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A TEXT BOOK OF HEAT

FOR JUNIOR STUDENTS

(INCLUDING KINETIC THEORY OF GASES, THERMODYNAMICS AND RADIATION)

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PREFACE

THE TEXT BOOK OF HEAT for Junior students has been written with a view to supplying the needs of the students of the pass course reading for the Bachelor's degree. It has grown out of the lectures which the senior author has been giving to the B.Sc. pass class of the Allahabad University for several years. The plan of the book closely follows that of the larger Text Book which is intended for B.Sc. honours and M.Sc. students. Separate chapters have been devoted to Kinetic Theory, Liquefaction of Gases and Heat Engines. The principles of Thermodynamics and their applications have been treated at considerable length. Throughout the book the methods of calculus have been freely employed. The supplementary chapter on Meteorology has been kindly written by Dr. A. K. Das of the Indian Meteorological Service and Mr. B. N. Srivastava. Meteorology is a growing science and is extremely useful to the public at large. It is not at present included in the curriculum of any Indian University (except Agra where it forms a special course for the M.Sc. degree), but this seems to be a cardinal omission. It is hoped that in future it will form a regular subject of study by degree students.

As this is the first edition of the book, it is feared that there may be several omissions and inaccuracies. The authors will be grateful if these are brought to their notice.

ALLAHABAD :
January, 1933

THE AUTHORS

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Müller Pouillets, *Lehrbuch der Physik.*

Henning, *Temperaturmessung.*

Nernst, *Grundlagen des neuen Wärmesatzes.*

Jellinek, *Lehrbuch der physikalischen Chemie* (1930 edition).

Ewing, *The Steam Engine and Other Heat Engines.*

Watson, *Practical Physics.*

Burgess and Le Chatelier, *The Measurement of High Temperatures.*

Proceedings of the Physical Society of London.

Physical Review.

Journal of the Optical Society of America, Vol. 10.

Proceedings of the Royal Society, London. Chap. II, Figs. 6, 7; Chap. VIII, Fig. 14.

Philosophical Transactions of the Royal Society Chap. II, Fig. 8; Chap. VII, Fig. 8.

Zeitschrift für Physik. Chap. V, Fig. 4.

Physikalische Zeitschrift. Chap. II, Fig. 17.

Annalen der Physik. Chap. V, Fig. 9; Chap. VII, Fig. 2.

Handbuch der Physik, Chap. IV, Fig. 6; Chap. VI, Fig. 9; Chap. X, Fig. 4; Chap. XI, Fig. 23.

Handbuch der Experimentalphysik. Chap. V, Fig. 10; Chap. VI, Figs. 8, 12; Chap. VIII, Fig. 8; Chap. XI, Figs. 11, 18, 19, 20.

Ezer Griffiths, *Methods of Measuring Temperature.* Chap. I, Figs. 5, 6, 7, 9; Chap. XI, Figs. 14, 15, 21, 22, 23 from diagrams on pp. 52, 52, 34, 71, 84, 84, 90, 90, 115 of the work respectively.

Andrade, *Engines.* Chap. VI, Figs. 2, 3; Chap. IX, Figs. 1, 2, 3, 4, 5, 6, 7, 8, 11, 14, 15 respectively from pages 235, 239, 61, 68, 75, 102, 86, 92, 107, 195, 211, 213 of the work by the kind permission of Messrs. G. Bell & Sons, Ltd. (London).

Partington and Shilling, *Specific Heats of Gases.* Chap. II, Figs. 14, 16, 18 respectively from pages 127, 76, 84 of the work.

Preston, *Theory of Heat.* Chap. I, Fig. 3; Chap. II, Figs. 5, 13; Chap. XI, Fig. 16. Reproduced by the kind permission of Messrs. Macmillan & Co.

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CHAPTER I

THERMOMETRY

1. Temperature.—The sensation of heat or cold is a matter of daily experience. By the mere sense of touch we can say whether a substance is hotter or colder than ourselves. The hot body is said to possess a higher temperature than the cold one. But temperature is not a measurable quantity in the sense that a length or mass is. The law of addition holds true in the latter case but not in the former: when two masses m_1 and m_2 are mixed together the resultant mass is $m_1 + m_2$, but when two substances at temperatures t_1 and t_2 are allowed to touch each other, the resultant temperature, in general, will not be $t_1 + t_2$. Temperature is rather an abstract concept and is measured by the effect which it produces.

Heat causes many changes in the physical properties of matter some of which are well-known, *e.g.*, expansion, change in electrical resistance, production of electromotive force at the junction of two dissimilar metals. All these effects have been utilised for the measurement of temperature. The earliest and commonest thermometers utilise the property of expansion. Mercury-in-glass is universally employed as a thermometer for ordinary purposes, but though it is simple, convenient to use and direct-reading, it is not sufficiently accurate for high-class scientific work.

2. Mercury Thermometer.*—Everybody is familiar with the ordinary centigrade thermometer. It consists of a glass bulb containing mercury to which a graduated capillary stem is attached. The freezing point of water is marked 0°C and the boiling point 100°C and the interval divided into 100 equal parts. This scale was first introduced by Celsius and is now adopted for all scientific work. Other scales in ordinary use today are those introduced by Fahrenheit and Réaumur. But Fahrenheit was the first to choose mercury as the thermometric substance on account of its many advantages. It does not wet glass, can be easily obtained

* For details of construction see Preston, *Theory of Heat*, Chapter 2.

pure, remains liquid over a fairly wide range, has a low specific heat and high conductivity; it is opaque and its expansion is approximately uniform and regular. But we must not forget its several drawbacks. The specific gravity and surface tension of mercury are large, and the angle of contact with glass when mercury is rising is different from that when it is falling. On account of these defects alcohol is sometimes used in place of mercury, and since it has a larger expansion it is more sensitive but it is likely to distil over to colder parts of the tube.

The range of an ordinary mercury thermometer is limited by the fact that mercury freezes at $-38{\cdot}8°C$ and boils at $356°C$ but the upper limit can be raised to about $500°C$ by filling the top of the tube with nitrogen under pressure. The thermometric glass must be of special quality: it should be stable and should rapidly return to its normal state after exposure to high temperatures. The glasses generally employed for the purpose are *verre dur* and Jena 16^{III} and 59^{III}.

Mercury thermometers are generally employed for rough work. If they are at all used for accurate work various corrections must be applied to get the true temperature. The important ones among them are the following:—

(1) Calibration Correction. This is due to want of uniformity in the bore of the capillary tube.

(2) Correction due to change in the fundamental interval from 100 to $100 + \delta$ (say) where δ has any value.

(3) Correction due to shift of the zero. This is very important since glass after exposure to high temperatures returns to its normal state only after a very long time.

(4) Exposed Stem Correction. Part of the stem and hence the contained mercury does not acquire the temperature of the bath.

(5) Correction due to changes in the size of the bulb caused by variable internal and external pressure.

(6) Correction for thermal expansion of the material.

For details concerning the application of these corrections see Preston, *Theory of Heat*, or Glazebrook, *A Dictionary of Applied Physics*, Vol. 1 (Article on Thermometry).

3. Special Types of Liquid Thermometers.*—The ordinary mercury thermometer is not suitable for certain purposes; for this reason special types of thermometers have been devised. They are modifications of the ordinary thermometer designed to serve the particular end in view.

* For further information see Glazebrook, *A Dictionary of Applied Physics*, Vol. 1 (Article on Thermometry).

For *meteorological* purposes thermometers are required to indicate the maximum and minimum temperatures to which they have been exposed during a certain period. Six devised a combined maximum and minimum thermometer which is indicated in Fig. 1. The bulb A and part of the tube is filled with alcohol up to the level B, then with mercury up to C above which again there is alcohol up to D. The glass indexes I, I, have each an iron wire attached (shown separately), and placed above B and C in each tube. When the temperature rises the alcohol in A expands and the expanding mercury pushes upwards the index above C to its maximum limit. With a fall in temperature this index is undisturbed while the index above B is pulled upwards by the contracting alcohol, but is left behind when the temperature rises. The iron wire attached to the glass index prevents it from falling under its own weight and enables its position to be adjusted from outside.

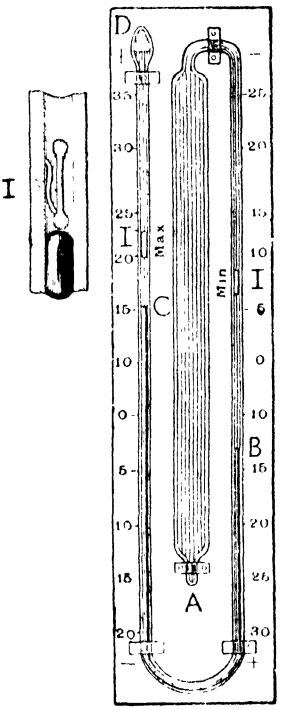

Fig. 1.—Six's maximum and minimum thermometer.

The clinical thermometers in ordinary use are mercury thermometers of short range of the maximum type. The stem just above the bulb has a constriction which the mercury passes when its temperature rises. On cooling, the mercury is unable to force its way back. The range of temperatures is 95°F to 110°F, and the bulb is very thin and the capillary bore very fine. The mercury thread is rendered easily visible by constructing lens-front thermometers.

For accurate work such as the determination of the boiling and melting points of organic substances several short-range thermometers are employed between the range 0 and 450°C. They are called *chemical* thermometers. Benzol and toluol thermometers are amongst the many that are in use.

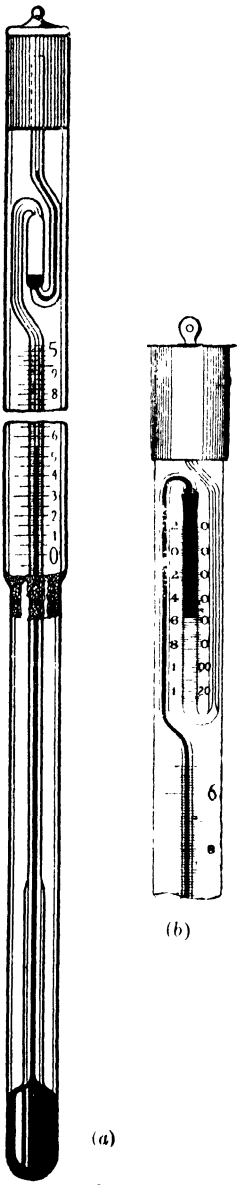

Fig. 2.—Beckmann thermometer.

The *Beckmann* thermometer indicated in Fig. 2 is used to measure small changes of temperature with a high degree of accuracy. The stem is here marked from 0 to 5 representing approximately degrees centigrade and every degree is divided into 100 equal parts. There is a reservoir at the top of the instrument shown separately at (*b*), to enable the range to be varied. To set the thermometer to any desired range the bulb is heated to expel mercury into the reservoir and the instrument gently tapped when the mercury column breaks near the reservoir and some mercury is transferred into it. Next the Beckmann thermometer is immersed along with an auxiliary thermometer in a bath whose temperature is varied till the mercury stands at 0 division of the former. The temperature corresponding to the zero of the Beckmann thermometer is thus observed on the auxiliary thermometer, and by varying the amount of mercury in the bulb this is adjusted to be near the desired range. The value of each scale division varies with the quantity of mercury in the bulb and a correction curve for different settings of the zero is supplied with the instrument from which the correction at any point of the scale may be obtained. The true value of a scale division may also be obtained by calculation if the expansion of mercury and glass be known.

4. Gas Thermometers.—The fundamental disadvantage of liquid thermometers is that two thermometers containing different liquids such as mercury and alcohol, and graduated as on page 1 will agree probably only at 0°C and 100°C and at no other

temperature. This is due to the fact that the expansion of the two liquids is not regular and similar. Thus the mercury thermometer of page 1 would give an arbitrary scale of temperature. In practice, however, all such thermometers are calibrated (sec. 8) by an actual comparison with the standard gas thermometer throughout the entire range.

Even then the mercury thermometer has been discarded for all accurate work. This is because the corrections to be applied to it (p. 2) are uncertain and known only approximately. Hence for all standard work gas thermometers are employed. Gases possess several advantages. Their expansion is large and regular; they can be obtained pure and remain gaseous over wide ranges of temperature. Further the scales furnished by different gases are practically identical; this is because the pressure and volume coefficients of all permanent gases are nearly equal. Hence gas thermometers are used as primary standards from which all others are calibrated.

The theoretical basis underlying the use of gas as thermometric substance is the laws of Boyle and Charles which state

$$\frac{p_2 v_2}{p_1 v_1} = \frac{1+\alpha t_2}{1+\alpha t_1} \quad . \quad . \quad . \quad . \quad (1)$$

where α is the coefficient of expansion at constant pressure and is nearly equal to $\frac{1}{273}$ for permanent gases, and t_1, t_2 are any two temperatures on the centigrade scale. If $t_2 = -\frac{1}{\alpha}$, $v_2 = 0$, *i.e.*, at temperature $\frac{1}{\alpha} = 273°C$ (nearly) below the ice-point, the volume of the gas would be zero provided the perfect gas equation is obeyed throughout the range. This temperature is, by definition, called the *absolute zero.* It is true the gas would liquefy and solidify before this state is reached and the perfect gas equation would cease to be valid. Further it is inconceivable that matter should at any time occupy no space ($v=0$). Nevertheless the idea of such a zero of temperature is very useful.* If we measure temperatures from this zero, the ice-point is given by $\frac{1}{\alpha}°$, the steam point by $\frac{1}{\alpha} + 100$, and generally any temperature $t_2°C$ by $\left(\frac{1}{\alpha} + t_2\right)° A = T°A$.

* The absolute zero thus defined is shown from thermodynamic considerations (Chap. X) to be the lowest temperature possible. Hence the idea of this absolute zero is very important [see further pp. 10-11].

Hence equation (1) becomes

$$\frac{p_2 v_2}{p_1 v_1} = \frac{\frac{1}{\alpha} + t_2}{\frac{1}{\alpha} + t_1} = \frac{T_2}{T_1},$$

$$\text{or} \quad \frac{p_2 v_2}{T_2} = \frac{p_1 v_1}{T_1} = \frac{p_0 v_0}{T_0} \text{ (say)} \quad . \quad . \quad (2)$$

where T_0* = 273·20°A, the ice-point. For a gram-molecule of gas $\frac{p_0 v_0}{T_0}$ = R = 8·313 × 10^7 ergs = 1·986 calories. Hence generally $pv = n$RT where n is the number of gram-molecules of the gas.

Equation (2) furnishes two ways of measuring temperature. The pressure may be kept constant and the volume observed at different temperatures giving us the constant pressure thermometer; or the volume may be kept constant and the change in pressure noted, a principle utilised in the constant volume thermometer.

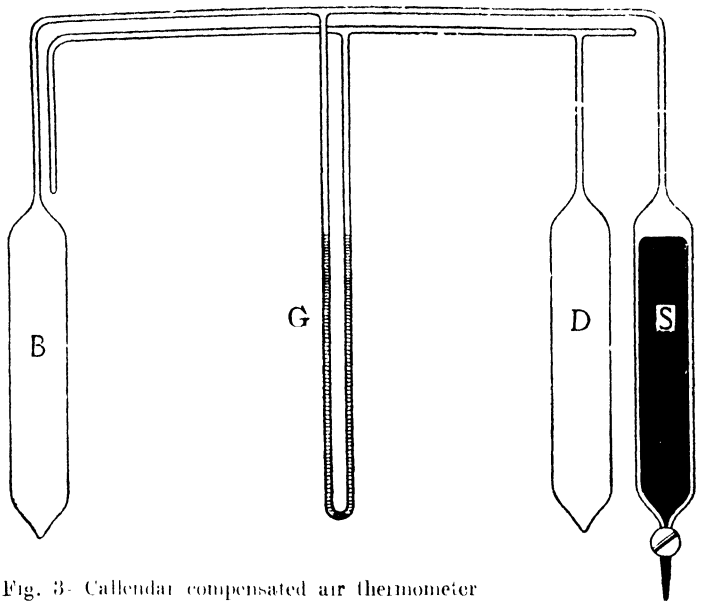

Fig. 3. Callendar compensated air thermometer

5. Callendar Compensated Air-Thermometer.—Accurate measurements with the constant-pressure gas thermometers are difficult as

* See p. 11.

the gas in the connecting tube and the manometer is at a temperature different from that of the bulb. To avoid this Callendar devised the compensated air-thermometer. In this instrument (Fig. 3) the pressure of the air in the thermometer bulb B is kept equal to the pressure of the air in D as indicated by the sulphuric acid gauge G. When B is heated, the pressure of the air in B increases and equality of pressure is restored by allowing mercury to flow out from the mercury reservoir S. The volume of the tube connecting B and S is eliminated by attaching to D an exactly similar tube placed close to it. This will be evident from the following consideration:—

Let v, v_1, v_2 be the volumes of the bulb B, the tube connecting B and S and the air in S respectively; θ, θ_1, θ_2 their respective temperatures, n the number of gram-molecules of air contained in B, S, and the connecting tube and p its pressure, we have from the gas laws

$$p\left(\frac{v}{\theta}+\frac{v_1}{\theta_1}+\frac{v_2}{\theta_2}\right)=n\,\mathrm{R}. \quad . \quad . \quad . \quad (3)$$

Similarly if v', v_1' be the volumes of the air in D and the tube attached, θ', θ_1' their respective temperatures, n' the number of gram-molecules and p' the pressure, we have

$$p'\left(\frac{v'}{\theta'}+\frac{v_1'}{\theta_1'}\right)=n'\,\mathrm{R}. \quad . \quad . \quad . \quad . \quad (4)$$

If $p=p'$, $n=n'$, $v_1=v_1'$, $\theta_1=\theta_1'$ we have from (3) and (4)

$$\frac{v}{\theta}+\frac{v_2}{\theta_2}=\frac{v'}{\theta'}.$$

If in addition S and D are immersed in melting ice, $\theta_2=\theta'=\theta_0$, the freezing point of water, and

$$\theta=\theta_0\,\frac{v}{v'-v_2},$$

or denoting v, v', v_2 by B, D, S,

$$\theta=\theta_0\,\frac{\mathrm{B}}{\mathrm{D}-\mathrm{S}}. \quad . \quad . \quad . \quad . \quad (5)$$

Thus we see that the influence of the connecting tubes is entirely eliminated if (1) the pressure in B is kept equal to that in D ($p=p'$); (2) the total mass of the gas in B, S, and the connecting tube is equal to that in D and the connecting tube ($n=n'$); (3) the volume of the connecting tubes are equal ($v_1=v_1'$). The condition $\theta_1=\theta_1'$ is automatically satisfied

since the two connecting tubes are placed side by side and are at the same temperature.

6. Standard Gas Thermometers.—The constant-pressure air-thermometer has been defended by Callendar on various grounds: (1) the apparatus and the calculations are simple; (2) the internal pressure on the bulb does not increase as the temperature rises; (3) accuracy of the result depends upon the accuracy of weighing. Nevertheless the instrument does not give concordant results and has been replaced by the constant-volume thermometer as a standard. The normal thermometer selected by the Bureau International des Poids et Mesures and everywhere adopted today is the constant-volume hydrogen thermometer filled with gas at a pressure of 1 metre of mercury at the temperature of melting ice. It consists essentially of two parts: the bulb enclosing the invariable gaseous mass and the manometer for measuring the pressure. Fig. 4 (*a*) represents the thermometer diagrammatically.

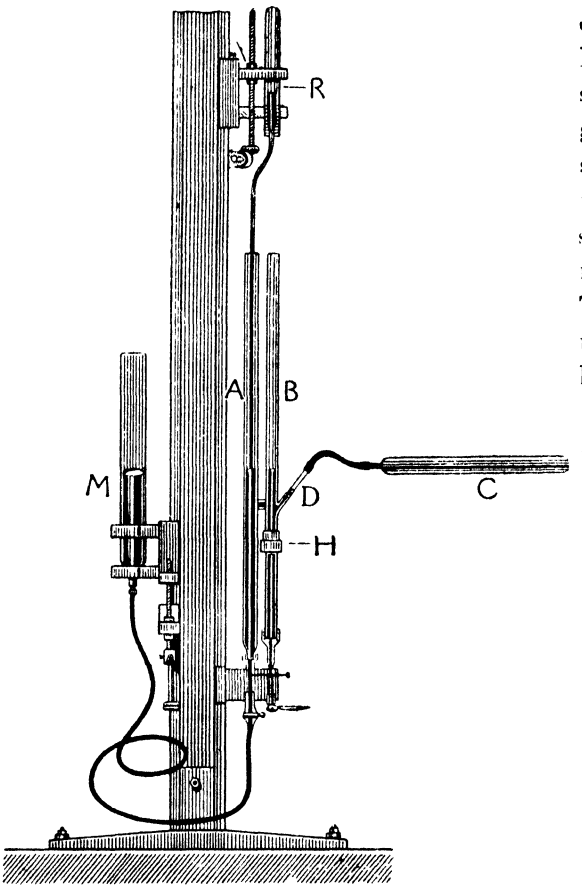

Fig. 4 (*a*).—Constant-volume Hydrogen Thermometer.

* For further information see *Encyclopædia Britannica*, Article on 'Thermometry.'

The bulb C is a platinum-iridium tube a litre in capacity, 1 metre in length and 36 mm. in diameter. It is attached to the manometer by a capillary tube of platinum 1 metre in length. The manometer consists of two tubes A and B, and the stem of the barometer R dips into A. The barometer tube is bent so that the upper surface of mercury in it is exactly above B and these levels can be read off by a cathetometer furnished with three telescopes. The number of observations to be taken is thus reduced to two. B consists of two columns of mercury separated by the steel-piece H and both these columns communicate with A. By raising or lowering the mercury reservoir M, the mercury surface in the lower part of B is arranged just to touch a fine platinum point P [shown separately in Fig. 4 (*b*)], projecting from the steel-piece H, and thus the volume of gas is kept constant.

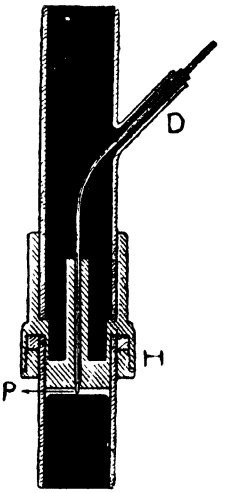

Fig. 4 (*b*).

The thermometer described above is suitable for measuring temperatures up to 500°C. For higher temperatures certain modifications are necessary which will be discussed under 'pyrometry' in Chapter XI. The range of gas thermometers with proper modifications can be extended to −260°C—1600°C.

To derive a formula for this thermometer let us start with the fundamental equation $pv=n\mathrm{R}T$. If p_0, p_{100} denote the pressures indicated by the manometer at the ice-point and steam-point respectively, then $p_0 v=n\mathrm{R}T_0$, $p_{100}v=n\mathrm{R}\,(T_0+100)$, where T_0 represents the ice-point on the perfect gas scale and the fundamental interval is 100°

$$\therefore \frac{p_{100}}{p_0}=\frac{T_0+100}{T_0},$$

$$\text{or } \frac{1}{T_0}=\frac{p_{100}-p_0}{100p_0}=\beta$$

where β is the coefficient of expansion at constant volume. Thus we know β for that gas from a measurement of p_{100} and p_0. To find the absolute

temperature corresponding to any observed pressure p_1, we have,

$$p_1 v = nRT_1$$

$$\therefore \frac{p_1}{p_0} = \frac{T_1}{T_0},$$

$$\text{or } T_1 = \frac{p_1}{p_0}\frac{1}{\beta}, \quad \text{since } T_0 = \frac{1}{\beta}. \quad . \quad . \quad (6)$$

Thus to determine an unknown temperature the corresponding pressure p_1 is observed on the thermometer and the temperature T_1 calculated either from the above relation or graphically.

In an actual measurement corrections have to be applied for the following:—

(*a*) the gas in the 'dead space' is not raised to the temperature of the bulb. The 'dead space' consists of the space inside the capillary tube and in the manometer between the mercury level and the steel-piece H. Its initial and final temperatures are also different.

(*b*) Increase in the volume of the bulb C with rise of temperature.

(*c*) Change in volume of the bulb due to changes in internal pressure.

(*d*) Changes in density of mercury on account of temperature changes.

For a discussion of these the authors' advanced book may be consulted.

THE THERMODYNAMIC OR ABSOLUTE SCALE OF TEMPERATURE

7. Perfect Gas Scale.—The formulæ developed for the gas thermometer assume that the gas in question accurately obeys the gas laws but experiments show that no real gas does so exactly. The coefficient of expansion α at constant pressure is not exactly the same for real gases as may be seen from any book of physical constants (see Kaye and Laby: '*Physical Constants*'). Further the two coefficients α, β are not exactly equal, and β also varies with the initial pressure. Thus different gases would furnish different scales of temperature if the thermometer is calibrated as indicated above, and the selection of any particular gas will be arbitrary and will give an arbitrary scale of temperature. To avoid this arbitrariness we must reduce our observations to that state of the gas in which the perfect gas equation is satisfied. The scale would then be independent of the nature of the gas used. This is the perfect gas scale or absolute scale.

Before discussing the methods of reducing the real gas scale to the perfect gas scale we may point out an important result arrived at in Chapter X. There it is shown how Lord Kelvin, from consideration of heat-engines, has developed an absolute scale *independent of the property of any particular substance.* This is the true scale of temperature and is known as the thermodynamic scale. It is shown there that the ratio of two temperatures on the thermodynamic scale is equal to the ratio of the two temperatures as obtained on the perfect gas scale. Thus if the zeros of the two scales are made to agree the thermodynamic scale will be identical with the perfect gas scale at all points. We thus see that the perfect gas scale which was hitherto shown to depend on the properties of gases now becomes independent of the properties of any particular substance. Hence it is called the absolute scale.

We shall now give the methods* of deducing the perfect gas scale from observations on real gases. This can be done when we have a knowledge of the deviation of gases from Boyle's law. The calculations are rather complicated and will not be given here. It is evident however that at infinitely low pressures all gases would obey Boyle's law accurately and this conclusion is borne out by experimental observation. Hence the same scale will be given by all gases at this pressure. For such a gas the coefficient of expansion γ can be calculated from the data given by Holborn and Otto.† The mean of several results gives $\gamma = 0{\cdot}0036604$ for a perfect gas. Thus T_0 the melting point of ice on the thermodynamic scale $= \frac{1}{\gamma} = 273{\cdot}20°\text{A}.$

Another good method of obtaining the correction to be applied to the real gas scale consists in performing the Joule-Thomson experiment (Chapter VI). But unfortunately the existing data are not sufficient to enable us to apply this method and we fall back upon the method already given.

8. Standardisation of Secondary Thermometers.—Gas thermometers are very cumbersome to use and require several corrections. Hence in laboratories they are replaced by secondary standards such as the resistance thermometer, the thermo-couple, etc., which have been carefully standardised by comparison with a standard gas thermometer in

* For fuller information see *A Treatise on Heat* by the authors.

† *Zeits. f. Physik*, Vol. 33, p. 5.

standardising laboratories. For this purpose comparison baths may be constructed suitable for the different ranges. Between 0° and 100°C a water bath, between 100° and 250°C an oil bath, between 250° and 600°C a mixture of sodium and potassium nitrate, and above that an air bath, electrically heated, may be employed.

The secondary thermometers may also be standardised by means of a series of easily reproducible fixed points whose temperatures have been accurately determined. A table of standard temperatures is given below. The values are generally those adopted by the Seventh General Conference of Weights and Measures* representing thirty-one nations which was held in October 1927, but some additional fixed points have also been included.

Table 1.—Standard Temperatures.

Temperature Centigrade	Substance	Temperature Centigrade	Substance
−252·78°	B. P. of Hydrogen	320·9	F. P. of Cadmium.
−195·81	B. P. of Nitrogen	327·3	M. P. of Lead
−182·962	B. P. of Oxygen	419·45	F. P. of Zinc
− 78·483	Sublimation of CO_2	444·60	B. P. of Sulphur
− 38·832	M. P. of Mercury	630·5	F. P. of Antimony
0·00	M. P. of Ice	960·5	M. P. of Silver
+ 32·38	Transition temperature of $Na_2SO_4.10H_2O$.	1063	M. P. of Gold
		1083	M. P. of Copper
		1452·3	M. P. of Nickel
100·000	B. P. of Water	1555	M. P. of Palladium
217·96	B. P. of Naphthalene.	1770	M. P. of Platinum
		2454	F. P. of Iridium
231·85	M. P. of Tin	2620	M. P. of Molybdenum
305·90	B. P. of Benzophenone.	3400 ± 50	M. P. of Tungsten
		3500 ± 50	M. P. of Carbon

9. Fixed Temperature Baths.—It is frequently convenient to calibrate the secondary thermometers by means of the fixed-point scale given above. The ice-point may be most conveniently obtained by dipping the thermometer in pure melting ice contained in a Dewar flask. This is

* See a Report by Burgess, *Bull. Bur. Stand.*, Vol. 22, p. 635 (1928). See also Heuse and Otto, *Ann. d Physik*, Vol. 9, p. 486 (1931), for later work.

a double-walled glass or metal vessel whose sides are silvered.* For the steam-point the hypsometer indicated in Fig. 5 is employed. The diagram explains itself. C is the condenser employed to prevent the water from being lost by evaporation, M is the manometer and T the thermometer. The path of steam is indicated by the arrows. For other fixed points a number of vapour baths in which sulphur, naphthalene, aniline, etc., are used, serves the purpose.

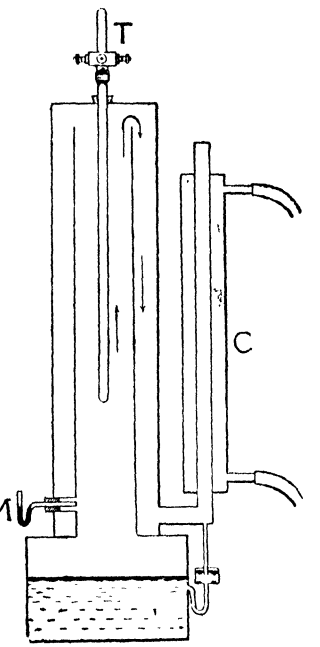

Fig. 5.—Hypsometer.

The sulphur boiling-point apparatus has been much improved during the last 30 years. Callendar and Griffiths found that the standard Meyer-tube apparatus was well adapted for the work. It consists of a hard glass cylinder A of diameter 5 cms. and length about 25 cms. to which a spherical bulb B is attached at the bottom (Fig. 6, p. 14). The whole is surrounded by an asbestos chamber C. The thermometer T is fitted with an asbestos or aluminium cone D. This cone serves in two ways: (1) it prevents the condensed sulphur from running down over the bulb and cooling it below the temperature of sulphur vapour; (2) it prevents the bulb from directly radiating to the cooler parts of the tube. Sulphur is placed in the bulb and heated over a flame. A side tube may be provided in the upper part of the chamber and serves to condense sulphur vapour.

Baths for naphthalene and aniline may be constructed by slightly modifying the above apparatus.

RESISTANCE THERMOMETRY

10. Platinum Thermometers.—The necessity of secondary standards has been clearly indicated above. Two types of such instruments

* For a complete description see Chap. VI.

based on two electrical properties of matter will be described in this chapter. The properties are—(1) variation of electrical resistance of metals with temperature; (2) variation of thermal electromotive force with temperature. First let us consider the former.

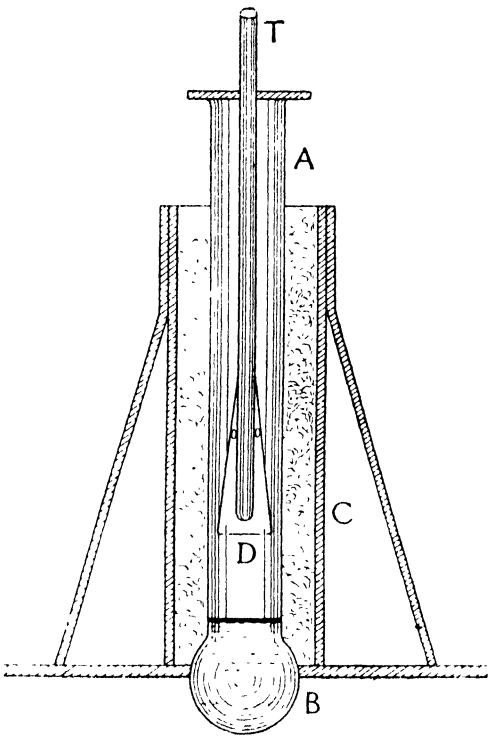

Fig. 6.—Sulphur-boiling apparatus.

Sir William Siemens was the first to construct thermometer in 1871 based on this principle but the constructional details were unsatisfactory. Platinum wire, wound on a fire-clay cylinder, was enclosed in a tube of wrought iron. Its resistance at a temperature was not found to be constant but to have increased after exposure to high temperatures due to contamination with impurities. Later improvements by Callendar and Griffiths have given the instrument its modern form. Fig. 7 (p. 15) represents an hermetically-sealed thermometer designed by Dr. E. H. Griffiths for laboratory work of high precision. Pure platinum wire free from silicon, carbon, tin and other impurities is selected. It is doubled on itself to avoid induction effects and then wound on a thin plate of insulating mica *m*. The ends of this wire are attached to platinum leads which pass through holes in mica sheets closely fitting the upper part of the tube, and the other ends of these leads are joined to terminals P, P at the top of the instrument. The mica sheets give the best insulation and prevent convection currents of air up and down the tube. The coil is sealed for, otherwise, moisture would deposit on the mica and break down

the insulation. To compensate for the resistance of the leads, an exactly similar pair of leads, with their lower ends joined together, is placed close to the platinum thermometer leads, and is connected to terminals marked C, C, on the instrument. These are called compensating leads and are joined in another arm of the Wheatstone bridge; thus the resistance of the thermometer leads is eliminated. For work up to 700°C copper leads may be used and the whole may be enclosed in a tube of hard glass. But for high temperatures platinum leads must be used and the whole must be enclosed in a tube of glazed porcelain.

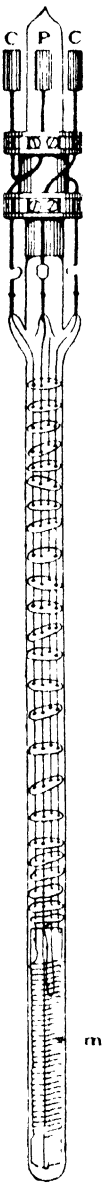

Fig. 7.—Platinum Thermometer.

The precision and reliability of modern resistance thermometers are entirely due to the work of Callendar* and Griffiths. They determined the resistance of pure platinum from 0° to 500°C and found that it was very accurately given by a parabolic formula of the type

$$R_t = R_0(1+\alpha t+\beta t^2), \quad . \quad . \quad . \quad (7)$$

where R_t, R_0 are the resistances at t°C and 0°C and α, β are constants. But Callendar further showed that it was unnecessary to solve this quadratic equation to find t from the value of R_t. He gave a special form to this relation and introduced nomenclature which has come into general use. Thus we assume the simple relation†

$$R_t = R_0(1+cp_t)$$

where c is the mean temperature coefficient of resistance between 0 and 100°C, and define the platinum temperature p_t, which is nearly equal to the true temperature t, by the relation

$$pt = \frac{R_t - R_0}{R_{100} - R_0}\,100. \quad . \quad (8)$$

* Callendar, *Phil. Trans.*, 178, p. 160 (1887); Callendar, *Phil. Mag.*, 32, p. 104 (1891); Callendar, *Phil. Mag.*, 47, p. 191 (1899).

† c is slightly different from α. The exact relation may be deduced to be

$$\alpha = c\left(1+\frac{\delta}{100}\right); \quad \beta = -\frac{c\delta}{(100)^2}.$$

where R_t, R_0, R_{100} respectively denote the resistances at $t°$, 0°, 100°C. The quantity $R_{100} - R_0$ is called the fundamental interval (F. I.) of the thermometer. Callendar further showed that the difference between the true temperature t and the platinum temperature p_t was accurately given by the parabolic formula

$$t - p_t = \delta \left\{ \left(\frac{t}{100} \right)^2 - \frac{t}{100} \right\}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where δ is a constant for that particular specimen of wire. To deduce (9) we have,

$$t - p_t = t - \frac{R_t - R_0}{R_{100} - R_0} 100$$

$$= t - \frac{\alpha t + \beta t^2}{(100)\alpha + (100)^2 \beta} 100 \text{ from } (7)$$

$$= -\frac{\beta (100)^2}{\alpha + 100\beta} \left[\left(\frac{t}{100} \right)^2 - \frac{t}{100} \right].$$

Thus δ in equation (9) is equal to

$$-\frac{\beta (100)^2}{\alpha + 100\beta}.$$

The value of δ for the specimens employed is about 1·5. The higher the purity the greater is α and the smaller is δ. δ is determined by finding the platinum temperature p_t for the boiling point of sulphur whose true temperature is known, and then substituting in (9). Later work by Heycock and Neville shows that if the platinum thermometer is standardised at 0°, 100°, and the boiling point of sulphur the parabolic formula (9) gives true readings as far as 1080°C.

11. Bridges.—The determination of temperature by this thermometer involves the accurate measurement of resistance. Various special types of resistance bridges are used for this purpose. In order to compensate for the resistance of the leads a bridge with equal ratio arms must be used. Further the bridge should be capable of measuring changes in resistance to a high degree of accuracy. For the fundamental interval is generally 1 ohm and measurement of temperature to hundredths of a degree requires resistance measurements to $\frac{1}{10000}$ th of an ohm.

The Callendar and Griffiths bridge* is quite suitable for this purpose. Fig. 8 indicates the connections. Q and S, the ratio arms, are kept equal

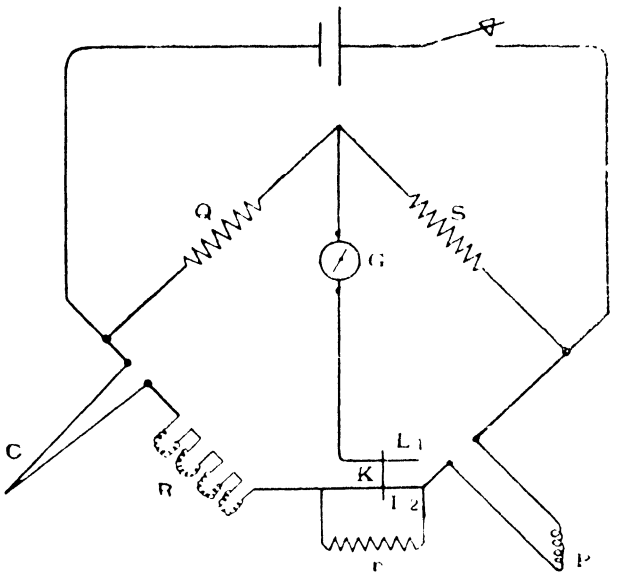

Fig. 8.- Callendar and Griffiths Bridge.

by the makers of the instrument. R consists of a set of resistances of 1, 2, 4, 8, 16, 32, 64 units. The usual plug contacts are here replaced by mercury cup contacts. L_1, L_2 are two parallel wires of the same material which can be connected to each other by the contact-maker K. This arrangement is adopted in order to eliminate thermo-electromotive forces. P represents the thermometer and C the compensating leads. The bridge is adjusted for no deflection of the galvanometer G. The resistance r acts as a shunt and makes the resistance of the wire exactly in the desired ratio. For accurate work, however, various precautions are necessary some of which are given below†:—

(1) The current flowing through the bridge heats the bridge coils and changes their resistance. The change in temperature may be observed on a thermometer and the corresponding change in resistance calculated. The correction can then be easily applied. Or the bridge may be placed in a thermostat.

(2) The thermometer coil has to be very thin (·15 mm. diameter) since it must have a large resistance and hence the heating effect is considerable. From Callendar's observations the

* For further details see Flint and Worsnop '*Practical Physics.*'

† For complete details see *Methods of Measuring Temperature* by E. Griffiths (Chap. 3).

heating effect for a current of ·01 ampere is 0·016° at 0°C and 0·017° at 100°C. According to him the best procedure is to pass the same current through the thermometer at all temperatures when the heating effect remains approximately constant.

(3) The bridge centre must be determined and the bridge wire calibrated.

(4) Due to temperature gradient along the conducting leads and the junctions thermo-electromotive forces are developed in the circuit whose magnitude may be found by closing the galvanometer circuit when the battery circuit is kept open. To eliminate these the galvanometer circuit should be permanently closed and balance obtained for reversals of the battery current. If induction effects are perceptible when the battery circuit is made or broken a thermo-electric key should be employed. This key first breaks the galvanometer circuit, then makes the battery and the galvanometer circuits in succession.

(5) The external leads connecting the terminals PP, CC to the bridge should be exactly similar and similarly placed.

12. As already mentioned, the platinum thermometer is standardised by measuring the resistance at the melting point of ice, boiling points of water and sulphur. The last gives δ, and hence t can be determined from any subsequent determination of ρ_t. Every such thermometer is however provided with a calibration curve drawn by an actual comparison with a standard gas thermometer in standardising laboratories. The temperature can be directly read from this temperature-resistance curve.

The great advantage of platinum thermometers lies in their wide range (−200°C to 1300°C). If carefully prepared, their readings are reliable to 0·01° up to 500°C and to 0·1° up to 1300°C. They are free from changes of zero for the wire when pure and well-annealed has always the same resistance at the same temperature. They are very convenient for ordinary use and, when once standardised by comparison with a gas thermometer, serve as reliable standards. Impurities in the platinum are highly detrimental to accurate work. Impure platinum does not obey the same resistance-temperature law as the pure metal.

Table 2 below gives the variation in resistance of a platinum thermometer over a wide range. It is taken from Henning's *Temperatur-messung*. The value of the quantity $R = R_t/R_0$ is given for various temperatures where R_t, R_0 are the resistances at temperatures t°C and 0°C.

Table 2.—Values of $R = R_t/R_0$.

Temp. °C	R	Temp. °C	R	Temp. °C	R
−190	0·21607	+60	1·23624	320	2·21154
−180	0·25927	80	1·31406	340	2·28330
−160	0·34505	100	1·39141	360	2·35460
−140	0·42986	120	1·46830	380	2·42543
−120	0·51347	140	1·54471	400	2·49580
−100	0·59612	160	1·62067	420	2·56570
− 80	0·67814	180	1·69616	440	2·63513
− 60	0·75948	200	1·77118	460	2·70410
− 40	0·84019	220	1·84574	480	2·77261
− 20	0·92033	240	1·91983		
0	1·00000	260	1·99345		
+ 20	1·07921	280	2·06661		
+ 40	1·15796	300	2·13931		

THERMO-ELECTRIC THERMOMETRY

13. Thermo-Couples.—Let us now return to the second electrical property utilised for temperature measurement. Starting from Seebeck's discovery in 1828 numerous attempts were made to construct a thermometer based on this principle, for instance, by Becquerel, Pouillet and Regnault. Pouillet used an iron-platinum couple but the chemical changes in the iron due to exposure to high temperatures vitiated his results and his systematic investigations became useless. At present, however, thermo-electric thermometry has attained a degree of precision inferior only to resistance thermometry below 1000°C, but for temperatures exceeding that, it is the only sensitive and convenient electrical method at our disposal.

A thermo-electric thermometer installation consists of the following parts:—

(1) The two elements constituting the thermo-element.

(2) The electrical insulation of these wires and the protecting tubes.

(3) Millivoltmeter or potentiometer for measuring the thermo-electro-motive force.

(4) Arrangements for controlling the cold-junction temperature.

The choice of the elements constituting the couple is determined by the temperature to which the couple is to be heated and the e.m.f. developed. For low temperatures up to 300°C couples of base metals

such as iron-constantan and copper-constantan are satisfactory, as they develop a large e.m.f. of about 40 to 60 microvolts per degree. For high temperatures these base metals cannot be used as they get oxidized and melt. Nickel-iron couple may be used up to 600° but above that platinum and an alloy of platinum with iridium or rhodium must be used. Le Chatelier in 1886 introduced the couple (pure platinum *v* 90% Pt 10% Rh) which is now largely employed for scientific work. The e.m.f. developed by these noble metals is however much less.

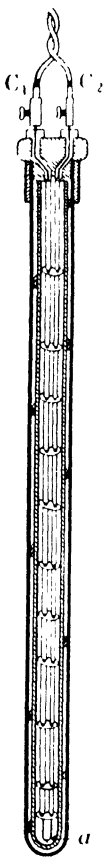

Fig. 9.
Thermo couple.

The two elements are taken in the form of a wire and one end of both is welded together electrically or in an oxyhydrogen flame. This end *a* (Fig. 9) forms the hot junction. The portions of the wires near the hot-junction are insulated with capillaries of fire-clay (or hard glass for lower temperatures) and are threaded through mica discs enclosed in outer protecting tube of porcelain, quartz or hard glass, depending upon the temperature for which it is meant. The protecting tube prevents the junction from contamination but necessarily introduces a lag. For rough use this may be further enclosed in a steel sheath (shown black in the figure). Where there is no risk of contamination the mica discs and the protecting tubes can be dispensed with. The wires are connected to terminals C_1 and C_2 on the instrument. To these terminals are connected flexible compensating leads leading to the cold junction. These leads are usually of the same material as the elements of the couple itself. Thus the cold junction is transferred to a convenient distant place where a constant temperature say 0°C. can be maintained. Usually the compensating leads are marked so that there is no difficulty in connecting to the proper terminals.

There are two ways of making the connections which are indicated in Fig. 10. The diagrams explain themselves. The cold junction is immersed in ice at 0°C. As a recording instrument either a millivoltmeter or a potentiometer is employed.

14. To find the temperature of the hot junction we must measure the e.m.f. developed between the ends of the copper leads. This can be done by means of a high resistance millivoltmeter which may be graduated to read temperatures directly and the temperature thus obtained can be relied upon to about ± 5°C. For attaining higher accuracy a potentiometer must be used. In principle this consists of

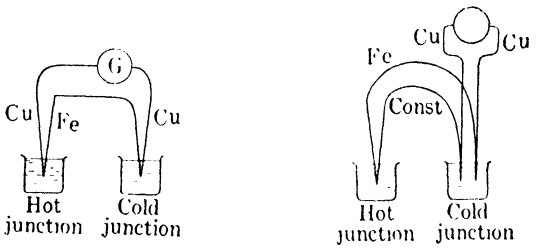

Fig. 10.—Measuring with a thermo-couple.

a uniform wire resistance AB (Fig. 11) in series with the resistance r, and through these a steady current is maintained by the battery E_1. The e.m.f. to be measured V_1 (may be a cell or the two leads of a thermo-couple as shown) is applied as indicated. The sliding contact K is adjusted for no deflection in the galvanometer G. Then if a standard cell of e.m.f. V_2 gives balance with the length AB and V_1 with the length AK, $V_1 = \frac{AK}{AB} V_2$. Various types of potentiometers based on this principle have been devised specially for this purpose.* With these instruments the e.m.f. can be measured accurately even

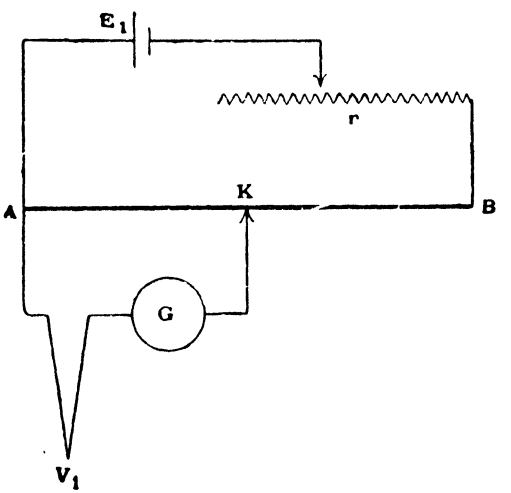

Fig. 11.—Illustration of the principle of potentiometer.

* A description of these will be found in *Methods of Measuring Temperature* by E. Griffiths.

to ·1 micro-volt which corresponds to about ·1°C for a Pt, Pt-Rh couple. For accurate work the cold junction must be maintained at 0°C otherwise corrections* will be required in that respect.

In order to deduce the temperature from an experimental determination of the e.m.f. a calibration curve is generally supplied with the instrument. This gives the temperature corresponding to different electromotive forces developed and has been drawn by the makers by an actual comparison with a standard thermo-couple throughout the range. If it is required to calibrate a thermo-couple in the absence of a standard one, the fixed points (Sec. 8) must be utilised. The e.m.f. at those points is measured and an empirical interpolation formula employed in order to give the e.m.f. corresponding to the intervening temperatures. For a Pt—Pt-Rh couple three different equations must be used for the different ranges. Thus

$$\text{from } 0° \text{ to } 400°\text{C}, \quad E = At + B\,(1 - c^{t})$$

$$300° \text{ to } 1200°\text{C}, \quad E = -A' + B't + C't^2$$

$$1100° \text{ to } 1750°\text{C}, \quad E = -A'' + B''t + C''t^2$$

where A, B, C are constants whose values are empirically determined.

The useful range of thermo-electric thermometers is about −200°C to 1600°C though couples of Ir and 90% Ir 10% Ru have been used up to 2100°C. Readings are reliable only when the composition of the couple does not change even slightly. In actual practice frequent calibration is necessary.

The following are the chief sources of error in thermo-electric thermometry:—

(1) Parasitic electromotive forces developed in the circuit. They are due to (*a*) Thomson effect or e.m.f. generated on account of temperature differences along the wire; (*b*) Peltier effect or e.m.f. developed due to heating of junction of dissimilar metals at other parts of the circuit; (*c*) Becquerel effect or e.m.f. generated due to inhomogenities in a single wire.

(2) Leakage from the light mains or furnace circuit. If leakage currents pass through the potentiometer their presence can be detected by short-circuiting the thermo-couple when the galvanometer continues to be deflected.

(3) Cold-junction correction if it is not kept at 0°C.

* See Ezer Griffiths, *Methods of Measuring Temperature*, p. 68.

For the methods of minimising or eliminating these errors the reader is referred to *Measurement of High Temperatures* by Le Chatelier and Burgess.

We give below a table, selected from Landolt and Börnstein's *Physikalisch-Chemische Tabellen*, which indicates the thermo-electric force for various couples in common use. The cold junction is maintained at 0°C while the hot junction at t°C.

Table 3.—E.m.f. in millivolts.

Temp.	Fe/Constantan.	Ag/Pt	Cu/Constantan.	Ag/Ni	90% Pt 10% Rh against pure Pt.
t°C	Hoffmann Schulze.	Holborn and Day.	Wick.	Hevesy and Wolff.	Day and Sosman.
—185	...	—0·16	— 5·20	..	...
— 80	...	—0·30	...	— 1·68	..
+100	+5·27	+0·72	+4·0	+ 2·18	+ 0·64
+200	10·8	+1·73	+8·8	+ 4·96	+ 1·43
300	16·2	2·96	14·9	+ 7·52	2·32
400	21·5	4·47	.	+ 9·83	3·25
500	26·8	6·26	...	+12·04	4·23
600	32·3	8·25		+14·50	5·23
700	38·3	10·60	.	+17·30	6·27
800	44·5	13·17	. .	+20·73	7·33
900	50·9	15·99	...	+24·19	8·43
1000	16·8	...	...	. .	9·57
1200	...	...	. .	...	11·93
1400	...	...	...		14·34
1600	...	...	...	...	16·75
1800	...	...	...	...	18·61

15. Certain methods of measuring temperature utilise the radiation emitted by the hot body whose temperature is to be measured. These methods will be discussed in detail later (see Chap. XI). They can be used for measuring temperatures from about 1000°C to any upper limit.

16. Other methods of measuring temperature which are more or less obsolete utilise any one of the following properties of matter:—

(1) Expansion of a bar of metal.

(2) Changes in vapour density with rise of temperature.

(3) Variation of refractive index of a gas with temperature in accordance with Gladstone and Dale's law.

(4) Calorimetric methods based on the measurement of quantity of heat.

(5) Change of vapour pressure with temperature.

17. Low Temperature Thermometry.*—The importance of accurate measurement in the low temperature range has been considerably increased by the recent work of Dewar, Onnes, Crommelin and others. The standard thermometer in this range is the constant volume hydrogen or helium thermometer. The difficulty is presented by the circumstance that gases liquefy and even solidify at these low temperatures. Prof. Dewar, however, showed that the boiling point of hydrogen as indicated by the hydrogen thermometer was $-253{\cdot}0°C$ and $-253{\cdot}4°C$, while a helium thermometer registered $-252{\cdot}7°C$ and $-252{\cdot}1°C$. Similarly he compared thermometers of other gases. These experiments evidently led to the conclusion that a gas could be relied upon even to its boiling point. Thus helium furnishes the scale down to its boiling point (5°A). The corrections necessary to convert this scale to the thermodynamic scale may be obtained and have been given by Onnes and Cath.† Now we shall consider the secondary standards.

Mercury freezes at $-38{\cdot}83°C$ and alcohol at $-111{\cdot}8°C$ and hence these thermometers cannot be used below the respective temperatures. A special liquid thermometer containing fractionally distilled petroleum ether can be used down to $-190°C$.

But for all accurate work, however, resistance thermometers are employed. It is absolutely essential that the substance of which the thermometer is made is perfectly pure. Pure metals show a regular decrease in resistance with decrease of temperature. Dewar and Fleming found that the presence of the slightest trace of impurity in a metal is sufficient to produce a considerable increase in resistance at these low temperatures. It is, therefore, difficult to trust the purity of any specimen for very low temperatures without actual comparison. Henning‡ found from a detailed investigation that the parabolic formula did not hold

* For pyrometry see Chap. XI.

† *Leiden Commun.*, No. 156(a), (1922).

‡ *Ann. d. Physik*, Vol. 40, p. 635 (1913).

below $-40°C$ and later on Henning and Heuse* showed that for temperatures lying between 0 and $-193°C$ the following relation holds

$$R_t = R_0 (1 + \alpha t + \beta t^2 + \gamma t^4)$$

Different platinum thermometers if standardised and calibrated according to Callendar's method give different platinum scales. Henning†, however, showed that the platinum temperatures p_t, p_t' given by two thermometers could be connected by a relation of the form

$$p_t' - p_t = c p_t (p_t - 100), \quad . \quad . \quad . \quad . \quad (10)$$

where c is a constant.‡ This constant can be determined by an actual comparison of two thermometers at any temperature, say of boiling oxygen.

In order to employ (10) we would require a standard platinum thermometer. Henning has, however, carefully compared a standard platinum thermometer with a hydrogen thermometer and we can utilise his results. Thus the procedure is as follows:—We find the platinum temperature p_t for our thermometer corresponding to any fixed point (say the boiling point of oxygen), and from the value p_t' on Henning's thermometer corresponding to the same temperature we find c for our thermometer with the help of (10). To determine the true temperature corresponding to any observed value p_t on our thermometer we employ this value of c to find p_t' from (10) and look for the corresponding true temperature given by Henning.

For temperatures lower than $-193°C$, platinum thermometers become insensitive, hence lead and gold thermometers are employed. Onnes§ has used lead down to $-259°C$ and Nernst|| has deduced a formula for calculating these temperatures. Below $-250°C$ resistance thermometers of constantan, manganin or phosphor-bronze have been employed.

For low temperatures copper-constantan and iron-constantan couples are very sensitive as they develop a large e.m.f. They can be used down

* *Zeits. f. Physik*, Vol. 23, p. 95 (1924).
† *Ann. d. Physik*, Vol. 40, p. 635 (1913).
‡ No relation has been found to exist between c and δ.
§ *Leiden Commun.* No. 99 (1907).
|| *Nernst Grundlagen des neuen Wärmesatzes*, p. 31.

to $-255°C$. They must be calibrated by direct comparison with a gas thermometer.

In order to measure temperatures below the temperature of boiling helium ($-268°C$) vapour-pressure thermometers alone can be employed. Their use is based on the well-known fact that the vapour pressure of a liquid varies uniquely with the temperature. Thus the method consists in measuring the vapour pressure of a liquid at the required temperature by means of an apparatus similar to that shown in Fig. 4, Chap. V and obtaining the corresponding temperature by means of a calibration curve or a theoretical formula.

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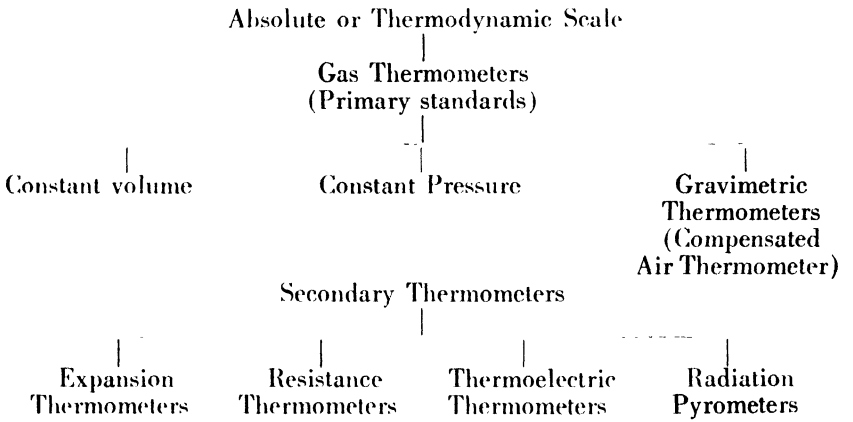
18. Illustration of the Principles of Thermometry.



Books Recommended.

Burgess and Le Chatelier—*The Measurement of High Temperatures.*
Ezer Griffiths—*Methods of Measuring Temperature.*
Henning—*Temperaturmessung.*

Chart of Fixed Points

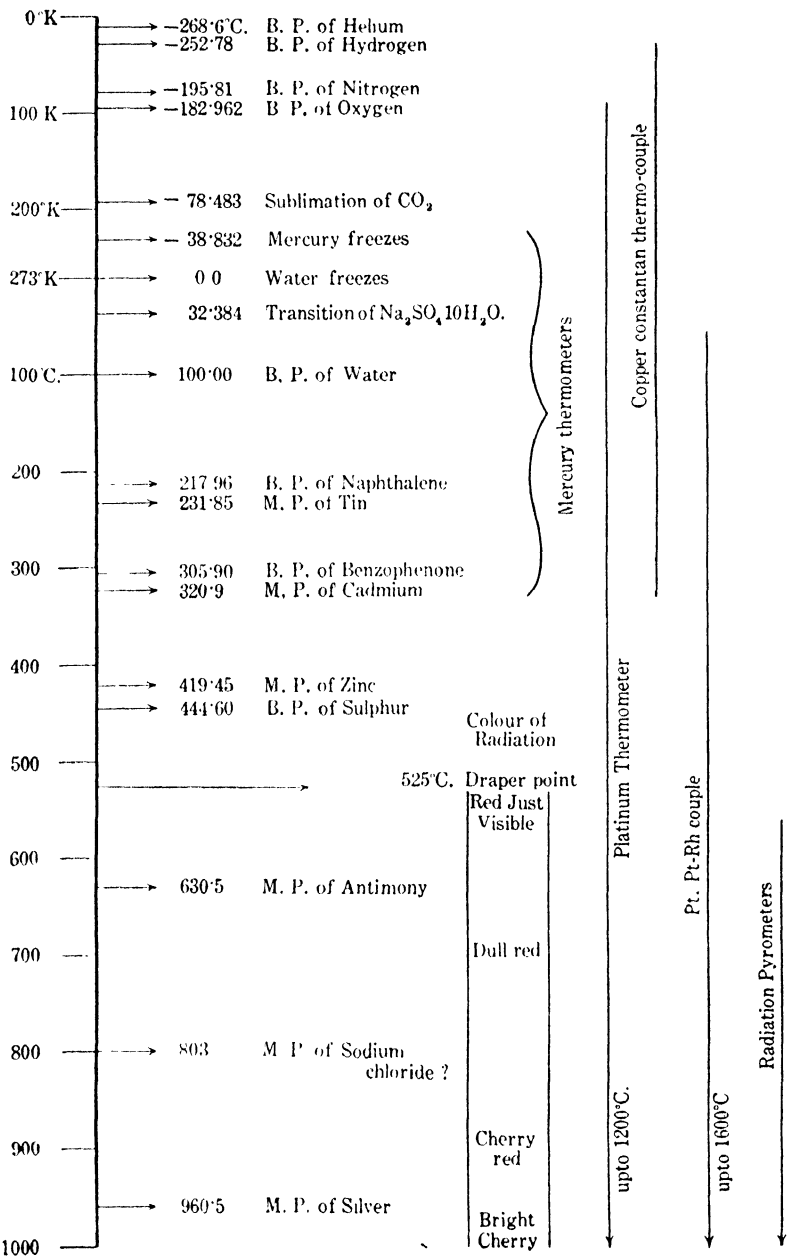
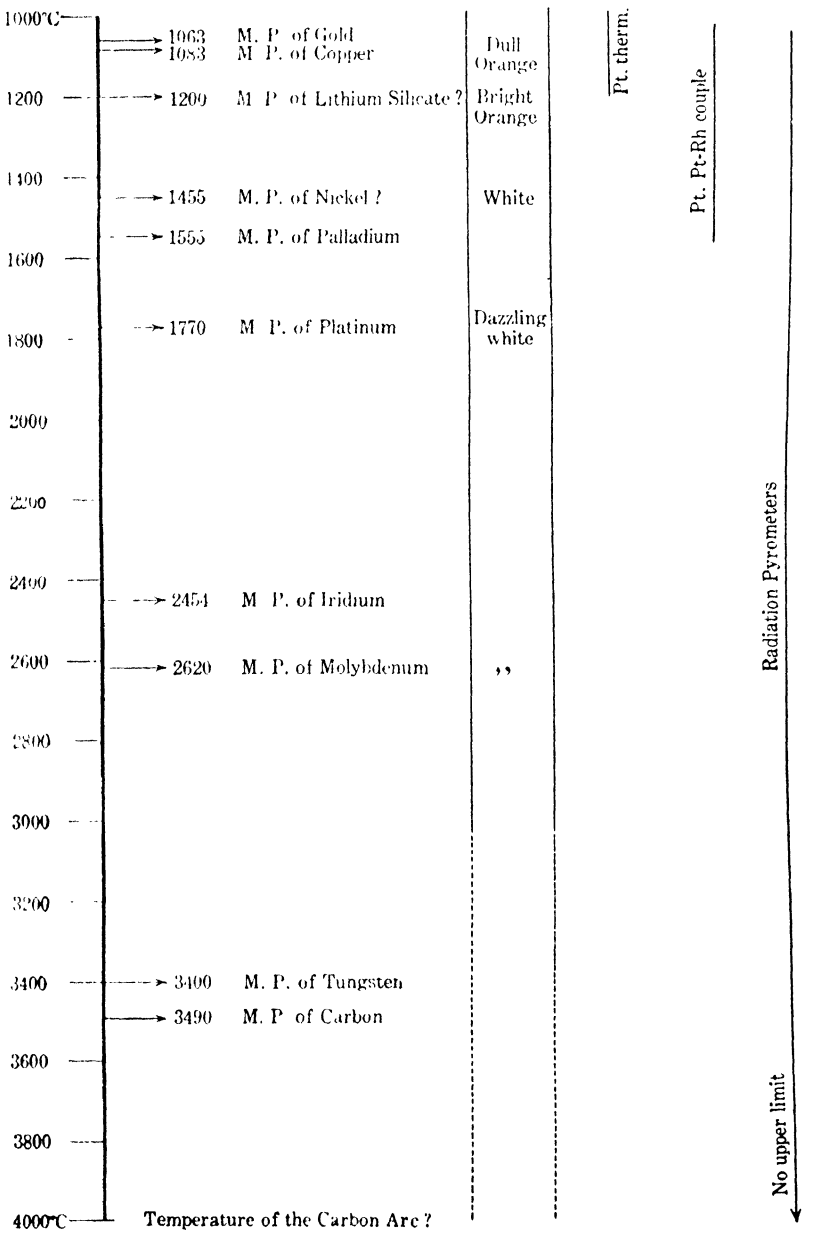


Chart of Fixed Points (Contd).



CHAPTER II

CALORIMETRY

1. General Idea.—It is a matter of common experience that when a hot body is placed in contact with a cold one, the former becomes colder and the latter warmer; we say that a certain quantity of heat has passed from the hot body to the cold one. But a simple experiment shows that when different bodies are raised to the same temperature and then allowed to share heat with a cold body the final temperature is different. If we take equal quantities of water in three different vessels at the same temperature and plunge equal masses of aluminium, lead and copper previously heated to 100°C into these vessels, one in each, the equilibrium temperature is highest for aluminium and least for lead. This indicates that, of these three metals, aluminium can yield the largest quantity of heat and lead the least.

The *capacity for heat* of a substance is defined as the quantity of heat required to raise the temperature of 1 gram of the substance through 1°C. For water this quantity is called the '*calorie*' which is also the unit in which quantities of heat are measured. The *calorie* is usually defined as the quantity of heat which would raise the temperature of one gram of water from 14·5°C. to 15·5°C. The *specific heat* of any substance is similarly defined as the number of calories required to raise 1 gram of the substance 1°C. This is strictly speaking not the same at all temperatures. Thus if a quantity of heat Q raises the temperature of m grams of a substance from θ to θ', s, the mean specific heat of the substance, is given by $\frac{Q}{m(\theta'-\theta)}$; while if a quantity dQ raises the temperature by $d\theta$, the specific heat at the temperature θ is $\frac{dQ}{m d\theta}$.

The *thermal capacity* or water equivalent of a substance is equal to the product of its mass and specific heat.

2. Methods in Calorimetry.—The following are the chief methods employed in Calorimetry*:—

(1) Method of Mixtures.
(2) Method of Cooling.
(3) Methods based on Change of State or Latent Heat Calorimetry.
(4) Electrical Methods.

In the following pages we shall discuss these methods one by one. Under each of these we shall consider the various forms of experimental arrangement that have been adopted. Solids and liquids will be considered first while gases will be taken up later in the chapter.

1. METHOD OF MIXTURES

3. Theory of the Method.—Regnault about the year 1840 made a careful study of the Method of Mixtures, and by care and skill obtained results of the highest accuracy. The principle of the method is to impart the quantity of heat to be measured to a certain mass of water contained in a vessel of known thermal capacity and to measure the rise of temperature produced. Thus if a substance of mass m_1, specific heat s_1 and initial temperature θ_1, be plunged into m_2 grams of water at temperature θ_2, and if W be the thermal capacity of the calorimeter, θ the final temperature of the mixture, we have, by equating the heat lost by the substance to the heat gained by the water and calorimeter,

$$m_1 s_1 (\theta_1 - \theta) = (m_2 + \mathrm{W})(\theta - \theta_2)$$

or

$$s_1 = \frac{(m_2 + \mathrm{W})(\theta - \theta_2)}{m_1 s_1 (\theta_1 - \theta)}$$

This gives the specific heat of the substance. Various corrections are however, necessary, for heat is lost by the system by conduction, convection and radiation. Thus for θ we must put $\theta + \triangle\theta$ where $\triangle\theta$ is the correction.

4. Radiation Correction.—In most experiments on calorimetry the calculation of this loss of heat due to radiation is important. Rumford first gave a simple method of doing this. His plan was to determine approximately from a preliminary experiment the rise of temperature and then so arranging the experiment that the initial temperature of the calorimeter is as much below the room temperature as the final temperature is

* A very good account of these methods is given in Glazebrook, *A Dictionary of Applied Physics*, Vol. I, article on 'Calorimetry.'

above it. Thus the heat absorbed by the calorimeter in the first part compensates for the heat lost during the second part. The compensation is, however, only imperfect, because the time taken in the first part is much less than in the second, since the rate of rise of temperature diminishes as the equilibrium is approached.

The radiation correction may however be accurately calculated with the help of Newton's Law of Cooling which states that for small differences of temperature the heat loss due to radiation is proportional to the temperature difference between the calorimeter and the surroundings. To illustrate its application let AB (Fig. 1) denote the observed rise of temperature during an experiment, BC the observed cooling at the end of it. We have to calculate the true rise in temperature. Divide the abscissa into n equal intervals $\delta t_1, \delta t_2, \ldots \delta t_n$ by means of ordinates $P_1M_1, P_2M_2 \ldots P_n M_n$ such that the small portions $AP_1, P_1P_2, \ldots P_{n-1} P_n$, may be treated as straight lines. Let us measure temperatures from the temperature of the surroundings. If $\theta_1, \theta_2 \ldots$ denote the mean temperatures during these intervals, $\theta_1', \theta_2' \ldots$ the temperatures at the ends of these intervals, represented by $P_1M_1, P_2M_2 \ldots$, then the temperature diminution due to radiation in the interval δt_1 is $k\theta_1 \delta t_1$. If $\theta_1'', \theta_2'' \ldots \theta_n''$ denote the

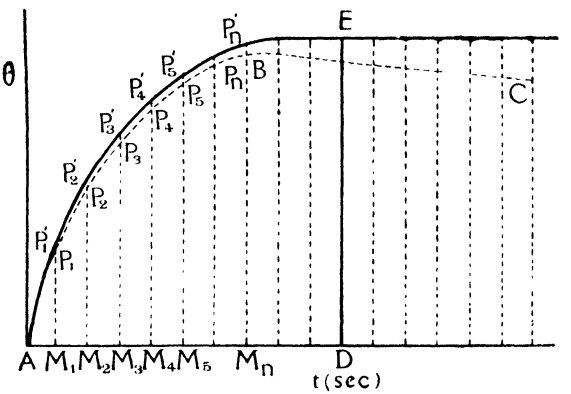


Fig. 1.—Illustration of Radiation Correction.

temperatures at the ends of these intervals had there been no loss due to radiation, then

$$\theta_1'' = \theta_1' + k\theta_1 \delta t_1 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\theta_2'' = \theta_2' + k\theta_1 \delta t_1 + k\theta_2 \delta t_2 \quad . \quad . \quad . \quad . \quad (2)$$

$$\therefore \theta_n'' = \theta_n' + k(\theta_1 \delta t_1 + \theta_2 \delta t_2 + \ldots . \theta_n \delta t_n)$$

$$= \theta_n' + k(\text{area of the curve } ABM_n A)$$

$$= \theta_n' + k \int_0^t \theta dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We can thus correct any temperature θ'_n if we determine the area $AP_n M_n A$ and k.

An alternative method is to plot the upper curve from the lower curve by increasing the ordinate M_1P_1 to M_1P_1', M_2P_2 to M_2P_2', etc., where $M_1P_1'=\theta_1''$, $M_2P_2'=\theta_2''$, etc. The highest ordinate on the curve (*viz.*, DE) gives the true rise of temperature in the experiment corrected for radiation.

To determine k we have to observe the rate of cooling at any temperature. The curve BC (Fig. 1) is obtained for this purpose experimentally. From this $\frac{d\theta}{dt}$ is calculated for any mean value θ. Now $k=\frac{1}{\theta}\frac{d\theta}{dt}$ hence k is known.*

Another method called the adiabatic method is to eliminate the heat loss by continuously adjusting the temperature of the bath enclosing the calorimeter to be always equal to the temperature of the calorimeter itself.†

5. Specific Heat of Solids.—For finding the specific heat of solids by this method the requisites are a calorimeter with an enclosure, a thermometer and a heater. For work at ordinary temperatures the calorimeter is made of thin copper, nickel-plated and polished on the outside, so as to reduce radiation losses. It is supported on pointed pieces of wood or by means of thread inside a larger double-walled vessel which has water maintained at a fixed temperature in the annular space between the walls. The heater is a steam-jacket in which the substance is heated by steam without becoming wet. An oil bath may also be used. The transference and radiation errors must be reduced by suitable mechanical devices as in Regnault's classical experiments.

For high temperatures the solid substance is heated in an electric furnace. White‡ in his work at high temperatures employed a furnace having a platinum coil wound on its interior surface. The substance is supported inside the furnace in a loop of platinum-wire and is allowed to drop into the calorimeter by a suitable mechanical device. Change in temperature is measured by a resistance thermometer.

* A simple but rough method sometimes adopted is to add to the observed rise half the cooling observed at the highest temperature in a time equal to the duration of the experiment. This is based on the assumption that the average excess of temperature of the calorimeter over the surroundings may be taken to be half the final excess, hence the cooling during the experiment is half the cooling at the final temperature.

† For other methods see Glazebrook, 1 *Dictionary of Applied Physics*, Vol. 1, pp. 61–63.

‡ *Phys. Rev.*, Vol. 31, p. 670 (1910); *Amer. Journ. of Science*, Vol. 47 (1919),

For work at low temperatures the substance is cooled down in a quartz vacuum-vessel* surrounded by liquid air before being dropped into the calorimeter.

The copper block calorimeter devised by Nernst, Lindemann and Koref† is suitable for low temperatures. It consists of a heavy copper block K (Fig. 2) cemented with Wood's metal to the inside of a Dewar flask D. It is essentially a calorimeter based on the method of mixtures in which copper replaces water as the standard substance. The heated substance is dropped into the copper block through the glass tube R and the change in temperature of the latter is read on thermo-couples T, T, whose one end is inside the copper block K and the other end in the block C. The copper block on account of its good conductivity keeps the temperature uniform. Magnus‡ has by a somewhat similar apparatus measured the specific heat of platinum up to about 900°C.

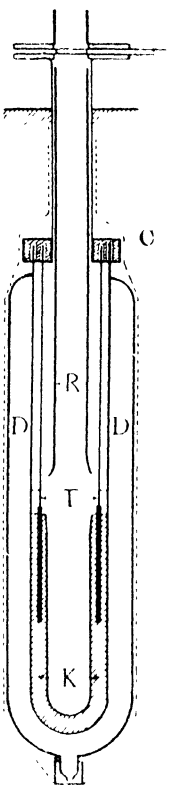


Fig. 2.—Copper Block Calorimeter

Awbery and Ezer Griffiths§ have determined the specific heat of solids and molten liquids as well as their latent heat by using an improved apparatus based on the method of mixtures. This is discussed in Chap. V.

6. Specific Heat of Liquids.—Specific heat of liquids which do not react chemically with water or any other substance of known specific heat may be obtained by direct mixture. For liquids which react in this way Regnault used a different form of apparatus. The liquid was not allowed to mix with water but was admitted when desired into a vessel immersed in water. The liquid was first heated and then forced into the vessel. The specific heat could be calculated as before.‖

* Koref, *Ann. d. Physik*, Vol. 36, p. 49 (1911).
† *Ber. d. Kgl. Pr. Akad. d. Wiss.*, vom. 3 (März), 1910.
‡ *Ann. d. Physik*, Vol 48, p. 983 (1915); *Zeits. f. Physik*, Vol. 7, p. 111 (1921).
§ *Proc. Phys Soc. London*, Vol. 38, p. 378 (1926).
‖ For details see Preston, *Theory of Heat*.

Another class of experiments for measuring the specific heat of liquids involves the expenditure of some mechanical energy and measurement of the consequent rise of temperature. To this class belong the classical experiments of Rowland for determining the mechanical equivalent of heat. They will be described in detail in Chapter III.

2. METHOD OF COOLING

7. This method, perfected by Dulong and Petit, is found to be most convenient for liquids but unsuitable for solids owing to variations of temperature within the latter. The method is based on the assumption that when a body cools in a given enclosure the heat dQ emitted in the time dt is given by the relation

$$dQ = Af(\theta)dt \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where A depends upon the area and the radiating power of the body; $f(\theta)$ is an unknown function of θ, the excess of the temperature of the body over that of the surroundings.

If this produces a cooling of the body through $-d\theta$, we have

$$dQ = -msd\theta$$

where m and s denote the mass and the specific heat of the body respectively.

Equating these two expressions for dQ we get

$$-msd\theta = Af(\theta)dt$$

$$\text{or } t = \frac{ms}{A}\int_{\theta_2}^{\theta_1}\frac{d\theta}{f(\theta)} \quad . \quad . \quad . \quad . \quad (5)$$

where t is the time the body takes in cooling from $\theta_1°$ to $\theta_2°$.

Similarly for another substance to cool through the same interval of temperature

$$t' = \frac{m's'}{A'}\int_{\theta_2}^{\theta_1}\frac{d\theta}{f(\theta)} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If $A = A'$, *i.e.*, the surface area and the radiating power of the two bodies be the same

$$\frac{ms}{t} = \frac{m's'}{t'} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If masses m, m' of two liquids be contained successively in a calorimeter of thermal capacity W and the calorimeter suspended inside a vessel kept at 0°C by immersion in melting ice, and then observations of the rate of cooling taken we have

$$\frac{W+ms}{t} = \frac{W+m's'}{t'} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If one liquid is water ($s=1$), the specific heat of the other is thus determined from a knowledge of t, t', m, m'.

The method is sometimes employed for determining the specific heat of liquids but is not capable of any great accuracy and is mainly of historical interest.

3. METHODS BASED ON CHANGE OF STATE

8. These methods may be subdivided into two: namely, the method of melting ice and the method of condensation of steam. These methods were of real advantage in the last century when accurate measurements of temperature were impossible, but with the recent development of accurate thermometers and electrical heaters they are now less in use, chiefly on account of their inherent defects. The second method is, however, very convenient for determining the specific heat of gases at constant volume and hence retains its importance.

9. Method of Melting Ice.—In this method the heat given out by a certain substance in cooling is imparted to ice and measured by the amount of ice thereby melted. The earliest form of the apparatus, devised by Black, consisted merely of a block of pure ice (Fig. 3) hollowed out to form a cavity which is covered over with another slab of ice to form an ice-chamber. This chamber is carefully dried with a sponge. Then the substance whose specific heat is required is heated to a known temperature and transferred to the ice-chamber where it melts some ice. The water thus produced is estimated by soaking it into a sponge previously weighed, and finding the increase in weight. Thus if M, s, θ denote the

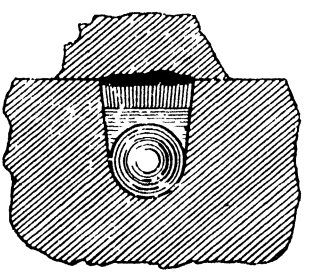


Fig. 3.—Black's Calorimeter.

mass, specific heat and initial temperature of the substance respectively and m the mass of water produced,

$$Ms\theta = mL \quad . \quad . \quad (9)$$

where L is the latent heat of fusion of ice. This gives s the required specific heat. The difficulty of obtaining large masses of pure ice for this experiment led Lavoisier and Laplace to modify the apparatus. Their calorimeter consists of three chambers, one within the other (Fig. 4). The substance B is introduced into the innermost chamber A and melts the ice in the chamber C which is allowed to run out through the tap T and weighed. The chamber D prevents external heat reaching the chamber C and vitiating the results. Considerable error is, however, introduced in estimating the amount of ice melted since water adheres to the broken pieces of ice and the amount of water drained off through the tap does not represent the total amount produced. Further the water in the interspaces between the ice is different initially and finally.

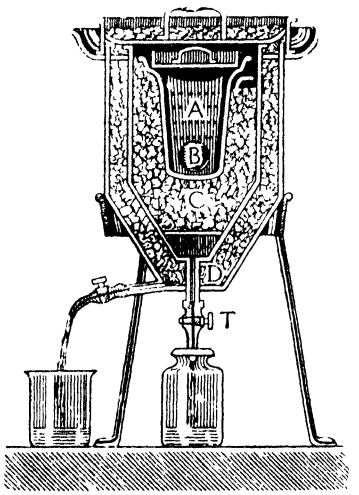


Fig. 4.—Lavoisier and Laplace's Calorimeter.

10. Bunsen's Ice Calorimeter.—The errors mentioned above are eliminated in this calorimeter. The water produced by the melting of ice is not drained off but is allowed to remain mixed with ice and the resulting change in volume observed. The calorimeter is illustrated in Fig. 5. The

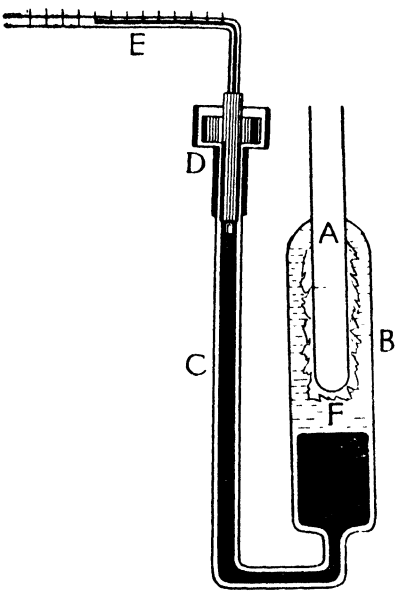


Fig. 5.—Bunsen's Ice Calorimeter

test-tube A is fused into the cylindrical glass bulb B which is provided with the glass stem C. B is nearly filled with boiled air-free water and the remaining space and the stem is filled with mercury. The stem terminates in an iron collar D containing mercury into which a graduated capillary tube E is pushed so that mercury stands at a certain graduation in E.

In conducting an experiment a stream of alcohol, cooled by a freezing mixture, is first passed through the test-tube A until a cap of ice F is formed round it in B. The whole instrument is then kept immersed in pure ice at 0°C for several days till all the water in B is frozen. It is then ready for use.

To calibrate the scale on E, let a mass m of water at a temperature θ°C be poured into the test-tube A. Some ice in B melts and the resulting contraction of mercury, say, n divisions on E is observed. Then if a recession of mercury by 1 division corresponds to q calories of heat

$$m\theta = nq, \text{ or } q = \frac{m\theta}{n}. \quad . \quad . \quad . \quad . \quad (10)$$

Next the substance under investigation, previously heated to a temperature θ' is dropped into some water at 0° contained in the test-tube A. Then if M, s denote the mass and the specific heat of the substance respectively, and n' the observed recession of mercury thread in E, we have

$$\mathrm{M}s\theta' = n'q$$

or

$$s = \frac{n'}{\mathrm{M}\theta'}q = \frac{mn'}{\mathrm{M}n}\frac{\theta}{\theta'}. \quad . \quad . \quad . \quad (11)$$

This gives the specific heat of the substance. The specific heat of rare metals which can be had in small quantities can be readily found by this method.

The accuracy attained by this apparatus is, however, limited. The ice in the surrounding vessel may not be at the same temperature as that in the vessel B, thus a progressive heating or cooling of ice in B may take place. The necessary correction may be obtained by observing the rate of recession of mercury before and after the experiment. The error due to this cause is minimised considerably by placing the instrument in an empty vessel surrounded by ice as proposed by Boys, or, better still, by enclosing it in a Dewar flask. But a serious objection to the use of the ice-calorimeter rests on the fact that a given specimen of water can freeze into ice of different densities.

11. Joly's Steam Calorimeter.—In the steam calorimeter devised by Prof. Joly* in 1886 the heat necessary to raise the temperature of a substance from the ordinary temperature to the temperature of steam is measured by the amount of vapour condensed into water at the same temperature. It consists of a thin metal enclosure A (Fig. 6), double-walled and covered with cloth, which is placed beneath a sensitive balance. One pan of the balance is removed and from this end of the beam hangs freely a wire *w* supporting a platinum pan P inside the enclosure. The substance whose specific heat is required is placed on this pan and weights added on the other pan till balance is attained. The temperature of the enclosure is observed by means of a thermometer inserted into the chamber, and in the meantime steam is prepared in the boiler. It is then admitted suddenly into the chamber through the wide opening O at the top and can escape through the narrow exit-tube *t* at the bottom. Steam condenses on the substance and the pan and weights are added on the other pan to maintain the equilibrium. When the pan ceases to increase in weight the readings are noted and the temperature

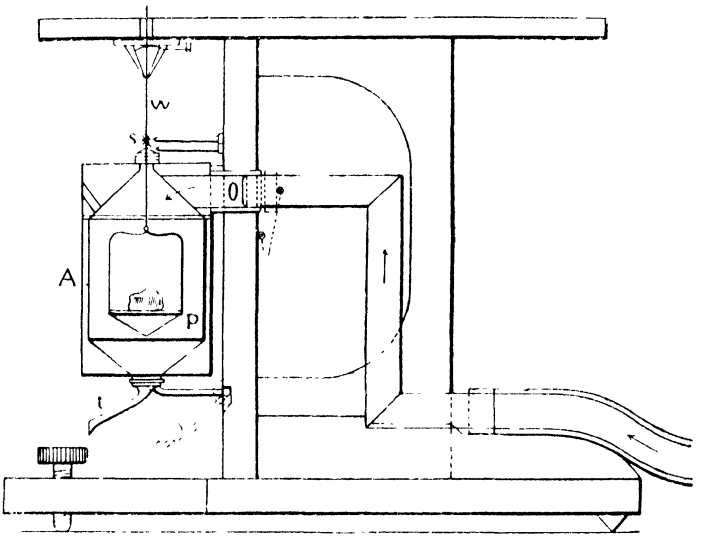


Fig. 6.—Joly's Steam Calorimeter.

of the steam read on a thermometer. During the final weighing the steam is allowed to enter the chamber through a narrow escape-tube so as not to

* *Proc. Roy Soc.*, Vol. 41, p. 352 (1886).

disturb the pan. The weight becomes practically constant in four or five minutes though a very slow increase of about 4 milligrams per hour may be observed due to radiation. The difference between the two weighings gives the weight of steam condensed.

If W is the weight of the substance,
w the increase in weight of the pan,
θ_1 the initial temperature of the enclosure,
θ_2 the temperature of steam,
k the thermal capacity of the pan,
L the latent heat of steam,
s the required specific heat,

then

$$Ws\,(\theta_2 - \theta_1) + k\,(\theta_2 - \theta_1) = w\mathrm{L}. \quad . \quad . \quad (12)$$

k is determined from a preliminary experiment without any substance on the pan and thus the specific heat of the substance is found.

For great accuracy various precautions and corrections are necessary. Steam condenses on the suspending wire where it leaves the chamber and then surface tension renders accurate weighing difficult. A thin spiral s of platinum wire in which a current flows, usually surrounds the suspending wire just above the opening, and is made to glow so that the heat developed is just sufficient to prevent condensation. A rapid introduction of steam is necessary in the early stages, for steam also condenses on the pan due to radiation to the cold air and the chamber, thus causing error. This is of course partially balanced by radiation from the steam to the substance later. Further w does not accurately represent the weight of steam condensed since the first weight is taken in air at θ_1°C and the second in steam at θ_2°C. All the weighings must be reduced to vacuum and then the increase in weight calculated. Specific heat of rare substances can be found by this method since small quantities of the substance are needed but a sensitive balance is indispensable. The specific heat of liquids and powders can be found by enclosing them in glass or metal spheres whose thermal capacity is taken into account. Gases can also be similarly enclosed, but then the modified form of the apparatus—the differential calorimeter—is used.

12. The Differential Steam Calorimeter.—In this form invented by Prof. Joly* in 1889, both the balance pans are made exactly similar and of equal thermal capacity and hang in the same steam-chamber (Fig. 7, p. 40). The substance to be tested is placed on one pan and the excess of steam condensing on this pan over that on the other pan is

* *Proc. Roy. Soc.*, Vol. 47, p. 218 (1889)

entirely due to the substance. Thermal capacity of the pans, radiation from them and all other sources of error common to them are eliminated, the substance bearing only its own share of the error. The chief use of this apparatus, however, consists in the determination of the specific heat of gases at constant volume. The pans are then replaced by two equal hollow spheres of copper furnished with "catch-waters" (shown in the figure). One sphere is filled with the dried experimental gas at any desired pressure while the other is empty. These spheres are counterpoised by adding necessary weights m which represent the mass of the contained gas. Steam is admitted and condenses on the pans. A larger amount of steam condenses on the sphere containing the gas, the excess, say w, giving the amount of steam required by the gas. Now the specific heat at constant volume, c_v may be calculated from the equation

$$mc_v(\theta_2-\theta_1)=wL \quad . \quad . \quad (13)$$

where θ_2, θ_1 are the final and initial temperatures of the chamber.

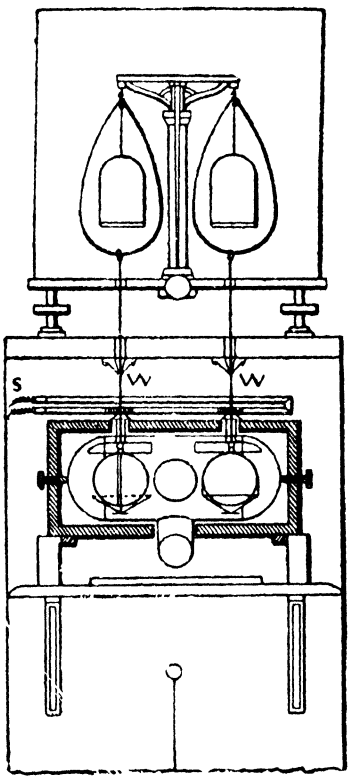


Fig. 7.—The Differential Steam Calorimeter

Prof. Joly used copper spheres of diameter 6·7 cms. and weighing 92·2 gms. and employed gases at different pressures. Corrections were applied for the following:

1. The expansion of the sphere due to increased temperature and the consequent work done by the gas in expanding to this volume.
2. The expansion of the sphere due to the increased pressure of the gas at the higher temperature.
3. The thermal effect of this stretching of the material of which the sphere is made.
4. The increased buoyancy of the sphere due to its increased volume at the higher temperature.
5. The unequal thermal capacities of the spheres.
6. The reduction of the weight of water condensed to its weight in vacuum.

Quite recently* the steam calorimeter has been employed to measure the latent heat directly in terms of the mean calorie.

Dewar† has devised calorimeters based on an analogous principle in which he employed a liquefied gas as the calorimetric substance. The heat to be measured is applied to the liquefied gas whereby the liquid evaporates absorbing its latent heat and the volume of gas given off by the liquid is measured. Using liquid oxygen and liquid hydrogen the apparatus can be adopted for very low temperatures.

4. ELECTRICAL METHODS

13. The electrical method was first employed by Joule in his attempts to determine the mechanical equivalent of heat. The electrical methods at present available may be subdivided into two:

(1) Method based on the observation of rise of temperature.

(2) Method employing the steady-flow electric calorimeter.

We shall first consider the application of these methods to liquids because historically the method was first applied to them.

14. Methods Based on the Rise of Temperature.—Following Joule this method was adopted by many workers the chief among them being Griffiths.‡ Schuster and Gannon.§ Bousfield and Bousfield.‖ They employed this method for determining the mechanical equivalent of heat and found that it was capable of the highest accuracy. The same arrangements may be employed for finding the specific heat of liquids.

The principle of the method is to generate heat by passing a current through a conducting wire. If i is the current through the wire of resistance R and E the potential difference across its ends, the energy spent in a time t seconds is Eit ergs, provided E and i are expressed in electromagnetic units. If this raises the temperature of M grams of a substance by $\delta\theta°$, the specific heat s of the substance is given by the relation

$$Eit = JMs\,\delta\theta \quad . \quad . \quad . \quad . \quad . \quad (14)$$

* *Proc. Roy. Soc.*, A, Vol. 93, p. 155 (1917).
† *Proc. Roy. Soc.*, A, Vol. 76, p. 325 (1905); Vol. 89, p. 158 (1913)
‡ *Phil. Trans.*, A, Vol. 211, p. 236 (1911).
§ *Phil. Trans.*, A (1893); *Proc. Roy. Soc.*, Vol. 55 (1894).
‖ *Phil. Trans.*, A (1895)

where J is the mechanical equivalent of heat (see Chap. III). If E is expressed in volts and i in amperes the energy spent is given in Joules (1 Joule $= 10^7$ ergs.).

Any two of the quantities E, i, and R may be measured, thus giving three methods. Griffiths, in his determination of the specific heat of water, chose to measure E and R which is rather difficult, for R must be measured during the heating experiment. He attempted to get over this difficulty by performing a series of subsidiary experiments to determine the temperature coefficient of the resistance of the wire and the difference in temperature between the liquid and the wire. He used the ordinary calorimeter containing water which was heated by the current carrying wire immersed in it and the rise in temperature observed. The foregoing formula gives the specific heat. His calorimeter was enclosed in a partially evacuated space surrounded by a constant temperature bath.

Griffiths' work is important since it first established the fact that the electrical method can accurately give the value of J in absolute units. Schuster and Gannon measured E and i.

Quite recently Jaeger and Steinwehr* have applied this method to determine the mechanical equivalent of heat and hence also the specific heat at different temperatures. They used a large mass of water (about 50 kgm.) and a very small rise of temperature (1·4°C). In their work they aimed at an accuracy of 1 in 10,000 and their results are very reliable.

15. The Method of Steady-flow Electric Calorimeter.—Very great accuracy has been attained by Callendar and Barnes† by using the

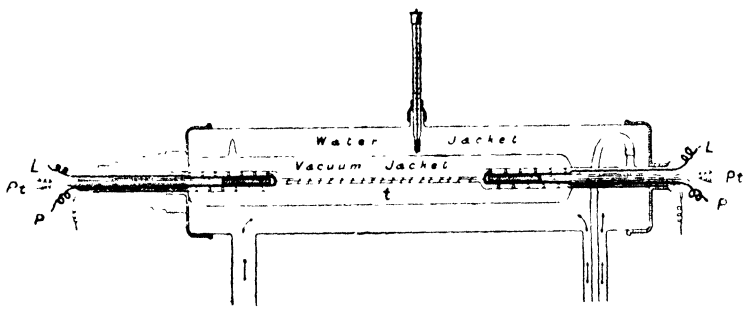


Fig. 8.—Steady-flow Electric Calorimeter

* *Ann. d. Physik*, Vol. 61, p. 305 (1921).
† *Phil. Trans.*, A, Vol. 199, p. 55 (1902).

steady-flow electric calorimeter shown in Fig. 8. A steady current of the experimental liquid flowing through the narrow glass-tube t, about 2 mm. in diameter, is heated by an electric current flowing through the central conductor of platinum. The steady difference of temperature $\delta\theta$ between the inflowing and outflowing water is measured by a pair of differential platinum thermometers *pt*, *pt* at the ends. The bulb of each thermometer is surrounded by a thick copper tube of negligible resistance attached to the central conductor. This on account of its good conductivity keeps the whole bulb at the temperature of the adjacent water, and due to its low resistance prevents the generation of any appreciable amount of heat by the current near the thermometer. The leads L, L and P, P are attached to this tube of copper, the former for introducing the heating current and the latter for measuring the potential difference across the central conductor in terms of a standard Clark cell by means of an accurately calibrated potentiometer. The potentiometer also serves to measure the heating current i by measuring the potential difference across a standard resistance included in the same circuit. In order to diminish the external loss of heat the flow tube is enclosed in a hermetically sealed glass vacuum-jacket surrounded by a constant temperature bath.

Neglecting small corrections the general equation is

$$Eit = JMs\,\delta\theta + h \quad . \quad . \quad . \quad . \quad . \quad (15)$$

employing the same notation as before, where h denotes the heat loss due to radiation, etc. The time of flow t in these experiments was 20 minutes and was recorded automatically on an electric chronograph. The mass of water M was measured by collecting the outflowing water. The difference in temperature $\delta\theta$ was from 8° to 10°C and was accurately read to ·001°C. The heat loss h was very small and regular, and was determined and eliminated by suitably adjusting the electric current so as to secure the same rise of temperature for different rates of flow of the liquid. The specific heat s thus determined is the average specific heat for the interval $\delta\theta$ and may be taken as the specific heat at the middle of the interval.

The great advantage of this steady-flow electric method is that no correction is necessary for the thermal capacity of the calorimeter since there is no change of temperature in any part of the instrument. Care must, however, be taken to secure perfect steadiness, as it is practically

impossible to correct for unsteady conditions. Further, since all conditions are steady, the observations can be taken with the highest degree of accuracy. The thermometers used are very sensitive and have no lag. It is essential, however, that the current of water be thoroughly mixed; this is secured by having the central conductor in the form of a spiral instead of a straight wire.

Callendar and Barnes used this method to find the specific heat of water at various temperatures. Their results are discussed in the next article. Callendar* found the specific heat of mercury by this method. The central conducting wire was dispensed with, the flowing mercury itself serving as the conductor. Griffiths† employed this method to determine the specific heat of aniline over the range 15° to 50°C.

16. Specific Heat of Water.—In ordinary calorimetric experiments the specific heat of water is supposed constant at all temperatures and equal to unity. Accurate investigations of the last article, however, show that it varies with temperature. The earliest experiments to determine this variation such as those of Regnault, Plaundler and Platter, Hirn and others, were based on the method of mixtures and showed in general that the specific heat increased with temperature. The first accurate experiments in this connection were those of Rowland‡ in connection with his determination of the mechanical equivalent of heat (Chap. III). He argued that if the specific heat of water at all temperatures were constant this mechanical equivalent must come out a constant quantity even if we used water at different temperatures. The variation in the value of J was due to the variation in specific heat. From his values of J he concluded that water had a minimum specific heat at about 30°C. Similar results were obtained later by Bartoli and Stracciati and by Ludin using the method of mixtures.

The most accurate experiments on the subject are those of Callendar and Barnes (sec. 15). By this method the specific heat can be accurately investigated at various temperatures. According to Barnes, the specific heat of water is minimum at 37·5°C. Jaeger and Steinwehr (sec. 14), however, find the minimum at 33·5° and their values at other temperatures differ slightly from those given by Callendar. But Callendar's results

* *Phil. Trans.*, A, Vol. 199, p. 104 (1902).
† *Phil. Mag.*, 1895 *Proc. Camb. Phil. Soc.* (1895), Vol. 8, part 4.
‡ *Proc. Amer. Acad. of Arts and Sciences*, Vol. 7, (1879-80).

have been confirmed later by an entirely different method and hence appear to be more reliable.

In Table 1 we give the specific heat of water according to Callendar and Barnes, and Jaeger and Steinwehr, together with the amount of energy in international Joules* required to raise the temperature of 1 gram of water by 1°C at various temperatures. The values given in the second column have been plotted in Fig. 9.

Table 1.—Specific Heat of Water at different temperatures.

Temp. °C.	Specific Heat (Callendar and Barnes)	Specific Heat (Jaeger and Steinwehr)	Heat capacity in int. Joules (J & S)	Temp. °C.	Specific Heat (Callendar and Barnes)
0	1·0093	(1·005)	(4·205)	60	0·9987
5	1·0047	1·0029	4·1966	70	1·0000
10	1·0019	1·0013	4·1897	80	1·0017
15	1·0000	1·0000	4·1842	90	1·0036
20	0·9988	0·9990	4·1800	100	1·0057
25	0·9980	0·9983	4·1771	120	1·0108
30	0·9976	0·9979	4·1755	140	1·0167
35	0·9973	0·9978	4·1753	160	1·0234
40	0·9973	0·9981	4·1764	180	1·0309
45	0·9975	0·9987	4·1788	200	1·0392
50	0·9978	0·9996	4·1855		

Since the specific heat varies with temperature the calorie must be defined with respect to any particular temperature. Callendar adopts

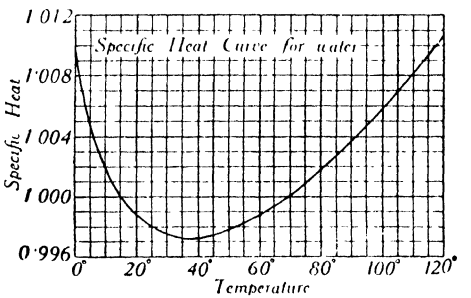


Fig. 9.—Specific Heat Curve for Water.

20°C, but the majority of scientists favour 15°C, *i.e.*, the amount of heat required to raise the temperature of 1 gram of water from 14·5°C to 15·5°C.

* 1 int. Joule = $1·0005 \times 10^7$ ergs.

Specific Heat of Solids.

17. Rise of Temperature Method.—The electrical method was first applied to solids by Gaede* in 1902. Griffiths and Griffiths† determined the specific heat of many metals over the range $-160°$ to $+100°$C. The substance was used in the form of a calorimeter and was first cooled below the desired temperature. Electrical energy was utilised in heating the calorimeter and the temperature indicated by a resistance thermometer. The calorimeter was enclosed in a constant temperature bath and radiation correction applied.

18. Nernst Vacuum Calorimeter.—A different form of the apparatus, known as the vacuum calorimeter, was used by Nernst and Lindemann‡ for measuring specific heat at very low temperatures.

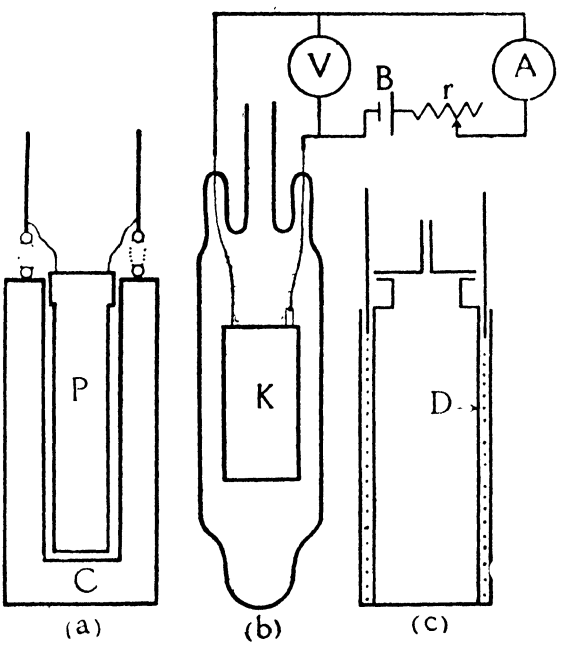


Fig. 10.—Nernst Vacuum Calorimeter.

* *Phys. Zeits.*, Vol. 4, p. 105 (1902).
† *Phil. Trans.*, A, Vol. 213 (1913). *Proc. Roy. Soc.* A, Vol. 89, p. 561 (1913).
‡ *Journal de Physique*, [4] 1910, Vol. 9; *Ann. d. Physik*, Vol. 36, p. 395 (1911).

This differed from Gaede's form essentially in having the calorimeter suspended in vacuum. The results achieved with its aid are of great theoretical importance and hence their apparatus will be considered in some detail. For good conducting solids such as metals the calorimeter shown in Fig. 10 (a) was used. The substance whose specific heat is to be determined is shaped into a cylinder C, having a cylindrical hole drilled almost through its entire length, and a closely fitting plug P made for it from the same material. The substance here acts as its own calorimeter. The plug is wound over with a spiral wire of purest platinum (shown dotted in the figure) which is insulated from it by means of thin paraffined paper, and finally liquid paraffin is poured over it. The upper part of the plug is somewhat thicker than the lower part, thus a good thermal contact is obtained. The calorimeter K thus constructed is suspended inside a pear-shaped glass bulb [shown at (b)] which can be filled with any gas or evacuated. The whole can be surrounded by suitable low temperature baths such as liquid air or liquid hydrogen. The platinum spiral, which serves both as electric heater and resistance thermometer, is connected in series with the battery B, resistance r and a precision ammeter A, the voltmeter V indicating the potential difference across the spiral. In order to bring the calorimeter to the desired temperature of experiment, hydrogen which is a good conductor of heat was first admitted into the pear-shaped vessel and the latter surrounded by a suitable bath. Next the vessel was completely evacuated so that the heat losses from conduction and radiation were almost entirely eliminated. In addition it was surrounded by liquid air or liquid hydrogen.

To carry out an experiment a current was allowed to flow through the heater for t seconds and the voltage across it was adjusted to be constant by varying the resistance r. If R_f, R_i and i_f, i_i denote the final and initial values of the resistance of the heater and the current through it respectively, and E the constant potential difference,

$$R_f = \frac{E}{i_f}; \quad R_i = \frac{E}{i_i}. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Thus an observation of i_f, i_i and E gives R_f and R_i, and from a previous determination of the resistance of the platinum spiral at various temperatures the rise in temperature $\delta\theta$ can be found. The energy supplied electrically is Eit where i is the average value of the current. Now if M

is the mass of the substance forming the calorimeter. s its specific heat. we have, as on p. 13

$$Eit = JMs\ \delta\theta + h. \quad . \quad . \quad . \quad . \quad (15)$$

This gives the specific heat at a single temperature since $\delta\theta$ is usually 1° or 2°. The heat capacity of the paper and paraffin can be found and eliminated by taking different amounts of the substance and at the same time arranging that the temperature rise is the same. The heat loss h is very small and is determined and accounted for by observing the rate of cooling.

For *non-conducting* solids the calorimeter shown in Fig. 10 (c) was employed. The heating wire was wound over a cylindrical silver vessel D and the whole covered with silver foil to diminish heat loss. This foil was soldered at the bottom of the cylinder as indicated. The solid whose specific heat is required was placed inside the silver cylinder and the latter closed with the lid. The silver on account of its high conductivity keeps the temperature uniform and this is further secured by filling the cylinder with hydrogen through the tube in the lid. The tube is then closed. Liquids and gases can be similarly admitted into the cylinder and their specific heat determined.

19. Results of Early Experiments.—In 1819 Dulong and Petit from their investigations concluded that the product of atomic weight and specific heat was constant for many substances, or in other words, *atoms of all substances have the same capacity for heat.* Regnault from his own researches found that for ordinary substances the mean value of the constant was 6·38 with extremes of 6·76 and 5·7. A more accurate value of the constant can be obtained from the kinetic theory (Chap. III). The atomic heat at constant volume is there shown to be equal to $3R = 5{\cdot}955$. According to Richarz, the value of the ratio c_p/c_v for many substances lies between 1·01 and 1·04, hence the atomic heat at constant pressure, the quantity commonly determined should lie between 6·01 and 6·19. This law is of great use in determining atomic weights. In illustration of the law, the following table* of specific heats is added.

* Taken from *Handbuch der Experimentalphysik*, Vol. 8, p. 193

Table 2.—Illustration of Dulong and Petit's law.

Element.	Atomic weight (1)	Mean specific heat (2).	Atomic heat (1)×(2)
Sodium	23·00	0·307	7·06
Magnesium	24·32	0·247	6·00
Aluminium	27·1	0·2175	5·83
Iron	55·84	0·110	6·14
Nickel	58·68	0·1092	6·41
Copper	63·57	0·0930	5·92
Zinc	65·37	0·0939	6·14
Silver	107·9	0·0559	6·03
Cadmium	112·4	0·0557	6·26
Tin	118·7	0·0556	6·60
Antimony	121·8	0·0502	6·10
Platinum . .	195·2	0·0318	6·21
Gold	197·2	0·0309	6·10
Lead	207·2	0·0310	6·43
Bismuth	209·0	0·0299	6·22

Mean value=6·24

In 1831 Neumann enunciated a similar law concerning molecular heats: the *product of the specific heat and the molecular weight of compounds of similar composition is nearly constant.* The value of the constant varies from one series of compounds to another. In illustration of the law the following table* is added.

Table 3.—Molecular Heat of Oxides

Compound.	Specific heat (1)	Molecular weight (2)	Molecular heat (1)×(2)
Fe_2O_3 .. .	0·1700	159·8	27·2
Cr_2O_3 . . .	0·1796	152·0	27·4
As_2O_3	0·1277	197·8	25·3
Sb_2O_3	0·0901	287·8	25·9
Bi_2O_3	0·0605	464·8	28·1

Mean value=26·8

* Taken from *Handbuch der Experimentalphysik*, Vol 8, p. 200.

Neumann's law can be considered as a particular case of the following law: The molecular heat of a compound may be considered as the sum of the atomic heats of its constituents. Thus, if a compound has the composition $A_a B_b C_c D_d$ its molecular heat C_p is given by the relation

$$C_p = aC_{p_A} + bC_{p_B} + cC_{p_C} + dC_{p_D} \quad . \quad . \quad (17)$$

where A, B, C, D stand for the different types of atoms composing the compound and C_{p_A}, C_{p_B}, etc., their atomic heats given by Dulong and Petit's Law. The law is of much use in evaluating the molecular heats of certain substances.

20. Variation of Specific Heat with Temperature.—The specific heat as determined by the foregoing methods is not found to be a constant quantity. For solids and liquids pressure has little or no effect on specific heat. Rise of temperature, however, in general, produces an increase in the specific heat. Various empirical formulæ have been proposed from time to time indicating the effect of pressure and temperature on the specific heat. The specific heat at very low temperatures shows a marked decrease. To illustrate this a short table indicating the specific heats at 50°A is appended below:—

Table 4.—Specific Heat at 50°A.

Substance	Specific heat	Substance	Specific heat
Lithium ...	0·1924	Magnesium .	0·063
Silver	0·0242	Bismuth ...	0·0218
Copper ...	0·0226	Aluminium ..	0·0413
Lead	0·0250	Antimony ...	0·0240

These variations have been successfully accounted for only in recent years by the quantum theory of specific heats.* The earlier observations are accounted for by the kinetic theory (Chap. III).

21. Two Specific Heats of a Gas.—The specific heat of a gas, as of solids and liquids, may be defined as the ratio of the heat absorbed to the rise in temperature, taking a unit mass of the gas. A little consideration will show that this definition requires to be restricted. Imagine a quantity of gas to be suddenly compressed. The temperature of the gas will be found to rise, though no heat has been added. The ratio,

* See the Authors' *Treatise on Heat*, Chap. XVI.

heat added/increase in temperature, i.e., specific heat, vanishes. Again let this compressed air expand suddenly; a cooling would take place. This is just prevented by applying some heat to the gas. In this case the ratio, *heat added/change in temperature*, becomes infinite. Thus we see that the original definition gives an infinite range of values for the specific heat. Hence external conditions are of paramount importance in determining the specific heat of gases. It has become customary to speak of two specific heats of a gas: the specific heat at constant volume denoted by c_v and the specific heat at constant pressure denoted by c_p. In the former process the gas is maintained at constant volume so that the whole heat applied goes to increase the intrinsic energy of the gas. In the latter case the gas is allowed to expand against a constant pressure and in so doing it does external work. This work is obtained by using up part of the heat energy applied to the gas.

Let us assume that the gas is perfect, *i.e.,* its molecules exert no influence on one another. This is approximately true for the permanent gases as Joule's experiment (sec. 22) shows. Hence in this expansion no internal work against molecular attractions is done by the gas and the excess of heat supplied in the second case is simply the thermal equivalent of the external work. Consider the gas enclosed at pressure p, in a cylinder of height x and cross-section A and let the gas on expansion occupy a length $x+\delta x$. The work done is $pA\delta x = p\delta V$ where δV is the change in volume. Suppose a gramme-molecule of the gas, occupying a volume V_1 at temperature T° A and pressure p, expands to a volume V_2 at temperature (T+1)° A. Let $Mc_p = C_p$, $Mc_v = C_v$ where M is the molecular weight of the gas. C_p and C_v may be called molecular specific heats. The work done by the gas in expanding from V_1 to V_2 is

$$p(V_2 - V_1) = R\,[(T+1) - T] = R \quad . \quad . \quad . \quad (18)$$

by the gas laws. The thermal equivalent* of this work is $J(C_p - C_v)$.

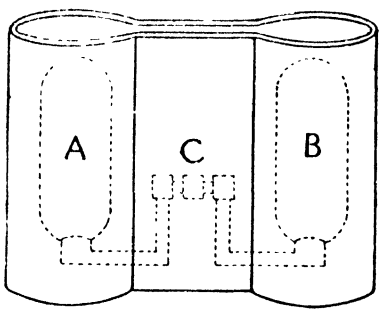
$$\therefore J(C_p - C_v) = R\dagger \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

or $C_p - C_v = R$, if either R is expressed in calories, or C_p, C_v measured in ergs.

* This assumes the First law of Thermodynamics which will be discussed in Chapter III.

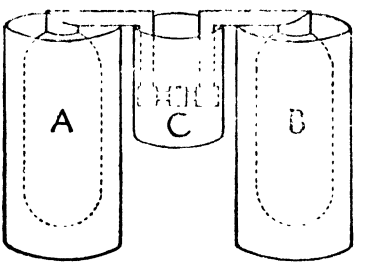
† This is true for a perfect gas only. For real gases it can be shown that $C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p$ where the differentials must be evaluated from the actual equation of state (Chapter IV) for the gas.

22. Experiments of Gay-Lussac and Joule.—Gay-Lussac first carried out experiments to determine whether a gas does any internal work in expanding. He allowed gas contained in a vessel at a high pressure to expand into an evacuated vessel and observed the fall of temperature in one and the rise of temperature in the other vessel. Somewhat later, Joule employed a similar apparatus but he immersed the vessels in calorimeters. His apparatus is indicated in Figs. 11 and 12. The two vessels A and B communicated with each other through a tube furnished with a stop-cock C. A was filled with dry air at 22 atmospheres while B was exhausted. First the whole apparatus was placed in a single calorimeter (Fig. 11) and the stop-cock C opened. No change in temperature of the water was observed showing that no internal work against molecular attractions was done by the gas in expanding. To investigate the point further, the parts A, B, C were placed in separate vessels (Fig. 12) containing water whose temperatures could be read by sensitive thermometers. On opening the stop-cock C the air expanded into B and the temperature of the vessel surrounding A fell while the temperatures of B and C rose. It was found that the heat lost by A was exactly equal to the sum of the



Joule's experiment with one calorimeter

Fig. 11.



Joule's experiment with two calorimeters

Fig. 12.

heats gained by B and C, thus the total change in the energy of the gas during expansion is zero, *i.e.*, $\left(\frac{\partial U}{\partial V}\right)_T = 0$ where U is the internal energy and V the volume. This is called Joule's law or Mayer's hypothesis. This shows clearly that no internal work is done by a gas in expanding. Joule's law holds only for the perfect gas to which the permanent gases

of Nature as helium, hydrogen, etc., approximate. For further discussion see Chap. VI, sec. 13 and Chap. X, sec. 33.

23. Adiabatic Transformations.—When the pressure and volume of a substance change but no heat is allowed to enter or leave it, the transformations are said to be adiabatic. In an isothermal change the temperature is kept constant by adding heat to or taking it away from the substance. Consider an amount of heat dQ applied to a perfect gas. This is spent in raising the temperature of the gas and in doing external work. If we consider a gramme-molecule of the gas, the former is equal to $C_v\,dT$ and the latter to $\frac{pdv}{J}$, both in calories. Hence

$$dQ=C_v dT+\frac{pdv}{J},$$

or, if dQ and C_v are measured in ergs,

$$dQ=C_v\,dT+pdv \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This equation combined with $pv=RT$ will give the solution of all problems on perfect gases.* In an adiabatic transformation $dQ=0$. Therefore

$$C_v\,dT+pdv=0 \quad . \quad . \quad . \quad . \quad . \quad (21)$$

In order to find a relation between p and v we must eliminate T from (21) by means of the gas equation $pv=RT$. Differentiating the latter, we have

$$pdv+vdp=R\,dT \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Substituting for dT from (22) in (21), we get

$$C_v\frac{pdv+vdp}{R}+pdv=0,$$

and replacing R by C_p-C_v,

$$C_v vdp+C_p pdv=0.$$

Denoting C_p/C_v by γ we obtain

$$\frac{dp}{p}+\gamma\frac{dv}{v}=0,$$

* For real gases instead of $pv=RT$, and $C_p-C_v=R$, we must substitute the actual equation of state and the true value of C_p-C_v. We shall then get the relation between p, v, and γ for real gases.

which on integration yields

$$\log p + \gamma \log v = \text{constant}$$

or
$$pv^{\gamma} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

This is the adiabatic relation between p and v.

To find the adiabatic relation between T and v or between T and p we must respectively eliminate p or v between equation (23) and the gas equation $pv = RT$. The results are

$$Tv^{\gamma - 1} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$Tp^{\frac{1-\gamma}{\gamma}} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (25)$$

24. Experimental Methods.*— Let us now consider the experimental methods of finding the specific heats of gases. Since for perfect gases $C_p - C_v = R$, a knowledge of one of the specific heats gives the other. Again if we determine γ, *i.e.*, C_p/C_v, the above relation will give both C_p and C_v. Hence the experimental methods may be divided into three classes:

(a) The measurement of C_p

(b) The measurement of C_v

(c) The determination of γ.

(a) MEASUREMENT OF C_p

25. The specific heat at constant pressure has been found either by the Method of Mixtures or by the Constant-Flow Method. The principle of these methods has already been described.

26. Method of Mixtures—Regnault's Apparatus.—This method was first applied to gases by Lavoisier and Laplace. Improvements were made later by Delaroche and Berard, Haycroft and Regnault. Regnault with his great experimental skill obtained results of high accuracy. His apparatus is indicated in Fig. 13. Pure dry gas was compressed in the reservoir A which was immersed in a thermostat. The reservoir was provided with a manometer (not shown). Gas could be allowed to flow through the stop-cock V at a uniform rate. This was effected by

* The reader will find a very good account of these methods in Partington and Shilling : *Specific Heat of Gases.*

continuously adjusting the stop-cock V (shown separately) so that the pressure indicated by the manometer R was constant. The gas then flowed through a spiral S immersed in a hot oil-bath and then into the calorimeter C finally escaping into the air. The gas acquired the temperature T of the bath and raised the temperature of the calorimeter say from θ_1 to θ_2.

If m is the mass of the gas that flows into the calorimeter, c_p its

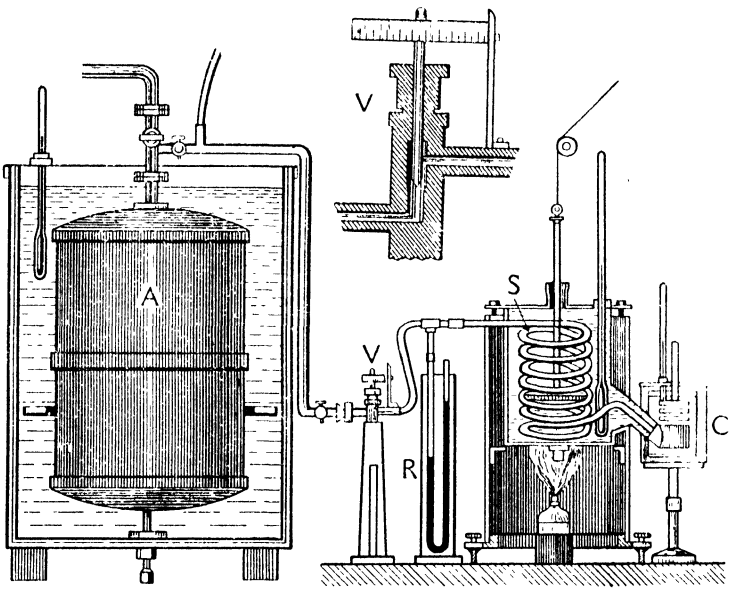


Fig. 13.—Regnault's Apparatus for C_p

specific heat is given by

$$mc_p \left(T - \frac{\theta_1+\theta_2}{2} \right) = w(\theta_2-\theta_1) . \quad . \quad (26)$$

where w is the thermal capacity of the calorimeter and its contents. The mass m of the gas was determined by Regnault as follows:—for any pressure p he assumed that the weight W of the gas contained in the reservoir at temperature θ was given by the relation

$$W(1+\alpha\theta) = Ap + Bp^2 + Cp^3$$

where A, B, C were determined from a series of preliminary experiments. Hence the weight W′ of gas corresponding to the observed pressure p' at the end of the experiment is given by

$$W'(1+\alpha\theta) = Ap' + Bp'^2 + Cp'^3.$$

Thus $W'-W$, *i.e.*, the weight of the gas that flowed out was found.

In practice corrections are necessary for the loss or gain of heat by conduction, convection and radiation which cannot be accurately determined. Regnault corrected for them by observing the variation in temperature of the calorimeter before and after the experiment. If $\delta\theta$, $\delta\theta'$ denote this variation in temperature of the calorimeter per minute, t_0, t_0' the mean temperature of the air and θ_0, θ_0' the mean temperature of the calorimeter before and after the experiment respectively,

$$\delta\theta = A\ (\theta_0 - t_0) + k$$

$$\delta\theta' = A\ (\theta_0' - t_0') + k$$

A is a factor depending upon radiation and k upon conduction from the oil-bath. These two equations give A and k. If the experiment lasts for n minutes and t_1, t_2 denote the temperature of the air initially and finally, the change in temperature $\Sigma d\theta$ due to these causes during the experiment is

$$\Sigma d\theta = n\left[A\left(\frac{\theta_1+\theta_2}{2} - \frac{t_1+t_2}{2}\right) + k\right]. \quad . \quad (27)$$

This can be calculated if the mean temperatures of the calorimeter and air are observed. The heat given by the gas is thus equal to

$$w(\theta_2 - \Sigma d\theta - \theta_1) \quad \text{and not } w(\theta_2 - \theta_1).$$

27. Other Experiments.—The experiments of Wiedemann* were essentially similar to those of Regnault. Lussana devised a high-pressure apparatus in which the same amount of gas enclosed at a high pressure can be repeatedly heated and passed through the calorimeter. The principle employed is the same as in Regnault's experiment. This apparatus can be used to find the specific heat of gases at very high pressures and possesses the advantage that the gas is not wasted. Lussana found that the specific heat at constant pressure increased with increasing pressure according to the relation

$$c_p = a + b(p-1)$$

where a, b are constants peculiar to the gas.

* *Ann. d. Physik*, Vol. 157, p. 1 (1876).

For determining the specific heat at high temperatures the experiment of Holborn and Henning* may be mentioned. Employing suitable electric heaters, resistance thermometers and well-designed calorimeter they were able to find the specific heats of nitrogen, carbon-dioxide and steam up to 1400°C. The same method has been used by Nernst† in finding the specific heat of ammonia up to 600°C.

28. Constant-flow Method.—For finding the variation of specific heat with temperature the constant-flow method is most suitable, and was first used by Swan.‡ The most recent form of the apparatus is that used by Scheel and Heuse in finding the specific heat down to very low temperatures.

The gas under test, previously brought to a steady temperature by passing through a suitable bath, flows through the calorimeter in a steady stream. Inside the calorimeter it is heated electrically by a heating coil of constantan and thus the energy supplied can be calculated. The temperatures of the incoming and outgoing gases are observed by resistance thermometers. The specific heat can be calculated by an equation similar to (15).

For work at low temperatures the gas was initially passed through a low temperature bath in which the calorimeter was also immersed. In studying helium and other rare gases Scheel and Heuse§ modified the apparatus so as to employ a closed circuit. These experimenters carried out measurements on various gases in the range 0 to −130°C.

For measurement of specific heat at high pressures the constant-flow method has been employed by Holborn and Jakob‖ and gives the most reliable results.

(*b*) METHODS BASED ON THE MEASUREMENT OF C_v

29. Steam Calorimeter.—The direct determination of C_v is best made by means of Joly's steam calorimeter (sec. 12). The method of carrying out the experiment and the necessary details will be found in that section.

* *Ann. d Physik*, Vol. 23, p. 809 (1907).
† *Zeits. f. Electrochemie*, Vol 16, p. 96 (1910).
‡ *Proc. Roy. Soc.*, A, Vol. 82, p. 147 (1909), or *Phil. Trans.*, A, Vol. 210, p. 199 (1910).
§ *Ann. d. Physik*, Vol. 37, p 79 (1912); Vol. 40, p. 473 (1913); Vol. 59, p. 86 (1919).
‖ *Berl. Ber.*, Vol 1, p 213 (1914).

30. Explosion Method.—Following the work of Bunsen, Vieille and others, Pier* improved the explosion method and devised the modern explosion bomb indicated in Fig. 14. Immersed in the water-bath B is a steel-bomb A which has a side-tube M through which the bomb can be

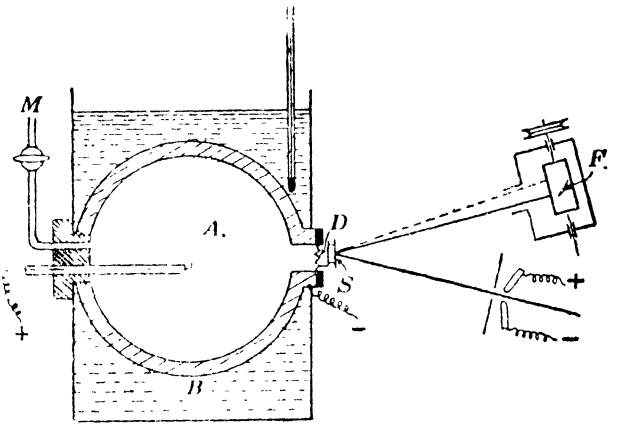


Fig. 14.—Pier's Explosion Bomb.

evacuated and various gases introduced at the desired partial pressures. D is a corrugated steel membrane closing an opening in the bomb and carrying a mirror S. Light reflected from the mirror falls on the photographic film F which revolves on a drum. By applying various known static pressures and noting the deflection of the light spot, the pressure attained in any experiment can be found simply from the record on the film. Any explosion mixture, say a mixture of hydrogen and oxygen, together with the inert gas whose specific heat is required is introduced in the bomb. By 'inert' is meant any gas which will not take part in the reaction either from want of chemical affinity or due to its presence in excess. The partial pressures of the various gases are known. The explosion is started by means of electric sparks and the final pressure reached (p_1) is observed. This takes about ·01 sec.

The calculation may be easily made. If the vessel were allowed to cool to the initial temperature T_2 (absolute), suppose it would record the pressure p_2. The maximum temperature T_1 reached during the explosion

* *Zeits. f. phys. Chem.*, Vol. 66, p. 759 (1909); *Zeits. f. Electrochemie*, Vol. 15, p. 536 (1909); Vol. 16, p. 897 (1910).

is calculated from the value of p_1, for, from the gas laws, since the volume remains constant,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

$$\therefore T_1 = \frac{p_1}{p_2} T_2$$

or if p_i denote the initial pressure and e the ratio $\frac{\text{final}}{\text{initial}}$ number of molecules (owing to the explosion the total number of molecules changes).

$$p_2 = e p_i \quad [\because \text{volume and temperature is the same}]$$

$$\therefore T_1 = \frac{p_1}{e p_i} \cdot T_2 = \frac{P}{e} T_2 \quad . \quad . \quad . \quad (28)$$

where P is the ratio $\frac{\text{Explosion}}{\text{Initial}}$ pressure. The relation connecting the specific heats and the heat of reaction is

$$m\, Q_{T_2} = (T_1 - T_2)\, [mC_{vr} + nC_{vi}] \quad . \quad . \quad . \quad . \quad (29)$$

where m is the number of gramme-molecules of the reaction products, n the number of gramme-molecules of the inert gas; C_{vr}, C_{vi} respectively their mean molecular specific heats over the range $(T_1 - T_2)$, and Q_{T_2} the heat of reaction for the explosion mixture at $T_2°$. Q_{T_2} is generally known. We can determine C_{vr} by exploding either with different amounts of a gas whose variation of specific heat with temperature is known, or with different quantities of argon a substance whose specific heat is constant. Then the same reacting gases may be exploded with any inert gas, and knowing C_{vr}, we can find C_{vi} for the inert gas.

The method is very suitable for measurements of specific heat at high temperatures and has been used to about 3000°C. Corrections* are however necessary for loss of heat, effects of dissociation, incomplete combustion, etc. For Argon, Pier found that the specific heat does not vary with temperature.

31. Nernst's vacuum-calorimeter method is employed to find C_p at low temperatures. The gas is enclosed in the calorimeter [Fig. 10 (c)]. Eucken† has in this way found the specific heat of hydrogen at low temperatures and obtained interesting results.

* *Zeits. f. Electrochemie*, Vol. 17, p. 731 (1911); Vol. 18, p. 101 (1912).
† *Berl. Ber.*, p. 141 (1912); p. 682 (1914).

(C) METHODS BASED ON DETERMINATION OF γ

32. As already pointed out this is an indirect method of finding the specific heats of gases. Though indirect it is capable of the highest accuracy so that the modern accepted values of specific heats are based on the values of γ thus obtained.

The methods for measuring γ, the ratio of the two specific heats, may be classified under two heads: (1) those depending on the *adiabatic expansion or compression* of a gas, (2) those depending on the *velocity of sound* in the gas. We shall first consider the former.

(1) Adiabatic Expansion Method.

33. Clément and Désormes* were the first to find γ by the adiabatic expansion method. Their original apparatus has been considerably improved and is indicated in Fig. 15. A large flask A of about 28 litres capacity is closed by a stop-cock M about 1·4 cm. in diameter. The flask is connected to the water manometer $P_i P_A$ by means of a side-tube and is plugged with cotton-wool to avoid loss of heat. First the flask is partially evacuated and the pressure P_i, recorded by the manometer, is observed. The stop-cock M is then opened and quickly closed. Air rushes into the flask till the pressure inside and outside becomes equal. The process is adiabatic since the loss of heat in the short interval for which the cock M is open, may be neglected. The temperature of the air in the flask rises on account of the inrush of the external air and the pressure becomes

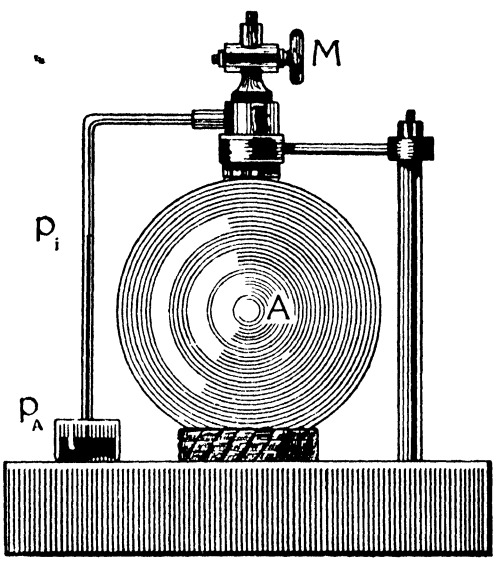


Fig. 15. Clément and Désormes' apparatus.

* *Observations sur la Physique*, Vol. 89, pp. 321, 428 (1819).

atmospheric. The flask is next allowed to cool to the temperature of the surroundings when the water in the manometer rises and finally indicates the pressure p_f.

Let the atmospheric pressure be p_A, and the specific volumes of air at the pressures p_i, p_A, p_f be respectively v_i, v_A, v_f. The first process is adiabatic and hence we have

$$p_i v_i^{\gamma} = p_A v_A^{\gamma} \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Since the final temperature is the same as the initial, we have, considering 1 gramme-molecule of the gas

$$p_i v_i = p_f v_f \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Again $$v_A = v_f \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

because the volume of the manometer tube is negligible compared with that of the flask and hence there will be no appreciable change in the specific volume of the gas due to rise of liquid in the manometer.

Combining (30), (31), and (32), we have,

$$\frac{p_i}{p_A} = \left(\frac{p_i}{p_f} \right)^{\gamma}$$

or $$\gamma = \frac{\log p_i - \log p_A}{\log p_i - \log p_f} \quad . \quad . \quad . \quad . \quad (33)$$

If as usual, the changes in pressure are small,

$$\gamma = \frac{p_i - p_A}{p_i - p_f}.$$

From measurement of Clément and Désormes, Laplace deduced the value of γ to be 1·354.

In this experiment there is a source of serious error. We have assumed that the pressure inside has become atmospheric when the stop-cock M is closed. Actually however oscillations set in; on account of the kinetic energy more air first rushes in than would make the pressure just atmospheric, and hence the pressure inside becomes greater than p_A. Next some air rushes out till the pressure inside is less than p_A and so on. After several such overshootings the pressure p_A is attained. This takes considerable time and, as a matter of fact, this to-and-fro motion has not subsided when the stop-cock is closed. It must be closed at the instant

when during an oscillation the pressure just becomes atmospheric. This is very difficult to secure and hence later investigators tried to avoid it by measuring the change in temperature resulting from adiabatic expansion. The stop-cock has not to be closed in this case. We shall consider shortly the experiments of Lummer and Pringsheim and of Partington and Shilling based on this principle.

We have assumed above that the incoming air has the same temperature as the air in the flask initially. To avoid correction in case it is not so, it is better to start with compressed gas in the flask. Further care must be taken to use perfectly dry air for γ is appreciably different for moist air. Consequently the water manometer is replaced by a sulphuric acid gauge. Röntgen* modified the apparatus and determined the cooling during expansion on account of radiation by making use of Newton's law of cooling and corrected his results for it. By taking different values for the ratio *surface/volume* he could determine and allow for the effect of the walls. He kept the stop-cock open for about 0·3 sec. The vessel had a volume of 70 litres, large volume being advantageous since the exchange of heat between the gas and the walls is thereby diminished. For air he got the mean value $\gamma = 1{\cdot}4053$.

34. Joule was the first to study the change in temperature by adiabatic expansion or compression. Various investigators later employed this method to determine γ. Air was compressed in a vessel and its temperature and pressure observed. It was then allowed to expand suddenly to atmospheric pressure and the change in temperature noted. The calculations can be easily made. If p_1, T_1 denote the pressure and temperature before expansion, p_2, T_2 the same quantities after the expansion, we have, from (25)

$$T_1 p_1^{\frac{1-\gamma}{\gamma}} = T_2 p_2^{\frac{1-\gamma}{\gamma}}$$

or
$$(1-\gamma)\log\frac{p_1}{p_2} = \gamma \log \frac{T_2}{T_1}$$

$$\therefore \quad \gamma = \frac{\log p_1 - \log p_2}{(\log p_1 - \log p_2) - (\log T_1 - \log T_2)} \quad . \quad . \quad (34)$$

Thus γ can be calculated.

Lummer and Pringsheim† made considerable improvements in the apparatus for determining γ by this method. They employed a 90-litre copper sphere and measured the change in temperature by the change

* *Ann. d. Physik*, Vol. 141, p. 552 (1870); Vol. 148, p. 580 (1873).
† *B.A. Reports*, p. 565 (1894).

in resistance of a thin bolometer wire hanging at the centre of this sphere. A Thomson galvanometer having a period of 4 sec. was used as a null instrument. Certain errors are, however, inherent in the apparatus.

In order to eliminate these errors Partington* has further improved the apparatus. He used a large expansion vessel (130 litres capacity) and a bolometer of very thin platinum wire (·001 to ·002 mm. in diameter) with compensating leads; thus there was no lag. Further an Einthoven string galvanometer capable of recording temperature in ·01 sec. is used so that a detailed record of changes in temperature of the gas during and after expansion is obtained. His apparatus is indicated in Fig. 16, p. 64. The vessel A is provided with the expansion valve C which can be manipulated by means of the spring P and whose size can also be varied. A is connected to the sulphuric acid manometer M, the mercury manometer *m*, and the drying tubes F. Thus carefully purified air enters A. Further the vessel A is kept immersed in a water-bath which is kept stirred by S. B is the bolometer wire (shown separately in the figure) and is connected in one arm of a Wheatstone bridge. G is the string galvanometer.

The initial temperature was read on a carefully standardised mercury thermometer T immersed in the bath and was given correct to ·01°. Then the resistance in one arm of the Wheatstone bridge was lowered to give some deflection in the galvanometer. It was so arranged by trials that immediately after expansion this deflection was reduced to zero. After the expansion experiment some ice was continuously added to the bath to keep its temperature constant and equal to that immediately after expansion. This was ascertained by keeping the galvanometer deflection steadily at zero, and the temperature of the bath was again read on the same mercury thermometer.

If the aperture is too large, oscillations of the gas take place and the galvanometer deflection is not quite steady, the initial deflection being somewhat greater than the true value. If the aperture is too narrow prolonged expansion results and the process is not adiabatic. In practice the aperture was gradually diminished and when overshooting was eliminated the deflection was instantaneous, and perfectly steady. The atmospheric pressure was read on a Fortin's barometer and γ calculated from the foregoing formula. γ was found to be 1·4034† at 17°C. This method cannot be used at high temperatures since it is impossible to determine accurately the cooling correction.

* *Proc. Roy. Soc.*, A, Vol. 100, p. 27 (1921).

† From this value of γ the velocity of sound in dry air at 0°C was calculated from equation (39) to be 331·38 metres which is in close agreement with Hebb's mean value 331·41 *m*/sec. (Sec. 37).

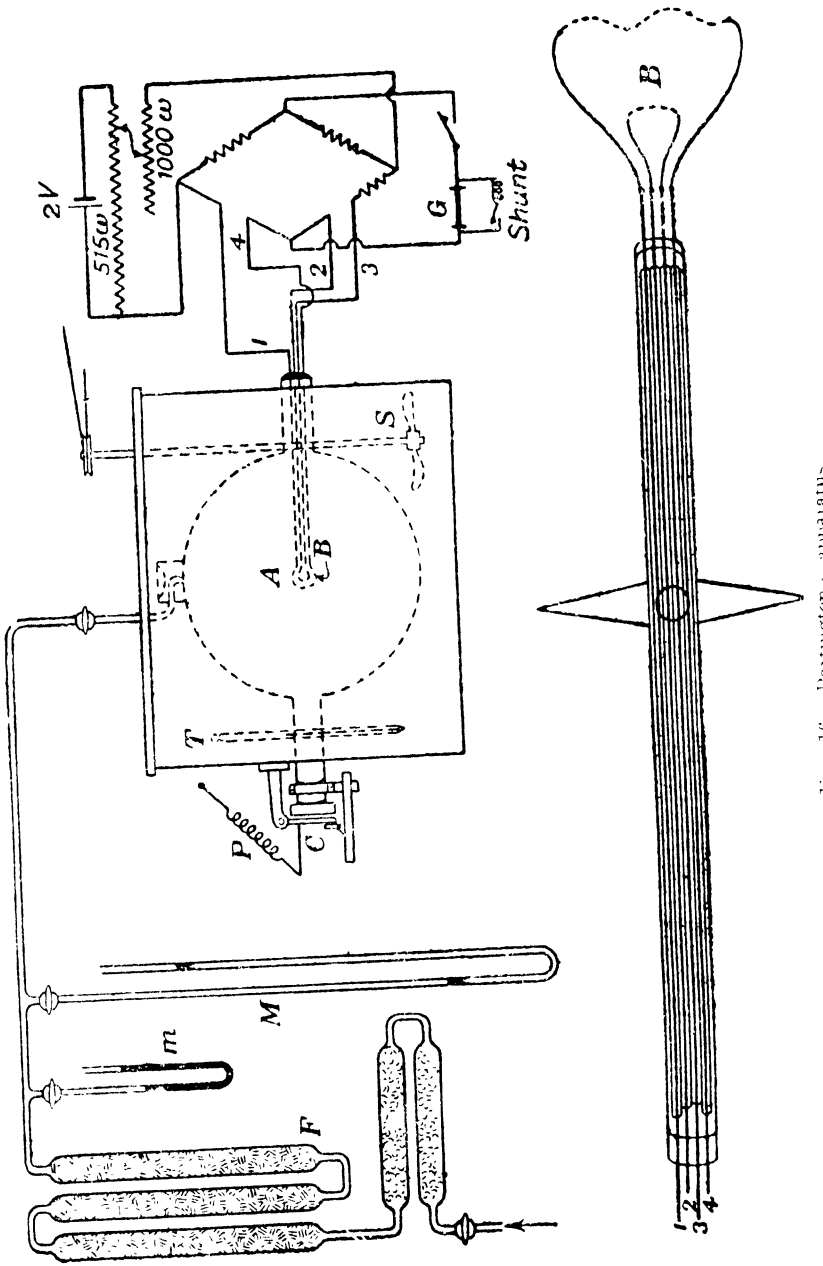


Fig. 16.—Partington's apparatus

35. A simple method for determining γ, which is suitable for class-room demonstration, has been described by E. Rüchardt.* The apparatus consists of a large glass bottle V (Fig. 17) fitted air-tight with a glass-tube at the top and a stop-cock H at the bottom. The glass tube has a very uniform bore in which a steel ball of mass m fits very accurately. If the ball is dropped into the tube, it begins to oscillate up and down and comes to rest after a few oscillations. If the period of oscillation be determined with a stop-watch, γ can be easily calculated.

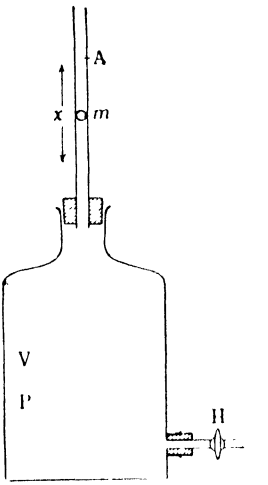


Fig. 17.

Let A be the cross-section of the glass tube, v the volume of the bottle, b the barometric pressure, and p the pressure in the flask. Then in the equilibrium position

$$p = b + \frac{mg}{A} \quad . \quad . \quad . \quad . \quad (35)$$

If the ball now moves a distance x downwards, it compresses the air adiabatically increasing the pressure to $p + dp$, hence its equation of motion is

$$m \frac{d^2x}{dt^2} = \text{Force of restitution}$$

$$= -A\,dp.$$

Now since $pv^\gamma =$ constant, we have

$$dp = -\gamma p \frac{dv}{v} \quad . \quad . \quad . \quad . \quad (36)$$

$$= -p\gamma \frac{Ax}{v}, \text{ for } dv = -Ax$$

$$\therefore m\frac{d^2x}{dt^2} = -\frac{\gamma p A^2}{v} x \quad . \quad . \quad . \quad . \quad (37)$$

* *Phys. Zeits.* Vol. 30, p. 57 (1929).

from which the period of oscillation comes out to be

$$T = 2\pi\sqrt{\frac{mv}{\gamma p A^2}},$$

or
$$\gamma = \frac{4\pi^2 mv}{pA^2 T^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Thus knowing T, p, and the constants of the apparatus, γ can be evaluated.

(2) Velocity of Sound Method

36. This method also depends upon the adiabatic expansion and compression of a gas but differs from the foregoing method in that no direct measurement of changes in temperature or pressure need be observed. The method has given us the most accurate data regarding specific heats for both high and low temperatures and so we shall consider it in some detail.

The velocity of sound in any fluid is given by the equation* $V = \sqrt{\frac{E_s}{\rho}}$ where E_s is the adiabatic elasticity of the fluid and ρ its density. For adiabatic changes in perfect gases† $pv^\gamma =$ a constant (p. 54). hence

$$E_s = -v\left(\frac{\partial p}{\partial v}\right)_s = \gamma p \text{ from (36).}$$

$$\therefore V = \sqrt{\frac{\gamma p}{\rho}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Thus if we determine the velocity of sound in the gas we can find γ.

37. We may adopt either of the *two following methods.* The absolute velocity of sound in the gas may be determined, or we may compare the velocity with that in another gas (say air) which has been determined accurately by other methods.

* See Barton, *Sound*

† For real gases we must take into account the true equation of state (Chap IV) and substitute the value of $\frac{\partial p}{\partial v}$ from that equation. In all accurate work this is done.

For our purpose we discard the large-scale determinations of the velocity of sound in air on account of the various defects inherent in them. The most accurate direct determination of the velocity of sound in air was made by Hebb* in 1905 by a method depending on the reflection of sound of known frequency from parabolic mirrors. His mean value after employing all corrections gives 331·41 metres/sec. as the velocity of sound in air at 0°C and 760 mm. pressure.

Now we must remember that practically all determinations of the velocity of sound in gases have been made in tubes, but the velocity in a tube is not the same as in free space. Corrections have to be applied to reduce this velocity to that in open space. In equation (39) the velocity in open space must be substituted. Dixon† has directly determined the velocity of sound in different gases from 15°C to 1000°C in a very satisfactory manner. His results may be employed to give γ.

Method based on the Measurement of Wavelength.

38. Kundt's Tube.—Kundt‡ first devised an apparatus by means of which he could find the velocity of sound in a gas. This consists simply of a glass tube about 1 metre in length and 3 cm. in diameter. One end of the tube was fitted with a movable stopper, while through the other end passed a loosely-fitting disc carried by a glass or metal sounding rod

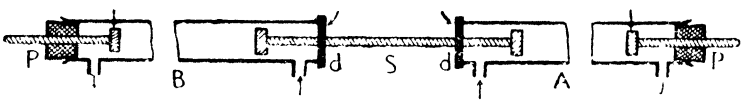


Fig. 18.—Kundt's Double-tube Apparatus

which was itself clamped at its centre. Later Kundt employed the double-tube apparatus indicated in Fig. 18. Two tubes A and B are connected by means of the sounding-rod S which is clamped at distances one-quarter of its length from either end. The two rubber corks d, d in the tubes A and B provide the clamping arrangement. The pistons P, P can be moved to bring the tubes in resonance with the rod S. Throughout the length of each tube is spread some light dust such as lycopodium powder or silica dust. One tube is filled with air and the other with the experimental gas. The sounding-rod S is excited by rubbing it at the centre when the dust is

* *Phys. Rev.*, Vol. 20, p. 89 (1905); Vol. 14, p. 74 (1919).
† *Proc. Roy. Soc.*, A, Vol. 100, p. 1 (1921).
‡ *Ann. d. Physik*, Vol. 127, p. 497 (1866); Vol. 135, pp. 337, 257 (1868).

thrown into violent agitation at the antinodes and collects at the nodes. The distance between successive nodes equals half-wavelength, and knowing the frequency of the sound the velocity is easily obtained. The double form of the apparatus is very convenient for comparing the velocity of sound in any gas with that in air for

$$\frac{V_{gas}}{V_{air}} = \frac{\lambda_{gas}}{\lambda_{air}}.$$

Various precautions are however necessary. The tube and the powder must be perfectly dry. Carefully purified air must be used or corrections for the various impurities must be made. Too much dust should not be used for excess of dust diminishes the velocity. A decrease in the diameter of the tube diminishes the velocity. Finally from the velocity in the tube the velocity in open space must be deduced. Though mathematical equations giving the requisite correction have been developed by Helmholtz, Kirchhoff and others, they are not quite true and the best method* is to express the velocity V′ in the tube as

$$V' = V(1 - kC)$$

where V = velocity in open space,

k = a constant depending on the tube (its radius, thickness, thermal conductivity, etc.)

C = a factor depending on the gas (its viscosity, density, ratio of specific heats, etc.).

For air from Hebb's experiments we know V, and by observing V′ and calculating C, k for the tube is determined. This value of k is employed to give V the velocity in open space for any other gas.

Kundt and Warburg† later employed this method to determine the velocity of sound in mercury vapour. One of the tubes contained mercury vapour and was heated in an air-bath to about 300°C. The distance between two nodes was measured when the tube cooled. They found $\gamma = 1{\cdot}666$. Ramsay‡ employed this method to find γ for argon but on account of certain difficulties he got a low value. Behn and Geiger§ improved the apparatus considerably. They dispensed with the sounding rod and employed a sealed tube containing the experimental gas as the source of sound. This tube was clamped in its middle and was excited like the sounding rod. The tube should be chosen properly and its length be adjustable so that the contained gas may give resonance with the sound emitted by the rod. The apparatus was eminently suited for gases at

* For full discussion see Partington and Shilling, *Specific Heats of Gases*, p. 52.

† *Ann. d Physik*, Vol. 157, p. 353 (1876).

‡ *Phil. Trans.*, A, Vol. 186, p. 228 (1895).

§ *Verh. d. deuts. Phys. Ges.*, Vol. 9, p. 657 (1907).

high temperatures. This method was later employed by different investigators particularly by Partington.

More recently Partington and Shilling determined the velocity of sound in various gases up to 1000°C by a resonance method* and obtained very reliable results. They found the successive lengths of a tube which resonates to a sound of known frequency. This gives the wavelength and hence the velocity of sound in the gas.

Cook† employed this method to find γ for air from 90° to 293°A. His apparatus may be visualized if we imagine the hot air-bath of Kundt and Warburg to be replaced by a long Dewar flask containing liquid air.

39. Results.– In the foregoing pages we have considered the various methods of finding specific heats. The following table‡ gives values which best represent the experimental data. We reserve our comments on these values for the next chapter.

Table 5.—Molecular Heats in Calories at 20°C and Atmospheric Pressure.

Gas	C_p	C_v	$\gamma = \frac{C_p}{C_v}$	Remarks
Argon ..	4·97	2·98	1·666	Monatomic
Helium ...	4·97	2·98	1·666	
Hydrogen ...	6·865	4·88	1·408	Diatomic
Oxygen ...	7·03	5·035	1·396	
Nitrogen ...	6·95	4·955	1·402	
Nitric oxide ...	7·10	5·10	1·39	
Hydrochloric acid	7·04	5·00	1·41	
Carbon monoxide	6·97	4·98	1·40	
Chlorine ...	8·29	6·15	1·35	
Air	6·950	4·955	1·402	
Carbon dioxide ...	8·83	6·80	1·299	Triatomic
Sulphur dioxide ...	9·65	7·50	1·29	
Hydrogen sulphide	8·3	6·2	1·34	
Methane .	8·50	6·50	1·31	Polyatomic
Ethane ...	12·355	10·30	1·20	
Acetylene ...	10·45	8·40	1·24	
Ethylene ...	10·25	8·20	1·25	
Ammonia ...	8·80	6·55	1·315	

* *Trans. Faraday Soc.*, Vol 18, p. 386 (1923)
† *Phys. Rev.*, Vol. 23, p. 212 (1906).
‡ Taken from *Handbuch der Experimentalphysik*, Vol. 8, p. 33.

40. Bomb Calorimeters.—Various other calorimeters have been devised for particular purposes such as the measurement of heat of combustion, heat of chemical reaction, etc., but they involve no new principles. Particular interest however attaches to the determination of heat of combustion in industries, for the value of fuel is judged mainly from its calorific value. To determine this, two types of calorimeters have been developed: (1) "Submerged bell" type, (2) "Bomb" type. The latter is generally preferred and hence a description of it is given below.

Fig. 19 indicates the calorimetric bomb. It consists of a stout steel-cylinder A fitted with a cover held down tightly by suitable means. The cover has a milled-head screw valve which varies the cavity k_1 and thereby regulates the admission of oxygen through the tubes B and C into the bomb. Through the centre of the cover but insulated from it passes the wire i which is connected to the platinum wire w, the other end of the latter being connected to e. There is another similar screw valve varying the cavity k_2 through which gas can go out of the bomb. To withstand the corrosive action of the products of combustion the bomb is plated inside with gold, though platinum would be better. The bomb is enclosed in an ordinary calorimeter such as is used for the method of mixtures. This calorimeter is provided with a stirrer and accurate mercury thermometer. The whole is surrounded by a constant-temperature jacket.

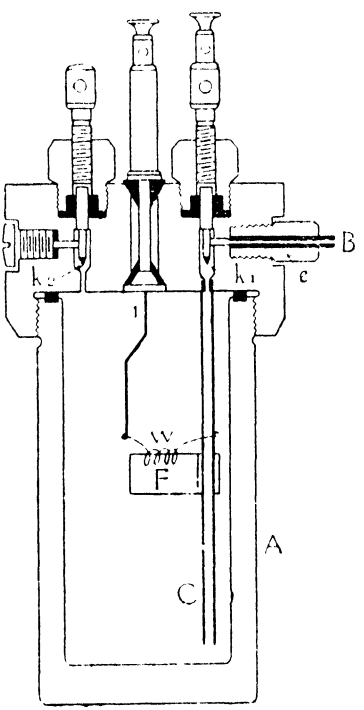


Fig. 19.—The Bomb.

To find the heat capacity of the bomb and its accessories a known amount of electrical energy may be spent in the system or a fuel of known calorific value burnt. The former method is adopted in standardising laboratories and the latter in actual practice. Benzoic acid is most suitable for this calibration. The

fuel, if solid, is formed into a small briquette; if liquid, it is soaked in pure cellulose and put in the platinum dish F and ignited. About three times the amount of oxygen just necessary for complete combustion is admitted through B. C. The oxygen is generally employed at a pressure of about 25 atmospheres and at this high pressure the combustion is almost instantaneous.

EXAMPLE

Dry air enclosed at 25°C and at atmospheric pressure is suddenly compressed to half its volume. Find (1) the resulting temperature. (2) the resulting pressure. Assume $\gamma = 1{\cdot}40$.

(1) From equation (24)

$$Tv^{\gamma-1} = T_1 v_1^{\gamma-1}$$

$$\therefore T_1 = T\left(\frac{v}{v_1}\right)^{\gamma-1} = (273+25)\,(2)^{(1{\cdot}4-1)}$$

$$= 298 \times 1{\cdot}319 = 393^\circ\text{A or } 120^\circ\text{C}.$$

(2) Again from equation (23)

$$pv^\gamma = p_1 v_1^\gamma$$

$$\therefore p_1 = p\left(\frac{v}{v_1}\right)^\gamma = p.\,2^{1{\cdot}4} = 2{\cdot}64 \text{ atmos.}$$

Books Recommended.

(1) Glazebrook. *A Dictionary of Applied Physics*, Vol. I, article on 'Calorimetry.'

(2) Partington and Shilling. *Specific Heats of Gases.*

CHAPTER III

KINETIC THEORY OF MATTER

The Nature of Heat

1. Historical.—In the legends of some ancient nations, it is said that fire was first made for man by some friendly god by rubbing together two pieces of stick. The legend probably refers to a prehistoric discovery of the art of making fire. But though this way of producing heat by friction clearly indicates the real nature of heat, the early philosophers had no correct notion about it. They philosophized from the observation that heat could pass spontaneously from a hot body to a cold one. Heat was, therefore, supposed to be a kind of fluid—the caloric fluid.

Various fictitious properties were assigned to this hypothetical fluid. It was supposed to possess no weight, since bodies did not increase in weight on mere heating. Further it was supposed to be highly elastic, all-pervading, indestructible and uncreatable by any process. Temperature was likened to potential or level. A substance, hot or cold, was supposed to contain the same quantity of caloric fluid. When the body was heated the caloric fluid was supposed to stand at a higher level than when cold. Production of heat by friction was compared to the oozing out of water from a sponge when squeezed.

Doubts on the caloric theory of heat began to be thrown towards the end of the eighteenth century. The earliest philosopher to have a correct notion of the physical nature of heat was Count Rumford, an American by birth, who being loyal to Great Britain during the American War of Independence had to flee from his country. He took service under the Elector of Bavaria as superintendent of the artillery. In those days guns were made by casting solid cylindrical pieces and scooping out the inside by a boring machine. Rumford observed that apparently an inexhaustible amount of heat could be produced by the friction of the spindle of the boring machine against the body of the gun, though the amount of iron scraped was very small. He undertook protracted experiments and found that the amount of heat produced (measured by the raising of water to a

high temperature) bore no relation to the amount of iron scraped, but was proportional to the amount of motion lost. He henceforth rejected the caloric theory and asserted that *Heat is only a kind of Motion. Whenever Motion disappears it reappears as Heat and there is an exact proportionality between the two.* He even made an estimate of what we now call the Mechanical Equivalent of Heat. His value is not much different from the value now adopted as standard.

In 1799, Davy showed that when two pieces of ice were rubbed together water is produced. It was admitted by all that water has greater quantity of heat than ice.* Now supporters of the caloric theory asserted that heat is generated in friction because the substance produced by friction has less capacity for heat than the original substance. But the substance produced in Davy's experiment (water) has greater heat capacity than ice, hence the caloric theory is untenable. Davy's experiment proved the greatest stumbling block for the caloric theory.

But the valuable work of Rumford and Davy was soon forgotten and it was only about forty years later that the first law of Thermodynamics gained general publicity through the researches of Joule in England, Mayer and Helmholtz in Germany, and Colding in Denmark.

2. Joule's Experiments.—In 1840 Dr. Joule of Manchester began his classical experiments for determining the relation between the work done and heat generated. We do not wish to describe these experiments here in detail as they are at present only of historical interest. The heat was produced by churning water contained in a cylinder by means of brass paddles. This could be kept revolving by means of a double thread wound over a solid cylinder and passing over pulleys, and carrying weights at either end. The amount of work done was calculated by observing the height through which the weights fell. The rise in temperature was measured by a mercury thermometer and hence the heat generated could be found. After applying various corrections Joule found that 772 ft.-lbs. of work at Manchester can raise the temperature of 1 pound of water 1°F. In 1878 Joule used a modified form of the apparatus in which the work done was measured by the application of an external couple as in Rowland's experiments to be described later.

* This was proved by Black's discovery of Latent Heat of Fusion. He hung equal masses of ice and ice-cold water alternately inside a room and observed that the water was raised 4°C. in half an hour, while the ice took about ten hours to melt into water, the temperature remaining constant.

3. First Law of Thermodynamics.—The conversion of work into heat was thus established by the experiments of Rumford and Joule. Now, between the times of Rumford and Joule, the steam-engine had been widely applied for various industrial purposes. As we shall see later, this is simply a contrivance for the conversion of heat into work. Thus it is established that heat and work are mutually convertible. Nay, we may go even further and say that when some work is spent in generating heat, a definite relation exists between the work spent and heat generated. These two facts, *viz.*, the possibility of converting work into heat and *vice versa* and the existence of a definite relation between the two, are expressed by the First Law of Thermodynamics. Mathematically the law may be stated thus:—

If W is the work done in generating an amount of heat H, we have

$$W = J\,H, \qquad \ldots\ldots (1)$$

where J is a constant, provided all the work done is spent in producing heat and no portion is wasted by friction, radiation, etc. If H is expressed in calories and W in ergs, $J = 4{\cdot}186 \times 10^7$. The truth of the second statement embodied in the law is amply proved by the fact that the various methods for finding J (secs. 4—7) yield almost an identical value.

4. Methods for determining J.—Various methods have been devised for finding the value of the mechanical equivalent of heat but the method of fluid friction and the electrical method are the only ones capable of yielding accurate results, and hence only these will be considered in detail. There is however an ingenious method of calculating the value of J, first given by *Mayer*. From the theoretical relation $J\,(C_p - C_v) = R$ (p. 51), he calculated the value of J. Thus for hydrogen

$$R = \frac{p_0 V_0}{T_0} = 8{\cdot}313 \times 10^7 \text{ ergs (p. 6) and } C_p - C_v = 1{\cdot}985 \text{ cal. (p. 69)}$$

$$\therefore\ J = \frac{8{\cdot}313 \times 10^7}{1{\cdot}985} = 4{\cdot}186 \times 10^7 \text{ ergs.}$$

Certain other methods* that have been employed are enumerated below:—

* For a complete list of the methods see Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, p. 480.

(1) Measurement of heat produced by compressing a gas —— Joule
(2) Heat produced by percussion —— Hirn
(3) Work done by a steam-engine —— Hirn
(4) Heat developed in a cylinder kept stationary in a rotating magnetic field produced by means of polyphase alternating electric current —— Baille and Ferry.

5. Rowland's Experiments.—Joule's thermometers were not standardised and thus errors of 1 or 2% may arise from this cause. The rate of rise of temperature in his experiments was rather slow (about 0·62°C per hour) and hence the radiation correction large. Professor

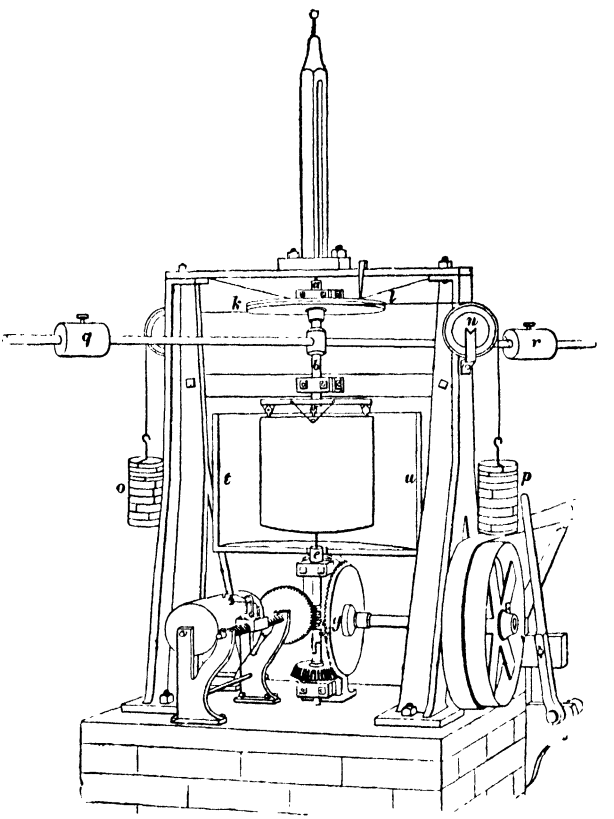


Fig. 1 (*a*).—Rowland's Apparatus.

Rowland* minimised this source of uncertainty by designing a special apparatus with the object of securing a rapid rate of rise of temperature (40°C per hour), the principle of the method being identical with that of Joule.

The calorimeter was firmly attached to a vertical shaft *ab* [Fig. 1 (*a*)] to which is fixed a wheel *kl* wound round with a string carrying weights *o*, *p* at either end, the whole being suspended by a torsion wire. The axis of the paddle [Fig. 1 (*b*)] passed through the bottom of the calorimeter and was attached to the shaft *ef*. The latter could be rotated uniformly by the wheel *g* driven by a steam-engine. The number of revolutions were automatically recorded on a chronograph worked by a screw on the shaft *ef*. The revolution of the paddle at an enormous rate tended to rotate the calorimeter in the same direction on account of fluid friction. This was prevented by the external couple produced by the weights *o*, *p* and the torsion wire. For the purpose of accurately determining the radiation correction a water jacket *tu* surrounded the calorimeter.

The paddle is indicated separately at (*c*). To a hollow cylindrical axis four rings were attached, each having eight vanes. Around these were the fixed vanes, consisting of five rows of ten each, which were fixed to the calorimeter. Thus the liquid could be vigorously churned. The rise

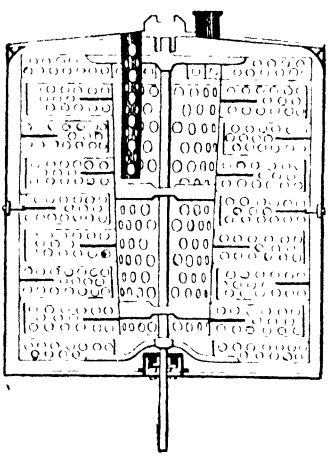


Fig. 1 (*b*).

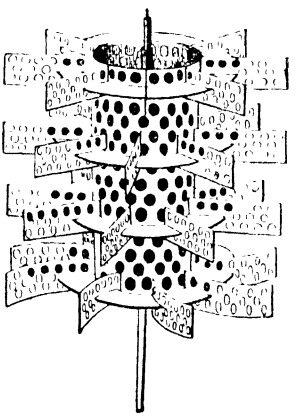


Fig. 1 (*c*).

* *Proc. Amer. Acad. Arts and Sciences*, Vol. 7 (1880).

of temperature was recorded by a thermometer suspended within the central sieve-like cylinder in which water circulated briskly.

If D denote the diameter of the torsion wheel and mg, mg, the weights suspended, the work done in n revolutions of the paddle is equal to *couple*×*angle of twist*,

$$= mg\mathrm{D}.\ 2\pi n \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If W denote the thermal capacity of the calorimeter and its contents, $\delta\theta$ the rise in temperature (corrected for radiation), the heat produced by friction is $\mathrm{W}\delta\theta$, hence

$$\mathrm{J} = \frac{2n\pi.\ mg\mathrm{D}}{\mathrm{W}.\ \delta\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If D is in cms. and mg in dynes, J comes out in ergs.

Corrections were applied for the torsional couple, for the weights in air which must be reduced to vacuum, for the expansion of the torsion wheel, etc. Rowland found $\mathrm{J} = 4{\cdot}179\times10^7$ ergs for the 20° calorie. Laby* recalculated from Rowland's observations by applying certain corrections and obtains the value $\mathrm{J} = 4{\cdot}187\times10^7$ ergs for the 15° calorie.

Reynolds and Moorby† obtained by a modified apparatus, the value of the mean calorie between 0° and 100°C to be $4{\cdot}1833\times10^7$ ergs. Quite recently Hereus and Laby‡ have employed what is in principle an induction motor, to find J, and obtain the value $\mathrm{J} = 4{\cdot}186\times10^7$.

6. A Simple Laboratory Method of Finding J.—For laboratory purposes a simple apparatus for finding J by the mechanical method is sketched in Fig. 2 but it is not capable of yielding results of the highest precision. A is a brass cone held rigidly in position by means of non-conducting ebonite pieces attached to a brass cylinder C, which can be made to revolve by means of a motor. Inside A is another brass cone B fitting smoothly into it and attached rigidly to a wooden disc D. The latter has a groove running round its circumference and carrying a cord which passes over the pulley P and supports a weight mg. When the outer cone rotates rapidly the inner one tends to move in the same direction on account of the friction between the two cones, but is held in position by

* *Proc. Phys. Soc. Lond.*, Vol. 38, p. 169 (1926).
† *Phil. Trans.*, p. 381 (1897).
‡ *Phil. Trans.*, Vol. 227, p. 63 (1927).

properly suspending a suitable weight mg at the end of the cord. The inner cone B contains some water, a thermometer and a stirrer (not shown).

When the weight mg is kept stationary the turning moment exerted by it just balances the frictional couple. If D is the diameter of the disc the frictional couple is $mgD/2$ and the work done by it in n revolutions of the cone is $2n\pi\ mgD/2$. If W be the water equivalent of the cones and

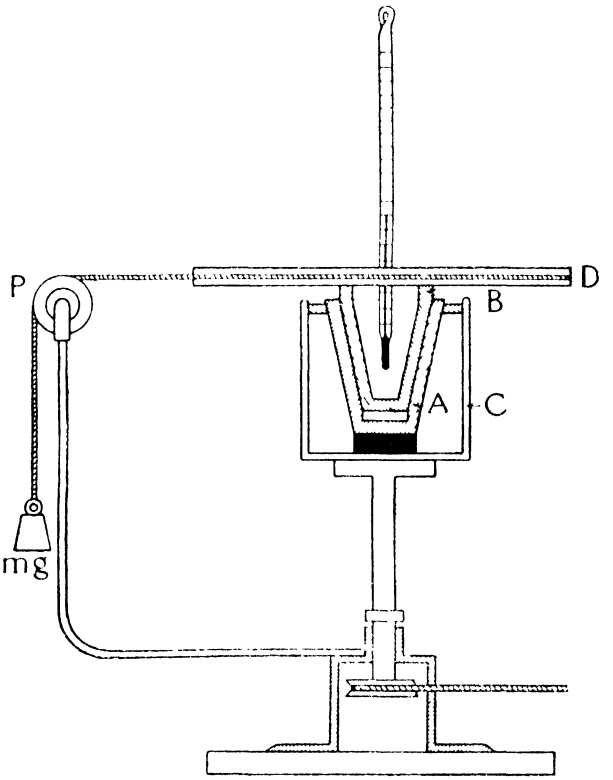


Fig. 2. A Simple Laboratory Apparatus for J.

the contents, $\delta\theta$ the rise of temperature produced by friction, then

$$n\pi mgD = W\delta\theta.\ J \quad . \quad . \quad . \quad . \quad . \quad (1)$$

whence J can be calculated.

7. Electrical Methods.—These methods have already been described (pp. 41—44) in full detail. It is easily seen that if the specific heat of the liquid be known, this method gives the mechanical equivalent of

heat. There are two methods:—(1) Steady-flow method. (2) Rise in temperature method. The former was employed by Callendar and Barnes who did their experiments with great care and skill, but the principal source of uncertainty in their work lies in the value of the electrical units employed. According to Laby* we may put the E.M.F. of the Clark cell used by Callendar and Barnes as 1·4335 volts at 15°C. They employed the international ohm which is equal to $1·0005\times10^9$ c.m. units. Reducing Callendar's results with the help of these data Laby gets for the mechanical equivalent of the 20° calorie a value of $4·1795\times10^7$ ergs. This yields $4·1845\times10^7$ ergs as the equivalent of the 15° calorie. The most accurate experiments on the subject are those of Jaeger and Steinwehr by the rise of temperature method, and of Laby and Hercus by a mechanical method, the respective values being $4·1863\times10^7$ and $4·1860\times10^7$ for the 15° calorie. Hence we can adopt the value $4·186\times10^7$ ergs.

8. Heat as Motion of Molecules.—From these experiments it is clearly established that heat is a kind of motion; the next question is—*motion of what?*—The answer was given by Clausius and Krönig in 1857 for the case of gases. The answer is that heat consists in the motion of molecules or the smallest particles of matter.

The idea that if we go on dividing matter we ultimately come to small particles which cannot be further subdivided dates from very ancient times. But it remained a barren speculation till Dalton gave to it a definite form in the middle of the last century. The history of the molecular theory is known to all our readers and no account of it need be given here. Suffice it to say that according to it all matter is composed of a large number of molecules, all molecules of the same substance being exactly identical as regards mass, size, etc., but differ in their motion. In the solid and liquid states these molecules are closely packed while in gases they are far apart from each other.

Now according to the Kinetic Theory of matter heat is supposed to consist in the motion of these molecules. The identification of heat with motion of molecules is not a mere hypothesis. It is able to explain and predict natural phenomena and at present there is little doubt that it rests upon foundations of truth.

* *Proc. Phys. Soc. Lond.*, Vol. 38, p. 169 (1926).

9. Growth of the Kinetic Theory.—The Kinetic Theory of matter rests upon two fundamental hypotheses (1) the molecular structure of matter, (2) the identification of heat with molecular motion. The first of these was established early in the 19th century while the second was established by the experiments of Rumford, Joule, Mayer and Colding. We may however consider Daniel Bernouilli (1730) as the founder of the modern kinetic theory as he was the first to explain Boyle's law by molecular motions. Clausius and Maxwell in the middle of the 19th century placed the theory on a firm mathematical basis. Among the other prominent contributors to the theory are Boltzmann, Mayer, Jeans, Van der Waals, Lorentz and Lord Rayleigh.

Up to the beginning of the present century, however, the theory had been developed entirely from a mathematical standpoint. There was no direct experimental proof of the actual existence of these molecules or of their motions. Gradually however much evidence has accumulated in favour of these views, the most important being the Brownian Movement phenomena investigated by Perrin in 1908.

10. Evidence of Molecular Agitation.—(1) The phenomena of diffusion and solution readily suggest the molecular agitation of matter. Hydrogen is found to diffuse into carbon dioxide against gravity when a cylinder of hydrogen is placed over a cylinder of CO_2. Alcohol poured over water diffuses into the entire mass of water. Even gold is found to diffuse into lead.

(2) A gas tends to expand. The moving molecules of the gas tend to fly away and produce this property of expansibility. The rectilinear motion of the molecules is observed in the experiment of Dunoyer. In this a vertical cylinder is divided into three parts by two horizontal diaphragms each containing a hole. Solid sodium kept in the lowest part is vaporised and deposits on the upper surface of the cylinder. This deposit is found to coincide with the geometrical projection of the second hole, formed by joining points in the two holes by straight lines.

(3) Phenomena of evaporation and vapour pressure.

(4) The gas laws can be deduced from the kinetic theory (sec. 13). Other results obtained from the kinetic theory as specific heat, Avogadro number, molecular diameter, etc., agree with experimental results or deductions from other branches of Physics.

(5) Brownian Movement*—This phenomenon was first discovered by the English botanist Brown in 1827. It can be readily observed if small particles suspended in a liquid, as in a colloidal solution are examined under a powerful microscope. The particles are seen to be moving to and fro, rapidly and continuously, in an entirely haphazard fashion. Each particle spins, rises, sinks and rises again. The irregular motion is called the Brownian movement of the particle. The Brownian movement never ceases it is eternal and spontaneous, and is independent of the nature of the suspended particles, all particles of the same size being equally agitated. Smaller particles are, however, much more vigorously agitated than bigger ones. Now it has been definitely established that the Brownian movement is due to the impact of the surrounding molecules of the liquid on the particle. The suspended particles are like buoys in a sea of molecules, and are tossed up and down in the wildest fashion by the impact of the molecules. Thus the phenomenon of Brownian movement is a direct proof of the existence of molecular motion.

The study of the kinetic theory is best approached by a study of gases. The kinetic theory of the liquid and solid states is comparatively undeveloped and will not be discussed in this book.

11. Pressure Exerted by Perfect Gas. It has been shown above that a gas consists of molecules in motion. As a consequence, it must exert pressure on the walls of its enclosure. To calculate this pressure we first make several simplifying assumptions. These are the following:—

(1) The molecules move about in all directions with very different velocities. They collide with one another and have their velocities altered considerably both in direction and magnitude. That is, the gas is in a state of molecular chaos. But in the steady state molecular collisions do not affect the molecular density of the gas. This fact is of considerable importance.

(2) Between two collisions a molecule moves in a straight line with uniform velocity. This is because the molecules are material bodies and must obey Newton's laws of motion.

(3) The dimensions† of a molecule may be neglected in comparison with the distance traversed by it between two collisions, called its free

* For detailed information see Perrin, *Atoms*.

† If we take the dimensions of the molecules and the forces of attraction we get Van der Waals' equation (Chapter IV)

path. The perfect gas theory treats the molecules as mere mass-points.

(4) The time during which a collision lasts is negligible compared with the time required to traverse the free path.

(5) The molecules are perfectly elastic* spheres and no appreciable force of attraction or repulsion is exerted by them on one another or on the walls, *i.e.*, all energy is kinetic. This is proved by Joule's experiment (p. 52).

We now proceed to calculate the pressure exerted by such a gas. We will employ the method of collisions, because it is very simple.

Imagine a perfect gas enclosed in a cube of unit side and consider a group of molecules moving with velocity u perpendicular to one surface. From the principles of conservation of energy and momentum it follows that they rebound with the same velocity. Hence the change in momentum suffered by a single molecule during collision is $2mu$. The molecule strikes that particular surface $u/2$ times per second, hence the change of momentum per second in $2mu$. $\frac{u}{2} = mu^2$. Since pressure is equal to change in momentum per second, the total pressure exerted on that surface is Σmu^2 where the summation extends over all the molecules.

$$\therefore p = \Sigma mu^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Now $\Sigma u^2 = nu^2$ where u^2 is the average of u^2 over all the n molecules.

$$\therefore p = mnu^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If v^2, w^2 denote the mean square velocities in the other two perpendicular directions,

$$u^2 = v^2 = w^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

since the molecules do not tend to accumulate in any part of the vessel. But

$$u^2 + v^2 + w^2 = c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

* The assumption of perfect elasticity is warranted by the fact that we can convert into work all the heat supplied to a perfect gas. For otherwise addition of heat would increase molecular velocities and hence also the force of collision, and if deformation of molecule results, all heat cannot be converted back to work. Nevertheless equation (9) can be deduced without this assumption. See Meyer, *Kinetic Theory of Gases*, Sec. 12.

where c^2 is the resultant mean square velocity. Hence from (7) and (8)

$$u^2 = \frac{1}{3}\overline{c^2}$$

and finally (6) yields $$p = \frac{1}{3}mn\,\overline{c^2} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

But $mn = \rho$, the density of the gas, since n is the number per c.c.

$$\therefore p = \frac{1}{3}\rho\overline{c^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$= \frac{2}{3}\cdot\frac{1}{2}\rho\overline{c^2} = \frac{2}{3}\,\mathrm{E}, \quad . \quad . \quad . \quad (11)$$

where E is the kinetic energy per unit volume. Thus we see that the pressure of a perfect gas is numerically equal to two-thirds of the kinetic energy of translation per unit volume.

We have considered a single molecule as if it suffered no collision with others. If a molecule encounters another it gives its whole momentum* to the other which by assumption (3) has to traverse exactly the same distance as the first one if there had been no collision. By assumption (4) no time is lost in this collision and hence our calculation holds true for a perfect gas.

12. Equation (10) enables us to calculate the mean square velocity $\overline{c^2}$ of the molecules of any gas, for $\overline{c^2} = 3p/\rho$. The pressure and density of a gas can be found experimentally and hence $\overline{c^2}$ calculated. Thus the density of nitrogen at 0°C and atmospheric pressure is 0·00125 gms. per c.c. Hence for nitrogen the *root mean square velocity*†

$$\mathrm{C} = \sqrt{\overline{c^2}} = \sqrt{\frac{3\times 76\times 13{\cdot}59\times 981}{0{\cdot}00125}}$$

$$= 4{\cdot}93\times 10^4 \text{ cm./sec.}$$

The formula also shows that the molecules of the lightest gas, *viz.*, hydrogen, would move faster than the molecules of any other gas under the same conditions.

* This result may be easily deduced from the laws of elastic impact (assumption 5).

† C is the square root of the mean square velocity and differs from the mean velocity $\bar{c}$. The relation between C and $\bar{c}$ is given later.

13. Deduction of Gas Laws.—From the above results we proceed to deduce the laws of perfect gases.

(1) *Avogadro's Law.*—If there are two gases at the same pressure p we have from (9)

$$p = \tfrac{1}{3} m_1 n_1 C_1^2 = \tfrac{1}{3} m_2 n_2 C_2^2 \quad . \quad . \quad . \quad (12)$$

where the subscripts 1 and 2 refer to the first and the second gas respectively. Further, if the two gases are also at the same temperature we know there will be no transfer of heat (or energy, since the two are equivalent by the First Law of Thermodynamics) from one to the other when they are mixed up. On mixing, the two types of molecules will collide against one another and there will be a mutual sharing of energy. Maxwell* showed purely from dynamical considerations that the condition for no resultant transfer of energy from one type of molecules to the other is that the mean translational energy of molecules of the one type is equal to that of the other. Hence if the two gases are at the same temperature it follows that

$$\tfrac{1}{2} m_1 C_1^2 = \tfrac{1}{2} m_2 C_2^2 \quad . \quad . \quad . \quad . \quad (13)$$

Combining (12) and (13) we get

$$n_1 = n_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

i.e., two gases at the same temperature and pressure contain the same number of molecules per c.c. This is Avogadro's Law.

(2) *Boyle's Law.*—Equation (10) states that the pressure of a gas is directly proportional to its density or inversely proportional to its volume. This is Boyle's Law. This holds provided C^2 remains constant which, as shown above, implies that the temperature remains constant.

(3) *Dalton's Law.*—If a number of gases of densities ρ_1, ρ_2, ρ_3 .... and mean square velocities C_1^2, C_2^2, C_3^2 ..... be mixed in the same volume, the resultant pressure p, considering each set of molecules, is given by

$$\begin{aligned} p &= \tfrac{1}{3} \rho_1 C_1^2 + \tfrac{1}{3} \rho_2 C_2^2 + \tfrac{1}{3} \rho_3 C_3^2 + \ldots\ldots \\ &= p_1 + p_2 + p_3 + \ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15) \end{aligned}$$

* He considered the collision of gaseous particles of two different types and possessing different amounts of energy. By applying the dynamical laws of impact he found that after each collision the difference in energy of the two molecules diminishes by a certain fraction, *i.e.*, the molecule possessing greater energy loses it while that possessing less energy gains. This process is repeated at each collision, and ultimately the energies of the two become equal. For details, see the Authors' *Treatise on Heat*, pp. 729—731.

i.e., the pressure exerted by the mixture is equal to the sum of the pressures exerted separately by its several components. This is Dalton's law of partial pressures.

14. Introduction of Temperature.—If we consider a gramme molecule of the gas which occupies a volume V, we get

$$pV = \tfrac{1}{3}MC^2 \quad . \quad . \quad . \quad . \quad . \quad (16)$$

M being the molecular weight. In order to introduce temperature in the foregoing kinetic considerations of a perfect gas we have to make use of the experimental law, *viz.*, $pV = RT$.

Hence, $$RT = \tfrac{1}{3}MC^2$$

or $$C^2 = \frac{3RT}{M} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Thus C^2 is proportional to the absolute temperature which may thus be considered proportional to the mean kinetic energy of translation of the molecules. This is the kinetic interpretation of temperature. Hence, according to the kinetic theory, the absolute temperature is the temperature at which the molecules are devoid of all motion. This deduction is, however, not quite justified since the perfect gas state does not hold down to the absolute zero.

We can put $R/N = k$ where N denotes the number of molecules in a gram-molecule and is usually called the Avogadro number. k is known as Boltzmann's constant. Hence we get

$$p = (N/V)kT = nkT$$

where n denotes the number of molecules per c.c.

15. Distribution of Velocities. Maxwell's Law.—In the above we were concerned only with the mean square velocity and did not care to find the velocity of every molecule. But for studying the properties of the gas further we must know the dynamical state of the whole system. It is easy to see that all the molecules cannot have the same speed for even if at any instant all the molecules possess the same speed, collisions at the next moment will augment the velocity of some while diminish that of the others. As the number of molecules is very large ($2{\cdot}7 \times 10^{19}$ per c.c. at N.T.P.) and they are invisible, we cannot find their actual velocity.

The problem is a statistical one and we can apply the theory of probability. We shall illustrate this by means of an example. In a big city there are persons of all ages and we find the number of persons whose ages lie between definite ranges, say between 10 and 15, 15 and 20, and so on. So in an assemblage of molecules where the molecules have all velocities lying between 0 and infinity we find the number of molecules possessing velocities lying between c and $c+dc$. In the steady state this number is found to remain constant and is not modified by collisions. This number dn_c is given by the distribution law of Maxwell which states:

$$dn_c = 4\pi n a^3 e^{-bc^2} c^2 dc, \quad . \quad . \quad . \quad . \quad (18)$$

where n is the molecular density, and $a = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi kT}}$. But we cannot say what the velocity of any individual molecule selected at random is. We can only say that the probability that its velocity lies between c and $c+dc$ is

$$4\pi a^3 e^{-bc^2} c^2 dc.$$

Thus the distribution law gives a complete knowledge of the gas only in a statistical sense.

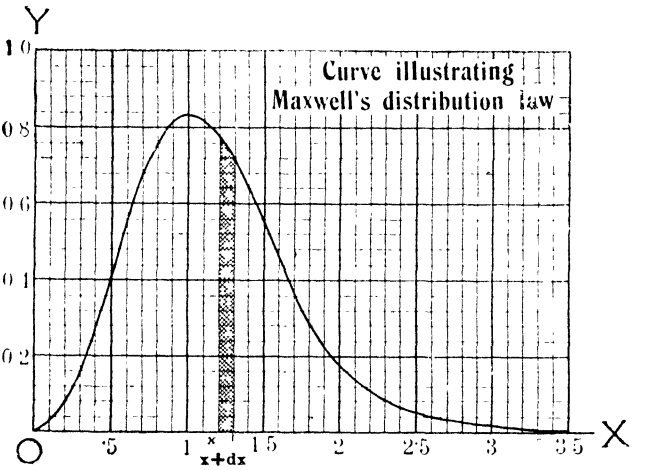


Fig. 3.—Curve illustrating Maxwell's Law.

A slight transformation (putting $bc^2 = x^2$) will show that the number $dn = 4n\pi^{-\frac{1}{2}} x^2 e^{-x^2} dx$, which helps us to represent the law graphically.

Let us plot the function $y=4\pi^{-\frac{1}{2}}e^{-x^2}x^2$ against x (Fig. 3). Then the number dn of molecules whose speed lies between x and $x+dx$ is proportional to the shaded area. The ordinate y gives the number of molecules possessing a speed corresponding to x, and from the curve it is obvious that the probability corresponding to $x=1$ is greatest, while it is considerably less for $x=2$ or $x=\frac{1}{2}$. Hence we can approximately treat the whole gas as endowed with the most probable velocity.

16. Average Velocities.—We must distinguish between two velocities, the square root C of the mean square velocity, and the mean velocity $\bar{c}$. The former is such that its square is the average of the squares of the velocities of the molecules.

Thus
$$C^2=\bar{c^2}=\frac{1}{n}\int_0^\infty c^2 dn_c=\frac{3kT}{m} \quad . \quad . \quad . \quad (19)$$

The mean velocity

$$\bar{c}=\frac{1}{n}\int_0^\infty c.\,dn_c=\sqrt{\frac{8kT}{m\pi}} \quad . \quad . \quad . \quad . \quad (20)$$

$$\therefore \frac{\bar{c}}{C}=\sqrt{\frac{8}{3\pi}}=\cdot 921 \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The most probable velocity α is that value of c for which N_c the number of molecules with velocity c is maximum. Hence for such value of c, $\frac{dN_c}{dc}=0$. This relation gives α. Substituting for N_c we get

$$\alpha=\sqrt{\frac{2kT}{m}}=\sqrt{\frac{2}{3}}C. \quad . \quad . \quad . \quad . \quad . \quad (22)$$

17. Law of Equipartition of Energy.—We next proceed to deal with the law of equipartition of energy. It is better to introduce here the idea of *degrees of freedom* of a system. A particle can move in any one of the three perpendicular directions and the motion along each direction is independent of the other. The particle is said to have three *degrees of freedom*. In general, the dynamical state of a body is defined by a number of coordinates of position x_1, $x_2 \ldots x_n$, and a number of coordinates of momenta or velocities u_1, $u_2 \ldots u_n$, all being independent, the energy corresponding to every such coordinate of either

class is the same, *i.e., the energy is equally distributed between the various degrees of freedom.* This is the law of equipartition of energy and was arrived at by Maxwell* in 1859. Boltzmann† extended it to the energy of rotation and vibration also. It can further be shown that the energy corresponding to each degree of freedom per molecule is $\frac{1}{2}kT$.‡ The law is very general, and we shall not attempt here to prove it.

In general if any dynamical system requires n coordinates, positional or momental, to define it, *i.e.,* if it has n degrees of freedom, the energy associated with the system at T°A is $n \times \frac{1}{2}kT$.

18. Molecular and Atomic Energy.—The above theorem is very useful in calculating molecular energy of substances. Let us calculate the specific heat of gases. In a *monatomic* gas the molecules are considered as elastic spheres, and the heat imparted to the gas at constant volume increases only the kinetic energy of translation of the molecules. The molecules possess only kinetic energy and no potential energy. They can move along any of the three mutually perpendicular directions and hence have three degrees of freedom. Therefore, the kinetic energy associated with a molecule is $3 \times \frac{1}{2}kT$. The total energy E associated with a gram-molecule is N times the above expression. It is thus equal to $\frac{3}{2}NkT = \frac{3}{2}RT$. The molar specific heat at constant volume is therefore

$$C_v = \frac{dE}{dT} = \frac{3}{2}R = 2{\cdot}98 \text{ cal./degree.}$$

For all perfect gases we have established the relation

$$C_p - C_v = R.$$

Therefore for a monatomic gas

$$C_p = \frac{3R}{2} + R = \frac{5}{2}R = 4{\cdot}96 \text{ cal./degree.}$$

and the ratio of the two specific heats

$$\gamma = 5/3 = 1{\cdot}66 \quad . \quad . \quad . \quad . \quad . \quad (23)$$

* Maxwell, *Collected Works*, Vol. I, p. 378

† *Sitzb. Akad. Wiss. Wien*, p. 58 (1861)

‡ From sec. 14 we have $pV = \frac{1}{3}MC^2 = RT$. The kinetic energy of translation of a gram-molecule is $\frac{1}{2}MC^2 = \frac{3}{2}RT$ from the above relation. If we assume that the energy is equally distributed between the three degrees of freedom, the energy associated with one degree of freedom per molecule becomes $\frac{1}{2}kT$. For a formal proof of the law see the Authors' *Treatise on Heat*, p. 140.

These theoretical conclusions agree with experimental results [see Table 5, Chap. II] for the monatomic gases as argon, helium, etc.

The specific heat of polyatomic gases can also be obtained by using the equipartition law. The molecule of a *diatomic* gas may be pictured as a system of two homogeneous elastic spheres joined rigidly to one another like a dumb-bell. This system possesses, in addition to the three components of the velocity of translation of the common centre of gravity, two components of the velocity of rotation about two axes perpendicular to the line of centres of the two spheres. Thus the system has five degrees of freedom and the total energy $E = \frac{5}{2}RT$. Hence

$$C_v = \frac{5}{2}R,\ C_p = \frac{7}{2}R,\ \gamma = 1{\cdot}4. \quad . \quad . \quad . \quad (24)$$

This is approximately the case for hydrogen, nitrogen, etc. At low temperatures, however, C_v falls to $\frac{3}{2}R$, as Eucken's experiments with hydrogen show, indicating that the rotation has disappeared. For chlorine C_v is greater than $\frac{3}{2}R$. This shows that the two atoms are not rigidly fixed but can vibrate in a restricted manner along the line of centres.

In a *triatomic* gas a molecule possesses three translational and three rotational degrees of freedom and hence

$$C_v = 6 \times \tfrac{1}{2}R = 3R,\ C_p = 4R,\ \gamma = 1{\cdot}33. \quad . \quad . \quad (25)$$

For more complex molecules γ approaches unity but is always greater than it. It is very difficult to know the vibrational degrees of freedom for them.

An expression for the specific heat of solids may also be obtained from the kinetic theory. We can consider molecules of a solid as elastic spheres held in position by the attraction of other molecules and capable of vibrating in a simple harmonic manner about a mean position. The molecule will have three components of velocity, and hence three degrees of freedom. The kinetic energy associated with each degree of freedom is $\frac{1}{2}kT$. On the average the harmonic vibration will have equal kinetic and potential energies and hence the total energy associated with a degree of freedom is kT. Therefore, the total energy for N molecules for the three degrees of freedom is 3RT, and the molar specific heat is $3R = 5{\cdot}955$. This yields Dulong and Petit's law.

But the kinetic theory of specific heat is unable to explain the variation of specific heat with temperature (p. 50), particularly the marked decrease

at extremely low temperatures. Further, the decrease is gradual and cannot be explained by the disappearance of any degree of freedom which would involve discontinuous changes by multiples of ½R. We cannot assume fractional degrees of freedom. Here the principles of classical dynamics and equipartition law fail completely. The quantum theory of specific heat has been developed which explains the existing facts satisfactorily.

MEAN FREE PATH PHENOMENA

19. Need for the Assumption that Molecules have got a finite Diameter.—We have seen in the previous sections that the molecules of a gas are moving at ordinary temperatures with very large velocities; in the case of air it amounts to about 400 metres per sec. There is no force to restrain the motion of the molecules. Hence the objection was raised that the assumption of such large rectilinear velocities were incompatible with many facts of observation. If the particles are moving with such enormous velocities, the gaseous mass contained in a vessel would disappear in no time. But we are all aware that the top of a cloud of smoke holds together for hours; hence there must be some factor which prevents the free escape of particles.

A very simple explanation was offered by Clausius. He showed that the difficulty disappears if we ascribe to the molecules a finite though very small volume. Then as a particle moves forward, it is sure to collide with another particle after a short interval, and its velocity and direction of motion will be completely changed. The path traversed between two successive collisions will be a straight line described with a constant velocity, since the molecules exert no force over one another except during collision. Hence the path of a single particle will consist of a series of short zig-zag paths as illustrated below:—

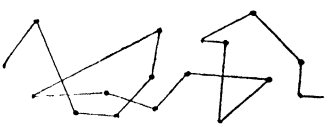


Fig. 1 – Illustration of free path.

Some of these paths will be long, others will be short. We can define a mean free path λ. Add up the lengths of a large number of paths

and divide it by the total number; this will give λ. This quantity is of great importance in studying a class of phenomena, called transport phenomena, such as viscosity, conduction of heat and diffusion.

20. Calculation of the Mean Free Path.—We shall give a very simple method of calculating the mean free path approximately. We make the simplifying assumption that all molecules except the one under consideration are at rest. The moving molecule will collide with all those molecules whose centres lie within a distance σ from its centre (σ being the diameter of the molecules), and are thus contained in a sphere of radius σ described about the centre of the moving molecule. This sphere is called the 'sphere of influence' of the molecule. As the molecule traverses the gas with velocity v it will collide with all the molecules lying in the region traversed by its sphere of influence. The space thus traversed in a second is a cylinder of base $\pi\sigma^2$ and height v, and hence of volume $\pi\sigma^2 v$. If the number of molecules per c.c. is n, this cylinder will enclose $\pi\sigma^2 vn$ centres of molecules and hence the number ν of collisions per second is $\pi\sigma^2 vn$. The length of the mean free path

$$\lambda = \frac{v}{\nu} = \frac{v}{\pi\sigma^2 vn} = \frac{1}{n\pi\sigma^2}. \quad . \quad . \quad . \quad . \quad (26)$$

In the above we assumed the other molecules to be at rest. Clausius removed this defect by assuming that all the molecules move with the same average velocity v. He obtained

$$\lambda = \frac{3}{4n\pi\sigma^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Maxwell further corrected the expression by introducing the law of distribution of molecular velocities and obtained the result

$$\lambda = \frac{1}{\sqrt{2}n\pi\sigma^2}. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

21. Transport Phenomena.—The distribution law expressed by (18) may also be put in the form

$$dn = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2}\frac{(u^2+v^2+w^2)}{kT}} du\, dv\, dw. \quad (29)$$

where dn is the number of molecules with velocity components lying between u and $u+du$, v and $v+dv$, w and $w+dw$ respectively. If the gas is endowed with mass motion represented by u_0, v_0, w_0, then

$$dn = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}(U^2+V^2+W^2)}\,dU\,dV\,dW \quad . \quad . \quad (30)$$

where $U=u-u_0$, $V=v-v_0$ and $W=w-w_0$.

If the gas is not in a steady state any one of the following cases, singly or jointly, may occur. (1) u_0, v_0, w_0 may not have the same value in all parts of the gas so that there will be a relative motion of the layers of the gas with respect to one another. We have then the phenomenon of viscosity. (2) Secondly, T may not be the same throughout, then we have the phenomenon of conduction, *viz.*, heat will pass from regions of higher T to regions of lower T. (3) Thirdly, if n is not the same everywhere we have the case of diffusion, *i.e.*, molecules diffuse from regions of higher concentration to regions of lower concentration. It is thus obvious that viscosity, conduction and diffusion represent respectively the transport of momentum, energy and mass. These are called transport phenomena. These phenomena are brought about by the thermal agitation of the molecules. But the molecules move with very large velocities, while these processes are comparatively very slow. The cause of this anomaly lies in the frequent molecular collisions. Hence the study of these phenomena is most conveniently done through the mechanism of mean free path. The molecules carry with them certain associated magnitudes and thereby tend to establish equilibrium.

22. Viscosity.—We shall first discuss the phenomenon of viscosity. Maxwell* was the first to explain this on the kinetic theory. Here we shall give an elementary treatment of the phenomenon based on considerations of mean free path. Consider a gas in motion and choose a horizontal plane xy such that there is a mass motion of the gas parallel to xy-plane but all the gas molecules in a layer parallel to that plane have the same velocity, and assume that the velocity increases as z increases. The molecules above the plane $z=z_0$ possess greater momentum than those below it, and hence when molecules from either side cross the plane there is greater transport of momentum downwards, since the number of mole-

* *Phil. Mag.*, Vol. 19, p. 20 (1860).

cules moving each way is the same, there being no mass motion parallel to the z-axis.

We can consider every molecule, on the average, to traverse a distance λ equal to the mean free path and then suffer a collision. If the velocity gradient is $\frac{du_0}{dz}$ the difference in the mean molecular velocity across two planes separated by a distance λ is $\lambda\frac{du_0}{dz}$. The mass of a molecule being m, the momentum transferred by it is $m\lambda\frac{du_0}{dz}$. Again due to heat motion, the number of molecules moving along the x-axis must be, on the average, the same as that moving along the y- or the z-axis. Hence one-third of the molecules move along the x-axis, both up or down. Thus the number of molecules crossing unit area of a layer per second, either up or down, will be $\frac{1}{3}n\bar{c}$ where n is the molecular density and $\bar{c}$ the mean molecular velocity corresponding to the temperature of the gas. Hence the total momentum transferred across the plane downwards is $\frac{1}{3}nm\bar{c}\,\lambda\frac{du_0}{dz}$. This will exert an accelerating force on the lower layers. Or the lower layers will retard this faster layer by a force equal to this. By definition of viscosity η this force must equal $\eta\frac{du_0}{dz}$. Hence

$$\eta = \tfrac{1}{3}nm\bar{c}\,\lambda = \tfrac{1}{3}\rho\bar{c}\lambda, \quad . \quad . \quad . \quad (31)$$

where ρ is the density of the gas.

23. Discussion of the Result.—We have established that $\eta = \frac{1}{3}\rho\bar{c}\lambda$ but $\lambda = \frac{1}{\sqrt{2}\,n\pi\sigma^2}$ (p. 91).

$$\therefore \eta = \frac{1}{3\sqrt{2}}\frac{m\bar{c}}{\pi\sigma^2}. \quad . \quad . \quad . \quad . \quad (32)$$

Now $\bar{c}$ is proportional to the square root of the absolute temperature, hence the coefficient of viscosity is independent of the pressure or the density of the gas, provided the temperature is constant. This deduction is rather surprising and was first regarded with suspicion. Meyer* and Maxwell† subsequently showed experimentally that the law actually held

* *Pogg. Ann.*, Vol. 125, pp. 40, 564 (1865); Vol. 143, p. 14 (1871).

† *Phil. Trans. Roy. Soc.*, Vol. 156, p. 249 (1866).

for pressures lying between 760 mm. and 10 mm.; this was a striking success for the Kinetic Theory. But beyond both limits the law fails. At higher pressures deviation from the law is expected since the intramolecular forces cannot be then ignored. At low pressures the mean free path λ gradually increases till it becomes comparable with the dimensions of the containing vessel, and then remains constant. Any further decrease of pressure reduces ρ and hence η. Thus at very low pressures the coefficient of viscosity rapidly decreases with decrease of pressure.

Again since $\bar{c}$ varies as $\sqrt{\frac{1}{m}}$, η for different gases should vary as $\sqrt{m}$. This is found to be approximately true.

24. Conduction.- Let us now find an expression for the conductivity of a gas which is a similar problem. In this case the temperature and hence the energy varies from layer to layer and it is the energy E which is transferred from one layer to another. Considering the energy gradient $\frac{dE}{dz}$ instead of the velocity gradient $\frac{du_0}{dz}$ the total transfer of energy per unit area becomes

$$-\tfrac{1}{3} n\bar{c}\lambda \frac{d\bar{E}}{dz},$$

where E denotes the mean molecular energy pertaining to any layer.

If K be the conductivity of the gas, $\frac{dT}{dz}$ the temperature gradient, the flow of heat across unit area will be $-K\frac{dT}{dz}$ and the flow of energy $-JK\frac{dT}{dz}$, where J is the mechanical equivalent of heat. Therefore

$$JK\frac{dT}{dz} = \tfrac{1}{3} n\bar{c}\lambda \frac{d\bar{E}}{dT}\frac{dT}{dz}.$$

$$K = \tfrac{1}{3} n\bar{c}\lambda \frac{d\bar{E}}{dT}\frac{1}{J}$$

$$= \tfrac{1}{3} n\bar{c}\lambda . mc_v = \eta c_v \quad . \quad . \quad . \quad (33)$$

when c_v is expressed in heat units. Further considerations show that the above result must be modified into $K = \varepsilon\eta c_v$ where ε is some constant.

Since $K = \varepsilon \eta c_v$ and the variation of c_v is small, the variation of conductivity with pressure and temperature follows in general the same course as the variation of viscosity. Thus conductivity like viscosity is independent of pressure. This was verified experimentally by Stefan* and others. We shall not consider the phenomenon of diffusion as it is somewhat more complicated.

25. Value of Constants.—We give below a number of constants which will give an idea of the several magnitudes involved in the Kinetic Theory of Gases. The gases are at 0°C and atmospheric pressure.

Table 1†

Gas	Mas of molecule $m \times 10^{24}$ gms.	Velocity in metres	Viscosity $\eta \times 10^6$	Thermal conductivity $K \times 10^6$	Mean free path $\lambda \times 10^6$ cms.	Molecular diameter $\sigma \times 10^8$ cm.
H_2	3·1	1839	86	318	18·3	2·47
N_2	43·1	493	166	52	9·44	3·5
O_2	49·2	461	187	56	9·95	3·39
He	6·1	1311	189	339	28·5	2·18
A	61·3	413	210	38·9	10·0	3·36
Cl_2	58·5	307	129	...	4·57	1·96

Book Recommended.

A good account of the subject matter of this chapter will be found in Eugéne Bloch, *Kinetic Theory of Gases*, English translation published by Methuen and Co.

Other References.

1. Loeb, *Kinetic Theory of Gases.*
2. Jeans, *Dynamical Theory of Gases.*
3. Meyer, *Kinetic Theory of Gases.*

* *Sitzb Akad Wiss Wien*, Vol. 65, pp. 2, 15 (1872).

† The table is largely taken from Kaye and Laby, *Physical Constants*. No great accuracy is claimed for the values given.

CHAPTER IV

EQUATIONS OF STATE FOR GASES

1. Deviation from the Perfect Gas Equation.—By the term "Equation of State" is meant the mathematical formula which expresses the relation between pressure, volume and temperature of a substance in any state of aggregation. If any two of these quantities be known, the third has a fixed value depending uniquely upon them, and can be determined if the equation of state is known, but this is seldom possible. According to the laws of Boyle and Charles, we have for a perfect gas,

$$pV=RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This is the equation for a perfect gas.

But even Boyle himself found that the law held only under ideal conditions, *viz.*, high temperature, low pressure, while under ordinary conditions it did not correctly represent the true state of affairs for any actual gas. For every temperature a curve can be drawn which has for its abscissa the volume and for its ordinate the corresponding pressure of the enclosed substance. These curves are called isothermals. If equation (1) were true the isothermals ought to be rectangular hyperbolas parallel to each other, but experiments show that this is not so. The most extended earlier investigations are due to Regnault.* He applied pressures up to 30 atmospheres while the temperature was varied from 0° to 100°C. He plotted the product pV as ordinate against p as abscissa (see Figs. 5, 6 supra this chapter). The curves ought to be straight lines parallel to the x-axis, actually however they were inclined to it. He found that for air, nitrogen and carbon dioxide the product pV decreases with increasing pressure, while for hydrogen it increases. He also found that hydrogen shows an abnormal Joule-Thomson effect (Chap. VI). These facts led him to describe hydrogen as "more than perfect." If equation (1) were true the product pV ought to remain constant; thus these permanent gases were shown to be imperfect.

* *Mem. Acad. Sciences*, Vol. 21 (1847).

Later work by Natterer, Andrews* and Cailletet using higher pressures confirmed the idea that the actual gases showed considerable deviations from equation (1). Andrews' experiments are of fundamental importance as they throw much light on the actual behaviour of gases and form the basis of an important equation of state first proposed by Van der Waals. Andrews' experiments are described in the next section.

The most thoroughgoing and exact experiments are due to Amagat† who investigated the behaviour of various gases up to a pressure of 3,000 atmospheres. His results particularly with CO_2 (Fig. 6) and ethylene showed that their behaviour is very complicated.

A different method has been utilized by K. Onnes,‡ who investigated the behaviour of several gases at very low temperatures and found that none of the numerous equations of state proposed correctly represents the results of experiments. He finds that at any temperature the result is best represented by an empirical equation of the type

$$pV = A + Bp + Cp^2 + Dp^3 + \ldots . \quad . \quad . \quad . \quad (2)$$

where A, B, C, ... are constants for a fixed temperature, but vary with temperature in a complicated manner. As many as twenty-five constants are used; they are called *virial coefficients.* A is simply equal to RT while the values of the coefficients of higher terms diminish rapidly. Holborn and Otto,§ following Onnes' method, studied several gases up to 100 atmospheres and between the temperatures of $-183°C$ and $+400°C$, and found that they need take only four constants. They give the values of these constants for various gases at different temperatures.

The coefficient B is of particular importance. For all gases it varies in a similar way: at low temperatures it has a negative value, then it gradually increases to zero and becomes positive. Now if at any temperature $B=0$, and C, D are negligible as usual, then

$$\frac{d(pV)}{dp} = B = 0.$$

* *Phil. Trans.*, Vol. 159, p. 575 (1869); Vol. 166, p. 421 (1876).

† *Ann. Chem. Phys.*, Vol. 19, p. 345 (1880); Vol. 22, p. 353 (1881); Vol. 28, pp. 456, 464 (1883); Vol. 29, p. 68 (1893).

‡ *Leiden Commun.*, No. 71 (1901).

§ *Zeits. f. Physik*, Vol. 33, p. 9 (1925).

Hence at this temperature Boyle's law will be obeyed up to fairly high pressures. This temperature is called the *Boyle Point.*

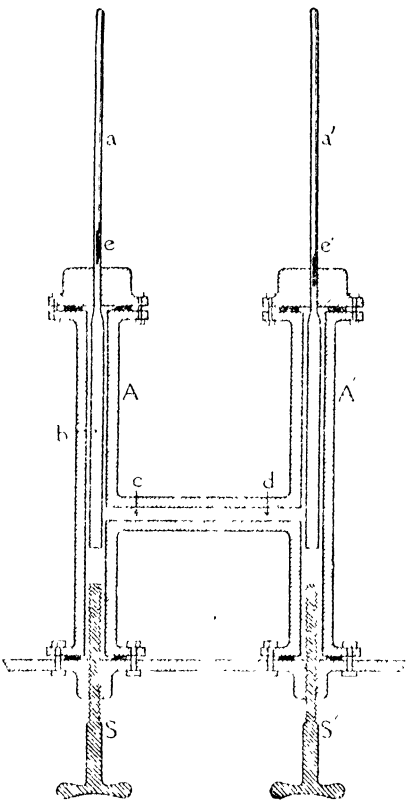


Fig. 1.—Andrews' apparatus.

2. Andrews' Experiments.—While engaged in the attempt to liquefy some of the so-called permanent gases—an important problem of the day, Dr. Andrews, in 1869, was led to study the isothermals of carbon dioxide. His apparatus is indicated in Fig. 1. *ab* is a glass tube whose upper portion consists of capillary tube and is narrower than the lower part. Carefully dried carbon dioxide was passed through the tube for several hours and then the tube sealed at both ends. The lower end of the tube was immersed under mercury and opened, and some of the gas expelled by heat, so that, on cooling, a small column of mercury *e* rose in the tube and enclosed the experimental gas.

The tube was surrounded by a strong copper tube A fitted with brass flanges at either end, to which brass pieces could be attached air-tight with the help of rubber washers. A screw S passed through the lower flange. The tube A contained water and hence by screwing in, pressures as high as 100 atmospheres could be applied to the carbon dioxide enclosed above *e*. To register the pressure a similar capillary tube containing air was placed on the right side, the steel tube A′ communicating with the tube A through the tube *cd*. The pressures in either tube could be varied by means of the screws S or S′. The capillary tube *ae* could be surrounded by any suitable constant temperature bath (not shown).

3. Discussion of Results.—The curves obtained by Andrews are shown in Fig. 2. In discussing them we must remember that the carbon dioxide employed by him contained about ·001% of air as impurity. Considering the isothermal corresponding to 13·1°C and starting from the right we see (portion AB) that as we increase the pressure, the volume diminishes considerably and finally liquefaction of the gas begins at a pressure of about 49 atmospheres. As long as liquefaction continues the pressure remains constant and the volume continually diminishes, more and more of the gas being precipitated as liquid. This is indicated by BC which is simply a horizontal line. (The slight inclination indicating an increase of pressure towards the end is due to the presence of air.) At C all the gas has condensed into liquid and the almost vertical part CD corresponds to the fact that liquids are only slightly compressible.

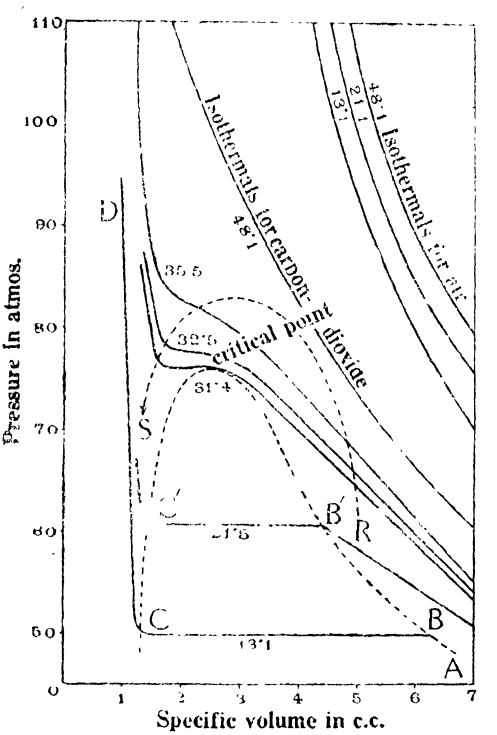


Fig. 2.—Andrews' Curves for Carbon dioxide

The isothermal corresponding to 21·5°C is of the same general form but the horizontal portion B′C′ is shorter. The specific volume of the vapour when condensation begins is smaller while that of the liquid when condensation has completed is greater than the corresponding volumes for the previous curve. As the temperature is raised these changes proceed in the same direction as above, till at 31·4°C the horizontal part has just disappeared and the two volumes have become identical. This is called the critical isothermal for carbon dioxide. Above this temperature, the horizontal part is absent from all the isothermals and as we increase

the pressure, there is no visible formation of liquid, but the volume diminishes rapidly till it becomes equal to that of the liquid. This peculiarity of the isothermal also disappears at higher temperatures as is evident from the isothermal for 48·1°C. which is much like the isothermals for air shown separately on the right-hand top. Thus if we want to convert gaseous CO_2 at 20°C. into liquid CO_2 at the same temperature without any discontinuity appearing, *i.e.*, the mass is not to separate into a liquid and a gaseous part with a layer between them, we must avoid reaching the inside of the dotted curve BB′C′C. Thus we heat it above 31·4° then compress it till the volume becomes equal to that of the liquid at that temperature. Next cool it to 20°C. and then reduce the pressure. Such a path is roughly indicated by the dotted curve RS in the figure. This idea is expressed by the statement that *there exists a continuity of the liquid and gaseous states*.

Thus we see that if gaseous CO_2 is compressed above 31·4°C. no liquid can make its appearance, however great the pressure may be. More accurate experiments show that this temperature is 31·0 and not 31·4°. The temperature 31·0°C. is called the *critical temperature* (T_c) for carbon dioxide. We may define critical temperature as the highest temperature at which a gas can be liquefied by pressure alone. This is why the earlier attempts to liquefy permanent gases failed, though enormous pressures amounting to as much as 3,000 atmospheres were sometimes employed. The pressure necessary to liquefy gases at the critical temperature is called the *critical pressure* (p_c), and the volume which the gas* then occupies is called the *critical volume* (V_c). These three quantities are called the *critical constants* of a gas. A table giving the critical constants for various gases is given on p. 112. It obviously follows that in trying to liquefy a gas, it is useless to apply pressure alone if the initial temperature is above the critical point, and no pressure greater than the critical need be employed.

As a point of historical interest, it may be mentioned that Cagniard de la Tour, as early as 1822, had pointed out the existence of a critical temperature, but the credit of clearing up the matter goes to Andrews.

4. Van der Waals' Equation of State.—The equation of state for perfect gases can be theoretically deduced from the kinetic theory of gases

* Of course the volume occupied by the gas and the liquid at the critical temperature is the same.

(Chap. III). Various investigators pointed out that the assumptions made in this deduction do not conform to actual facts for any real gas. Clausius first pointed out the importance of the finite volume occupied by molecules, and showed that V should be replaced by $V-b$, where b is related to the total volume occupied by the molecules. A preliminary consideration may suggest that b is simply equal to the total volume occupied by the gas molecules. A detailed consideration*, however, shows that b is equal to *four* times the volume occupied by the molecules.

Hirn, in 1864, pointed out that as the particles exert forces of attraction on one another, the energy cannot be wholly kinetic, and potential energy due to forces of cohesion must also be taken into account. The correction for forces of cohesion can be very simply obtained. These forces are of the same nature which give the phenomenon of surface tension in liquids. Now the molecules of the gas near the boundary must be attracted inwards by the molecules in the interior with a force which must be proportional to the number of molecules per unit area of the outermost layer and to the density of the molecules in the interior. This additional force is thus proportional to the square of the density of the gas. Hence p in the perfect gas equation must be increased by $p_1=c\rho^2$. Thus the perfect gas equation finally becomes

$$(p+p_1)\ (V-b)=RT$$

or

$$(p+c\rho^2)\ (V-b)=RT \quad . \quad . \quad . \quad . \quad (3)$$

where ρ is the density of the gas and equals $\frac{Nm}{V}$ where N is the Avogadro number, m the mass of the molecule and V the gram-molecular volume. Hence putting $cN^2m^2=a$, we have

$$\left(p+\frac{a}{V^2}\right)\left(V-b\right)=RT. \quad . \quad . \quad . \quad (4)$$

This is Van der Waals' Equation.† Van der Waals was the first to work out a systematic theory, taking into account both these factors, *viz.*, the finite size of molecules and the forces of cohesion. He first discussed the matter clearly in 1872 in his essay *on the Continuity of Liquid and Gaseous States*. Van der Waals' equation is found to hold true for small deviations from the perfect gas equation. A comparison of this with the

* For the proof of this result see the Authors' *Treatise on Heat*, pp. 206-207.

† For the various methods of deducing this equation see the Authors' *Treatise on Heat*, Chap. IV.

experimental results is given in Sec. 6. Various other equations of state have been proposed. Some of them are more accurate than Van der Waals' equation in certain regions; nevertheless, the latter, considering its simplicity gives in general, the most satisfactory first approximation to the behaviour of actual gases. We shall discuss this equation in more detail.

5. Method of Finding the Values of 'a' and 'b.'—A method of finding the values of 'a' and 'b' occurring in Van der Waals' equation is given below:—

Determination of 'a' and 'b' from Critical Data.—In the next section it will be shown from theoretical considerations that the critical temperature T_c, critical pressure p_c and critical volume V_c for a gas obeying Van der Waals' equation are respectively given by

$$T_c = \frac{8a}{27bR}\ ;\ p_c = \frac{a}{27b^2}\ ;\ V_c = 3b \quad . \quad . \quad . \quad (5)$$

$$\therefore\ a = \frac{27R^2}{64}.\frac{T_c^{\,2}}{p_c}\ ;\ b = \frac{R}{8}.\frac{T_c}{p_c} \quad . \quad . \quad . \quad (6)$$

Thus if T_c, p_c are experimentally determined 'a' and 'b' can be calculated with the help of equation (6). It may, however, be pointed out that the method is not very accurate as the gas does not obey Van der Waals' law accurately near the critical point. But this is not of much consequence as 'a' and 'b' themselves depend upon temperature and volume.

The values of 'a' and 'b' for a few important gases are given in

Table 1.—Values of 'a' and 'b' for some gases.*

Substance	$a \times 10^6$ in atmospheres	$b \times 10^6$ in cc.
Helium	6·8	106
Argon	268	143
Oxygen	273	143
Nitrogen	272	173
Hydrogen	48·7	118
Carbon dioxide .	717	191
Ammonia	833	166

table 1. They refer to 1 c.c.† of gas at N.T.P., and are determined by this

* Taken from Landolt and Börnstein, *Physikalisch-Chemische Tabellen.*

† If we consider a gram-molecule we have to multiply 'a' in the table by $(22{\cdot}4 \times 10^3)^2$ and 'b' by $(22{\cdot}4 \times 10^3)$. This is obvious from relation (6) since R for a gram-molecule in these units is $22.4 \times 10^3/273$.

method from equation (5). They may be taken to represent average values.

6. Discussion of Van der Waals' Equation.—We shall now discuss Van der Waals' equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT. \quad . \quad . \quad . \quad . \quad (4)$$

This is an equation of the third degree in V, hence it follows that for every value of p, V must have three values. Further, from theory of equations, either all the three values are real or one is real and two imaginary.

Again writing the equation in the form

$$p = \frac{RT}{V - b} - \frac{a}{V^2}, \qquad (7)$$

we see that for very large values of V, p is small and in the limit $p=0$ when $V=\infty$. Again when V is very small approaching b, p tends to infinity. Hence the curve must have a concavity upwards. For $V<b$, p is negative, hence this case is devoid of any physical significance. If in (7) we substitute the values of 'a' and 'b' for carbon dioxide, *viz.*, $a=0.00717$ atmos. $b=.00191$ c.c., and then represent the resulting equation by means of graphs for every temperature (p=ordinate, V=abscissa), curves of the type shown in Fig. 3 are obtained. It is readily seen that the curves resemble, in general, the experimental curves (Fig. 2) obtained by Andrews, but if we look for quantitative agreement by trying to make the two sets of curves coincide we are greatly

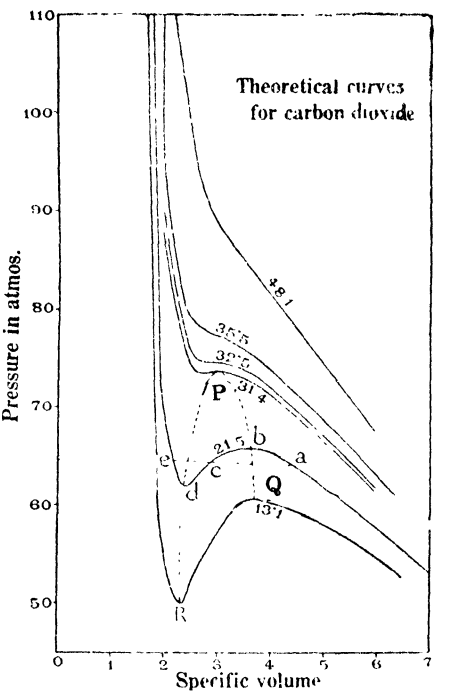


Fig. 3.—Theoretical curves for CO_2 according to Van der Waals' Equation

disappointed. In fact the agreement is only approximate and qualitative; partly because of errors in the assumed values of 'a' and 'b,' and partly because the equation holds only approximately.

There is however a remarkable divergence between the theoretical and the experimental curves in one region. The theoretical curves drawn from Van der Waals' equation give maxima and minima in the region represented by a straight line in Andrews' curves. Experimentally this is the region where condensation or vaporisation begins and the pressure remains constant as long as the process continues.

This difference is easily explained when the theoretical curve is properly interpreted. The part *bd* inside the dotted curve corresponds to the fact that the volume decreases with decrease of pressure which is quite contrary to experience. This would be a collapsible state, for any decrease of volume is accompanied by a decrease of pressure which tends to further decrease the volume. (This is apparent if we imagine the fluid to be confined in a cylinder.) Thus the state of the fluid inside the dotted curve represents a state of unstable equilibrium, and consequently can never be realised in practice. The portion *ab* of the theoretical curve also represents an unstable equilibrium and is sometimes obtained experimentally when vapour is supercooled, but as is well-known, this state can be easily disturbed mechanically. Similarly, the part *de* represents a superheated liquid which is also in an unstable state. Thus the apparent divergence is explained.

Van der Waals' theory, however, does not tell us when condensation begins, *i.e.*, where the straight part commences. A simple thermodynamic argument* shows that the straight portion should be so drawn that the area *abc* = area *cde*.

The maxima and minima points on the theoretical curve can be obtained by putting $\frac{\partial p}{\partial V} = 0$. Hence from (7), by differentiation,

$$\frac{\partial p}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0, \quad . \quad . \quad . \quad (8)$$

* Let the substance represented by the point a form the working substance of a heat engine (Chap. IX) and let it be taken through the cyclic operation represented by the path *abcdeca*. Since the temperature remains constant throughout the process, it follows from the theory of heat engines (Chap. IX) that the total work done by the working substance, *i.e.*, the area of the enclosed curve is zero. Hence the two areas *abca* and *cdec* since they are described in opposite senses, must be equal.

or
$$T = \frac{2a(V-b)^2}{RV^3} \quad . \quad . \quad . \quad . \quad (9)$$

This is also a cubic equation. Hence for every isothermal there are three real or one real and two imaginary points of maxima or minima. The curves below P in Fig. 3 are seen to possess one maxima and one minima points while those above it have none at all. A slight mathematical transformation will show that the other point of minima lies in the region $V<b$ and hence has no physical meaning. Equations (7) and (9) when combined yield

$$p = \frac{a(V-2b)}{V^3} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This is the curve passing through the maxima and minima points and is shown by the dotted curve QPR.

For temperatures below P, the isothermals have maxima and minima points, and these go on approaching each other as the temperature is increased. Above the point P there are no such points; therefore P may be identified with the critical point, and the isothermal through it with the critical isothermal. At P the dotted curve has its maximum, hence for this point we have, by differentiating (10) with respect to V and equating to zero,

$$\frac{a}{V^3} - \frac{3a(V-2b)}{V^4} = 0,$$

or
$$V_c = 3b.$$

From (10)
$$p_c = \frac{a}{27b^2}$$

and from (7)
$$T_c = \frac{8a}{27Rb}. \quad . \quad . \quad . \quad . \quad (11)$$

The critical constants may be very easily deduced from (7), since for the critical isothermal the point P is a maximum point as well as a point of inflexion, and for it both $\frac{\partial p}{\partial V}$ and $\frac{\partial^2 p}{\partial V^2}$ are equal to zero. Hence from (8)

$$\frac{\partial p}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0, \quad . \quad . \quad . \quad (8)$$

$$\frac{\partial^2 p}{\partial V^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0. \quad . \quad . \quad . \quad (12)$$

Combining (8) and (12) we get $V_c = 3b$, and with the help of (8), $T_c = \frac{8a}{27Rb}$. Finally from (7) $p_c = \frac{a}{27b^2}$, and $\frac{RT_c}{p_c V_c} = \frac{8}{3}$.

7. Defects in Van der Waals' Equation.—In spite of general agreement, deductions from Van der Waals' equation show considerable deviation from experimental results. We have already shown that for carbon dioxide the curves drawn from Van der Waals' equation do not quite agree with the experimental curves of Andrews. A particular isothermal may be made to agree much more closely with suitably chosen values of 'a' and 'b,' but then for the same values the agreement is not so good for other isothermals. This only implies that 'a' and 'b' vary with temperature as has been directly found from experiments but Van der Waals' theory assumes them to be constant. This is a great defect of the theory.

Another discrepancy however lies in the value of the critical coefficient $\frac{RT_c}{p_c V_c}$. From equation (5) this should be $\frac{8}{3}$ for all gases independent of their nature. Actually, however, it varies from gas to gas with an average value of 3·77 for most substances. This appears to depend upon the molecular structure of the gas. The critical coefficients for various gases are given in table 2* below.

Table 2.—Critical Coefficients for various fluids.

Substance	Critical coefficient	Substance	Critical coefficient
Helium	3·27	Chlorobenzol ...	3·78
Hydrogen	3·276	Iodobenzol ...	3·78
Neon	3·249	Bromobenzol ...	3·80
Nitrogen	3·412	Ethyl ether ...	3·81
Argon	3·424	Hexane	3·83
Oxygen	3·419	Heptane ...	3·86
Carbon dioxide ...	3·45	Octane	3·86
Ethane	3·55		
Methyl chloride ...	3·48	Propyl alcohol ...	4·00
Sulphur dioxide ...	3·62	Ethyl alcohol ...	4·02
Carbon-tetrachloride ..	3·67	Methyl alcohol ...	4·55
Isopentane . .	3·73	Acetic acid ...	4·99
Benzol	3·75		
Pentane ...	3·76		

* Taken from *Handbuch der Physik*, Vol. 10, p. 143.

Again Van der Waals' equation gives $V_c = 3b$, while experimentally it is found that V_c is more nearly equal to $2b$.

8. Experimental Study of the Equation of State.—The methods of determining isothermals for gases and liquids fall into two classes: (*a*) In the one we observe the change in volume when different pressures are applied. (*b*) In the other the volume remains constant, the quantity of matter being varied. The latter method is less common and has been employed by Holborn and Schultze* and by Kamerlingh Onnes.† The apparatus is somewhat complicated and will not be described here. Onnes' results have already been given on p. 97.

(*a*) *Apparatus based on the principle of variable volume.*—When the pressure is small, the apparatus is quite simple and is given in elementary text-books as the Boyle's law apparatus. For higher pressures up to 100 atmos. an apparatus due to Cailletet is used. This is described below. The same apparatus with certain modifications has been used by Regnault, Andrews and Amagat in their researches.

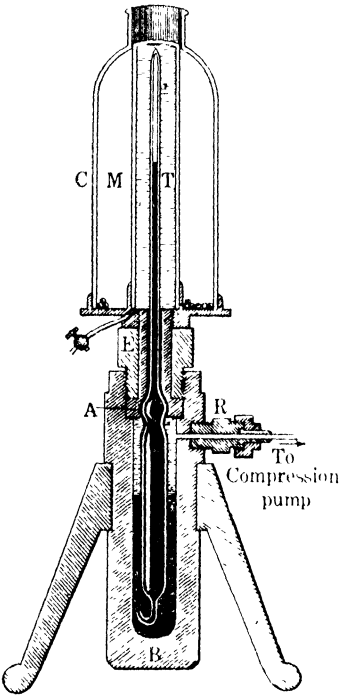


Fig. 4.—Cailletet's apparatus.

The apparatus is shown in Fig. 4. T is the measuring vessel made of stout glass which ends in a carefully calibrated capillary tube. The lower part of the vessel is placed in a steel cylinder. By means of a brass piece A and a screw E the vessel is held in the steel cylinder. M is a thermostat surrounding the upper narrow part of the tube which is again closed by means of a mantle C. The vessel T is filled with the gas under investigation at atmospheric pressure, the space between T and the inner wall B

* *Ann. d Physik*, Vol. 17, p. 1089 (1915), *Zeits f Physik*, Vol. 10, p. 367 (1922); Vol. 23, p. 77 (1924), Vol. 30, p. 320 (1924).

† *Leiden Commun.*, Nos. 69, 78, 97.

being filled with a sufficient quantity of mercury over which a quantity of glycerine or paraffin oil is poured. Pressure is communicated from a compression pump through glycerine to the measuring vessel. At high pressures mercury will rise up to the capillary tube and the volume can be easily read off from the calibration. When the pressure is high, it is measured by a compression manometer. If the pressure is about 300 atmos. and is exerted only from the inside the capillaries are generally smashed, hence the experimental tube must be subjected to pressure from all sides. Such a pressure tube was built by Amagat.*

Amagat carried out an exhaustive study of the behaviour of several gases by the above method. In one set of experiments he employed pressures up to 450 atmos., while in the next series pressures as high as 3000 atmospheres were used.† We shall now discuss his results.

Amagat represented his results by graphs in which pV denotes the ordinate and p the abscissa. The curves for hydrogen and nitrogen for several temperatures are shown in Fig. 5. As already mentioned, for H_2 the product pV increases with pressure, but for nitrogen it first decreases and then increases. The curves are straight lines *inclined* to the pressure axis, while if Boyle's law held true, they would be straight lines *parallel* to the pressure axis. The curves‡ for CO_2 (Fig. 6) are typical of all gases. The isothermals below about 30° have a portion of them parallel to the pV-axis. This indicates that the pressure remains constant while the volume varies, and corresponds to the condensation of vapours. Further, it is seen that the curvature

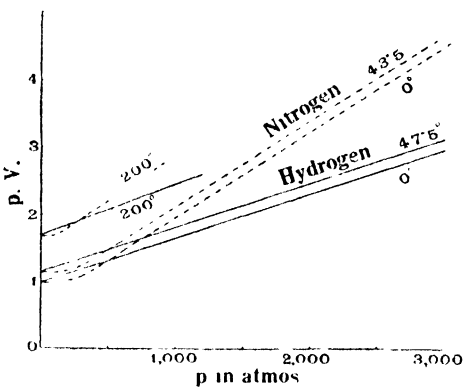


Fig. 5.—Amagat's curves (pV against p) for different gases.

* For a detailed description see Muller-Pouillet, *Lehrbuch der Physik*, Vol. 3, Part I, p. 242.

† A very good account of these experiments is given in Jellinek, *Physikalische Chemie*, Vol. 1, pp. 334–354.

‡ These curves can be fully understood and interpreted with the help of Van der Waals' equation and will be found to show striking concordance with Andrews' curves.

of the isothermals diminishes as the temperature rises. The minima points on isothermals gradually recede away from the origin, and the dotted curve through them is a parabola. At still higher temperatures no minima point is found and carbon dioxide behaves like H_2 or N_2. The equation of these

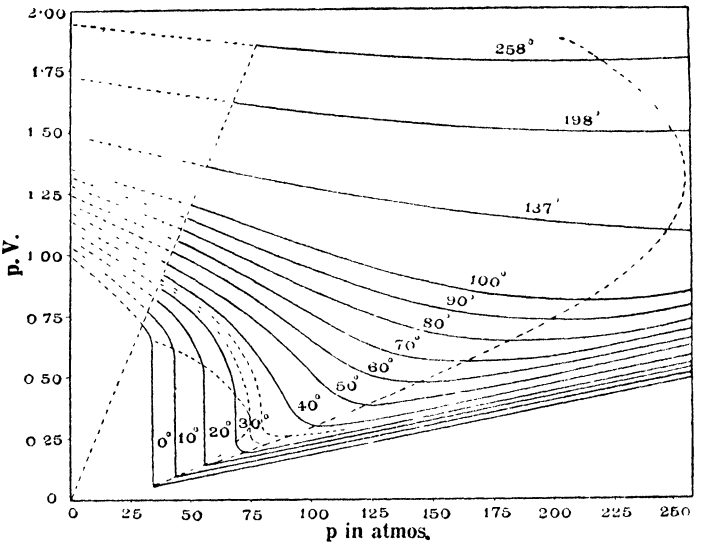


Fig. 6.—Curves for CO_2

straight inclined lines is of the form

$$pV = \beta p + \alpha$$

or

$$p(V - \beta) = \alpha$$

which is a first step to Van der Waals' equation.

9. Experimental Determination of Critical Constants.—We have defined the critical constants in sec. 3. They are constants characteristic of every substance, and are of fundamental importance as they occur in certain equations of state. Their importance in the study of liquefaction is discussed in Chapter VI.

The determination of these critical values is often a task of considerable difficulty. Of these the *critical temperature* is the easiest to measure accurately. For ordinary substances a hard glass tube like that of Andrews and connected to a manometer may be employed. Sufficient quantity of the liquid is introduced and the tube surrounded by a thermostat which can be maintained at constant temperatures differing by very small

amounts. The temperatures at which the liquid suddenly disappears and reappears are observed, the mean of these giving the critical temperature. The *critical pressure* is the pressure at the critical temperature and can be read easily from the manometer. The critical volume is much more difficult to measure accurately for even a small variation of temperature by 0·1°C. produces large change in volume, and hence the substance has to be kept exactly at the critical temperature. The pressure must also be exactly equal to the critical pressure since the compressibility of the substance in this region is very great. The method adopted was to arrange in such a way that a very slight increase of volume lowered the temperature by a small amount and caused the separation of the mass into liquid and vapour, the liquid appearing at the top. This initial volume is called the *critical volume*. The amount of substance initially contained in the tube has to be thus adjusted.

The most accurate method, however, is to make use of the *Law of Rectilinear Diameters* or mean densities, discovered by Cailletet and Mathias.* If the density of a liquid and of its saturated vapour be represented by ordinates and the corresponding temperatures by abscissæ, a curve roughly parabolic in shape is obtained (Fig. 7). In the figure the vapour density of nitrogen is plotted from the observations of Onnes and Crommelin† and is typical of all substances. The densities in the two states go on approaching each other till they become equal at the critical temperature. The curve AB is a line passing through the mean of the vapour and liquid densities and will consequently pass through the critical temperature. It was first observed by Cailletet and Mathias that for all substances this line was straight or very nearly so. The equation for this line is $y = \frac{1}{2}(\rho_l + \rho_v) = a + bt$ where

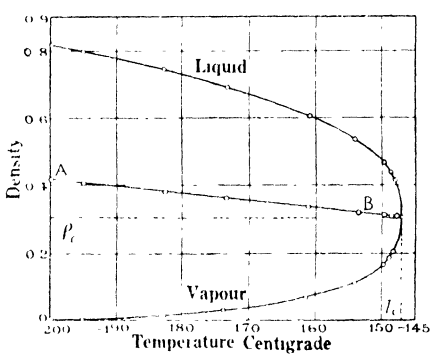


Fig. 7.—Law of Rectilinear Diameters.

* *Comptes Rendus*, Vol. 104, p. 1563 (1887), *Journal de Physique* (2), Vol. 5, p. 549 (1886).

† *Leiden Commun.*, No. 145 (*c*).

y is the ordinate and t the abscissa* and ρ_l, ρ_v denote the densities of the liquid and the vapour respectively. This law enables us to find the critical density or the critical volume, for we determine the densities of the saturated vapour and the liquid as near to the critical temperature as possible, then draw the rectilinear diameter and find ρ_c. The intersection of this line with the ordinate at the critical temperature gives the critical density or critical volume.

For substances like water which attack glass at high temperatures Cailletet and Colardeau† employed the apparatus shown in Fig. 8. The strong steel tube AB, platinized inside to prevent attack, contains the water or the substance to be investigated. It is immersed in a temperature bath LL which is heated by a gas regulated burner, and thus its temperature can be kept constant. The tube AB is connected to a similar steel tube FG by means of the flexible steel spiral CDE. Mercury fills part of the tube AB, the spiral CDE and the tube FG up to the level S_1. The tube FG is connected to a manometer M and a force pump. At S_1 an

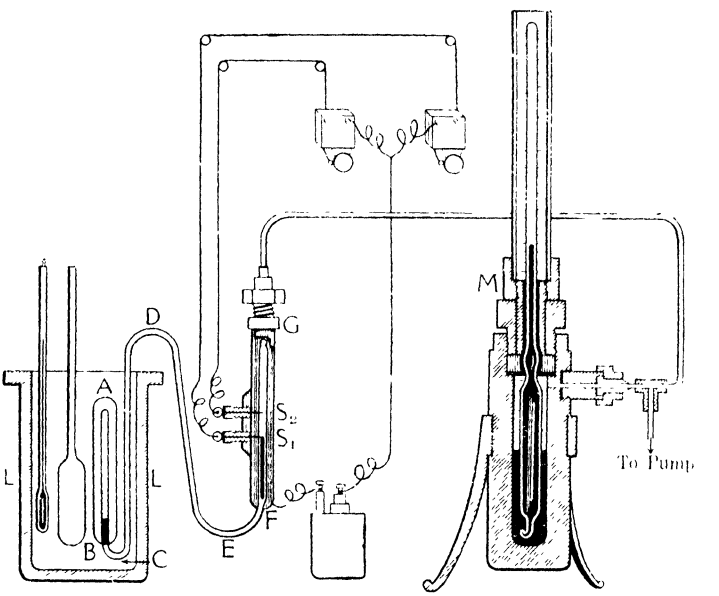


Fig. 8.—Cailletet and Colardeau's apparatus.

* For some substances the line is not quite straight. See *Handbuch der Physik*, Vol. 10, p. 171.

† *Comptes Rendus*, Vol. 112, p. 56 (1891); *Ann. de Chemie et de Physique* 6e, Vol. 25, p. 519.

insulated platinum wire is sealed in the side of the wall and completes an electric bell circuit. When the temperature of the bath is raised the pressure of the vapour in AB rises, mercury is forced past S_1 in FG and the bell sets ringing. Water is forced in by the pump to keep the level of mercury constantly at S_1 and thus the volume occupied by the water and water vapour in AB remains constant. The platinum wire at S_2 completes another electric circuit and serves to sound a warning that the whole mercury is about to be expelled out of AB.

We thus get the vapour pressure curve of the substance. The curve is perfectly continuous and characteristic of the substance. For water this is shown in Fig. 9. If, however, we start with different quantities of the liquid we get the same curve as far as M, but above it we get different curves. The vapour pressure thus appears to branch off at M, a point whose position was found by Cailletet to be practically independent of the quantity of liquid taken. This temperature is the critical temperature for the substance and for water it is 365°C.

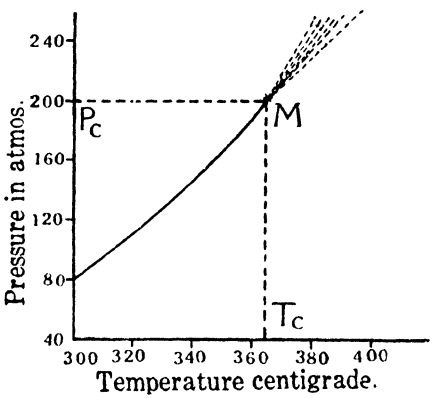


Fig. 9.—Vapour Pressure Curve for Water.

10. We give below a table of critical constants, taken from Landolt and Börnstein's *Physikalisch-Chemische Tabellen*.

Table 3.—Critical data.

Gas	T_c in °C.	P_c in atmos.	v_c specific volume	$\frac{RT_c}{P_c V_c}$
Helium	−267·9	2·25	15·4	3·13
Hydrogen	−239·9	12·8	32·2	3·28
Argon .. .	−122·4	48	1·88	3·43
Oxygen	−118·8	49·7	2·32	3·42
Nitrogen	−147·1	33·5	3·21	3·42
Carbon-dioxide ...	31·0	72·8	2·17	3·48
Ammonia	132·2	112·3	4·24	4·12
Ether	193·8	35·6	3·85	3·81
Sulphur dioxide ...	157·2	77·6	1·95	3·60
Methyl chloride .	143·1	65·9	2·71	3·80

11. Matter Near the Critical Point.—There has been much discussion about the state of matter near the critical point since the time of Andrews. The properties actually observed are:—(1) the densities of the liquid and the vapour gradually approach each other till they become equal at the critical point; (2) at the critical temperature the boundary line between the liquid and the vapour disappears, and hence there must be mutual diffusion, and the surface tension must vanish, *i.e.*, the molecular attraction in the liquid and vapour states must become equal; (3) the whole mass presents a very flickering appearance which suggests that there might be variations of density inside the mass. This was experimentally observed to be so by Hein* and others. They suspended spheres of different densities inside the fluid when each sphere comes to rest at a horizontal surface having a density equal to its own; (4) The compressibility of vapour at the critical point is infinite and is very great near that point. As pointed out by Guoy,† this explains the variation of density throughout the mass observed in (3), for the superincumbent vapour causes the density of lower parts to increase.

From these considerations the simplest and probably the most correct view appears to be that just beyond the critical temperature the whole mass is converted into vapour consisting of a single constituent and should behave like a gas near its point of liquefaction.

According to this theory the critical phenomenon, *i.e.*, the disappearance of the boundary between the liquid and the vapour and not its motion, should occur only when the amount of liquid in the tube is such that it will fill the whole tube with vapour of critical density. If more liquid is present the meniscus should go on rising till at the critical temperature the whole tube becomes filled with liquid. If less liquid is present, the meniscus goes on falling till at the critical temperature the whole tube should become filled with vapour alone. Experimentally, however, Hein‡ found that the critical phenomenon is observable when the initial density varies from 0·735 to 1·269 times the critical density. This is probably due to the property (4) as the variation of density inside the mass allows the excess or deficit amount to be adjusted. The branching of the vapour pressure curve at M observed by Cailletet and Colardeau may be explained in a similar way.

* *Zeits. f. physik. Chemie*, Vol. 86, p. 385 (1914).
† *Comptes Rendus*, Vol. 116, p. 1289 (1893).
‡ *Loc. cit.* The paper contains full references on critical phenomena.

An alternative view was put forward by Cailletet, Colardeau, Ramsay and others that the liquid state exists beyond the critical point, *i.e.*, both the liquid and the gaseous state simultaneously exist under these conditions. If we heat a mixture of liquids like ethyl alcohol and amyl alcohol which are partially miscible at ordinary temperatures but completely miscible beyond a certain temperature t, the two liquids will have a boundary of separation which will disappear at $t°$. Arguing from this analogy these physicists proposed that the liquid and vapour of the same substance though similar in chemical properties may probably differ in polymerisation and thus behave as the two liquids above. According to this view, above the critical temperature the upper part is solution of liquid in vapour while the lower part is a solution of vapour in liquid. It may be mentioned that the experimental evidence* for the simultaneous existence of the two states beyond the critical point is not quite conclusive. There appears to be no reason to suppose, *a priori*, that the liquid and vapour states can behave as two different fluids.

Books for Reference

1. Jeans, *Dynamical Theory of Gases.*
2. Loeb, *Kinetic Theory of Gases.*
3. Glazebrook, *A Dictionary of Applied Physics*, Vol. 1.

* For this evidence and other interesting discussions see Preston, *Theory of Heat.*

CHAPTER V

CHANGE OF STATE

FUSION—VAPORISATION—SUBLIMATION

1. It is a matter of common experience that on the application of heat, substances change their state of aggregation. Thus water exists in the solid form (ice) up to 0°C. If further heated, it becomes liquid. At 100°C the liquid passes completely into the vapour state under atmospheric pressure.

The temperature at which any change of state takes place is generally fixed, provided the external pressure is fixed and the substance is pure. The fusion point usually varies very little with the pressure (it requires a pressure of 130 atmos. to lower the melting point of ice by 1°C), but the variation of the boiling point with pressure is very great. As a matter of fact, it can be easily shown that water can be made to boil at any temperature up to 0°C, provided the pressure is sufficiently reduced. Conversely, the boiling point can also be raised considerably if the pressure be sufficiently increased. These facts can be readily verified by considering evaporation in a closed space.

2. Evaporation in a Closed Space.—If we fill a glass vessel partly with water and evacuate it with a pump, then water will begin to boil even at room temperature. If the pump be now cut off, the pressure can be measured by a manometer. For a certain definite temperature of the liquid, there is always a definite vapour pressure. If we increase the total space, more liquid will evaporate and fill up the extra space. If we reduce the space, some vapour will condense till the remaining vapour exerts the same pressure. If there is a third gas, not reacting with the vapour, the partial pressure of the liquid will be equal to the vapour pressure in the absence of the third gas. It is an important experimental task in Physics to determine the vapour pressure of a liquid at different temperatures.

3. Latent Heat.—Black found that the change from one state to another is not abrupt, but a large amount of heat must be absorbed before

the entire mass is converted from one state to another at the same temperature.* Thus to convert 1 gram of ice at 0°C to 1 gram of water at 0°C, 80 calories of heat are required. This amount of heat is required for loosening the particles of water in ice, so that they become mobile enough to form a liquid. The amount of heat required to convert 1 gram of a solid into a liquid without raising the temperature is called the *latent heat of fusion*. Similarly to convert water at 100°C to vapour at 100°C, 538·7 calories are required. This heat, which is necessary for pulling the molecules of water so far apart that they become quite independent of each other (vapour state) is known as the *latent heat of vaporisation*. It will be seen that the latent heat varies greatly with the temperature of vaporisation.

4. Sublimation.—Sometimes a solid may pass to a vapour state without passing through the intermediate liquid state. Camphor furnishes a good example of this class. On being heated it does not melt, but simply evaporates. Such a process is called *sublimation*, and the substance is said to be volatile.

But we shall see that the term is a relative one. All solid substances possess finite vapour tension at even ordinary temperatures. When this vapour tension is too small, we take no notice of it, but with the aid of delicate apparatus, it can be measured. A substance is said to be volatile only when the boiling point at atmospheric pressure is less than the melting point. Thus under an atmosphere different from our own, even ice which we do not consider volatile would have to be treated as such. The moon is supposed to have a very thin atmosphere (<1 *mm.* of mercury), and the temperature is below 0°C. If we consider ourselves transported to the moon, our studies will say that ice is volatile, because on being heated, it will evaporate to the gaseous state without passing through the liquid state. If we want liquid water in the moon we must artificially produce a high pressure and apply heat to ice under this pressure. Similarly camphor can be melted to a liquid form when it is heated under high pressure.

5. Amorphous Solids.—Only crystalline substances have got a definite melting point, the amorphous substances have no such property. They merely soften on heating and pass gradually to a liquid state.

* We have already discussed in Chap. II, pp. 35–41, the methods of measuring quantity of heat by Change of State.

Their viscosity diminishes and they become mobile. Such substances are not solids in the strict sense of the word, but are supercooled liquids. To this class belong glasses, fats, wax, pitch, etc.

6. Change of Properties on Melting.—Several properties of substances change in a very marked way when a substance melts. The following are among the important ones:

(1) *Change of Volume.* Most substances expand on solidification while a few others contract. To the former class belong ice, iron, bismuth, antimony, etc.; paraffin wax and most metals belong to the latter class. Good castings can only be made from substances of the former class. Often enormous force is exerted by water when it freezes into ice. The bursting of water pipes and of plant cells and the splitting of rocks is due to this cause.

(2) *Change of Vapour Pressure.* The vapour pressure abruptly changes at the melting point. The vapour pressure curves of the solid and liquid states are different and there is a sharp discontinuity at the melting point.

(3) *Change of Electrical Resistance.* The electrical resistance of metals undergoes a sudden change on melting. When the substance contracts on melting the conductivity increases and when it expands on melting the conductivity decreases. Table 1* below gives the ratio of the resistance of the fluid metal to that of the solid form at the melting point.

Table 1.—The Ratio $\frac{\text{resistance of fluid metal}}{\text{resistance of crystallised metal}}$ *for some metals.*

Substance.	Ratio.	Substance.	Ratio.
Al	1·65	Cu	1·97
Sb	0·70	Li	1·96
Pb	2·0	Na	1·34
Cd	1·97	Ag	1·98
Cs	1·65	Bi	0·45
Ga	0·58	Zn	2·00
Au	2·28	Sn	2·01
K	1·39		

(4) It is also found that molten metals show a discontinuity in their power of dissolving gases at their melting point.

* Taken from *Handbuch der Physik*, Vol. X, p. 37.

7. Determination of the Melting Point.—The melting point under normal conditions can be determined with very simple apparatus. The substance may be heated in a crucible electrically or otherwise. For high temperatures, the crucible must be of graphite or some other suitable material, and the substance heated in a non-oxidizing atmosphere. If the substance is rare, it can be employed in the form of a wire (wire-method). As thermometers, the secondary standards are very convenient to use, the thermo-couple or the resistance thermometer being generally chosen; such thermocouples or resistance wires must not be thrust directly into the melting substance, but should be protected by a sheath of protecting material, say porcelain, hard glass or magnesia tubes. Now as long as the substance is melting the temperature remains constant and hence the E.M.F. of the thermo-couple or the resistance of the thermometer is also stationary. A curve is plotted with the E.M.F. or the resistance as ordinate and time as abscissa. The horizontal part represents the freezing of the metal and the corresponding E.M.F. gives its melting point. Such a curve for copper is shown in Fig. 1 where 90 Pt-10Rh, Pt couple is used and the time is represented in minutes. The constant E.M.F. of the horizontal part is about 10·5 mV, which corresponds to 1084°C.

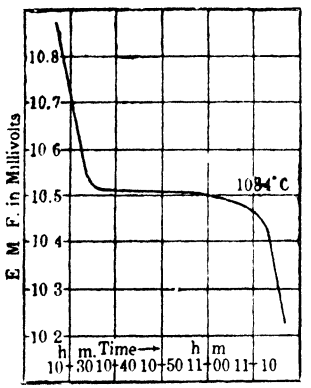


Fig. 1.—Melting Point of Copper.

8. Determination of the Latent Heat of Fusion.—For determining the latent heat of fusion, an ordinary calorimetric method (Chap. II) may be employed, *e.g.*—(1) the method of mixtures, (2) the Bunsen ice calorimeter, (3) the method of cooling, and (4) electrical methods. Method (3) is unimportant and will not be considered here.

The Method of Mixtures.—It is quite simple and has been explained in Chap. II. Most of the early determinations of the latent heat of ice were made by this method. Thus if M grams of ice at 0°C are added to a calorimeter containing water whose total thermal capacity is W and initial temperature θ_1 and if θ_2 be the final temperature, the latent heat L is given by the relation

$$ML+M\theta_2=W(\theta_1-\theta_2) \quad . \quad . \quad . \quad . \quad (1)$$

An important source of error in the above method lies in the fact that some water adheres to the crystals of ice at 0°C. To eliminate this, ice below 0°C is frequently chosen which requires a knowledge of the specific heat of ice. In this method we are required to find the heat taken up by ice in being heated. A converse method may also be employed, *viz.*, the heat given out by water in solidification may be found. The most accurate experiments give the value L=79·6 cal. for the latent heat of fusion of ice.

The method of mixtures has been very conveniently adopted to the simultaneous determination of the melting point and the latent heat of fusion of metals and their salts. Goodwin and Kalmus* employed this method for finding the latent heat of fusion of various salts. A known weight of the substance contained in a sealed platinum vessel is heated in an electric furnace to a high accurately measurable temperature. It is then dropped into a calorimeter and the quantity of heat liberated is determined in the usual manner. The platinum vessel is cylindrical in shape and water-tight. The electric furnace is specially designed to secure a uniform temperature throughout the platinum cylinder which is measured by a Pt-Rh thermo-couple. As calorimetric liquid, water was employed below 450°C while aniline above that temperature.

First a blank experiment gives the heat capacity of the platinum vessel. The experiment is then performed with the substance heated to different initial temperatures extending over a range of about 50°C both above and below the melting point, and the final temperature of the calorimeter noted. From these, after correcting for the heat capacity of the vessel, the quantity of heat Q necessary to raise 1 gram of the substance from the room temperature to its initial temperature could be calculated. Plotting Q as ordinate and T the corresponding initial temperature as abscissa curves of the type shown in Fig. 2 are obtained. The discontinuity in the value of Q indicated by the vertical line gives the latent heat of

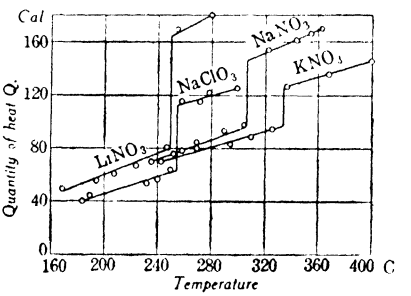


Fig. 2.—Latent Heat of Fusion of Salts.

* *Phys. Rev.*, I, Vol. 28, p. 1 (1909).

fusion, the temperature at which this discontinuity appears is the melting point T_m, and the slope of the curve at any temperature gives the specific heat of the substance at that temperature.

This method has been considerably improved by Awbery and E. Griffiths* who have made accurate determination of the latent heat of fusion of several metals. They employed a very special type of calorimeter which was so designed that the heated substance could be kept surrounded by water inside the calorimeter and the lid of the latter closed before any water had access to it, so that the loss of liquid by evaporation was eliminated.

In the above the quantity of heat with which the substance could part is measured by the method of mixtures. A *Bunsen ice calorimeter* may, however, be used for measuring that quantity of heat. The method is, however, not capable of great accuracy.

Electrical Method.—This consists in measuring the amount of electrical energy required to heat a mass of the substance below its melting point to a temperature above it. The method was employed by Dickinson, Harper, and Osborne† for finding the latent heat of fusion of ice. Electrical energy was supplied to a special calorimeter similar to that of Nernst in which ice below 0°C. was placed. Then

$$E = \int_{T_1}^{T_m} c_{p_1}\, dT + L + \int_{T_m}^{T_2} c_{p_2}\, dT \quad . \quad . \quad . \quad (2)$$

where E denotes the electrical energy supplied per gram, T_1, T_2 its initial and final temperatures and c_{p_1}, c_{p_2} the specific heats of ice and water respectively. From this relation L can be calculated. This method is very convenient for finding the latent heat at low temperatures.

Methods similar to the foregoing can also be employed for finding the heat of transformation of one allotropic modification to another but we are not concerned with them here.

9. Indirect Method.—Another method of finding the latent heat consists in making use of the Clausius-Clapeyron relation (Chap. X)

$$L = T \frac{\partial p}{\partial T} (v_1 - v_2) \quad . \quad . \quad . \quad . \quad (3)$$

* *Proc. Phys. Soc. Lond.*, Vol. 38, p. 378 (1926).
† *Bull. Bur. of Stand.*, Vol. 10, p. 235 (1914).

where v_1, v_2 denote the specific volumes of the liquid and solid respectively, and $\frac{\partial p}{\partial T}$ the ratio of the change of pressure with change of the freezing point. In this way L can be easily found.

10. Empirical Relationships.—It was observed by Richards that if ML denotes the latent heat multiplied by the atomic weight, $\frac{ML}{T}$ is approximately constant for all substances and its value lies between 2 and 3. This generalisation is known as *Trouton's Rule*. But the relation is only approximately true, and the value of the constant seems to depend upon the nature of the crystal form in which the matter solidifies. The following table* will show how far the generalisation holds:

Table 2.—Illustration of Trouton's Rule.

Substance	Atomic latent heat.	Melting Point T_m.	$\frac{ML}{T_m}$	Crystal system.
Na	630	371	1·7	Space-centred cube.
K	570	336	1·7	
Rb	520	312	1·7	
Cs	590	300	1·7	
Cu	2750	1356	2·03	Body-centred cube
Ag	2630	1234	2·13	
Au	3100	1337	2·32	
Pb	1170	600	1·96	
Al	2500	930	2·70	
Mg	1130	927	1·22	Hexagonal.
Zn	1800	692	2·60	
Cd	1500	594	2·53	
Hg	560	234	2·40	

11. Effect of Pressure on Melting Point. Regelation.—As already mentioned the melting point of a substance is not quite fixed; it changes when the external pressure is varied. In Chapter X a mathematical expression is deduced from thermodynamics for the change in

* Largely taken from *Handbuch der Experimental-physik*, Vol. 8, Part 1, p. 592.

melting point due to pressure. This expression clearly shows that the melting point of substances which expand on solidification is lowered by increase of pressure while the converse is the case for the other class of substances. This deduction is quite consistent with commonsense argument for substances of the former class will contract on melting and consequently excess of pressure will facilitate the change, *i.e.*, the substance will melt at a lower temperature. An analogous explanation can be given for the second class of substances.

Ice belongs to the first category. It is this property of ice which accounts for the well-known phenomenon of *Regelation*, *i.e.*, the melting of ice under pressure and its resolidification when the pressure is released. In virtue of this property we can explain the elegant experiment of Tyndall in which a piece of wire loaded at either end with weights and placed on a block of ice finds its way through the latter though the latter remains intact. The well-known phenomenon of glacier motion is partly due to the same cause. Snow goes on depositing on a mountain and when the mass attains sufficient height the ice at the bottom melts under pressure and begins to flow, but as soon as the pressure is released it resolidifies. The block of ice thus continuously shifts down the slope and we have the phenomenon of glacier motion.

12. Fusion of Alloys.—Most alloys melt like amorphous solids. They first become pasty or partially liquefied at the melting point of the more fusible component and liquefy completely when the melting point of the less fusible component is reached. On cooling the molten alloy, the temperature remains stationary when the melting point of the less fusible component is reached, then it falls gradually and again becomes stationary at the melting point of the more fusible component.

Certain alloys, however, have one definite melting point just like crystalline solids. They possess the peculiar property that their melting point is much less than that of any of the constituents. Thus an alloy of tin and lead (tin, 5; lead, 1) melts at 194°C; Rose's fusible metal (tin, 1; lead, 1; bismuth, 2) melts at 94°C; Wood's fusible metal (tin, 1; lead, 2; cadmium, 1; bismuth, 4) melts at 60·5°C though the melting points of bismuth, lead and tin are 269, 327, 232°C respectively. Sodium and potassium which are both solids form a silvery white liquid mixture at ordinary temperatures.

13. Phenomenon of Supercooling.—It has been said above that when a liquid is cooled it solidifies at a definite temperature (its freezing point). Most liquids, however, if slowly and continuously cooled, can be reduced to a temperature much below the normal freezing point. This is known as the phenomenon of supercooling. It can be conveniently observed with a Na_2SO_4 solution. Dufour suspended a minute drop of water in a mixture of chloroform and oil of sweet almonds which had a specific gravity equal to that of the water drop and managed to cool the latter to $-20°C$ without solidification while a drop of naphthalene could be supercooled to 40°C. (normal melting point 80°C.).

Supercooling is, however, essentially an unstable phenomenon. The introduction of the smallest quantity of the solid in which the liquid would freeze at once starts the solidification. Mechanical disturbances such as shaking the tube, stirring or rubbing the sides with a glass rod, or addition of some other solid is often sufficient to start solidification. If solidification has once started it will continue with evolution of heat till the normal freezing point is reached. After that further solidification will take place only when heat is lost by radiation, etc. Absence of air favours supercooling probably because the dust particles contained in it are then absent.

VAPORISATION

14. We have already seen that liquids as well as solids possess definite vapour tension at definite temperatures. We shall now describe some methods for determining the vapour pressure.

The range of pressure to be measured varies from 10^{-4} mm. to 400 atmospheres. In certain cases, pressures as low as 10^{-7} mm. have been measured. It is clear that such wide range of values requires various kinds of apparatus.

15. Vapour Pressure of Water.—The first accurate determination of the pressure of saturated vapour was made by Dalton.* A similar but improved apparatus was later employed by Regnault† for finding the vapour pressure at temperatures lying between 0° and 50°C. Regnault's experiments were performed with the greatest care and extend over a wide range of temperatures. His apparatus for the range $0°-50°$ is

* *Memoir of the Manchester Soc.*, Vol. XV, p. 109

† *Relation des Experiences, tom* 1, p. 467.

shown in Fig. 3. Two barometer tubes A and B were arranged side by side, fed from the same cistern of mercury M. The space *a* above the mercury level in the tube B is vacuum, while water is gradually introduced at the bottom of A till it rises through the mercury column and evaporates on reaching *b*. More water is introduced till a small layer remains floating over the mercury surface in A. A constant temperature bath DD furnished with stirrer (not shown), and a thermometer surrounds *a*, *b*, as well as some length of the mercury column. The difference in the heights of the two mercury columns, which are observed through a glass window with a cathetometer, gives the saturated vapour pressure of water at the temperature of the bath. Correction must be made for the weight of water in B, for effects of capillarity, refraction, etc.

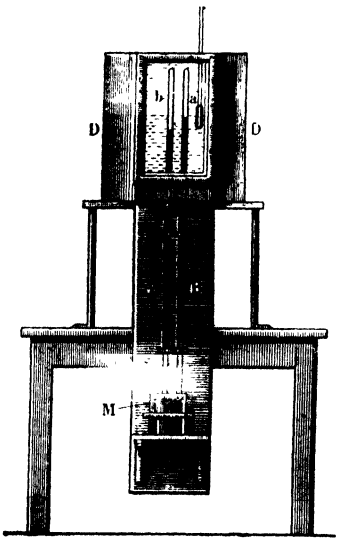


Fig. 3.—Regnault's vapour pressure apparatus.

For temperatures below 0°C Regnault modified his apparatus to that of Gay Lussac. The top of the tube A was bent round and terminated in a spherical bulb which contained water or ice and was surrounded by a suitable bath. For temperatures not much above 50°C the apparatus already described (Fig. 3) could be used when a longer bath would be necessary, but Regnault preferred the boiling point apparatus (Sec. 18).

16. General Methods.—The methods used for measuring saturated vapour pressure can be broadly divided into two classes:

(*i*) Methods in which the temperature is kept fixed and the pressure is determined either manometrically or by measuring the density of saturated vapour. This is called the *direct* or *static* method.

(*ii*) Methods in which the pressure is given and the temperature at which the liquid begins to boil is determined. This is called the *dynamic* method.

17. Static Methods.—Regnault's method is illustrative of class (*i*). The same method can be adopted for finding the vapour pressure of any liquid provided it does not react with mercury and the vapour pressure is neither too high nor too low. Quite a number of investigators have employed this method. Their apparatus differ only in unessential details. We have here a general scheme of apparatus (Fig. 1) which clearly illustrates the principle of the method. A is a small glass sphere, a few c.c. in capacity, to which is attached a glass tube C and another glass tube D with a smaller bore. This is connected to a bigger globe G and a mercury manometer M about 90 cms. long. The whole apparatus is first evacuated through the stop-cock S_1, and then the latter is closed. Next the gas under investigation is introduced through the stop-cock S_2 and condensed in A by suitably cooling the latter; finally S_2 is also closed. The sphere A is then surrounded by temperature baths and the vapour pressure corresponding to the temperature of the bath is indicated by the manometer M. B is a barometer to indicate the atmospheric pressure. The apparatus is convenient for measuring vapour pressures from a few cms. to the atmospheric pressure. For higher pressures a compressed air manometer may be employed when the whole apparatus has to be made of steel.

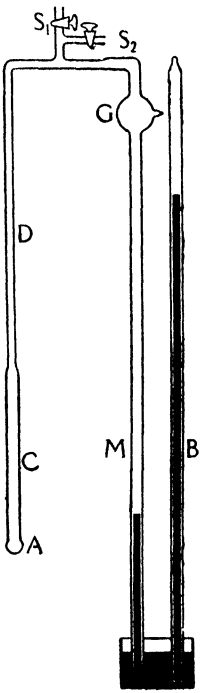


Fig. 4.—Determination of vapour pressure by statical method.

A similar apparatus was employed by Henning and Stock* for finding the vapour pressure of a number of gases between +10 and −181°C. On the same principle Siemens† has developed vapour pressure thermometry at low temperatures. For high pressures we may mention the classical experiments of Cailletet and Colardeau (p. 111) with water. Andrews' apparatus (p. 98) may also be used. In recent times also, Holborn and Baumann‡ determined the vapour pressure of water above 200°C by the statical method. The same method has also been employed by Smith and Menzies§ though their apparatus is much different.

* *Zeits. f. Physik*, Vol. 4, p. 226 (1921)
† *Ann. d. Physik*, Vol. 31, p. 915 (1910)
‡ *Ann. d. Physik*, Vol. 42, p. 871 (1913)
§ *Journ. Amer. Chem. Soc.*, Vol. 43, p. 547 (1921).

In the experiments mentioned above the pressure was measured manometrically, but the pressure may also be found by determining the density of saturated vapour, for assuming that the perfect gas equation holds, we have

$$p = \frac{\rho RT}{M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus knowing M, ρ, we can calculate p. Recently Isnardi and Gans* employed this method. Their apparatus is very simple. A portion of the vapour is isolated and its density determined.

18. Dynamic or Boiling Point Method.—This method is based on the fact that when a liquid boils its vapour pressure equals the external pressure on the surface of the liquid. A definite external pressure is applied on the liquid surface by means of a pump and then the liquid heated. The liquid will boil at the temperature at which its vapour pressure equals the external pressure, *viz.*, that set up by the pump. Hence the vapour pressure corresponding to the temperature of ebullition is the pressure exerted by the pump and can be read on a manometer.

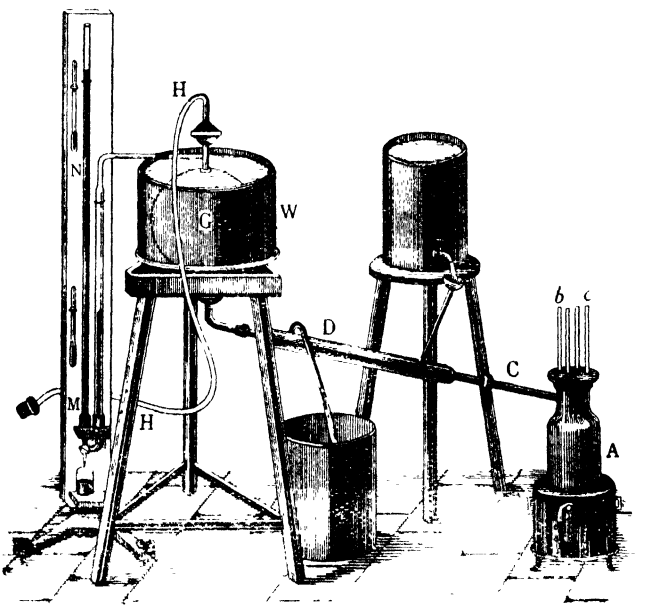


Fig. 5.—Regnault's Vapour Pressure Apparatus (Dynamical method.)

Regnault employed this method for finding the vapour pressure of water between 50°C. and 200°C. His apparatus is indicated in Fig. 5. The copper boiler A is partly filled with the experimental liquid

* *Ann. d. Physik*, Vol. 61, p. 267 (1920).

and contains four thermometers *bc* immersed to different depths inside the vapour and the liquid. The upper part of the boiler is connected to a large copper sphere G by means of a tube C which is itself enclosed in a water-cooling jacket D. The reservoir G is connected by means of H to a pump, the pressure being indicated by the mercury manometer NM. The reservoir is kept immersed in a water-bath W and serves to transmit the pressure from the boiler to the manometer as well as to smoothen the fluctuations due to the pump. The vapour of the liquid condenses in C and returns to the boiler, thus the same quantity of liquid is used over and over again. First, a definite pressure is established by the pump and the boiler heated. In a short time the readings indicated by the thermometers *b*, *c* become steady. The manometer indicates the vapour pressure corresponding to this temperature.

The apparatus can be adapted for all pressures. For high pressure all the parts must be made of copper and the pump must be a force pump. Regnault used pressures varying from a fraction of an atmosphere to 28 atmospheres. The method is capable of great accuracy. By this method Holborn and Henning* have very accurately determined the vapour pressure of water between 50 and 200°C (½ to 16 atmos.). Smith and Menzies† have devised an ingenious modification of the boiling-point method. Their apparatus is indicated in Fig. 6. The substance under investigation is kept in the sphere A close to the bulb of the thermometer T, both being immersed in some liquid contained in the test-tube B. The test-tube is closed air-tight and communicates with a pump and manometer (not shown). It is further surrounded by a bath whose temperature can be varied. A definite pressure is first established by the pump and the temperature of the bath gradually raised. When the vapour pressure of the substance contained in A becomes equal to the external pressure on the surface of the liquid in the tube, any further increase of temperature increases the pressure of the

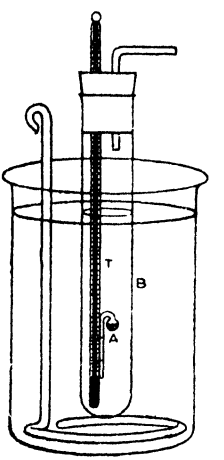


Fig. 6.—Smith and Menzies' Apparatus.

* *Ann. d. Physik*, Vol. 26, p. 833 (1908).

† *Zeits. f. phys. Chem.*, Vol. 75, p. 500 (1911); *Journ. Amer. Chem. Soc.*, Vol. 32, pp. 897, 907 (1910); *Ann. d. Physik*, Vol. 33, p. 989 (1910); *Journ Amer. Chem. Soc.*, Vol. 32, p. 1448 (1910).

vapour in A which consequently bubbles through the liquid in the tube. When this just happens the pressure recorded by the manometer gives the vapour pressure corresponding to the temperature indicated by the thermometer.

The boiling-point method has also been applied to metals by Braun.* Zinc or cadmium was heated electrically in a quartz or porcelain tube and the temperature of the vapour was measured by a thermo-couple.

19. Discussion of Results.—Experiments show that the saturated vapour pressure of every substance increases as the temperature is raised. Hence the vapour pressure p must be a function of the temperature, *viz.*, $p = f(T)$ where $f(T)$ must be of such form that its value increases with the temperature T. Various empirical relationships between p and T have been proposed at different times. They hold for a limited range and are by no means quite exact and universal. Further they had little or no theoretical basis until recently.

In 1820 Young proposed a very simple formula

$$\log p = A + \frac{B}{T}, \quad . \quad . \quad . \quad . \quad (5)$$

where T is the absolute temperature and A, B are constants. Rankine in 1849, from certain considerations, deduced the formula

$$\log p = A - \frac{B}{T} - \frac{C}{T^2}, \quad . \quad . \quad . \quad . \quad (6)$$

which appeared to agree with the experimental results of Regnault from $-30°C$ to $+230°C$. Kirchhoff in 1858 and Rankine in 1866 proposed quite independently the formula

$$\log p = A + \frac{B}{T} + C \log T. \quad . \quad . \quad . \quad (7)$$

This formula agrees with experimental results very closely and can also be deduced from theoretical considerations. It is shown in Chapter X that

$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)}, \quad . \quad . \quad . \quad . \quad (8)$$

where p is the vapour pressure, L the latent heat of vaporization, T the boiling point and v_1, v_2, the specific volumes of the substance in the

* *Zeits. f. anorg. Chem.*, Vol. 3, p. 119 (1920).

liquid and vapour states. Neglecting v_1 in comparison with v_2 and replacing v_2 by $\frac{RT}{Mp}$ from the gas laws we get

$$\log p = \frac{M}{R}\int \frac{L dT}{T^2} + i \quad . \quad . \quad . \quad . \quad (9)$$

Assuming L constant, equation (9) yields Young's formula (5). If however we assume L to vary linearly with temperature, *i.e.*,

$$L = L_0 - \alpha T,$$

equation (9) yields us formula (7). Equation (13) may be employed to give the exact value of pressure corresponding to any temperature.

The above holds for the saturated vapour pressure of a pure liquid; when mixtures of two liquids are investigated they yield interesting results. Regnault as early as 1854 deduced the following laws:—(1) In case of liquids which do not at all mix the vapour pressure of the mixture is equal to the sum of the vapour pressures of the constituents, *e.g.*, water and benzene. (2) In case the liquids are partially miscible the vapour pressure is less than the sum of the vapour pressures of the constituents or even less than that of one of them, *e.g.*, water and ether. (3) In case the liquids are miscible in all proportions the vapour pressure may become still less, *e.g.*, water and alcohol.

LATENT HEAT OF VAPORIZATION

20. In the measurement of latent heat of vaporization we have to remember two points; first, that its absolute value is relatively high; secondly, that the latent heat is absorbed or evolved in an isothermal change of state. The consequence is that its experimental determination is very little affected by the usual sources of error which are present in all calorimetric measurements. The methods can be grouped under three broad headings:

(A) *Condensation Methods.*—Those in which the amount of heat evolved when a certain amount of vapour condenses is measured.

(B) *Evaporation Methods.*—Those in which the amount of heat required to vaporize a given mass of the liquid is measured directly. The heat is generally added in the form of electrical energy and can be easily determined.

(C) *Indirect Methods.*—Those in which the latent heat is calculated with the help of certain thermodynamical relationships such as Clausius-Clapeyron relation (Chap. X). The first method is historically the oldest.

A. Condensation Methods

21. Berthelot's Apparatus.—Regnault's experiments are rather of historical interest. We describe below the apparatus of Berthelot (Fig. 7). In this apparatus which is wholly of glass the liquid is kept in the vessel D and heated by the ring burner B. The rest of the apparatus is protected by an insulating mantle M. The evaporated gas passes through the tube T into the spiral S placed within the calorimeter C. The spiral S is fitted to T by a conical ground piece and can be easily removed. The vapour condenses within the spiral and gives off its latent heat of vaporization to the calorimeter which can be easily measured by the rise of temperature on a thermometer placed inside the calorimeter. The calorimeter is placed inside a water jacket. The amount of water condensed is obtained by weighing the spiral S before and after the experiment. The heat measured represents the heat of vaporization plus the heat given up by the condensed liquid in cooling from the boiling point to the final temperature of the calorimeter. The open end of S is connected to a pump to regulate the pressure under which the boiling takes place.

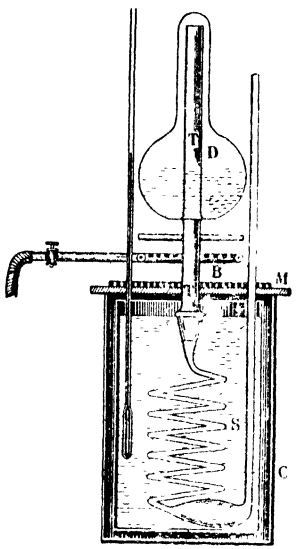


Fig. 7.—Berthelot's Latent Heat Apparatus.

Errors are likely to arise owing (1) to superheating of the liquid, (2) to the minute drops of water being carried over by the vapour. The use of a ring burner causes the heating to be sometimes irregular. Kahlenberg* replaced the ring burner by a metallic spiral placed inside the liquid and heated electrically. Trautz and Dechend† used an electrically heated wire as a boiling accelerator. Richards and Mathews‡ placed the upper part of the apparatus within a Dewar flask maintained at a constant temperature. The part between D and the spiral was made as short as possible to prevent condensation of steam in the leading tube TT.

* *Journ. Phys. Chem.*, Vol. 5, p. 215 (1901).
† *Zeits. f. Electrochemie*, Vol. 14, p 275 (1908).
‡ *Journ. Amer. Chem. Soc.*, Vol. 33, p. 863 (1911).

22. Awbery and Griffiths* used a slightly modified apparatus in which the usual calorimeter was replaced by a continuous flow calorimeter. The apparatus is shown in Fig. 8. The boiling chamber is heated electrically by an inner coil. The vapour passes down the vertical tube which is surrounded by a jacket of water through which a stream of water flows at a constant rate. The temperatures of the inflowing and outflowing water are determined by two thermo-couples. There is a third thermo-couple at the mouth of the vertical tube which gives the temperature of the condensed liquid as it leaves the apparatus. In this experiment the vapour must be produced at a steady rate and this is achieved by the use of electrical heating. The latent heat is obtained from the formula

$$M\theta = m\,[L + s(t_2 - t_1)] \quad . \quad (10)$$

where θ is the excess of temperature of the outflow water over the inflow water, M is the quantity of water flowing per unit time. m is the rate at which the liquid is being distilled, t_2 is the boiling point of the liquid, t_1 the temperature of the liquid as it leaves the apparatus.

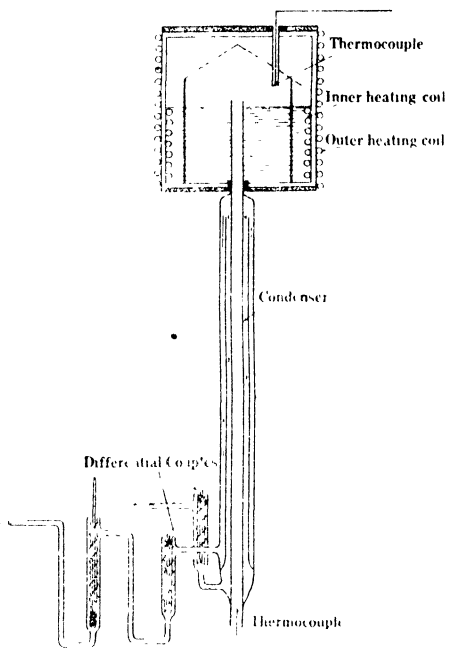


Fig. 8.—Awbery and Griffiths' Latent Heat Apparatus.

B. Evaporation Methods

23. This method was employed by Dieterici† who measured the heat required to evaporate a given mass of water with the help of a Bunsen ice-calorimeter. The water was contained in the tube and the heat was measured by finding the mass of mercury expelled. Griffiths‡ found the electrical energy required to vaporize a given mass of water. We shall describe

* *Proc. Phys. Soc. Lond.*, Vol. 36, p. 305 (1924).
† *Wied. Ann.* Vol. 37, p. 506 (1898).
‡ *Phil. Trans.*, p. 261 (1895).

the apparatus used by Henning* for precision measurement of the heat of vaporization between 30° and 100°C.

24. Henning's Experiments.—The apparatus employed by Henning is indicated in Fig. 9. C is a copper vessel, one litre in capacity, in which the liquid is allowed to evaporate. This is surrounded by an oil-bath A maintained at a constant temperature. The heating takes place through the spiral D, of constantan wire wound on a quadrilateral mica frame. E is a platinum resistance thermometer. The vapour which is evolved passes through the German silver tube H downwards through the German silver tube KK to the vessel P in which it is condensed and weighed. The end of H is bent downwards so that no liquid drops can be carried. By turning the stop-cock R the vapour can be turned to any one of the vessels P. The vapour is first led to one of the vessels P, and when the conditions become steady the stop-cock R is turned, and steam is led to the other vessel P. After a sufficient quantity of steam has been led to P the stop-cock R is turned to the other side.

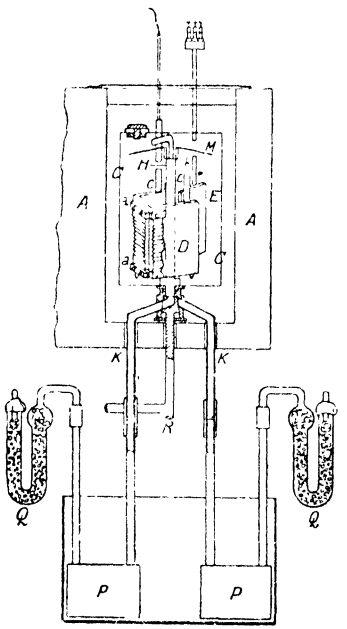


Fig. 9.—Henning's Latent Heat Apparatus.

The quantity of vapour deposited in the second vessel is now found by weighing and the quantity of heat supplied is obtained from observations of the electrical measuring apparatus. For determining the heat of evaporation at lower pressures P is connected to a large vessel of about 5 litres capacity which is maintained by means of a water pump at the required pressure.

A similar apparatus was employed by Henning† for finding the heat of vaporization of water up to 180°C. when the pressure reaches about 10 atmospheres. Smith‡ employed a current of air for the evaporation of

* *Ann. d. Physik*, Vol. 21, p. 849 (1906); Vol. 29, p. 441 (1909).
† *Ann. d. Physik*, Vol. 29, p. 441 (1909).
‡ *Phys. Rev.*, Vol. 33, p. 181 (1911).

water. Fogler and Rodebush* used this method for determining the latent heat of evaporation of mercury up to 200°C.

For determining the latent heat of evaporation of substances like nitrogen, hydrogen, helium, etc., which become liquid at very low temperatures, the above principle has been utilized by Dana and Onnes.† Simon and Lange.‡

C. Indirect Methods

25. The latent heat can be determined indirectly by means of the thermodynamic relation (8) which may be written in the form

$$L = T\left(\frac{dp}{dT}\right)(v_2 - v_1).$$

Thus from the vapour pressure curve, L can be calculated (*vide* Chap. X).

DISCUSSION OF LATENT HEAT DATA

26. Variation of the Latent Heat with Temperature.—Experiments show that the latent heat diminishes as the temperature at which boiling takes place is raised. This was noticed even by early investigators who proposed various empirical formulæ. Of these Thiesen's formula appears to have been most satisfactory and states

$$L = L_1 (t_c - t)^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad (11)$$

where t_c is the critical temperature and L_1 a constant which denotes the value of L at $t = t_c - 1$. This is of course based on the assumption that the latent heat vanishes at the critical temperature. Henning showed that between 30° and 100°C the latent heat is given by the formula

$$L = 538{\cdot}86 + 0{\cdot}5994\,(100 - t) \quad . \quad . \quad . \quad . (12)$$

* *Journ. Amer. Chem. Soc.*, Vol. 45, p. 2080 (1923).
† *Leiden Commun.*, *No.* 179 *c.*
‡ *Zeits. f. Physik*, Vol. 15, p. 312 (1923).

A typical curve showing the latent heat of carbon dioxide at various temperatures is given in Fig. 10. It is drawn from the results of several investigators and represents mean values. The figure shows clearly that the latent heat vanishes at the critical temperature of CO_2 which is about 31°C. This result is quite universal. The exact variation of latent heat with temperature for all substances is given by the thermodynamic formula

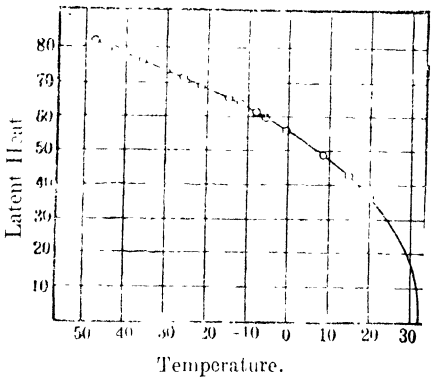


Fig. 10.—Variation of Latent Heat of CO_2 with Temperature.

$$\frac{dL}{dT} - \frac{L}{T} = c_g - c_l - \frac{L}{v_2 - v_1}\left\{\left(\frac{\partial v_2}{\partial T}\right)_p - \left(\frac{\partial v_1}{\partial T}\right)_p\right\}, \quad . \quad (13)$$

where c_g, c_l, denote the specific heat of the substance in the gaseous and liquid states respectively and v_2, v_1 the respective specific volumes.

27. Trouton's Rule.—As in the case of latent heat of fusion, we have here also an important generalization known as Trouton's Rule which states that *the ratio of the molar latent heat of vaporization to the boiling point is a constant for most substances;* or symbolically,

$$\frac{ML}{T} = \text{constant}, \quad . \quad . \quad . \quad . \quad (14)$$

where M is the molecular weight and T the boiling point. The value of the constant is about 21. The law does not hold for associated vapours. Table 3 (p. 135) shows that the law holds approximately for most substances.

It will be seen however that $\frac{ML}{T}$ is really not quite constant for all substances. A simple theoretical discussion shows that it cannot be so, for the boiling point under atmospheric pressure is purely an artificial point and has no physical significance. It varies enormously with the external pressure, while the latent heat varies neither in the same direction nor to the same extent. In the case of water the Trouton quotient at a few temperatures is given in Table 4.

Table 3.—Illustration of Trouton's Rule.

Substance	Molecular latent heat in calories ML	Boiling point T	Value of $\frac{ML}{T}$ experimentally
Helium. . ..	22	4·29	5·1
Hydrogen ...	219	20 4	10·8
Nitrogen .	1340	77·3	17·3
Oxygen .	1630	90 1	18·1
Hydrochloric acid	3890	188·1	20·7
Chlorine . .	4600	239·5	19·2
Pentane . .	6100	309 0	19·75
Carbon disulphide .	6490	319·2	21·0
Benzene ...	7350	353	20 8
Aniline ..	10000	457 0	21·9
Mercury	14200	630 0	22 6
Caesium .	15600	858	18 2
Rubidium ...	18700	942	19·9
Sodium ...	23300	1155	20·2
Zinc	27730	1180	23·5
Lead . .	46000	1887	24·4

Table 4.—Trouton quotient for water at different temperatures.

Pressure	B.P.	Latent heat	Trouton quotient
4·6 mm.	0°C.	606·5	40
760 „	100°C.	535·9	25 9
20950 „	230°C.	446	16

At the critical temperature the latent heat vanishes, hence Trouton quotient varies from 0 to 40 and can be made to assume any value. It is merely an accident that for most substances boiling under atmospheric pressure, the value is about 20.

DETERMINATION OF VAPOUR DENSITY

28. By vapour density we mean the specific gravity of the vapour referred to air or hydrogen as unity. The vapour density can be easily found if we find the volume occupied by a known weight of vapour at a certain pressure and temperature. Thus if w grams of the vapour occupy v c.c. at the pressure p and temperature T and w_0 be the weight of

1 c.c. of the standard substance (air) at 273° and 760 mm., then the vapour density is given by

$$\frac{w}{w_0 v} \cdot \frac{T}{273} \cdot \frac{760}{p} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The density of the *unsaturated* vapour can be easily and accurately found by any one of the standard methods,* *viz.*, of Victor Meyer, Dumas, Hofmann and others. But before 1860 there was no method for directly determining the density of *saturated* vapours. The methods adopted were all indirect in which the density of the unsaturated vapour was first determined and assuming the perfect gas laws to hold up to the saturated state, the density of the saturated vapour was determined. This assumption is, however, not quite justifiable, hence these methods can never give accurately the density of saturated vapour. Still however they are frequently used especially that of Victor Meyer, which is consequently described below.

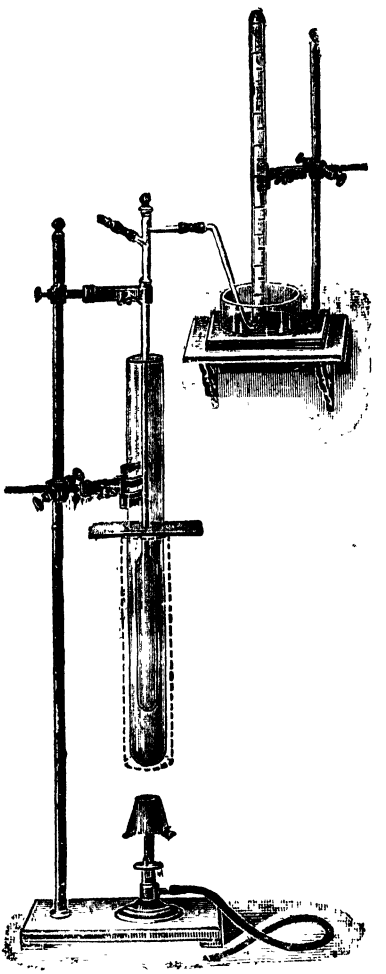


Fig. 11.—Victor Meyer's Vapour Density Apparatus.

Victor Meyer's method is of considerable practical importance. The apparatus (Fig. 11) consists of a cylindrical bulb with a long narrow stem, near the top of which there is a side-tube. The lower part of the tube is surrounded with a bath kept at the desired temperature. Air inside the tube gets heated and is expelled at the top;

* Full details of these methods will be found in any text-book on Physical Chemistry.

after a time however a steady state is attained when no more air escapes. The substance whose vapour density is to be determined is enclosed in a thin-walled stoppered bottle and gently dropped in the tube and the latter closed instantaneously. The liquid becomes vaporized and thereby displaces an equal volume of air which escapes at the side-tube and is collected in the measuring vessel. Knowing the mass of this air, the vapour density of the vapour is obtained by dividing the mass of the liquid taken by the mass of displaced air.

Nernst* has modified the apparatus and could thereby measure the vapour density of KCl and NaCl up to 2000°C while Wartenberg† found the vapour density of several metals up to 2000°C. For a description see Arndt *Physikalisch-chemische Technik*, Chap. IX.

29. Accurate Determination of the Density of Saturated Vapour.—In 1860 Fairbairn and Tate‡ devised an apparatus by means of which they measured the density of saturated vapour directly. Fig. 12 explains the principle of their apparatus. A is a spherical glass bulb whose narrow stem dips into mercury contained in the outer wider glass tube. The latter communicates with the metal reservoir B. Both A and B contain some water above the mercury levels, the latter containing a larger quantity than the former. All air is expelled from the apparatus and then both the vessels are surrounded by a bath whose temperature is gradually raised. The levels of the mercury in the two vessels remain constant, that in A being always higher than in B due to the excess of water in B. This is so as long as there is any liquid water in A. But as soon as the liquid in A disappears, the level of mercury in A suddenly rises. This is so because the saturated vapour pressure increases much faster than the pressure of unsaturated vapour obeying Boyle's law. The temperature at which this sudden rise of mercury column in A appears is noted. At

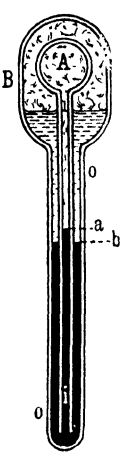


Fig. 12.—Fairbairn and Tate's apparatus.

* *Zeits. f. Electrochemie*, Vol. 9, p. 622 (1903).
† *Zeits. f. anorg. Chemie.*, Vol. 56, p. 320 (1908).
‡ *Phil. Trans.*, Vol. 150, p. 185 (1860); *Phil. Mag.*, Vol. 21, p. 230 (1861).

this temperature the vessel A becomes filled with saturated vapour whose pressure may be found by means of a gauge connected to B. Knowing the mass of water in A and the volume of the enclosed space, the density of the vapour at the particular temperature and pressure can be calculated.

Somewhat later Perot* attempted to isolate a portion of the saturated vapour and to weigh it. This could be very conveniently done by isolating by means of a stop-cock and getting the vapour absorbed in dry calcium chloride and weighing the latter. K. Onnes† has quite recently employed a very simple method. In a graduated vacuous tube different masses of the liquid are introduced and the volumes of the vapour and the liquid observed. Thus if m and m' grams of the substance are introduced and the volumes occupied by the gas and the liquid are v_1 and v_2 in the first case, and v_1', v_2' in the second case, and ρ_g, ρ_l represent the densities of the gas and the liquid, we have

$$m = v_1 \rho_g + v_2 \rho_l$$

$$m' = v_1' \rho_g + v_2' \rho_l$$

whence

$$\rho_g = \frac{m v_2' - m' v_2}{v_1 v_2' - v_1' v_2} \quad . \quad . \quad . \quad . \quad (16)$$

Book Recommended

(1) Glazebrook.—*A Dictionary of Applied Physics*, Vol. 1, article on Latent Heat.'

* *Comptes Rendus*, Vol. 102, p. 1369 (1886).
† *Leiden Commun.*, No. 117.

CHAPTER VI

LIQUEFACTION OF GASES

1. Introduction.—It is not quite clear whether the early philosophers did not regard the temperature of melting ice as the lowest attainable, but their selection of this point as the zero of scale seems to indicate that such was their belief. The observation of Fahrenheit that his mercury thermometer recorded a still lower temperature when placed in a mixture of ice and common salt constituted a step in advance. We know that Fahrenheit's zero is not the lowest temperature available. The study of the laws of perfect gases and definition of the absolute scale (Chap. X) tells us that we can, at least theoretically, proceed 273 degrees below the melting point of ice, and that this is the lowest temperature conceivable. This is taken as the zero of the absolute temperature scale. In this chapter we shall discuss the principles and contrivances by which the low temperature region can be reached.

PRINCIPLES USED IN REFRIGERATION

2. For reaching such low temperatures, we have to look to processes by which a body can be deprived of its total heat content. The following methods may be employed to achieve this end:—

(*i*) By adding a salt to water or ice.
(*ii*) By boiling a liquid under reduced pressure.
(*iii*) By the adiabatic expansion of a gas doing external work.
(*iv*) By utilizing the cooling due to Peltier effect.
(*v*) By the application of the Joule-Thomson effect.
(*vi*) By utilizing the heat of adsorption.
(*vii*) By the process of adiabatic demagnetisation.

The last method is too complicated to be described here. With its aid the lowest temperatures (below 1°A) have been reached.

A general theory of refrigeration will be given later in the chapter on Thermodynamics; here we shall simply discuss the principles and contrivances for utilizing them.

(*i*) Adding a Salt to Ice

3. Low temperatures may be attained *by adding a salt to ice.* This is the same process which was first utilised by Fahrenheit. The cause of this lowering of temperature is easily understood. Pieces of ice have generally some water adhering to them, and if salt be added to this ice, it is dissolved by the water and more ice melts. The necessary heat for this process, *viz.*, the heat of solution and the latent heat required to melt the ice, is extracted from the mixture itself whose temperature consequently falls down. This is the principle of *freezing mixtures.* In Table 1 is given the lowest temperature which is possible to attain by dissolving different salts in ice at 0°C.

Table 1.—Freezing Mixtures.*

Salt	Anhydrous salt per 100 grams of the mixture	Eutectic temperature
$MgSO_4$	19·0	−3·9°C.
$ZnSO_4$	27·2	−6·5
KCl	19·7	−11·1
NH_4Cl	18·6	−15·8
NH_4NO_3	41·2	−17·4
$NaNO_3$	37	−18·5
NaCl	22·4	−21·2
$MgCl_2$	21·6	−33·6
$CaCl_2$	29·8	−55
KOH	31·5	−65

The amount of cooling produced is limited by the existence of the eutectic point, *i.e.*, only so much salt can be dissolved that the solution reaches saturation. If more salt be added it remains undissolved, and no further cooling can be produced. In practice even the eutectic temperature is not easily reached on account of mechanical difficulties.

(*ii*) Boiling a Liquid under Reduced Pressure

4. Low temperature may also be attained by allowing a liquid to boil under reduced pressure. When a liquid evaporates it requires heat for conversion from the liquid to the gaseous state (latent heat of vaporization). Thus one gram of water at 100°C. requires 536 calories for complete evaporation. If such liquid be forced by some contrivance to evaporate rapidly, and if the liquid be isolated, this heat is supplied at the expense of its total heat content and intense cooling may be produced.

The oldest contrivance for utilising this process is the cryophorus indicated in Fig. 1. The bulb B contains water or some more volatile liquid and the rest of the space is filled with the vapour of the same liquid. When A is immersed in ice the vapour in it condenses and the pressure of the vapour in B becomes so much lowered that the liquid in B boils. The latent heat necessary for this purpose is extracted from the rest of the liquid which consequently freezes.

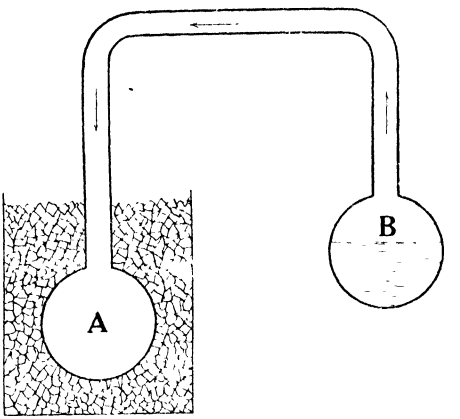


Fig. 1.—The Cryophorus.

5. Absorption Machines. *Sulphuric acid machine*—Carré employed the same principle in constructing a refrigerating machine. The principle of the machine is illustrated in Fig. 2. The flask A contains water and is connected to a chamber B containing concentrated sulphuric acid and to a vacuum-pump with a high rate of suction.

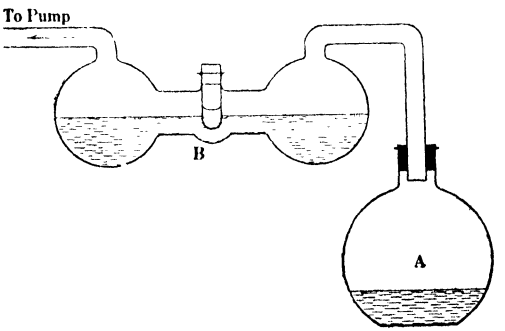


Fig. 2.—Sulphuric Acid Refrigeration.

When the space is completely evacuated the water in A boils, but the vapour is absorbed by the sulphuric acid as soon as it forms, causing more of the liquid to boil. Due to this rapid continuous boiling, the water in A freezes. The machine was later improved so that it could produce ice in about two minutes but it proved uneconomical and was consequently given up. Further the sulphuric acid became dilute in a short time and had to be concentrated for use again. Thus the action was intermittent.

Ammonia absorption machine.—Carré again devised an ammonia absorption machine which worked in two stages. Its action was not continuous* and hence it will not be described here. We shall however describe a continuous form of ammonia absorption freezing machine due to Carré which was formerly employed on a large scale. The working of the machine will be understood from Fig. 3. The generator A contains a strong solution of ammonia gas in water and is heated by a burner. Ammonia gas is expelled from the solution and passes into the coils immersed in the condenser B through which cold water continuously flows. The gas condenses there under its own pressure into liquid ammonia. The liquid ammonia thus formed passes through a narrow regulating valve V to the spiral immersed in the refrigerator C, where on account of the low pressure it evaporates. The valve is adjusted to maintain the desired difference of pressure on the two sides. Through the refrigerator flows a stream of brine water which becomes cooled by the evaporation of ammonia. The cool brine solution may be taken to any place for refrigerating purposes.

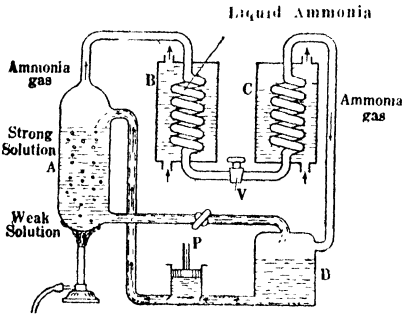


Fig. 3.—Ammonia Absorption machine

The ammonia gas formed in the coils in C is absorbed by water† or dilute ammonia solution contained in the absorber D and thus the pressure is kept low. The solution in D becomes concentrated and is transferred by the pump P to the generator at the top. Thus the supply of concentrated ammonia solution is kept up. Dilute ammonia from the bottom of the generator may be run to the absorber and concentrated. Thus the cycle is repeated and the action is quite continuous.

6. Vapour Compression Machines.—The absorption machines have rather a low efficiency and are consequently rarely used for commercial purposes. They have been almost completely replaced by the vapour compression machines. Fig. 4 shows a form of this machine.

* *Comptes Rendus*, Dec. 24 (1860).

† The water here plays the part of sulphuric acid and the ammonia gas that of water vapour in the sulphuric acid machine.

There are three principal parts—the compressor P, the condenser C and the refrigerator R. The refrigerator is connected to the suction side of the pump while the condenser is connected to the delivery side. The other ends of the condenser and the refrigerator are connected to a regulating valve V. The liquid, say anhydrous ammonia, sulphur dioxide or carbon dioxide, passes from the condenser C through V to the refrigerator R and boils there under low pressure.

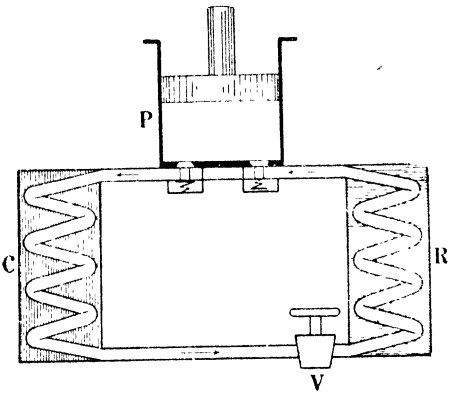


Fig. 4.—Vapour Compression Machine.

The substance to be cooled, say brine water, surrounds the refrigerating coils and hence becomes cooled. The low pressure vapour now passes to the pump, is compressed and delivered to the condenser which is cooled by water. The process is thus cyclic.

In addition to ammonia which is generally used in such machines, other volatile liquids may be used. The criteria for selecting a liquid are (1) large latent heat of evaporation, and (2) sufficient vapour pressure at low temperatures. Water is not suitable for though it has a large latent heat, the vapour pressure at low temperatures is small. Methyl and ethyl alcohol are more suitable because they have large vapour pressure even at $-20°C$. Besides ammonia, CO_2 and SO_2 are also used. The method may be employed to obtain extremely low temperatures by using liquid hydrogen and helium. These liquids are allowed to boil under reduced pressure when temperatures lower than their normal boiling points are reached.

The vapour compression machines are now extensively employed in ice-making, in preserving meat and other foodstuffs, and for various other industrial purposes.

(*iii*) Adiabatic Expansion of Compressed Gases

7. Cooling produced by the sudden Adiabatic Expansion of compressed gases.—If a highly compressed gas be suddenly allowed to

xpand adiabatically, it cools very considerably on account of the work it loes in expanding. The cooling may be so great that the gas may even olidify.

An example which may be easily tested in a big town is afforded by ylinders containing carbon dioxide. If such a cylinder be suddenly pened and a piece of cloth held before it, the issuing gas is deposited n the form of fine snow (called dry snow commercially).

This principle was utilised by Cailletet* who first liquefied oxygen n 1877. He compressed oxygen to a pressure of 300 atmospheres in a trong capillary tube cooled to −29°C. and suddenly relieved the pressure. A mist of liquid oxygen was formed which disappeared in a few seconds. Pictet compressed oxygen to a pressure of 500 atmos. and cooled it to bout −130°C. by liquid carbon dioxide evaporating under reduced ressure. Then he suddenly released the pressure. Oxygen in the form f a white solid was thereby obtained. In 1884 Wroblewski obtained a ist of hydrogen while in 1893 Olszewski obtained liquid hydrogen in ufficient quantities, by cooling compressed hydrogen with liquid oxygen nd then suddenly releasing the pressure.

The process is however essentially discontinuous and cannot be adopted for the continuous production of liquefied gases. Hence for commercial urposes it was almost discarded; but a novel way of utilizing the rinciple has been invented by Claude and Heylandt for liquefying air nd by Kapitza† for liquefying hydrogen and helium.

(*iv*) Cooling due to Peltier effect

8. It is well known that when an electric current flows in a circuit rom bismuth to antimony through a junction, this junction is cooled. his is known as the Peltier effect and may be utilized in producing ooling; but no successful application of the method has yet been made.

(*v*) Cooling by Joule-Thomson expansion

9. This method is of considerable importance and will be considered n detail later in this chapter.

(*vi*) Cooling due to Adsorption

10. Charcoal adsorbs a number of gases which are released on

* *Comptes Rendus*, Vol. 85, pp. 1213, 1270 (1877).
† *Proc. Roy. Soc. Lond.*, Vol. 147, p. 189 (1934).

lowering the pressure, and when these gases escape, a cooling results. This may be utilised in producing cooling.

LIQUEFACTION OF GASES

11. Liquefaction by application of pressure and low temperature.—Substances which are gaseous at ordinary temperatures may be converted to the liquid state if they are sufficiently cooled, and simultaneously a large pressure be applied to the mass. When pressure is applied the molecules come closer together, and if heat motion be sufficiently small, they may coalesce and form a liquid mass. If the liquid so cooled be allowed further to evaporate rapidly, still lower temperatures may be obtained. The production of extremely low temperatures is thus intimately connected with the problem of liquefaction of such gases which ordinarily show themselves to be very refractory.

The earliest scientist to try this effect of combined cooling and compression was Faraday* who, as early as 1823, employed the apparatus shown in Fig. 5 for liquefying chlorine. One end of the bent glass tube contains the substance from which chlorine is liberated by heat while the other end is immersed in a freezing mixture. Gaseous chlorine collects in the other end and finally liquefies under its own pressure. Thilorier in 1835 liquefied carbon dioxide by a similar apparatus.

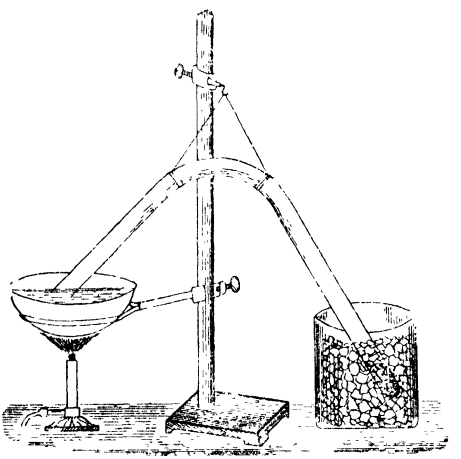


Fig. 5.—Faraday's Apparatus for Liquefaction of Chlorine.

By applying this process Faraday† and others succeeded in liquefying a large number of gases but some, *viz.*, oxygen, nitrogen, hydrogen, carbon monoxide, nitrogen monoxide and methane baffled all attempts at liquefaction, though sometimes enormous pressures up to 3000 atmos. were used. They were therefore termed *permanent* gases.

* *Phil. Trans.*, pp 160, 189 (1823).
† *Phil. Trans.*, p. 155 (1815).

Discovery of the Critical Point.—The cause of these failures became apparent with Andrews' discovery of the critical temperature in 1863. This subject has already been treated in Chapter IV. Andrews' experiments first clearly showed the importance of the critical phenomena. They established clearly that for every substance, which usually occurs in the gaseous form, there exists a temperature above which it cannot be liquefied however high may be the pressure to which it is subjected. Hence in order to liquefy a gas by this method it must be pre-cooled below its critical temperature.

The determination of the critical point (p. 109) is not however easy. The early workers did not in fact wait for its determination. They cooled the gases by ordinary methods as much as they could, and then applied high pressures.

12. The Principle of Cascades or Series Refrigeration.—This method was first employed by R. Pictet in 1878.* In principle it may

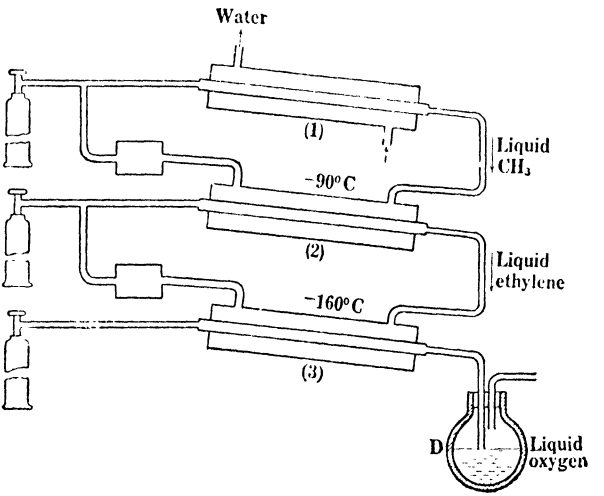


Fig. 6.—Illustration of the Method of Cascades.

be described as a number of compression machines in series. Pictet employed machines containing sulphur dioxide, carbon dioxide and nitrous oxide for the liquefaction of air. Kamerlingh Onnes† later employed the combination of methyl chloride and ethylene for liquefying oxygen. The principle of the method is illustrated in Fig. 6. Machine 1

* *Comptes Rendus.*, Vol. 85, pp. 1214 & 1220 (1878).
† *Leiden Commun.*, No. 87, p. 3 (1903); No. 14, p. 17 (1894).

utilizes methyl chloride. This has got a critical temperature of 143°C. and hence at room temperature it can be easily liquefied by the pressure of a few atmospheres only. Water at room temperature flows in the jacket in (1). Liquid CH_3Cl falls into the jacket in (2) which is connected to the suction side of the compression pump. Thus the liquid evaporates under reduced pressure and its temperature falls to about −90°C. The compressor returns compressed CH_3Cl gas through the tube inside jacket (1), which is shown straight but is really in the form of spirals.

Inside the jacket (2) passes the condenser coils through which ethylene passes from the compressor or the gas cylinder. It liquefies and then enters the jacket (3). There it evaporates under reduced pressure and lowers the temperature to about −160°C. Through the tube inside jacket (3) oxygen from a cylinder passes and liquefies under pressure. Liquid oxygen is collected in the Dewar flask D. The lowest temperature obtained by boiling oxygen under reduced pressure is −218°C which is much higher than the critical temperature of hydrogen (−240°C.) and hence the method of cascades failed to liquefy hydrogen.

Table 2.—Critical temperature, normal boiling point and triple point of gases.

Gas	B. P. at 1 atmos pressure.	Critical temperature	Triple point.
Methyl chloride . . .	−24·09°C.	143·3°C.	−102·9°C.
Sulphur dioxide . . .	−10·1	15·7	...
Carbon dioxide . . .	−78·6	31·0	...
Nitric oxide . . .	−89·8	36·50	−102·3
Ethylene	−103·72	+9·50	−169
Methane	−161·37	−82·85	−183·15
Carbon monoxide . . .	−190·0	−138·7	...
Oxygen	−182·95	−118·82	−218·4
Nitrogen	−195·78	−147·13	−248·86
Neon	−245·92	−228·82	−248·67
Hydrogen	−252·76	−239·91	−259·14
Helium	−268·83	−267·84	∠−272

The method of cascades is very useful for laboratory purposes. The use of the compressor can be entirely dispensed with by the use of suitable liquids boiling under atmospheric or reduced pressures. The suitable liquids can be selected from Table 2 which gives the normal

boiling point, the critical temperature and the triple point for the common gases. The interval between the critical temperature and the triple point represents the range in which the liquid is available.

13. Production of Low Temperatures by Utilising the Joule-Thomson Effect.—None of the above methods is however very suitable for a continuous conversion of gases to liquids and further they were incapable of liquefying helium at all. By 1898 another process began to be utilized. This is the Joule-Thomson effect discovered* in 1852. A full mathematical analysis of the phenomenon is postponed to Chapter X. We shall describe the phenomenon here.

We have already described Joule's experiment (p. 52) which showed that for permanent gases the internal energy does not depend upon volume, *i.e.*, $\left(\frac{\partial U}{\partial v}\right)_T = 0$. This is called Joule's law or Meyer's hypothesis and is the characteristic property of a perfect gas (for perfect monatomic gases $U = \frac{3}{2}NkT$ per mol.). But this is not strictly true for the actual gases of nature; they show deviations from this law of perfect gases, and for them U is not independent of volume. A slight change in the temperature of the gas should occur in Joule's experiment, but since the capacity for heat of the contained air is negligible as compared to the heat capacity of the surrounding water, no change in temperature could be observed. In 1852 Lord Kelvin, in collaboration with Joule, devised a modification of Joule's experiment in which very small changes in temperature produced by expansion could be easily measured. This is called the "Porous plug" experiment and provides an unfailing test of Meyer's hypothesis. With its help we can easily find how far a gas deviates from the state of being perfect. Before proceeding to describe this experiment we shall discuss the theory underlying it.

14. Elementary Theory of the Porous Plug Experiment.—In this experiment a highly compressed gas is continuously forced at a constant pressure through a constricted nozzle or porous plug. The plug, as its name implies, consists simply of a porous material, say cotton-wool, silk, etc., having a number of fine holes or pores and is thus equivalent to a number of narrow orifices in parallel. The gas during its passage through the pores becomes throttled or wire-drawn, *viz.*, molecules of the

* *Phil. Mag.*, Vol. 14 (1852); Joule, *Scientific Papers*, Vol. II, p. 216.

gas are drawn further apart from one another. This is always the case whenever a fluid has to escape through a partly obstructed passage. On either side of the plug constant pressures are maintained, the pressure on the side from which the gas flows being much greater than on the other side since the plug offers great resistance to the flow of the gas. During such a process the function $H=u+pv$ (Chap. X) remains constant.

To prove this theorem, let us consider a mass of the fluid traversing the porous plug C from left to right as indicated in Fig. 7. Let p_A, v_A, T_A, u_A, and p_B, v_B, T_B, u_B be the pressure, volume, temperature and internal energy of one gram of the fluid before and after traversing the orifice respectively. Suppose that one gram of the gas is contained between the porous plug and some point M on the left and also between the plug and some point N on the right. For visualising the process we may assume an imaginary piston A at M separating this quantity of the gas, and that the flow of the gas is caused by the forward motion of the piston A. Actually however the rest of the gas exerts a pressure p_A at M which is maintained by the source of supply. The gas after traversing the plug pushes forward the imaginary piston B whose motion is opposed by the pressure p_B of the gas to the right of B. The initial and final states are shown respectively at (a) and (b) in the figure, the initial volume of the gas being equal to ML and the final volume equal to ON.

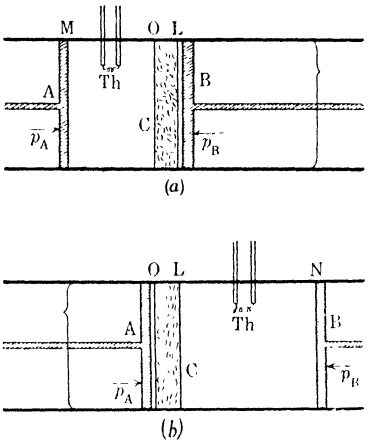


Fig. 7.—The Porous Plug Experiment.

The gas during its passage through the orifices in the plug has to overcome friction, viscosity, etc., and hence loses energy. The escaping gas issues in the form of eddies and its temperature falls considerably just at the jet (and this effect is spurious) because some thermal energy is now converted to the energy of mass motion. The eddies however subside after

traversing a short distance and the temperature consequently rises. Let us consider only the steady flow before and after transmission through the orifice, *i.e.*, at points far removed from the plug where eddies are not present. We assume that the gas moves very slowly so that the energy of mass motion is very small and negligible in comparison to the energy of thermal motions. Now our initial system is ML and the final system is ON. But the plug OL is initially and finally in the same state; hence the change simply consists in a change from MO to LN. If in addition, the tube is surrounded by a non-conducting material, no heat is supplied to or withdrawn from the system. If we consider the passage of a unit quantity of the gas through the plug, the work done on the gas by the forces at A in pushing the gas from M to O is $p_A v_A$, that done by the gas in pushing the piston B is $p_B v_B$. Hence by the first law of thermodynamics, since $dQ=0$, the decrease in internal energy of the gas is equal to the work done by it, *viz.*,

$$u_A - u_B = p_B v_B - p_A v_A \quad . \quad . \quad . \quad . \quad (1)$$

or

$$u_A + p_A v_A = u_B + p_B v_B \quad . \quad . \quad . \quad (2)$$

hence $u+pv$ remains constant in the throttling process.

For perfect gases Boyle's law $(pv)_T = \text{constant}$ and Joule's law $u=cT$ hold true, and therefore $u+pv$ would depend upon temperature only. We have just shown that $u+pv$ for the porous plug experiment is constant whether the gas is perfect or not. Hence for perfect gases the temperature on both sides of the plug would remain the same. In actual experiments, however, a cooling effect was observed for most gases such as air, O_2, N_2, CO_2, and a heating effect in case of H_2. Thus none of the gases examined was perfect except hydrogen which was apparently found to be more than perfect (*plus que perfait*—Regnault).

The lack of perfectness may be due either to deviations from Boyle's law or from Joule's law or both. If we know the former, as from Amagat's experiments (p. 108) we can find the latter by performing the porous plug experiment. If at the particular pressure and temperature in A, the gas is more compressible than at low pressures [*cf.* curves of N_2, CO_2 before the bend (p. 109)], $p_A v_A < p_B v_B$. Therefore due to deviations from Boyle's law alone $u_B < u_A$, *i.e.*, the gas would show a cooling effect. If the gas is less compressible (*cf.* H_2) there would be a heating effect.

Upon these effects will be superposed, the effect due to deviations from Joule's law. Since in actual gases, cohesive forces are present, work will be done in drawing the molecules further apart during expansion and the gas would become cooled. This would always be a cooling effect. Thus the effect observed is the resultant of these two effects and may be a heating or cooling effect depending upon the sign and magnitude of the former effect.

15. The Porous Plug Experiment.—We shall now describe an actual experiment. Joule* and Thomson were the first to carry out these experiments. They employed a cylindrical plug, which is indicated in Fig. 8. The compressed gas flows through a copper spiral immersed in a thermostat and after having acquired its temperature, passes through the porous plug W. The plug consists of silk, or cotton-wool or other porous material, kept in position between two pieces of wire gauze and enclosed in a cylinder of some non-conducting wood *bb*. The plug and part of the tube is surrounded by asbestos contained in a tin cylinder *zz* so that no heat reaches it from the bath. Joule and Thomson worked with air, O_2, N_2, CO_2 between 4° and 100°C., the initial and final pressures being 4·5 atmospheres and 1 atmosphere respectively.

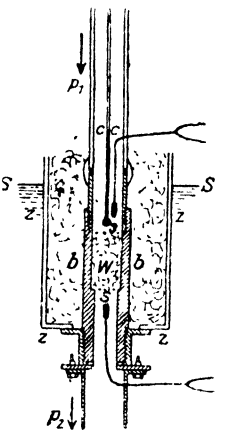


Fig. 8.—Joule-Thomson's porous plug.

Most gases when treated by this process gave a cooling effect while hydrogen gave a heating effect. Joule and Thomson found that the fall in temperature was proportional to the difference in pressure on the two sides of the plug, *i.e.*, $\delta\theta = k\ (p_A - p_B)$ where k is a constant, characteristic of the fluid. They found empirically that $k = A/T^2$ where T is the absolute temperature of the gas, while Ross-Innes found $k = A + B/T$. Hoxton however found that his results were best represented by the formula

$$k = A + \frac{B}{T} + \frac{Cp}{T^2}. \quad . \quad . \quad . \quad . \quad (3)$$

We can find a value of k from theoretical considerations. If the gas be supposed to obey Van der Waals' equation of state, it can be shown

* Joule, *Scientific Papers*, Vol. II, p. 216.

that the Joule-Thomson effect

$$\frac{\triangle\theta}{\triangle p} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right) \text{ approx.} \quad . \quad . \quad (4)$$

16. Principle of Regenerative Cooling.*—The Joule-Thomson cooling observed for most gases is very small. Thus for air, at a temperature of 20°C. when the pressures on the two sides are 50 atmospheres and 1 atmosphere respectively, Joule and Thomson found that the temperature falls by 11·7°C. But the effect is intensified by employing what is called the *regenerative* process. A portion of the gas which first suffers Joule-Thomson expansion and becomes cooled, is employed to cool other portions of the incoming gas before the latter reaches the nozzle. The incoming gas becomes still more cooled after traversing the nozzle. In this way the cooling effect can be made cumulative. In actual practice, this is secured by using either concentric tubes as in Linde's process or by means of Hampson spirals (sec. 18). Two or more concentric tubes are arranged in the form of spirals, the inner one carrying the high-pressure inflowing gas while the outer one the low-pressure outflowing gas. In the regenerative method a further advantage is gained by the fact that the lower the temperature the greater is the Joule-Thomson cooling.

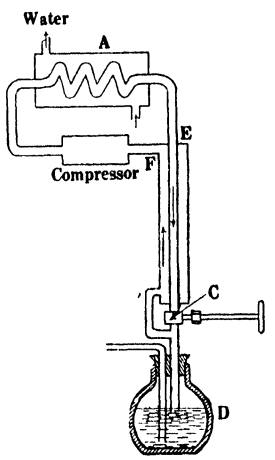


Fig. 9.—Illustration of the Regenerative cooling.

The regenerative principle is illustrated diagrammatically in Fig. 9 where the high-pressure gas from the compressor enters the spirals contained in the water-cooled jacket A. The gas next enters the regenerator coils at E and by expansion at the valve C becomes cooled by a small amount. This returns by the outer tube abstracting heat from the high pressure gas, and reaches F almost at the same temperature as the incoming gas at E. The gas is again compressed, cooled by

* Pollitzer, *Zeits. f. d. ges. Kälte-Ind.*, Vol. 28, p. 125 (1921); Linde, *Zeits. d. Verh. d. Ind.*, Vol. 65, p. 356 (1921); Seligmann, *Zeits. f. techn. Physik*, Vol. 6, p. 237 (1925); Meissner, *Zeits. f. Physik*, Vol. 18, p. 12 (1923).

A and re-enters at E. As time passes, the gas approaching C becomes cooled more and more till the Joule-Thomson cooling at C is sufficient to liquefy it, *viz.*, its temperature reaches the value at which the gas would liquefy under the pressure prevailing at F. A portion of the escaping gas then condenses inside the Dewar flask D. At this stage the temperature throughout the apparatus becomes steady and may be represented by the curve (Fig. 10). The part LM represents the continuous decrease of temperature of the gas as we approach the nozzle through the inner tube while MN represents the Joule-Thomson cooling. NL represents the temperature of the low-pressure gas which is less than that of the adjacent high-pressure gas. Thus the cooler low-pressure gas abstracts heat from the incoming stream. In the ideal case the temperature of the low-pressure gas at F is the same as that of the high-pressure gas at the entrance E.

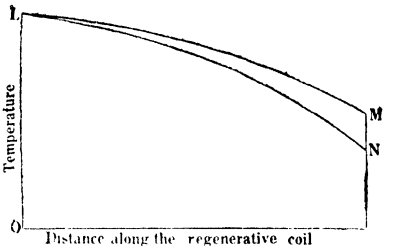


Fig. 10.—Temperature distribution in Regenerative cooling.

17. Linde's Machine for Liquefying Air.—The principle of regeneration (applied to heating) was discovered by W. Siemens in 1857, but its application to cooling processes came later. Linde* in Germany and Hampson in England almost simultaneously (1895) built air-liquefying machines based on the above principle. At the present time, such machines have become quite common and many laboratories in the world are fitted up with such machines. Fig. 11 shows a commercial form of Linde's machine; *e*, *d*, is a two, or better three stage compressor, the machine *e* compressing the gas from 1 to 20 atmospheres while *d* compresses it from 20 to 200 atmos. A charge of atmospheric air is taken in at *e* and compressed by *e* to 20 atmos. It is then cooled by passage through water-cooled tubes and is delivered to the suction side of the second stage compressor. The compressed gas then passes through the cylinder *f* which contains caustic soda. This absorbs the carbon dioxide (if this is not done, carbon dioxide will become solidified and choke the valves in the liquefier proper). The gas then passes to the tubes *g* which

* *Zeits. f. d. ges. Kälte-Ind.*, Vol. 5, p. 23 (1897).

are cooled by a freezing mixture to −20°C. From here it passes on through the metallic tubes P_2 to the inner coils of the liquefier proper. At *a* we have got the plug which is a throttle valve operated by the handle T. As the gas expands (in the first stage to 2 atmos.), the temperature falls to about −78°C., and the air again passes through the outer coils cooling the incoming gas; it is then led through the pipe P_1 to the second stage compression cylinder, where it is again compressed and allowed to pass through the refrigerator and the inner coils to *a*. After the completion of a few cycles the temperature of the incoming gas falls so low that the second throttle valve is opened. The air is now allowed to expand to 1

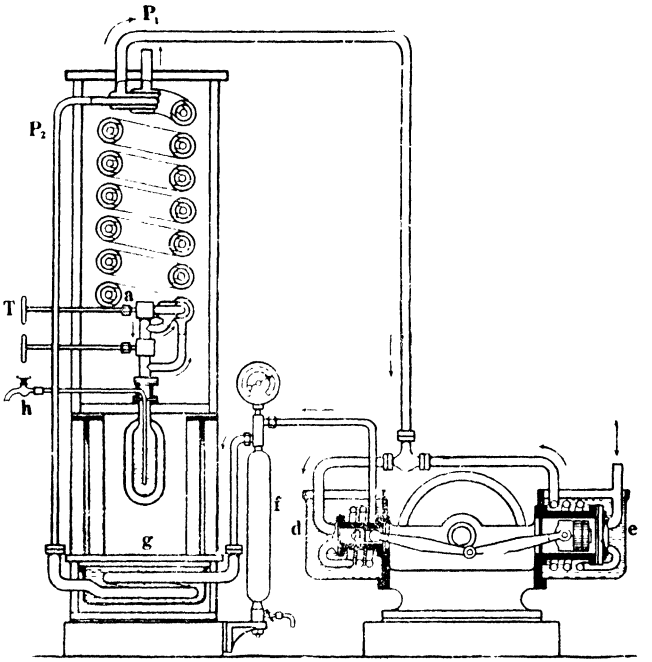


Fig. 11 – Linde's apparatus for liquefying air.

atmosphere when it becomes liquid and collects in the Dewar flask, from which it can be removed by the siphon *h*. The unliquefied gas is again led back through the outermost coils to the compressor *e* as indicated by the arrows. Fresh charge of air is being continuously taken in at *e* and the process continues.

18. Hampson's Air Liquefier.—This liquefier also utilizes the Joule-Thomson effect and the regenerative principle, but differs from

Linde's apparatus in details of construction. The special feature about it is the Hampson spiral. The high-pressure inflowing gas passes through copper tubes coiled in the form of concentric spirals arranged in layers; it then suffers the throttle expansion and becomes cooled. This cooled air rises through the interstices between the layers of spiral and thereby cools the incoming high-pressure gas. After some time the high-pressure gas becomes sufficiently cooled so that on suffering the throttle expansion, it liquefies. The apparatus thus differs from that of Linde only in the manner of cooling the incoming gas. The apparatus was later improved by Olszewski.* The Hampson construction has been utilized later by Dewar, Onnes and Meissner for liquefying hydrogen and helium.

19. Liquefaction of Hydrogen.—The method of cascades failed to liquefy hydrogen. Wroblewski thereupon studied the isotherms of hydrogen at low temperatures, and from that calculated the values of a and b, and thence the critical constants (p. 105). The critical temperature was found to be very low ($-240°$C.) and Olszewski pointed out that this temperature could not be reached by the evaporation of liquid nitrogen, which was the most intensive cooling agent then known. The physicists then turned to the Joule-Thomson method.

This method, however, first appeared to be inapplicable to hydrogen and helium, for Regnault had shown that when hydrogen is subjected to this process, it gets heated instead of being cooled. That the difficulty is not fundamental and insuperable can be seen from the expression for the Joule-Thomson effect, *viz.*,

$$\frac{\triangle\theta}{\triangle p} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right) \quad . \quad . \quad . \quad . \quad (4)$$

It is thus proportional to $2a/RT - b$ but in hydrogen and helium a is so small that at ordinary temperatures $2a/RT < b$, and the term on the right-hand side becomes negative. Hence for a negative value of $\triangle p$, *i.e.*, expansion of the gas, $\triangle\theta$ is positive at ordinary temperatures, and the gas shows a heating effect.

If T be sufficiently reduced, the right-hand term in (4) eventually becomes positive and the gas shows the cooling effect. There is just a

* *Ann. d. Physik*, Vol. 10, p. 768 (1903).

temperature where $\frac{2a}{RT} - b = 0$, *i.e.*, where the Joule-Thomson effect changes sign; this temperature is called the '*temperature of inversion*' T_i which is thus equal to $2a/bR$. This relation gives, after substituting the values of a and b for hydrogen, T_i to be $-73°C$. Olszewski* experimentally found the Joule-Thomson effect for hydrogen at various temperatures and found the temperature of inversion to be $-80{\cdot}5°C$.

Similar is the case with all gases. There is a fixed temperature of inversion for all of them which depends upon the initial pressure to a large extent. Even the Joule-Thomson effect depends very much upon the initial pressure. It is thus clear that the behaviour of hydrogen and helium is not anomalous; they differ from other gases only in having a low temperature of inversion.

Now since T_c, the critical temperature, is equal to $\frac{8a}{27bR}$ (p. 105), and $T_i = \frac{2a}{bR}$, it follows that $T_i = \frac{27}{4} T_c$. This relation is found to hold true approximately.

Hydrogen must therefore be cooled below $-80°C$. for liquefaction. But for practical success it should be pre-cooled to the Boyle point T_B (p. 98) which is defined as the point at which $\frac{\partial (pV)}{\partial p} = 0$.

Calculation with the help of Van der Waals' equation shows that this temperature $T_B = a/bR$

$$\therefore \quad T_B = \tfrac{1}{2} T_i$$

We thus see that hydrogen should be pre-cooled to about $96°A$ $(-177°C.)$. This temperature is easily attained if we immerse the hydrogen-liquefying apparatus in a bath of liquid air.

20. Hydrogen Liquefying Apparatus.—Dewar† first succeeded in liquefying hydrogen in this manner in the year 1898. Travers‡ later improved the apparatus. In this, hydrogen prepared from zinc and

Nature, Vol. 65, p. 576 (1902).

† *Jour. Chem. Soc.*, Vol. 73, p. 529 (1898); *Comptes Rendus*, Vol. 126, p. 1408 (1898); *Chemical News*, March 1900.

‡ *Phil. Mag.*, April 1901, p. 411; *Nature*, Vol. 67, p. 443 (1903).

sulphuric acid is compressed to about 150 atmos. and then passed through coils immersed in water in order to deprive the gas of the heat of compression. Next it passes through cylinders of caustic potash and some dehydrating agent and is deprived of its carbon dioxide and moisture. This is essential as these impurities would solidify much before the liquefaction of hydrogen sets in and choke the tubes. The gas then enters the liquefier and traverses the regenerative coils which are cooled by the outgoing gas, and in the final steady state, becomes cooled to about $-170°$C. Next the gas passes through a refrigerating coil immersed in liquid air, and then through another refrigerating coil immersed in liquid air boiling at a pressure of 100 mm. The temperature of the hydrogen gas falls to about $-200°$C. and it liquefies as it escapes at the nozzle under atmospheric pressure.

Many later investigators devised apparatus which have a large output. Amongst them may be mentioned Nernst,* Kamerlingh Onnes† and Meissner.‡ Onnes' apparatus is very similar to his helium liquefier. Meissner's apparatus is somewhat different in construction but similar in principle.

Liquid hydrogen boils at $-252{\cdot}76°$C. under atmospheric pressure. By causing it to boil under reduced pressure it can be frozen to a white solid.

21. Liquefaction of Helium.—Helium could not be liquefied for a long time. Dewar attempted to obtain liquid helium by allowing highly compressed helium, which had been pre-cooled by solid hydrogen, to expand suddenly, but his efforts were fruitless. Olszewski's attempts were also unsuccessful.

Kamerlingh Onnes proceeded in his efforts very systematically. He studied the isotherms of helium down to liquid hydrogen temperatures (up to $-259°$C.) and obtained the critical constants for helium. He found the following values:—$T_c = 5{\cdot}25°$A. $p_c = 2{\cdot}26$ atmos. and normal boiling point $4{\cdot}26°$A. The Joule-Thomson inversion point came out to be about 35°A and the Boyle point 17°A. This temperature could therefore be reached by pre-cooling the gas with liquid hydrogen. Kamerlingh Onnes

* *Zeits. f. Electrochemie*, Vol. 17, p. 735 (1911).

† *Leiden Commun.*, No. 94 *f.* (1906).

‡ *Naturwissenschaften*, Vol. 13, p. 695 (1925); *Phys. Zeits.*, Vol. 26, p. 689 (1925).

was thus convinced of the possibility of being able to liquefy helium by the Linde process. He succeeded in actually liquefying it in 1908.*

There are at present only a few helium liquefiers in the world. One is at Leiden, another at Berlin and a third one at Toronto. Since helium is rather costly, arrangement is to be such that it can work in cycles. In principle they are all similar. In the apparatus used at the cryogenic laboratory at Leiden gaseous helium compressed to 36 atmos. is passed through spirals immersed in cold hydrogen vapour, then through other spirals immersed in liquid hydrogen boiling under reduced pressure, then through helium vapour. The gas then suffers Joule-Thomson expansion and becomes liquefied. The industrial plant for liquefying helium is therefore complicated by the presence of an air and a hydrogen liquefying plant.

22. Solidification of Helium.—Kamerlingh Onnes tried to solidify helium by pressure, but though he claimed to have reached 1·15°A in 1910, helium still remained a fluid. In 1921 he again tackled the problem and by employing a battery of large diffusion pumps he reduced the vapour pressure to 0·013 mm. and the temperature to 0·82°A, but helium still remained fluid. After the death of Onnes, his collaborator and successor Dr. Keesom† succeeded in solidifying helium by subjecting it to an enormous pressure. Helium was compressed in a narrow brass tube under a pressure of 130 atmospheres, the tube itself being immersed in a liquid helium bath. It was found that the tube was blocked indicating that part of the gas had solidified. If the pressure was reduced by 1 or 2 atmospheres, the tube became clear again. Later experiments showed that helium at 4·2°A solidified at 140 atmospheres while at 1·1°A it solidified only under 23 atmospheres.

23. Low Temperature Technique. *Dewar flask.*—The discovery of Dewar flask by Sir James Dewar in the Royal Institution of London provided a very convenient apparatus for low temperature storage. Though very low temperatures had been produced, it was difficult to maintain the liquids at these temperatures as even by packing the bottles with the best heat insulating material, the leakage of heat from outside

* *Leiden Commun., Suppl.*, 45 (1922).
† *Nature*, Vol. 118, p. 81 (1926); *Leiden Commun.*, No. 184 *b*.

could not be prevented. But the problem was solved by Dewar in a very ingenious way.

The Dewar flask (shown in Fig. 12 together with a siphon) consists of a double-walled glass vessel, the inside walls being silvered. The air is completely evacuated from the interspace between the walls which is then sealed. If some substance be now placed inside such a vessel and the top closed, it is perfectly heat insulated, except for the small amount of heat which may creep in by conduction along the sides. The silver coatings protect the inside from radiation, and the absence of air prevents the passage of heat by conduction through the walls. If the substance be hung by thin wires inside the flask and the latter evacuated by pump and sealed, the insulation is complete. Such an arrangement was used by Nernst in his low temperature calorimetry (p. 46). Dewar flasks are now sold in the market under the trade name "Thermos flask." They have lately been made entirely of metal with a long neck of some badly conducting alloy as German silver.

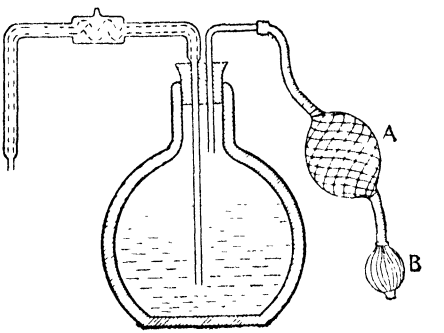


Fig. 12.—Dewar Flask.

Low Temperature Siphons.—For transferring liquid air from one vessel to another, special types of siphons are used. One such siphon is shown in Fig. 15, connected to the Dewar flask. It is formed of a double-walled tube silvered inside, the space between the walls being evacuated. On the application of gentle pressure to the rubber compressors A or B, liquid air rises up the siphon and can be transferred to a second vessel.

Cryostats.—For low temperature work constant temperature baths are necessary; they are called cryostats. The substance to be investigated is kept immersed in these baths. From Table 2 (p. 148) it is easy to find out which liquids are suitable in a particular range of temperatures. If there is no such liquid, then vapours of suitable liquids can be employed.

24. Use of Liquid Air and Other Liquefied Gases.—The importance of liquid air is being increasingly felt so much so that it has now

become essential for several purposes. Bottles of liquid air can now be obtained in any important modern town at a comparatively small cost. We shall give some of the important uses to which liquid air has been put.

(*i*) *Production of High Vacuum.*—High vacuum can be obtained by using liquefied gases with or without charcoal. For instance, if a vessel is first filled with a less volatile gas than air, say sulphurous acid or water vapour, and be then surrounded by liquid air, all the gas inside becomes solidified and thus high vacuum is produced. If the vessel contains air, liquid hydrogen may be employed to condense it. This process is greatly assisted by charcoal which possesses the remarkable property of occluding gases at very low temperatures and the lower its temperature the greater is the adsorption. Further also the adsorption is selective; as a general rule it may be said that the more volatile the gas, the less it is adsorbed.

We shall give a numerical example. During a certain experiment a vessel containing air at a pressure of 1·7 mm. at 15°C. when cooled by charcoal immersed in liquid air, gave a pressure of 0·000047 mm. in an hour and using liquid hydrogen as the cooler the pressure was reduced to 0·0000058 mm. Indeed such a high vacuum may be reached by employing pure nitrogen in place of air and charcoal cooled in liquid hydrogen to solidify it, that the pressure cannot be measured with a MacLeod gauge.

(*ii*) *Analytical Uses of Air.*—Liquid air is of great use in drying and purifying gases. Water vapour and the less volatile impurities are easily removed by surrounding the gas in question (say H_2) with liquid air, and for this purpose it is now a common laboratory reagent.

(*iii*) *Preparation of Gases from Liquid Air.*—Oxygen is now prepared commercially from liquid air by fractional distillation. Since the boiling point of nitrogen is −194°C., and that of oxygen is −182°C., the fraction to evaporate first will be rich in nitrogen while that evaporating last will be rich in oxygen. A few fractional distillations will suffice to separate these completely. Several rectifiers have been devised to effect this separation. In Linde's rectifier, liquid air trickles down a rectifying column where it meets an upgoing stream of gas. The temperature at the top of the column is slightly below −194°C. (B. P. of liquid air) while at the bottom it is −182°C. (B. P. of oxygen). The rising gas is pure oxygen at the bottom but as it comes in contact with the down-coming liquid some of the rising oxygen is condensed, while some of the nitrogen

in the down-coming liquid evaporates. and the liquid also becomes warmer. The process continues till the liquid reaches the bottom when it contains nearly pure oxygen. while nitrogen passes off as vapour at the top. This oxygen is almost pure but the nitrogen contains about 7% of oxygen. Claude later devised a better rectifier. For details see Glazebrook. *A Dictionary of Applied Physics*, Vol. 1. p. 570.

Again atmospheric air may be utilised for the production of the rare gases, particularly helium since its supply from monazite sand is limited. Roughly five volumes of helium are found in million volumes of air but this is sufficient for our purpose. Liquid air may be separated into two fractions the less volatile part consisting of oxygen and nitrogen and the more volatile part consisting of He, H_2. A. Kr. etc. Cooling the latter part by liquid hydrogen will remove all others except hydrogen which may be subsequently removed by sparking with oxygen. Thus oxygen, nitrogen and helium may be obtained from air.*

(*iv*) *Calorimetric Applications.*—Dewar constructed calorimeters of liquid air, oxygen, and hydrogen. He employed pure lead as the heater. and the volume of the gas evaporated by the application of this heat was measured. These calorimeters have the advantage that a large quantity of gas is formed which makes it possible to detect as little as $\frac{1}{300}$ calorie with liquid hydrogen. In this way the specific heat of lead and other substances may be investigated at low temperatures. More recently. Nernst, and his school carried out very valuable calorimetric experiments at liquid air temperatures.

(*v*) *Use of Liquid Air in Scientific Research.*—The extremely low temperatures which are now available to us by the use of liquid air and liquid hydrogen have opened for the investigator a new and vast field for research. This has made a liquid air plant essential for every modern laboratory. Most of the important properties of matter have been investigated at low temperatures and have yielded results of far-reaching importance. This has been extended even to biological research. where it has been shown that bacteria as well as seeds retain their activity unimpaired even after exposure to liquid air temperatures though a moderately high temperature is fatal.

(*vi*) *Industrial Uses of Liquid Air.*—The industrial uses of liquid air are not so numerous partly because these low temperatures are not

* For full details see *Encyc. Brit.*, Article on 'Liquid Gases.'

required commercially. An important use however is the preparation of oxygen from liquid air which has already been discussed. For submarines it may be found useful to store liquid air or liquid oxygen for respiration but the low thermodynamic efficiency inherent in the Linde machine prevents the use of liquid air in a heat engine (Chap. IX). Liquid oxygen is however employed on a small scale for preparing explosives, for when mixed with powdered charcoal and detonated, it explodes with great violence.

Books Recommended.

1. Andrade—*Engines.*
2. Claude—*Liquid Air.*
3. Glazebrook—*A Dictionary of Applied Physics*, Vol. I. articles on 'Refrigeration' and 'Liquefaction.'

CHAPTER VII

THERMAL EXPANSION

1. The size of all material bodies changes on being heated. In the majority of cases, the size increases with rise in temperature, the important exceptions being water and some aqueous solutions in the range 0—4°C. and the iodide of silver (resolidified) below 142°C. We shall first consider the expansion of solids.

EXPANSION OF SOLIDS

2. The cubical expansion of solids is somewhat difficult to measure directly (a method is given in section 17), and is generally calculated from the linear expansion. Hence experiments on the expansion of solids generally consist in measuring the linear expansion of bars or rods of the solid. For isotropic bodies, whose properties are the same in all directions, the expansion is also the same in all directions. To this class belong amorphous solids (*e.g.*, glass) and regular systems of crystals (*e.g.*, rock salt). Metals may also be included because though they are composed of a very large number of small crystals, these crystals are oriented at random and the *average* properties are independent of direction. In anisotropic bodies which include crystals, the expansion is different in different directions and may be even of different sign. We shall first consider isotropic bodies while anisotropic bodies will be considered later.

Isotropic Solids

3. Linear Expansion.—If a bar of length l_0 at 0°C. occupies a length l_t when raised to t°C., l_t can always be expressed by a relation of the form

$$l_t = l_0 \ (1+\lambda t) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where λ is called the mean coefficient of linear expansion between 0 and t°C., and is a very small quantity. This differs very little from the true coefficient of linear expansion at the temperature t which is equal to $\frac{1}{l}\frac{dl}{dt}$. The mean coefficient may be put equal to the coefficient of expansion at $t/2$ °C., if the range of temperature is small.

The mean coefficient λ itself is found to vary with temperature. This implies that the relation connecting length and temperature is not a linear one and equation (1) must be modified into

$$l_t = l_0 (1 + \lambda_1 t + \lambda_2 t^2 + \ldots) \quad . \quad . \quad . \quad (2)$$

where the successive coefficients go on decreasing rapidly. An equation of this type is entirely empirical. The molecular theory of matter has not yet been developed sufficiently to yield an exact theoretical formula. Generally it is sufficient to include terms up to the square of t; the relation then becomes parabolic. In most cases both the coefficients λ_1 and λ_2 are positive, the body becoming more expansible as the temperature rises.

4. Earlier Measurements of Linear Expansion.—The linear expansion of solids is very small: a bar of iron one metre long when heated from 0 to 100°C., increases in length by about 1·2 mm. To measure such small changes in length accurately, special devices are necessary. The increase in length may be obtained from the readings of a spherometer or directly observed by means of a microscope. Again the expansion may be multiplied in a known ratio by utilising the principle of the lever. The most satisfactory method, however, consists in utilising the interference fringes, which is considered in detail later. In this section, we shall consider the earlier experiments.

The spherometer or a milled-head screw was generally employed to measure the expansion and is suitable for ordinary work. The experimental bar, about a metre long, has its one end pressed against a fixed screw while the other end is free to expand. There is a micrometer screw or a spherometer which can be brought into contact with this end. By noting the micrometer readings when the screw is in contact at 0°C. and at any other temperature t°C., the expansion of the rod is found, whence the mean coefficient of linear expansion can be calculated from equation (1).

Roy and Ramsden employed microscopes to measure the expansion and were able to obtain results of considerable accuracy. The experimental bar was placed horizontally in a trough between two standard bars, and parallel to them. One standard bar carried a cross-mark at each end while the other carried at either end an eye-piece provided with cross-wires. The experimental bar carried an object glass at both ends so that the eye-piece on the standard rod and the object glass on the experimental bar

together formed a microscope focussed on the cross-mark on the second standard bar. The standard bars were always kept in ice. One end of the experimental bar was fixed while the other end was free to move when the bar was heated. The object glass was brought back to its initial position by a fine micrometer screw, whose initial and final readings gave the expansion.

Laplace and Lavoisier employed the lever principle to magnify the expansion. The change in length was converted into a change in angle by means of a lever arrangement and the angular change was measured by a scale and a mirror or telescope. The principle of their apparatus is indicated in Fig. 1. One end A of the experimental bar AB is fixed while the other end B pushes against a vertical lever OB attached at right angles to the axis of a telescope LL, which is itself pivoted at O and is focussed on a distant vertical scale CC'. The bar AB is first placed in melting ice and the scale division C seen through the telescope is noted. Next the bar is enclosed in a hot-water bath. The rod AB expands to B' thereby tilting the telescope LOL to the position L'OL' and the scale division C' is now seen through the telescope. The expansion BB' is equal to $\frac{OB}{OC} \cdot CC'$.

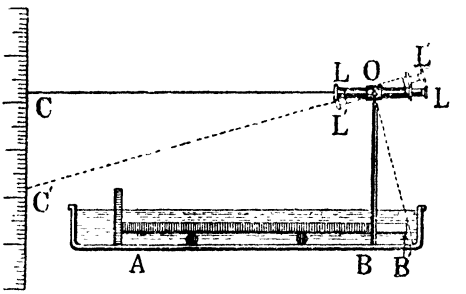


Fig. 1 Apparatus of Laplace and Lavoisier.

Paschen employed a combination of the micrometer screw and the lever. The expansion was multiplied in the ratio 1 : 5 by the lever and this magnified change in length was measured by the micrometer screw.

5. Standard Methods.—At the present time the standard methods employed for measuring expansion are:

(1) Comparator Method. (2) Henning's Tube Method. (3) Method of Interference Fringes. Methods (1) and (3) are direct while (2) is indirect.

6. Comparator Method.—If the substance is in the form of a long rod or bar it is supported horizontally, while if it is in the form of a

wire or strip it is supported vertically, a load being attached at its lower end. Two fine marks are made on this rod. A standard metre, always kept at a fixed temperature, serves to measure the distance between the two marks. Two graduations on the standard bar, approximately the same distance apart, are first observed through two vertical microscopes. These microscopes are provided either with an eye-piece micrometer or can be moved parallel to the direction of the expansion by means of a micrometer screw, and are supported independently of the rest of the apparatus.

Next the experimental bar is brought beneath the microscopes and by means of the micrometer arrangement the microscopes are focussed on the two marks. From the change in the micrometer reading, the length of the rod at room temperature is calculated. The bar is then raised to some temperature and its length at this temperature is also found in a similar way. For measurements at low temperature the experimental rod is immersed in a liquid bath* (*e.g.*, liquid air).

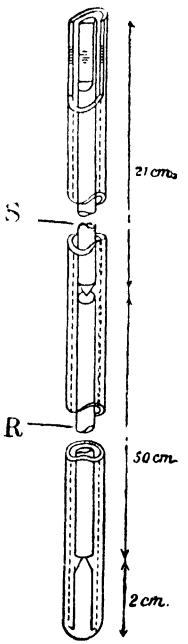


Fig. 2.—Henning's Apparatus.

7. Henning's Tube Method† of Measuring Relative Expansion.—In this method the experimental and the comparison bodies are together brought to the same temperature and the differential change of their lengths is measured. The comparison body is so chosen that its expansion in the temperature region is accurately known and, if possible, is also very small. Fused silica serves this purpose well. Inside a long vertical tube made of some well-defined glass (fused silica, Jena glass), there is a ground point, molten and drawn out of the same glass at its lower end. Upon this point rests the experimental rod R (Fig. 2), about 50 cms. long and having both of its end faces ground plane. Upon the upper surface of R rests a pointed end of another glass rod S made of the same glass as the outer wider tube. To the upper end of this rod as well as of the outer tube are attached end-pieces carrying scales. The whole tube

* Scheel and Heuse, *Verh. d. Phys. Ges.*, Vol. 9, p. 449 (1907).

† *Ann. d. Physik*, Vol. 22, p. 631 (1907); Holborn and Henning, *Zeits. f. Instrkde*, Vol. 32, p. 122 (1912).

up to half of the height of the rod S is immersed in a hot or cold bath and the relative shift of the end-pieces is measured with a microscope provided with a micrometer eye-piece. The shift gives the relative expansion of the experimental rod against a glass tube of equal length. This is so on the assumption that the temperature of the rod and of the outer tube is the same at the same height. For high* and low† temperatures suitable baths may be employed.

8. Fizeau's Interference Method.—Fizeau‡ has devised an optical method depending upon the observation of interference fringes. This method is capable of very great accuracy and is specially suitable when small specimens of the experimental substance are available, as in the case of crystals. The crystal is cut into a plate P with parallel faces less than a cm. in thickness. The plate P (Fig. 3) is placed on a plane metal disc AB through which project three levelling screws. These screws support a glass plate CD whose position is adjusted so that it lies very nearly parallel to, and at a small distance from, the upper surface of P. Fizeau allowed a beam of white light to fall perpendicularly on the glass plate. Part of the beam is reflected at the lower surface of CD while the remainder traverses the air film and suffers successive reflections backwards and forwards within it, a portion of it always emerging upwards at each incidence on the plate CD. These emerging rays produce interference fringes, formed as in the case of Michelson or Fabry Perot's interferometer. The lower surface of CD and the upper surface of P must be optically plane. If these surfaces are exactly parallel the fringes are circular and are formed at infinity; in practice, however, they make a very small angle between them. The fringes are then very nearly straight lines formed at the film itself and are observed with respect to lines drawn on the lower surface of the glass plate.

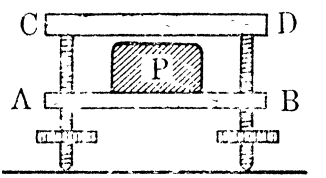


Fig. 3.—Fizeau's arrangement for expansion of crystals.

* Holborn and Day, *Ann. d. Physik*, Vol. 2, p. 505 (1900); Vol. 4, p. 104 (1901). Holborn and Valentiner, *Ann. d. Physik*, Vol. 22, p. 1 (1907).

† Grüneisen and Goens, *Zeits f. Physik*, Vol. 29, p. 141 (1924). Lindemann, *Phys. Zeits.*, Vol. 12, p. 1197 (1911).

‡ *Ann. Chim. Phys.* (4), Vol 2, p. 143 (1864); Vol. 8, p. 335 (1860). *Pogg. Ann.*, Vol. 123, p. 515 (1864); Vol. 128, p. 564 (1866).

When the above arrangement is placed in a chamber which is heated, the thickness of the air film changes due to the differential expansion of the screws and the test-plate, and the fringes become displaced. From a knowledge of this shift the differential expansion can be calculated. Thus in order to find the expansion of the crystal, we must know the expansion of the levelling screws. This can be done by making observations without the crystal. Tutton has, however, eliminated the expansion of the screws by devising an aluminium compensator above which the sample P is placed. The thickness of the compensator is such that its expansion compensates for the expansion of the levelling screws. The compensation however cannot be perfect at all temperatures.

Abbe* and Pulfrich† improved Fizeau's apparatus by replacing the screws by a system of quartz rings and slabs as shown in Fig. 4. G and D are two quartz plates and R is a hollow cylindrical tripod, also of quartz, cut with its generating axis parallel to the optic axis, and placed between G and D. The specimen is placed inside R and the fringes are formed by the air film enclosed between the lower surface of D and the upper surface of the specimen. The light from a Geissler tube (Fig. 5) is used. It enters the telescope at right angles, is deviated through a right angle by means of a right-angled prism, and then traverses the

Fig. 4.—Quartz rings of Abbe.

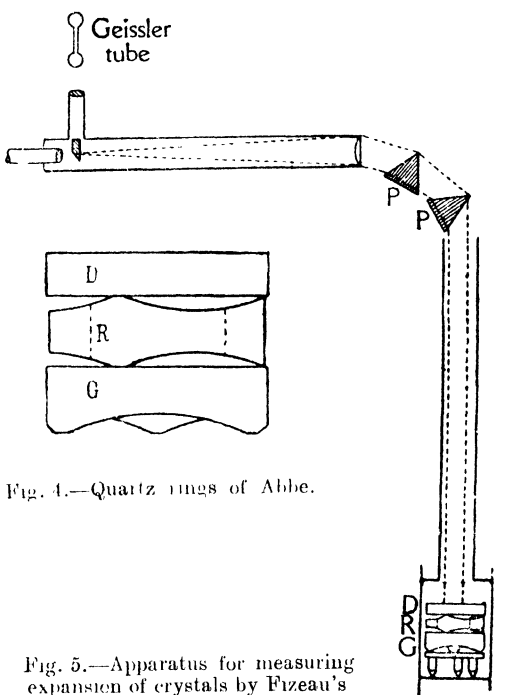


Fig. 5.—Apparatus for measuring expansion of crystals by Fizeau's method.

* *Wied. Ann.*, Vol. 38, p. 453 (1889).
† *Zeits. f. Instrkde.*, Vol. 13, p. 365 (1893); Vol. 18, p. 261 (1898).

prisms P, P and falls upon the system. The fringes are formed in the focal plane of the objective and measurements can be made by means of a micrometer in the eye-piece. The use of quartz rings, however, requires a careful investigation of the expansion of quartz itself. For high or low temperatures, the quartz system is enclosed in a suitable bath.*

With such arrangements very minute changes in the thickness of the air film can be measured. Thus if sodium light is used and the centre of one bright band is displaced through the distance between the centres of two bright bands, the air film must have changed in thickness by about $\lambda/2 = 0{\cdot}0000294$ cms. Fractions of this amount can also be accurately measured, for if λ_1, λ_2, λ_3 ... denote the various wavelengths of light employed and $x_1+\xi_1$, $x_2+\xi_2$, $x_3+\xi_3$ ... the number of interference bands displaced across a fixed line (x representing a whole number and ξ a fraction), the increase $\triangle$ in the thickness of the air film is given by

$$\triangle = \frac{\lambda_1}{2}\left(x_1+\xi_1\right) = \frac{\lambda_2}{2}\left(x_2+\xi_2\right) = \frac{\lambda_3}{2}\left(x_3+\xi_3\right). \quad . \quad (3)$$

The fractions ξ_1, ξ_2 . . . are measured with the help of the micrometer. For a method of calculating x_1, x_2 . . . see *Handbuch der Physik*, Vol. 10, p. 58.

9. Discussion of Results.—Table 1 below gives the mean coefficient of expansion of several substances between 0 and 100°C. The mean coefficient λ is multiplied by 10^6 and given in the table.

But as already mentioned in section 3, these values change appreciably if the final temperature is different from 100°C. The mean coefficient λ is a function of the temperature. As the final temperature is lowered the coefficient decreases. Grüneisen† has found the value of the quantity $\frac{1}{l_0}\frac{dl}{dt}$ for very low temperatures and has developed an important law connecting the coefficient of expansion and the specific heat. Grüneisen's law states that *for a metal the ratio of the coefficient of linear expansion to its specific heat at constant pressure is constant at all temperatures.*

* Scheel, *Ann. d. Physik*, Vol. 9, p 837 (1902). Valentiner and Wallot, *Ann d Physik*, Vol. 16, p. 837 (1915).

† *Ann. d. Physik*, Vol. 26, p. 211 (1908)

Table 1.—Coefficient of Linear Expansion of Substances.

Substance.	$\lambda \times 10^6$	Substance.	$\lambda \times 10^6$
Aluminium ...	23·8	Nickel	13·0
Copper	16·66	Platinum .	8·86
Cadmium	31·59	Palladium . .	11·04
Chromium .	8·4	Silver	19·68
Lead	28·0	Tungsten	4·5
Magnesium	26·0		
Manganese	22·8	Quartz glass ..	0·510
Molybdenum . .	5·20	Jena glass	8·08

10. Surface and Volume Expansion.—The change in area and volume can be easily calculated from a knowledge of the coefficient of linear expansion. A rectangle of sides l and b will, on being heated, have sides of lengths $l(1+\lambda t)$ and $b(1+\lambda t)$, and its area will become $lb(1+\lambda t)^2$. If the initial and final areas be A_0 and A we have

$$A = A_0 (1+2\lambda t) \text{ approx.} \quad . \quad . \quad . \quad . \quad (4)$$

since λ is small. Thus the coefficient of surface expansion is 2λ. Similarly the coefficient of volume expansion can be shown to be 3λ.

11. Expansion of Silica Glass, Invar.—Silica glass (quartz which has been fused and resolidified into the non-crystalline form) is now commonly employed for the construction of thermometers. Several experimenters have investigated its expansion and a summary of these results has been given by Kaye.* The expansion of silica is very small ($\lambda = \cdot 5 \times 10^{-6}$) and is very conveniently determined by Fizeau's method. Hence vessels made of this material can be heated without any fear of breaking. The curve connecting the coefficient of expansion and temperature is a straight line between the room temperature and 1000°C., but at both limits it bends. The coefficient is negative below −80°C.

Invar is another special substance, being an alloy of nickel and steel. Its coefficient of expansion at ordinary temperatures is almost zero and hence it is generally employed for making secondary standards of length, and in the manufacture of precision clocks and watches.

* *Phil. Mag.*, Vol. 115, p. 723 (1910).

Anisotropic Bodies

12. It was first observed by Mitscherlich* that the angles between the faces of cleavage of a crystal of Iceland spar change when the crystal is heated. He gave the correct explanation of the phenomenon, *viz.*, that the expansion of the crystal is different in different directions and this is the cause of the change in angle. Such substances are called anisotropic or non-isotropic. Crystals belong to this class.

For every crystal, however, there can be found three mutually perpendicular directions such that if a cube is cut out of the crystal with its sides parallel to these directions, and heated, the angles will remain right angles though the sides will become unequal. These directions are called the *principal axes of dilatation* and the coefficients of expansion in those directions are called the *principal coefficients of expansion*. Denote these by λ_x, λ_y, λ_z. Then a cube of sides l_0 will, on being heated to t°C., become a parallelopiped whose edges will be given by

$$l_x = l_0(1+\lambda_x t),\quad l_y = l_0(1+\lambda_y t),\quad l_z = l_0(1+\lambda_z t) \quad . \quad . \quad (5)$$

and volume by

$$l_x\, l_y\, l_z = l_0^3\left[1+(\lambda_x+\lambda_y+\lambda_z)t\right] \quad . \quad . \quad . \quad (6)$$

The volume coefficient of expansion is thus $\lambda_x+\lambda_y+\lambda_z$. The linear expansion in any other direction can be readily calculated in terms of the principal coefficients and the direction cosines.†

13. Experimental Methods.—Crystals are best investigated by the interference method. The crystal is cut in the manner desired, into a plate with parallel faces from 1 to 10 mm. thick, and is placed between the glass plate and the metal disc. The details of these experiments have already been given.

14. Results.—When the expansion along the various axes of different crystals is investigated very interesting results are obtained. In the hexagonal system, for optically negative crystals the expansion along the axis is always greater than that along an axis at right angles to it: while for optically positive crystals the reverse is the case. Thus for

* *Pogg. Ann.*, Vol. 41, pp. 213, 448 (1867).
† Further, see Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, p 876.

Iceland spar there is expansion parallel to the axis while contraction perpendicular to it. The contraction is always much less than the expansion so that the volume coefficient remains positive.

EXPANSION OF LIQUIDS

15. In case of liquids we have to consider only the cubical expansion. As before, the volume can again be expressed as a function of the temperature; thus

$$V = V_0 (1 + \alpha_1 t + \alpha_2 t^2 + \ldots) \quad . \quad . \quad . \quad . \quad (7)$$

or approximately

$$V = V_0 (1 + \alpha t) \quad . \quad . \quad . \quad . \quad (8)$$

The expansion of liquids is much greater than that of solids, yet it is more difficult to measure, for it is complicated by the expansion of the containing vessel. The expansion observed is called the apparent expansion and is a combination of the two effects, *viz.*, expansion of the liquid and of the containing vessel. It can be shown that the coefficient of absolute expansion of the liquid is approximately equal to the sum of the coefficients of expansion of the containing vessel and the coefficient of apparent expansion of the liquid. Thus the former can be determined if the latter two quantities are known.

There are three well-known methods for determining the apparent or relative expansion:—

(*i*) The Volume Thermometer Method. (*ii*) the Weight Thermometer Method. and (*iii*) the Hydrostatic Method.

16. The Dilatometer or Volume Thermometer Method.—The thermometer consists of a bulb to which a graduated stem is attached. It is nearly filled with the liquid to be experimented upon. If the liquid stands to the mark x_0 on the stem at 0°C., and to the mark x_1 at t°C., and if the volume of the bulb at 0°C. is V_0 and of each division of the stem v_0, then the volumes of the liquid at the two temperatures are

$$V_0 + x_0 v_0 \text{ and } (V_0 + x_1 v_0)(1 + \gamma t),$$

γ being the expansion of the containing vessel. The volume at t°C. is also equal to

$$(V_0 + x_0 v_0)(1 + \alpha t)$$

where α is the coefficient of absolute expansion of the liquid. Equating we have

$$(V_0 + x_0 v_0)\ (1+\alpha t) = (V_0 + x_1\ v_0)\ (1+\gamma t) \quad . \quad . \quad . \quad (9)$$

Knowing γ the true coefficient α is calculated, or if γ is not known, the relative expansion $\alpha - \gamma$ can be evaluated.

17. The Weight Thermometer Method.—A more accurate method, depending upon the determination of weights and not of volumes, is furnished by the weight thermometer. The thermometer is of the shape shown in Fig. 6, and is made of glass or fused silica. It is first weighed and then completely filled with the liquid by alternate heating and cooling with the open end dipping in a cup of the liquid. Some air often adheres to the neck of the thermometer; to remove it completely the liquid in the thermometer is boiled until half of it is evaporated, and then cooled. The process may be repeated.

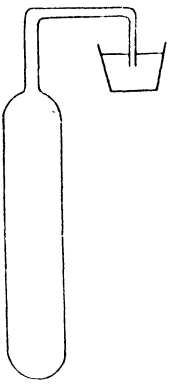


Fig. 6.—The Weight Thermometer.

The experiment consists in weighing the thermometer filled with the liquid at two temperatures. Let w_1, w_2 represent the weights of the liquid filling the thermometer at temperatures t_1 and t_2 respectively. If V_1, V_2 are the volumes of the vessel at the two temperatures and ρ_1, ρ_2 the corresponding densities of the liquid, then

$$w_1 = V_1\ \rho_1,\ w_2 = V_2\ \rho_2 \quad . \quad . \quad . \quad . \quad (10)$$

But if α, γ denote the expansion coefficient of the liquid and the vessel,

$$\frac{V_2}{V_1} = \frac{1+\gamma t_2}{1+\gamma t_1} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\frac{\rho_2}{\rho_1} = \frac{1+\alpha t_1}{1+\alpha t_2} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\therefore \frac{w_1}{w_2} = \frac{1+\gamma t_1}{1+\gamma t_2} \cdot \frac{1+\alpha t_2}{1+\alpha t_1}$$

$$= \frac{1+\alpha(t_2-t_1)}{1+\gamma(t_2-t_1)} \text{ approx.}$$

$$= 1+(\alpha-\gamma)(t_2-t_1) \text{ approx.} \quad . \quad (13)$$

Thus the relative expansion $\alpha - \gamma$ is readily obtained. More accurately, however,

$$\alpha - \frac{w_1}{w_2}\gamma = \frac{w_1 - w_2}{w_2(t_2 - t_1)}. \quad . \quad . \quad . \quad . \quad (14)$$

Knowing γ, the absolute expansion α can be calculated.

The thermometer can also be employed to find the cubical expansion of solids indirectly by enclosing the specimen inside the thermometer.*

18. Hydrostatic Method.—This consists in finding the apparent weight of a solid when immersed in the liquid at two temperatures t_1, t_2 respectively. The loss in weight of the solid is by Archimedes' principle equal to the weight of a volume of the liquid equal to that of the solid; denote this quantity by w. Then

$$w_1 = V_1\rho_1, \; w_2 = V_2\rho_2$$

where V_1, V_2 denote the volumes of the solid at the two temperatures t_1, t_2 respectively. Then

$$\frac{V_1}{V_2} = \frac{1+\gamma t_1}{1+\gamma t_2}, \quad \frac{\rho_1}{\rho_2} = \frac{1+\alpha t_2}{1+\alpha t_1}$$

and proceeding as before.

$$\alpha - \frac{w_1}{w_2}\gamma = \frac{w_1 - w_2}{w_2(t_2 - t_1)}. \quad . \quad . \quad . \quad . \quad (15)$$

19. Absolute Expansion of Liquids.—As already mentioned, the three foregoing methods may be employed to find the absolute expansion of a liquid provided the cubical expansion of the containing vessel [or of the immersed solid in case (*iii*)] be known. One way of finding the latter is by calculating from the linear expansion. This is however open to objection for the linear expansion is determined from bars of the material, and it cannot be assumed *a priori* that the physical properties of the material do not change when it is annealed and worked into a vessel of some shape. For this reason it is best to select vessels of fused silica for which the volume coefficient is extremely small (about 0·0000015).

* See Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, p. 878.

20. Hydrostatic Balance Method.—There is only one direct method of determining the absolute expansion of a liquid which was first given by Dulong and Petit.* It depends on the hydrostatic balancing of two liquid columns at different temperatures. Dulong and Petit employed a simple U-tube for the purpose. Regnault brought the upper ends of the tube close together, an improvement which made it easier to observe the difference in height of the two columns. The diagram (Fig. 7) serves to illustrate the principle of the method. A glass or metal tube, bent as shown in the figure, contains mercury. The vertical columns AB, CD, C′D′ are surrounded by melting ice and are thereby maintained at 0°C., while the column A′B′ is surrounded by an oil bath maintained at any temperature t°C. Suppose that AA′ is horizontal. Let H, H′, h, h' denote the heights of mercury in the various columns as shown, and ρ, ρ_0 the densities of mercury at t°C. and 0°C. Then since the pressures at D and D′ are equal, we have by equating the two expressions for the hydrostatic pressure at A

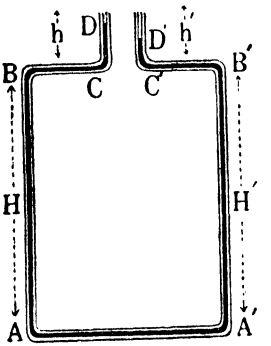


Fig. 7.– Hydrostatic Balance Method.

$$h'\rho_0 + H'\rho = H\rho_0 + h\rho_0 \quad . \quad . \quad . \quad . \quad (16)$$

But

$$\rho = \rho_0/(1+ct),$$

where c is the coefficient of absolute expansion of mercury. Hence

$$\frac{H'}{1+ct} + h' = H + h \quad . \quad . \quad . \quad . \quad (17)$$

whence c can be calculated.

If the columns H, h, h' are not at 0°C. but at temperatures t_1, t_2, t_3 respectively, we shall get

$$\frac{H'}{1+ct} + \frac{h'}{1+c_{t_3}t_3} = \frac{H}{1+c_{t_1}t_1} + \frac{h}{1+c_{t_2}t_2} \quad . \quad . \quad (18)$$

* *Ann. Chim. Phys.* (2) Vol. 7, p. 127 (1818).

where the quantities α_{t_1}, α_t, α_{t_2} denote the mean coefficients of expansion between the different ranges. These can be determined by having the temperature of A′B′ to be t_1, t_2, t_3 successively. If the height of A′ above A is h_1, a corresponding term can be added to the right-hand side.

Regnault* again devised another modification in which the U-tube is connected at the top by a horizontal tube and at the bottom by an inverted tube leading to a pump.

Regnault's observations, though carried out with great skill, must be corrected for various sources of error and hence cannot yield results of high accuracy. Callendar and Moss† repeated the experiments aiming at a high degree of accuracy. Instead of a single pair of hot and cold columns 1·5 m. long employed by Regnault, they used six pairs of hot and cold columns each 2 m. long and connected in series as shown diagrammatically in Fig. 8. The difference in heights of the first and the last column is six times that due to a single pair. The hot and cold columns are marked H and C respectively. The difference in height of the first and the last column (*viz.*, *ab*) is six times that due to a single pair.

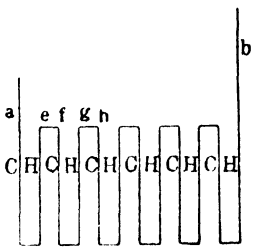


Fig. 8.—Arrangement of Callendar and Moss's apparatus.

In the actual apparatus *ef*, *gh*, . . . were doubled back so that all the columns marked C were one behind the other: and similar was the case with H columns. All the H columns were placed in one limb of a rectangle and all the C columns in one limb of another rectangle, while the other limbs of these rectangles contained electrically heated oil and ice cooled baths respectively. These were kept circulating by means of an electric motor and their temperatures were determined by a long 'bulb' resistance thermometer. Experiments were performed in the range 0 to 300°C. and an accuracy of 1 in 10,000 was aimed at.

21. Results for Mercury.—Their values for mercury are, however, systematically different from the mean of earlier investigators such as Regnault and Chappuis. Harlow has also made accurate determinations with the help of a weight thermometer of silica and aimed at an accuracy

* *Mem. Acad. Science*, Vol. 21, p. 251 (1847).
† *Phil. Trans*, Vol. 211, p. 1 (1911).

of 1 in 18,000. The concordance of results with bulbs of different shapes showed that silica was quite isotropic. The coefficient of expansion in the region 0 to 100°C. is according to Calendar and Moss 0·0001820530.

22. Expansion of Water.—It is well known that the expansion of water is anomalous in the region 0 to 4°C. When water at 0°C. is heated it goes on contracting as long as the temperature is below 4°C. Above 4°C. it expands on heating. This anomalous behaviour is explained on the assumption that there exist three types of molecules H_2O. $2H_2O$. $3H_2O$. which have different specific volumes and are mixed in different proportions at different temperatures. The total volume occupied is assumed to be the sum of the specific volumes, though there seems to be little justification for such an assumption.

23. Expansion of Gases.—The expansion of gases at constant pressure and at constant volume has been treated in Chapter I and forms the very basis of the system of thermometry adopted. The subject has again been dealt with in Chapter IV and will not be considered further.

Book recommended.

1. Glazebrook. *A Dictionary of Applied Physics*. Vol. 1. pp. 872–900.

CHAPTER VIII

CONDUCTION OF HEAT

1. Methods of Heat Propagation. When a bar of metal is heated at one end and held at the other by the hand we feel the sensation of heat. Heat travels from the hot end along the bar and produces this sensation in the hand. The power of transmitting heat in this manner is possessed by all substances to a varying degree and this phenomenon is called *conduction of heat*. In the process of *convection*, heat is transferred by the actual motion of heated particles of matter whether liquid or gaseous. This is best illustrated by placing gently some crystals of potassium permanganate at the bottom of a beaker containing water and heating it. Heated water rises up and curls down forming a closed path which is rendered visible by the red colour imparted to the water. In conduction, heat is transferred 'by contact' and there is no apparent transfer of matter.

In both the above processes the intervening medium takes an active part in heat propagation, but in addition to these there is another process in which the intervening medium takes no part. If we stand near a coal furnace, we feel the sensation of heat. If we are in the sun, we feel warm. Here the source of heat is the coal-furnace or the sun, and in the latter case it is at an enormous distance from us. There is absolutely no material medium between us and the sun, still heat continues to reach us. This phenomenon is called *Radiation*. The processes of conduction and convection are necessarily slow due to the action of the intervening medium while radiation travels with the enormous velocity of light. In this chapter we shall consider only the conduction of heat.

2. Conductivity of Different Kinds of Matter. Common observations show that different substances vary enormously in their conducting power. A glass rod can be melted in a flame by holding it at a point two or three inches away from the flame, while a copper rod under similar conditions becomes too hot to touch. Copper is thus a better conductor of heat than glass. Metals in general are good conductors of heat; glass, wood and other non-metals are bad conductors. Hold inside a flame two blocks, one of wood and the other of copper, each

covered with paper. The paper covering the copper block is not burnt, for heat is rapidly conducted away by copper and the temperature does not rise to the ignition point. The paper covering the wood is burnt. Similarly water may be boiled in a cup of paper.

Liquids in general are worse conductors of heat than solids and gases are the worst. A very simple experiment shows that water is a very bad conductor of heat. Take some water in a test-tube and sink into it a piece of ice by weighting it. The water at the top can be boiled by heating it locally while the ice at the bottom does not even melt. Air and gases in general are even worse conductors than water. Woollen clothing protects us from cold on account of the fact that it contains air in the interstices which renders it a very bad conductor of heat.

The good conductivity of metals is utilised in the construction of the Davy safety lamp. The flame is enclosed in an iron gauze chamber (Fig. 1) and can be taken down a mine. Any combustible gas, if present, comes in contact with the naked flame and burns inside the chamber. But the iron gauze conducts away heat so quickly that the temperature at any point of it does not rise to the ignition point and the outer gas does not ignite.

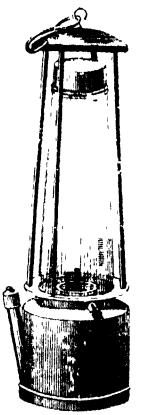


Fig. 1.—Davy Safety Lamp.

3. Definition of Conductivity. The first to give a precise definition of conductivity was Fourier who in his memorable *Théorie Analytique de la chaleur* (1822) treated the subject of heat conduction in a masterly way and placed it on firm mathematical basis. We shall first discuss the flow of heat inside a bar heated at one end. Consider a thin wall of the material with parallel faces such that heat flows in a direction perpendicular to the faces. Let θ_1, θ_2 be the temperatures of the two faces, l the thickness of the wall, A the area of each face then it can be shown experimentally that the amount of heat Q flowing through the wall in a time t, when the temperature at every point of the bar is steady, is directly proportional to (*i*) $\theta_1 - \theta_2$, (*ii*) the area A of the surface, (*iii*) the time t and (*iv*) inversely proportional to l, that is,

$$Q = K A \frac{\theta_1 - \theta_2}{l} t \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The coefficient K is a quantity depending upon the nature of the substance and is called its *thermal conductivity*. From this relation conductivity may be defined as the quantity of heat flowing per second through a unit area of plate of unit thickness, when the difference of temperature between the faces is unity. In analogy with the electrical resistance, the inverse of K may be called the *thermal resistance* of a unit cube.

Now imagine the thickness of the plate to be diminished indefinitely. The limiting value of $\frac{\theta_1-\theta_2}{l}$ or $-\frac{\theta_2-\theta_1}{l}$ is $-\frac{d\theta}{dx}$ and denotes the temperature gradient at any point. The minus sign has been used before $\frac{d\theta}{dx}$ because the symbol d always stands for the increase. Hence the quantity of heat Q flowing in the positive direction of x in time dt across the isothermal surface of area A at any point x is given by

$$Q = -KA\frac{d\theta}{dx}\,dt \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This equation is of fundamental importance in the theory of heat conduction. The units in which conductivity is measured on the C. G. S. system are the calorie per second per square centimetre of area for a temperature gradient of 1°C. per cm. [cal. $cm.^{-1}$ $sec.^{-1}$ $degree^{-1}$]

CONDUCTIVITY OF METALS

4. We shall now give the various methods of determining the thermal conductivity of metals. Methods I to III employ stationary heat-flow while in IV a stationary periodic flow of heat is used.

I. Conductivity from Calorimetric Measurement

5. The definition of conductivity from equation (1) provides a simple method of determining the conductivity of a substance. We need have only a slab of the material of known cross-section heated at one end, and measure the amount of heat that flows out at the other end in a known time, as well as the temperature of the two faces. Thus all the other quantities except K in equation (1) is known, and hence K can be evaluated.

The method though simple presents considerable experimental difficulties. It is difficult to measure accurately the temperature of the two faces. The early experimenters used steam to heat the slab at one end and ice or water to cool it at the other end, and assumed that the temperature of the end faces of the slab was that of steam and water respectively. But if proper precautions be not taken, the method sometimes gives absurd results. This is on account of the fact that a thin film of fluid, always at rest, is formed in contact with the surface, and this has a large temperature gradient. Hence it is essential that we should observe the temperature inside the slab itself by means of thermometers. There are many apparatus based on this method, and one due to Searle is described below.

Fig. 2 shows the apparatus diagrammatically. One end B of the rod AB is enclosed in the steam-chamber S while the other end A projects into another chamber C through which cold water circulates as indicated, the temperatures at entry and exit being T_3 and T_4 respectively. Temperatures at two points along the bar are measured by thermometers T_1 and T_2: let these be T_1 and T_2. The whole rod is wrapped round with some

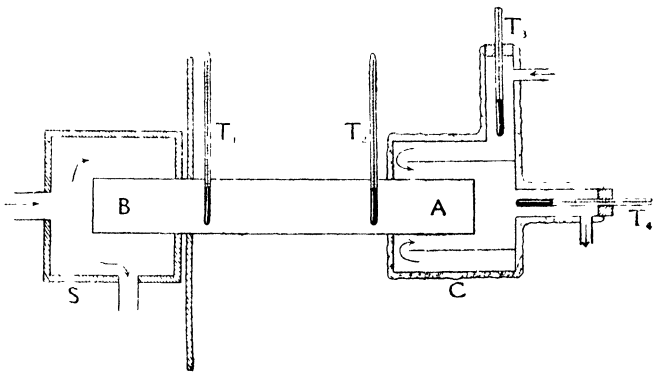


Fig. 2.—Searle's apparatus.

non-conducting material like wool, felt, etc. In the steady state if m grams of water flow past the cold end of the bar per second, the heat conducted by the bar per second is $m(T_4 - T_3)$, and this equals $KA\frac{T_1 - T_2}{d}$ where d is the distance between the thermometers T_1, T_2. Thus the conductivity K is determined.

In the foregoing experiment some heat was lost by radiation from the sides of the bar. This is a source of error and is very easily eliminated

if the bar be surrounded with some material at the same temperature as the adjacent portions of the bar. There will be no flow of heat perpendicular to the length of the bar as no temperature gradient exists in that direction. The surrounding material is called the 'guard-ring.'

Berget* utilised this guard-ring method for determining the conductivity of various substances such as copper, iron, brass and mercury. A vertical cylindrical column of mercury was surrounded by an annular ring of mercury which acts as a guard-ring and prevents radiation from the sides of the experimental column. The upper surface of mercury is heated by steam while the lower surface rests on a metal plate cooled by ice. The experimental column projects into the bulb of a Bunsen ice-calorimeter and the heat flowing out at the lower end is found from the indications of the mercury thread. The difference of temperature between several points along the column is determined by four differential thermocouples. The conductivity K can be calculated from the formula

$$K = \frac{Q}{A t} \cdot \frac{x}{\theta_1 - \theta_2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Berget's value for mercury is 0·0201 which is in good agreement with recent values.

II. Conductivity from Temperature Measurement—Indirect Method

6. Rectilinear flow of heat. Mathematical Investigation.

Consider a metal rod heated at one end, the isothermal surfaces being

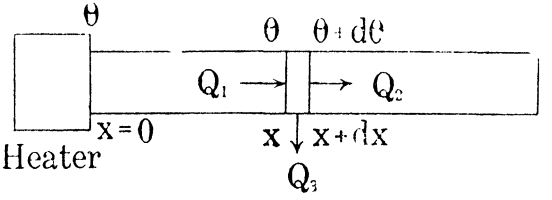


Fig. 3.—Flow of heat in a rod.

parallel planes perpendicular to the length of the rod, and let the axis of x be normal to these planes. At a distance x from the hot end (Fig. 3) let θ be the temperature and $\frac{d\theta}{dx}$ the temperature gradient, and consider

* *Journ. de Phys.*, Vol. 7, p. 503 (1888).

a layer of thickness dx at this point. The amount of heat Q_1, which enters the layer per second is $-KA\frac{d\theta}{dx}$ (from equation 2). Q_2 the heat which leaves the layer at the face $x + dx$ is

$$-KA\frac{d}{dx}\left(\theta + \frac{d\theta}{dx}dx\right),$$

since $\theta + \frac{d\theta}{dx}dx$ is the temperature of that face. Hence the gain of heat by the layer is

$$= -KA\frac{d\theta}{dx} - \left[-KA\frac{d}{dx}\left(\theta + \frac{d\theta}{dx}dx\right)\right]$$

$$= KA\frac{d^2\theta}{dx^2}dx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now before the steady state is reached this amount of heat raises the temperature of the layer of thickness dx. Let ρ be the density and c the specific heat of the material per unit mass, and let the rate of rise of temperature be denoted by $\frac{d\theta}{dt}$. The mass of the layer is $\rho A dx$. Hence if we neglect the heat lost by radiation from the surface

$$KA\frac{d^2\theta}{dx^2}dx = \rho A dx.\, c\frac{d\theta}{dt} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\therefore \frac{d\theta}{dt} = \frac{K}{\rho c}\frac{d^2\theta}{dx^2} = h\frac{d^2\theta}{dx^2} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $h = \frac{K}{\rho c}$. h is thus equal to the thermal conductivity divided by the thermal capacity per unit volume, and consequently determines the rapidity with which temperature changes take place in a given rod. This constant has been called *diffusivity* by Kelvin and *thermometric conductivity* by Maxwell but the former term is more commonly used.

If in addition, the sides of the bar are allowed to lose heat by radiation, this must be taken into account. If E is the emissive power of the surface, p its perimeter and θ the excess of the temperature of the surface over that of the surroundings, this radiation loss Q_3, assuming Newton's Law of cooling to hold true, is equal to $Ep\theta dx$. Hence we should rewrite (5) as

$$KA\frac{d^2\theta}{dx^2}dx = \rho A dx.\, c\frac{d\theta}{dt} + Ep\theta dx$$

or $$\frac{d\theta}{dt} = h\frac{d^2\theta}{dx^2} - \mu\theta \quad . \quad . \quad . \quad . \quad (7)$$

where $$\mu = \frac{Ep}{\rho A c}.$$

This is the standard Fourier equation for one dimensional flow of heat and we shall deduce all other cases from it.

Steady State.—A state is said to be steady when the temperature at every point of the rod is stationary, *i.e.*, $\frac{d\theta}{dt} = 0$. We have then

$$\frac{d^2\theta}{dx^2} = \frac{\mu}{h}\theta = m^2\theta \quad . \quad . \quad . \quad (8)$$

where $$m^2 = \frac{\mu}{h} = \frac{Ep}{AK}.$$

If the radiation losses from the sides can be neglected, this equation further reduces to

$$\frac{d^2\theta}{dx^2} = 0$$

$$\therefore \theta = Ax + B$$

where the constants A and B can be determined from the boundary conditions. Let these conditions be (1) $\theta = \theta_0$ at $x = 0$, θ_0 being the temperature of the source; (2) $\theta = \theta_1$ at $x = l$. Then

$$\theta = \theta_0 - \frac{\theta_0 - \theta_1}{l}$$

where θ is the temperature at any point x.

If radiation losses are not negligible, let us solve the differential equation (8).

Assume $\theta = e^{nx}$ to be the solution. Hence by substitution

$$n^2 = m^2 \text{ or } n = \pm m.$$

Therefore the complete solution is

$$\theta = Ae^{mx} + Be^{-mx} \quad . \quad . \quad . \quad . \quad (9)$$

where A, B are constants.

7. Ingen-Hausz's Experiment.—A very simple method of comparing the conductivity of different substances was given by Ingen-Hausz as early as 1789 and is generally shown as a demonstration experiment. Bars of different substances are coated with wax and have their one end immersed in a hot bath of oil (Fig. 4). The wax melts to different lengths along different bars. Before the steady state is reached the temperature at any point depends both on the thermal capacity and the thermal conductivity as indicated by equation (7). This is why initially the temperature wave is observed to travel faster along bismuth than along copper, for the low thermal capacity of the former more than compensates for the larger conductivity of the latter. In the steady state, however, the wax melts on the copper over a longer length showing the better conductivity of copper.

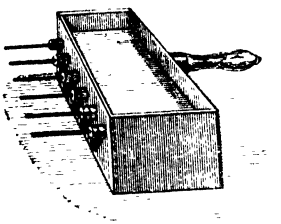


Fig. 4. Apparatus of Ingen-Hausz

Let l_1, l_2 ... denote the lengths along which the wax has melted on the different bars. θ_0 the temperature of the bath measured above that of the surroundings, and θ_1 the temperature of melting wax similarly measured. If the bars are long enough the temperature at their other ends is the same as that of the surroundings, *i.e.*, $\theta = 0$. We shall employ the solution (9) to investigate this problem. The boundary conditions for all the bars are

$$(a)\quad \theta = 0 \text{ at } x = \infty$$

$$(b)\quad \theta = \theta_0 \text{ at } x = 0$$

$$(c)\quad \theta = \theta_1 \text{ at } x = l.$$

Condition (a) gives

$$0 = Ae^{m\infty} + Be^{-m\infty},$$

so that $$Ae^{\infty} = 0, \text{ or } A = 0.$$

Condition (b) then gives

$$\theta_0 = Be^{-m.0}, \text{ or } B = \theta_0.$$

The solution then becomes

$$\theta = \theta_0 e^{-mx}.$$

Condition (c) then gives

$$\theta_1 = \theta_0 e^{-ml} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

or

$$ml = \log_e \frac{\theta_0}{\theta_1}.$$

Since $\log_e \frac{\theta_0}{\theta_1}$ is the same for all the bars we have

$$m_1 l_1 = m_2 l_2 = m_3 l_3 = \ldots = \text{constant}$$

which from the definition of m implies that

$$\frac{K_1}{l_1^2} = \frac{K_2}{l_2^2} = \frac{K_3}{l_3^2} = \ldots = \text{constant}. \quad . \quad . \quad . \quad (11)$$

provided the different bars have the same cross-section, perimeter and coefficient of emission. Thus

$$\frac{K_1}{K_2} = \frac{l_1^2}{l_2^2} \quad . \quad . \quad . \quad . \quad (12)$$

Therefore the conductivities are in the simple ratio of the squares of the lengths along which the wax has melted, and if the conductivity of one of the bars be known the conductivity of the others can be calculated. This is an indirect method. In order to secure the same coefficient of emission the bars are electroplated and polished.

8. Experiments of Despretz, Wiedemann and Franz. Despretz,* as early as 1822, compared the conductivity of two substances by means of three temperatures at equal distances. The bars were heated at one end and were provided with a number of equidistant holes throughout their entire length. These holes contained mercury in which the bulbs of mercury thermometers were immersed for recording the temperature. The theory of the method can be worked out with the help of equation (9).

Wiedemann and Franz† following the same principle devised a more accurate apparatus. The bars under test were about half a metre long and 6 mm. in diameter and were electroplated. One end of the bar was heated by steam and the remainder surrounded by a constant-temperature jacket. The temperatures at equidistant points were measured by a sliding thermo-couple which could be manipulated from outside.

* *Ann. Chim. Phys.*, Vol. 19, p. 97 (1822); Vol. 36, p. 422 (1827).
† *Ann. de Chimie*, Vol. 41, p. 107 (1854).

III. Conductivity by a Combination of the Steady and Variable Heat Flow

9. Forbes' Method.- One of the earliest methods of determining the absolute conductivity of a substance is that due to Forbes.* Though simple in principle, it is exceedingly tedious in practice. Forbes used a bar of wrought iron 8 ft. long and 1½ inch square section. One end of the bar (Fig. 5) was heated by being fixed into an iron crucible contain-

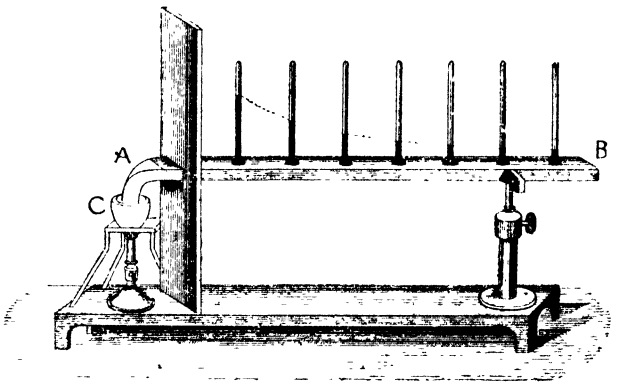


Fig. 5.— Forbes' apparatus. Statical experiment.
(The dotted curve shows fall of temperature along the bar and the tangent to the curve gives the temperature gradient.)

ing molten lead or silver. A number of thermometers, with their bulbs immersed in holes drilled into the bar, were employed to indicate its temperature throughout its entire length. After about six hours the temperatures at all points become steady and are read on the thermometers. This is called the *statical experiment* since it deals with the steady state of heat flow.

To obtain the heat flowing across a particular cross-section Forbes determined the amount of heat lost by radiation by the portion of the bar lying between the cross-section and the cold end. These two quantities are obviously equal in the steady state. Forbes achieved it by performing the *dynamical experiment*, so called because the temperature in this case is changing. For this purpose a bar only 20 inches long but in all respects exactly similar to the previous bar was used. First a high

* *Trans. Roy. Soc. Edin.*, Vol. 23, p. 133 (1864); Vol. 24, p. 73 (1867).

uniform temperature is communicated to this bar which is then allowed to cool in exactly the same surroundings as the statical bar, and a cooling curve plotted for it (Fig. 6).

Let us now calculate the amount of heat lost by the statical bar from the point $x=x_1$, to the end of the bar ($x=l$). The amount of heat lost per second by radiation from the surface of the bar from x to $x+dx$ in the steady state, is

$$-A dx.\ \rho c \frac{d\theta}{dt}$$

where ρ is the density of the material, c its specific heat and $-\frac{d\theta}{dt}$ the rate of cooling of that element. Hence the total heat lost by the portion of the bar from $x=x_1$ to $x=l$ in a second is

$$-A\rho c \int_{x=x_1}^{x=l} \frac{d\theta}{dt}\, dx .$$

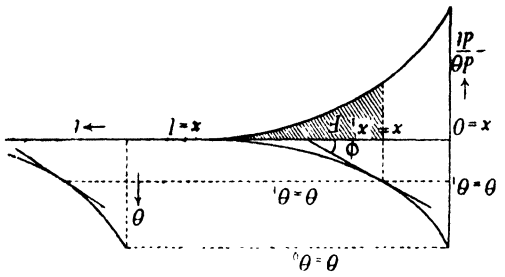


Fig. 6. Temperature curves in Forbes' bar.

We suppose that the bar is long enough so that its other end is at the room temperature. This will also be equal to the heat crossing the surface at $x=x_1$, *viz.*,

$$-KA\left(\frac{d\theta}{dx}\right)_{x=x_1}.$$

Equating these two quantities we have

$$\frac{K}{\rho c}\left(\frac{d\theta}{dx}\right)_{x=x_1} = \int_{x=x_1}^{x=l} \frac{d\theta}{dt}\, dx$$

or

$$\frac{K}{\rho c} \tan\phi = F. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where tan ϕ and F are denoted in Fig. 6. The figure is self-explanatory. The θ, x, and θ, t curves are drawn from actual observations, while the values of $-\frac{d\theta}{dt}$ are computed from the θ, t curve. Thus knowing tan ϕ and the area F of the shaded portion the conductivity K is determined.

There are several sources of error in Forbes' method and hence the method fails to give accurate results. The specific heat does not remain constant at different temperatures as assumed by Forbes. Further the distribution of temperature inside the bar in the statical and dynamical experiments are different. Forbes' method has been improved by, among others, Callendar, and Nicholson and Griffiths. The bar, shorter in length, was lagged to reduce heat loss which could be computed, and the amount of heat passing out at the other end was found by surrounding it with a calorimeter through which a stream of water flowed.

IV. Conductivity by Periodic Flow Method

10. Ångström's Method.—The conductivity of a metallic bar can also be found by periodically heating and cooling a portion of the bar and observing the temperature at different times at two points along the bar. This method was first employed by Ångström.

In his early experiments a small portion of the bar was enclosed in a chamber through which steam and water at any temperature could be alternately passed. In later experiments the end instead of the middle was heated. The bar was heated for 12 minutes and cooled also for the same time, the periodic time being 24 minutes. Temperatures were observed every minute at two points along the bar by means of two thermocouples. The mathematical analysis of this case is somewhat complicated and will not be given here. We have to solve equation (6) such that the solution is a periodic function of time.

11. Conductivity of the Earth's Crust.—The periodic flow method is very suitable for finding the conductivity of the earth's crust. The earth's surface is heated by day and cooled by night. This alternate heating and cooling effect travels into the interior of the earth and gives rise to the *diurnal* temperature wave. Again the earth receives a larger amount of heat in summer than in winter and this *annual* wave is also propagated into the interior of the earth. Assuming the waves to be simple harmonic as a first approximation (the annual wave in particular departs considerably from this ideal state), let us find how they progress into the earth. The problem is that of a bar periodically heated and cooled at one end and provided with a guard-right ($\mu = 0$).

A simple harmonic solution of (6) is

$$\theta = \theta_0 e^{-\alpha x} \sin(\omega t + \beta x + \gamma), \quad . \quad . \quad . \quad (14)$$

which gives the temperature fluctuations at any point x. This is the equation of a damped progressive wave and is graphically represented in Fig. 7. The wave moves forward with the velocity $\frac{\omega}{\beta}$ while its amplitude goes on diminishing exponentially (given by $\theta_0 e^{-\alpha x}$) which is shown by the dotted curve. These fluctuations will be superposed on the mean temperature at any point which will also diminish as we go further from the hot end.

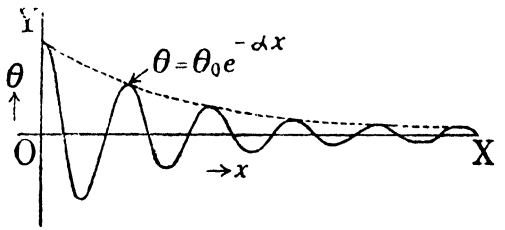


Fig. 7.—Temperature wave at a particular instant.

It can be easily seen that the *wavelength of the temperature wave* is $\lambda = -\frac{2\pi}{\beta}$. Again by substitution from (14) in (6) we get

$$\alpha = -\beta$$

and

$$h = \frac{\omega}{2\beta^2} = \frac{\lambda^2}{4\pi T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Now if a number of thermometers are embedded in the earth at different depths, the progress of the temperature wave inside the earth can be investigated, and knowing the wavelength, the diffusivity h can be calculated. In the same way we can find the conductivity of any bar if we heat one end in a simple harmonic manner as was done by King.*

12. Applications.—The above mathematical treatment can be utilised for solving the geological problem, *viz.*, the penetration of the daily and annual changes of temperature within the earth's crust. It will be easily seen from (14) that the range of amplitude R at any point is

$$R = 2\theta_0 \, e^{-x\sqrt{\pi/hT}} \quad . \quad . \quad . \quad . \quad (16)$$

* *Phys. Rev.*, Vol. 6, p. 437 (1915).

and velocity of propagation

$$v=2\sqrt{\frac{\pi h}{\mathrm{T}}} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and wavelength $$\lambda=2\sqrt{\pi h\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The "lag," *i.e.*, the time which any temperature applied at the surface takes to travel to a point x is

$$t=\frac{x}{v}=\frac{x}{2}\sqrt{\frac{\mathrm{T}}{\pi h}} \quad . \quad . \quad . \quad . \quad (19)$$

Let us calculate the range of temperature variations due to the diurnal and annual waves at different depths. For the diurnal wave for temperature variations from 45°C. to 35°C. in case of ordinary moist soil ($h=0{\cdot}0049$), the range is reduced to ·7°C.. at 30 cms. depth and to about ·002°C. at 1 metre depth. For the annual wave for temperature variations from 40°C. to 15°C. the range will be reduced to 16° at 1 m. depth and to 0·28° at 10 m. depth. The depth at which the amplitude will be reduced to $\frac{1}{e}$th of its value is $\sqrt{\frac{\mathrm{T}_1}{\mathrm{T}_2}}=\sqrt{\frac{365}{1}}=$ about 19 times larger for the annual wave than for the diurnal wave. Thus the annual wave is able to penetrate to a depth which is 19 times larger.

The velocity of the annual wave is however 19 times slower, being equal to 0·000045 cm. per second or 3·9 cms. per day. The maximum temperature inside the interior consequently lags behind the temperature at the surface by an amount given by (19). Thus the maximum temperature of the surface at 2 p.m. will reach a depth of 10 cms. at about 5-15 p. m. and 30 cms. at 11-45 p. m. Similarly the annual wave will penetrate a depth of about 120 cms. in a month. The wavelength λ of the annual and daily waves will be about 14 m. and ·74 m. Thus at a depth of $x=\frac{\lambda}{2}=7$ m.. the times of the year are exchanged but the amplitude becomes only $e^{-\pi}=\frac{1}{23}$. Most of these conclusions have been verified experimentally.

These theoretical considerations are amply borne out by experience. The fact that variations of temperature on the earth's surface are unable to penetrate great depths, explains the basis of a very interesting method of storing ice frequently adopted in Persia and many other tropical

countries. In winter when the sandy planes have sometimes temperatures below 0°C., the people dig deep trenches in the desert, fill it with water, and when the water freezes to ice, they cover it with a deep layer of sand. The scorching heat of summer is unable to melt this underground ice which is consequently dug out when needed and utilised for various purposes.

The slow velocity of the daily heat waves must have been experienced by everybody who is familiar with the housing conditions in tropical countries with the continental type of climate. In the morning hours, even up to about 11 a.m., the inside of the room is quite cool, though the external temperature may be 40°C., provided of course the windows are kept closed. This is because the lowest temperature on the roof was reached at about 6 a.m., and this wave takes from five to six hours to penetrate to the lower walls. The temperature inside the room reaches its maximum in the earlier part of the night because the roof has its maximum temperature at 2 p.m. and the wave takes several hours to reach the lower walls. Thus it becomes impossible to sleep indoors in the night, as the heated walls begin to radiate copiously. Underground chambers are free from such large temperature variations and are often to be found in the houses of rich men.

13. Relation between the Thermal and Electrical Conductivities of Metals. Wiedemann-Franz Law.—A table of thermal conductivities is given on p. 204. The table shows unmistakably that all good conductors of electricity are also good conductors of heat, and even before any theory was proposed, Wiedemann and Franz* gave the empirical law that *the ratio of the thermal and electrical conductivities at a particular temperature, is the same for all metals.* Lorenz† extended the law and showed that this ratio is proportional to the absolute temperature, *viz.*, $\frac{K}{\sigma T}$ = constant, where K is the thermal conductivity and σ the electrical conductivity.

Drude explained this remarkable result by assuming that the conduction of heat and electricity in metals takes place by means of free electrons. He even found theoretically the value of $\frac{K}{\sigma T}$.

* *Pogg. Ann.*, Vol. 89, p. 497 (1853).
† *Pogg. Ann.*, Vol. 147, p. 429 (1872).

These conclusions have been experimentally verified by Jaegar and Diesselhorst* and by Lees.† They obtained the values of $\frac{K}{\sigma T}$ experimentally for various metals which are given in Table 1. It will be seen that the value of $\frac{K}{\sigma T}$ remains practically constant for all metals.

Table 1.—Values of $\frac{K}{\sigma T} \times 10^8$

Metal	From Lees' experiment				Jaegar and Diesselhorst	
	−170°C	−100°C.	0°C.	18°C.	18°C.	100°C.
Aluminium ...	1·50	1·81	2·09	2·13	2·19	2·27
Copper ..	1·85	2·17	2·30	2·32	2·29	2·32
Silver	2·04	2·29	2·33	2·33	2·36	2·37
Zinc	2·20	2·39	2·45	2·43	2·31	2·33
Cadmium ..	2·39	2·43	2·40	2·39	2·43	2·44
Tin	2·48	2·51	2·49	2·47	2·53	2·49
Lead	2·55	2·54	2·53	2·51	2·46	2·51
Iron	3·10	2·98	2·97	2·99	2·76	2·85
Brass	2·78	2·54	2·45	2·45	...	...
Manganin ...	5·94	4·16	3·41	3·34	3·14	2·97

A closer examination of the table shows that the value falls off at low temperatures. Now at these temperatures both the thermal and electrical conductivities are found to increase. Hence it follows that the

* *Berlin-sitzungsber*, Vol. 38, p. 719 (1899).

† *Phil. Trans.*, Vol. 208, p. 381.

thermal and the electrical conductivity do not increase in the same ratio as the temperature falls, the electrical conductivity increasing much more rapidly. In fact the latter appears to become infinite at the absolute zero.

14. Heat Conduction in Three Dimensions.—Till now we have considered the flow of heat in one direction only, generally along bars of great length but small width and thickness. We shall now consider the conduction of heat in three dimensions inside an isotropic body. It can be shown by an amplification of the ideas given in sec. 6 that for flow in three dimensions, the equation of conduction is given by

$$K\left(\frac{d^2\theta}{dx^2}+\frac{d^2\theta}{dy^2}+\frac{d^2\theta}{dz^2}\right)=\rho c\frac{d\theta}{dt}$$

or

$$h\nabla^2\theta=\frac{d\theta}{dt} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where h is the diffusivity. This is the Fourier equation of heat conduction in general and we can solve it when the initial conditions are given. Equation (20) is of great importance in studying problems on heat conduction.

V. Conductivity of Poorly Conducting Solids

15. In finding the conductivity of poor conductors the substance cannot be employed in the form of long bars or rods as was the case with metals, for the heat loss from the sides would be considerable compared with the heat actually conducted away through the substance itself. For this reason the substance is generally used in the form of thin plate, sphere or cylinder. To this class belong all non-metallic bodies. Cork, asbestos, clay, wood, bricks, etc., are among the many substances of common occurrence. The conductivity of these varies from 0·01 to 0·00008. We shall now give some of the important methods of finding the conductivity of these substances.

In the methods commonly employed for finding conductivity of poorly conducting solids, energy is supplied electrically to a separate heating body, and the flow of heat through the experimental substance investigated.

16. Spherical Shell Method.—The simplest case of heat conduction in three dimensions is that of a sphere. If the source of heat is placed at the centre of the sphere the isothermal surfaces will be spherical surfaces described about the centre. The method has been employed by Nusselt* and others. Nusselt's apparatus is shown in Fig. 8.

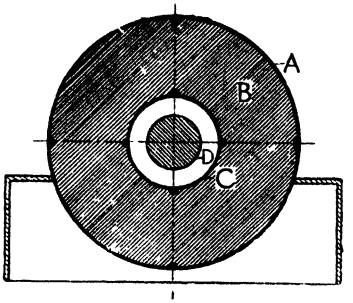


Fig. 8.—Nusselt's apparatus.

The external hollow sphere A is 30 cms. in diameter and made of copper. Inside it and concentric with it, is another hollow sphere C of aluminium, 15 cms. in diameter. The spheres can be split into two and reunited. The space between the spheres is filled with the material B under test such as asbestos, powdered cork, charcoal, etc. An electrically heated body D is placed at the centre of the sphere inside C and electrical energy is supplied at a constant rate. Temperatures are determined by means of thermo-couples placed in B at different distances from the centre and along one or more radii. Knowing the electrical energy spent and the radii of the shells, the conductivity can be calculated.

We shall solve the problem from elementary principles. On account of the symmetry about the centre the isothermal surfaces are spherical. The flux of heat across a spherical surface of radius r outwards in unit time is $-\mathrm{K}.\,4\pi r^2\frac{d\theta}{dr}$. This must equal the amount of electrical energy Q supplied per second to the heating body. Hence†

$$\mathrm{Q} = -4\pi\mathrm{K}.\,r^2\frac{d\theta}{dr}$$

or
$$d\theta = -\frac{\mathrm{Q}}{4\pi\mathrm{K}}\cdot\frac{dr}{r^2}. \quad . \quad . \quad . \quad . \quad (21)$$

Since Q does not vary with r we have on integrating (21)

$$\theta = \frac{\mathrm{Q}}{4\pi\mathrm{K}}\cdot\frac{1}{r} + \mathrm{A}. \quad . \quad . \quad . \quad . \quad (22)$$

* *Zeits. d. Ver. deutsch. Ing.*, Vol. 52, p. 906 (1908); *Forsch. Ver. d. Ing.*, Vols. 63 and 64 (1909).

† We can also proceed as in sec. 6.

If the two surfaces of the shell of radii r_1, r_2 acquire temperatures θ_1, θ_2 in the steady state,

$$\theta_1 = \frac{Q}{4\pi K} \cdot \frac{1}{r_1} + A$$

$$\theta_2 = \frac{Q}{4\pi K} \cdot \frac{1}{r_2} + A$$

whence

$$Q = \frac{4\pi K (\theta_1 - \theta_2) r_1 r_2}{r_2 - r_1} \quad . \quad . \quad . \quad (23)$$

Knowing Q, θ_1, θ_2 and r_1, r_2 as in the above experiment the conductivity K can be calculated. Again solving the simultaneous equation for Q and A, and substituting these values of Q and A in (22), the temperature distribution in the material can also be found, and is given by the expression

$$\theta = \frac{1}{r_2 - r_1} \left[(r_2\theta_2 - r_1\theta_1) + \frac{(\theta_1 - \theta_2) r_1 r_2}{r} \right] \quad . \quad . \quad . \quad (24)$$

17. Cylindrical Shell Method.—Let us consider the radial flow of heat in a cylinder which has an electrically heated wire along its axis. By suitably transforming equation (20) we can get the equation for this case. We shall however, as before, deduce it from elementary considerations. Since the cylinder is symmetrical about its axis, the isothermal surfaces are cylindrical. The amount of heat Q flowing per second across such an isothermal surface is

$$Q = -2\pi r l . K . \frac{d\theta}{dr}, \quad . \quad . \quad . \quad . \quad (25)$$

where l is the length of the cylinder. Now Q must remain constant, being equal to the electrical energy supplied per second. On integrating between the inner and outer radii of the cylindrical shell with corresponding temperatures θ_1, θ_2, we have

$$2\pi l K (\theta_1 - \theta_2) = Q \log_e (r_2/r_1)$$

or

$$K = \frac{Q}{2\pi l} \cdot \frac{\log_e (r_2/r_1)}{\theta_1 - \theta_2} \quad . \quad . \quad . \quad . \quad . \quad (26)$$

The temperature θ at a distance r can be shown to be given by

$$\theta = \frac{1}{\log_e (r_2/r_1)} \left[(\theta_1 \log r_2 - \theta_2 \log r_1) - (\theta_1 - \theta_2) \log r \right] \qquad (27)$$

Niven* has devised a method of determining conductivities based on this method. The cylinder of the material is formed by filling the space between two hollow concentric cylinders with that material. Heat is supplied by a wire carrying an electric current along the axis of the cylinder, and when the steady state is reached, temperatures at two points within the material are observed, as well as their distance from the axis. Knowing the electrical energy spent, equation (26) gives the conductivity.

A simple laboratory experiment based on this method may be devised for finding the conductivity of rubber and glass in the form of a tube. For rubber the arrangement shown in Fig. 9 is most convenient. Steam from the boiler A traverses through a rubber tube B, a length l of which is immersed in a weighed amount of water contained in the calorimeter C. The radial flow of heat Q from the tube to the water in C is given by

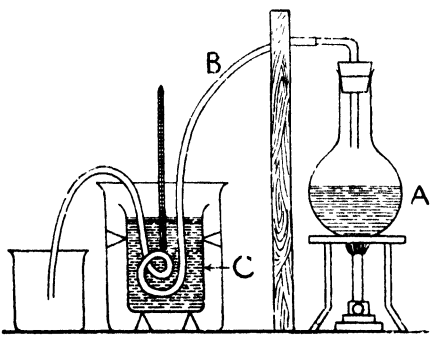


Fig. 9.—Apparatus for finding conductivity of rubber.

$$Q = \frac{2\pi K l (\theta_1 - \theta_2)}{\log_e \frac{r_2}{r_1}} \qquad . \quad . \quad . \quad . \quad (28)$$

where θ_1 represents the temperature of steam. and θ_2 the mean of the initial and final temperatures of the calorimeter. This heat can be calculated from the rise in temperature of the calorimeter and its thermal

* *Proc. Roy. Soc. Lond.*, Vol. 76, p. 34 (1905).

capacity, and hence equating these two quantities we get K, provided r_1, r_2 are known.*

For glass the arrangement shown in Fig. 10 is convenient. The glass

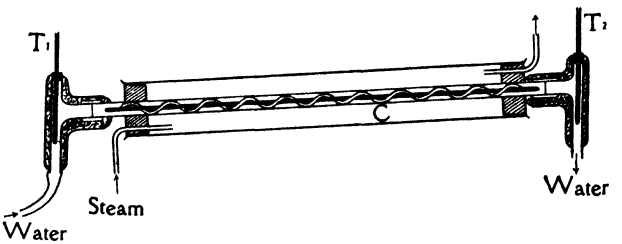


Fig. 10.—Apparatus for finding conductivity of glass.

tube C has a spiral wire along its axis and is surrounded by a steam jacket, while a steady current of water flows through the tube. The method of calculation is similar to the preceding one.

Another convenient method for finding the conductivity has been given by Lees. A thin plate of the experimental substance is placed between two copper plates. A coil of insulated wire is placed above the upper copper plate and heated electrically. The amount of heat passing through the experimental disc can be obtained from the electrical energy supplied and loss due to surface emission. Knowing the temperature of the copper plates the conductivity can be calculated.

CONDUCTIVITY OF CRYSTALS

18. Senarmont's Work.—We have so far considered isotropic bodies for which the conductivity is the same in all directions. But the conductivity of crystalline and anisotropic bodies is different in different directions. Thus Tyndal found by Despretz's method that the conductivity of wood was greatest along the fibre and least in the direction perpendicular to the fibre and the ligneous layers. Jannettaz found for laminated rocks that the conductivity was best parallel to the planes of cleavage and worst perpendicular to them.

* For experimental details see Worsnop and Flint, *Practical Physics.*

The first systematic and extensive investigation of the conductivity of crystals was carried out by De Senarmont.* A thin plate with parallel faces was cut from the crystal in any desired direction and the two faces were thinly coated with wax. Heat was applied at one point in the plate in any of the following ways. Either the sun's rays were concentrated by a short focus lens to a point on the surface of the plate or a wire passed through a hole in the plate and was heated electrically. In some experiments a fine silver tube passed through the hole and was heated by a flame. As portions of the plate became heated the wax on them melted. Finally in the steady state the bounding line of the melted wax represents an isothermal line corresponding to the temperature of melting point of wax. The conductivity in different directions can be calculated from the lengths along which the wax melts, much in the same way as in Ingen-Hausz's experiment.

Senarmont obtained very interesting results. For isotropic substances such as glass and cubic crystals, the isothermal curve was always a circle, while for other crystals in general it was an ellipse. The isothermal surfaces round the heated point were in general a system of concentric ellipsoids of revolution. The axes of these ellipsoids which are called the *thermic axes* of the crystal always coincided with the crystallographic axes of symmetry. Thus in the rhombohedral system the isothermal surface is an ellipsoid of revolution about the axis of the crystal which is the only axis of symmetry. For these the isothermal curves were found to be circles in plates cut perpendicular to the axis and ellipses in plates cut parallel to the axis. Fig. 11 shows such curves for a quartz crystal cut perpendicular and parallel to the axis. The rule was found to hold for all crystals. Later experiments confirmed these conclusions.

Fig. 11.—Isothermal surfaces in quartz cut (1) perpendicular (2) parallel to the axis.

CONDUCTIVITY OF LIQUIDS

19. The determination of the conductivity of a liquid is complicated by the presence of convection currents. If we heat a column of liquid at

* *Ann. de Chimie et de Physique*, 3e, Vols. 21, 22, 23 (1847-48).

the bottom, the liquid at the top receives heat both by conduction and convection. The laws governing convection currents are complicated, hence it is preferable to eliminate them. This is accomplished either by taking a column of liquid and heating it at the top, or by taking a thin film of liquid.

20. Column Method.—The column method was employed by Despretz long ago. The liquid at the top was kept heated and temperatures along the axis of the column were observed by mercury thermometers. He found that Fourier's equation already derived for a bar holds true in this case also, and hence the conductivities of two liquids can be compared with the help of equation (11). Weber* surrounded the column with a guard-ring and used as the source of heat an electrically heated oil bath. The bottom of the column was cooled by a copper plate standing in ice. The heat conducted away was found from the amount of ice melted. Knowing the temperature distribution along the column the absolute conductivity can be calculated in the same manner as for mercury in Berget's experiment.

21. Film Method.—This was employed by Lees,† Milner and Chattock‡ and by Jakob.§ We shall describe the apparatus used by Lees, which is simply a modification of his disc method for finding the conductivity of poor conductors. The liquid L under test is enclosed in an ebonite ring E (Fig. 12) and placed between copper blocks C_1, C_2. To determine the quantity of heat flowing through the liquid a glass disc G is inserted, above which another copper plate C_3 is cemented with a layer of shellac. Above C_3 and insulated from it by

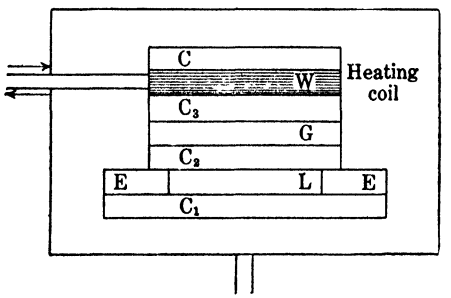


Fig. 12.—Lees' apparatus for finding the conductivity of liquids.

* *Ann. d. Physik*, Vol. 11, p. 1047 (1903).
† *Phil. Trans.* Vol. 191, p. 418 (1898).
‡ *Phil. Mag.*, Vol. 48, p. 46 (1899).
§ *Ann. d. Physik*, Vol. 63, p. 537 (1920).

mica is placed a flat spiral coil of heating wire W which is held down by another copper plate C. The whole pile is varnished and enclosed in an air-bath. Temperatures are recorded by thermo-couples soldered to the faces of the copper plate.

The amount of heat flowing across G is known (equation 1) if we know the conductivity of glass and the temperatures of C_2, C_3. Subtracting from it the heat lost by radiation from the surface of C_2 and the lower half of G we get the heat flowing across L. The conductivity of the liquid can then be easily calculated from equation (3) if we find the temperatures of C_1, C_2, and the thickness as well as the surface area of L.

22. Hot-wire Method.—Goldschmidt employed the "hot-wire" method of Andrews and Schleiermacher, the theory of which is discussed in sec. 17. The liquid was contained in a silver capillary tube 2 mm. in diameter and heated by a wire running along its axis.

CONDUCTIVITY OF GASES

23. The determination of the conductivity of gases is difficult for the phenomenon is always accompanied by radiation, and sometimes by convection currents also. Kundt and Warburg* showed that the rate of cooling of a thermometer immersed in air remained constant for pressures lying between 150 mm. and 1 mm. Hence the effect of convection currents is negligible in this region, and heat is lost only by conduction and radiation. To determine the radiation loss, the air was exhausted as completely as possible, and then the rate of cooling was found to be independent of the size of the enclosure, showing that the effect of conduction was negligible and heat was lost only by radiation. Subtracting this radiation loss, we get the heat lost by conduction alone. For finding the conductivity of a gas at pressures higher than 150 mm. the gas may be exhausted to this pressure (between 150 mm. and 1 mm.) and its conductivity determined. Now since the conductivity of a gas is independent of the pressure (see Chapter III, Sec. 24) this will give the required

* *Pogg. Ann.*, Vols. 155 & 156; *Jour. de. Physique*, Vol. 5, p. 118 (1876).

conductivity. Another procedure consists in taking a thin film of gas and heating it at the top when convection will be absent.

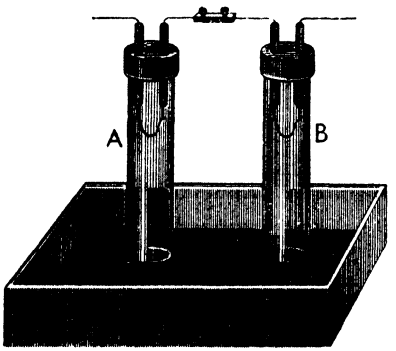


Fig. 13.—Apparatus to show the better conductivity of hydrogen.

A very simple experiment described by Andrews* and Grove† shows qualitatively that hydrogen is a far better conductor of heat than any other gas. A fine platinum wire was supported inside a glass tube (Fig. 13) which could be filled with any gas. The wire could be heated by an electric current and made to glow. Two such tubes were arranged side by side, one filled with air and the other with hydrogen. The same electric current was allowed to flow through both the wires. The wire in the air-tube can be seen glowing while the wire in the hydrogen tube does not glow at all. The glass tube containing hydrogen also becomes hot. Heat is very quickly conducted away by hydrogen and hence the wire is not raised to the temperature of incandescence. Replacing hydrogen with air restores the incandescence.

The important methods of finding the absolute conductivity of a gas are:—

(1) Hot-wire Method, (2) Film Method.

24. Hot-wire Method.—This method, first given by Andrews, was employed by Schleiermacher‡ for determining the absolute conductivity of a gas. An electrically heated wire is surrounded by a coaxial cylinder filled with the experimental gas. The temperature of the wire is known from its resistance, and the amount of heat flowing across the curved surface of the cylinder is found from the rate of energy supplied to the wire. Convection and radiation effects are eliminated as pointed out in sec. 23. The conductivity can be calculated from equation (26) where r_1, r_2 now denote the radii of the wire and the tube respectively.

* *Proc. Roy. Irish Academy*, Vol. 1, p. 465 (1840).
† Grove, "*Bakerian Lecture*," *Phil. Trans.*, 1847. *Phil. Mag.*, Vol. 27, p. 445.
‡ *Wied. Ann.*, Vol. 34, p. 623 (1888).

25. Film Method.—The film method, originally used by Todd,* has been recently employed by Hercus and Laby.† The principle underlying it is the same as in Lees' experiments (sec. 21). The thin film of gas under test was enclosed between two copper plates B and C (Fig. 14), the latter of which was cooled by a current of water. The upper plate B was made up of two sheets of copper clamped together with a heating coil between them. To prevent loss of heat by radiation from the upper surface of B, there was another plate A above it at the same temperature and a guard-ring D surrounding it. All the plates A, B, D contained

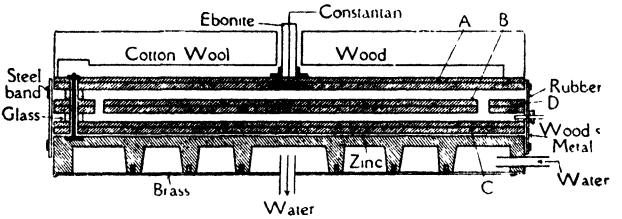


Fig. 14.—Apparatus of Hercus and Laby.

separate heating coils and thermo-couples and were kept at the same temperature. The whole apparatus was made air-tight. The temperature of A was generally kept a little above that of B in order to eliminate any possibility of convection. This however necessitated a small correction. The radiation correction was determined by a separate experiment on a silvered Dewar flask and was very small. Convection effects are entirely absent since the gas is heated at the top. The energy spent in B was known electrically and subtracting from it the heat lost by radiation, the heat transmitted to C by conduction through the air film was found. Knowing the temperature of C the conductivity of the gas can be calculated from equation (3).

26. Results.—The thermal conductivity of a number of substances is given in Table 2 (p. 204). The value of K is given in calorie $cm.^{-1}$ $sec.^{-1}$ $degree^{-1}$.

It will be seen from the table that silver is the best conductor of heat (K=1) and copper comes next. The conductivity is less for liquids and least for gases. The conductivity of gases is extremely low (of the order of 10^{-5}).

* *Proc. Roy. Soc. London*, Vol. 83, p. 19 (1909).
† *Proc. Roy. Soc. London*, Vol. 95, p. 190 (1918).

We have already considered on p. 94, Chap. III, the relation between thermal conductivity and viscosity of gases, as well as the variation of the thermal conductivity of gases with pressure.

Table 2.—Thermal conductivities of different substances.*

Substance	Conductivity	Substance	Conductivity
Metals (0°C.)		Asbestos paper ...	$0{\cdot}6\times10^{-3}$
Aluminium ...	0·48	Cardboard ...	0·5
Cadmium ...	0·23	Cork ($\rho=\cdot16$) ...	0·11
Copper ...	0·93	Paper ...	0·3
Iron (pure) ...	0·16	Ebonite ...	0·42
Lead ...	0·085	Mica ...	1·8
Mercury ...	0·025	Paraffin wax ...	0·6
Nickel ...	0·14	Pine wood ...	0·4
Silver ...	1·0	Rubber ...	0·45
Platinum ...	0·17	*Liquids.*	
Tin ...	0·155		
Zinc ...	0·265	Water (20°) ...	$14{\cdot}3\times10^{-4}$
Alloys (0°C.)		Alcohol (25°) ...	4·3
		Glycerine (25°) ...	6·8
Brass ...	0·23		
Constantan ...	0·05	*Gases* (0°C.)	
Manganin ...	0·05		
German silver ...	0·06	Hydrogen ...	$31{\cdot}\times10^{-5}$
Poor Conducting Solids (18°C.)		Helium ...	33·
		Argon ...	3·89
		Air ...	5·40
Crown glass ...	$2{\cdot}5\times10^{-3}$	Oxygen ...	5·63
Flint glass ...	2	Carbon dioxide . .	3·07

Books Recommended.

1. Glazebrook, *A Dictionary of Applied Physics*, Vol. 1.
2. Ingersoll and Zobel, *Mathematical Theory of Heat Conduction.*

* Taken partly from Landolt and Bornstein, *Physikalisch-Chemischen Tabellen* and partly from Kaye and Laby, *Tables of Physical and Chemical Constants.*

CHAPTER IX

HEAT ENGINES

1. Introduction to Thermodynamics.—Thermodynamics is literally that branch of science which discusses the relation of heat to mechanical energy. But in a broad sense. it comprises the relation of heat to other forms of energy also, such as electrical and chemical energy, light energy, etc. The principles of Thermodynamics are very general in their scope, and have been applied widely to problems in Physics, Chemistry and other sciences. The theory of heat engines forms an integral part of the subject, and as the early developments were largely in connection with the problem of conversion of heat energy to mechanical work, we shall devote a chapter to the Theory of Heat Engines.

HEAT ENGINES*

2. The progress of civilisation has been intimately bound up with man's capacity for the development and control of power. History tells us that whenever man has been able to make a great discovery leading to a substantial increase in his power, a fresh epoch in civilisation has begun.

The present age has sometimes been styled as the 'Steam Age,' indicating the profound influence exerted by the invention of the 'Steam Engine' on the course of human progress. In this chapter, we shall make a brief survey of this "great event."

At the present time we know that Heat is a kind of motion. Whenever motion disappears it reappears as heat, and experiments show that 1 calorie of heat is equivalent to $4{\cdot}18\times10^{7}$ ergs of work. The question naturally arises: "Can we not reverse the process? Can we not, by some contrivance, convert heat which is in so much excess about us, to useful work?" This is in fact the function of heat engines which we are going to discuss. They are contrivances to convert heat to work.

* In preparing this chapter, we have drawn very freely from the admirable little book by Prof. E. N. da. C. Andrade on "Engines," and we wish at this place to acknowledge our grateful thanks to the author.

But the early investigators were profoundly ignorant of the "Nature of Heat," hence the problem did not present itself to them in this form. They however observed that generally when bodies get heated, they develop power. We may take three examples familiar to every body:—

1. The expansive power of steam which we observe every day whenever water is boiled in a kettle.

2. Generation of impulsive power when gunpowder is exploded.

3. The development of wind power due to heating of air by the Sun.

The three illustrations chosen above have served as the starting point for three different classes of engines which convert heat to work, *viz.*: (1) the steam engine, (2) the internal combustion engines used in motor cars, aeroplanes, and for numerous other purposes, (3) the windmills and steam turbines.

Many of the principles utilised in these engines are quite common to all classes, and we shall begin by describing the evolution of the steam engine. Though the mechanical details are outside the scope of this book, an elementary discussion is included for the sake of completeness and continuity of treatment.

3. Early History of the Steam Engine.—The earliest record of human attempt to make a heat engine is found in the writings of Hero of Alexandria, a member of the famous Alexandrian school of philosophers. Hero describes a scientific toy in which air was heated in a closed box and allowed to expand through a pipe into a vessel below containing water. The water was thus forced up through another pipe into a vertical column producing an artificial fountain. There was, however, no suggestion to employ it on a large scale. In 1606, about two milleniums after Hero, Marquess Della Porta, founder of the Neapolitan Academy and one of the pioneers of scientific research in Europe, employed steam in place of air in Hero's experiment in order to produce a fountain. He also suggested that in order to fill up the vessel with water, it may be connected by a pipe to a water reservoir below. If the vessel filled up with steam be now cooled with water from the outside, steam inside will condense, a vacuum will be produced, and water will be forced up from the reservoir, replenishing the vessel again. This principle was utilised by Thomas Savery in 1698 to construct a water-pumping machine which is described below. He was the first man to produce a commercially suc-

cessful steam engine which was extensively used for pumping water out of mines, and supplying water from wells.

The principle utilised in this engine is illustrated in Fig. 1. V is a steam boiler, from which steam passes through the valve A to the vessel P, and presses upon the water contained in P. The valve B is kept closed in this stage, and C opened. Thus the water is forced up through C into the vessel D and the vessel P is emptied. Then A and C are closed, B is opened, and cold water is sprinkled on P. The steam condenses producing vacuum in P and water is forced up by atmospheric pressure and fills up P. Then B is closed, and A and C are opened and a fresh cycle begins.

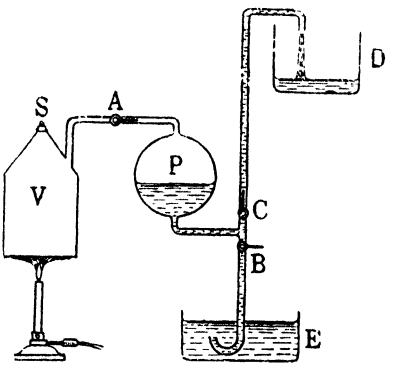


Fig. 1.—Principle of Savery's engine.

Savery's engine could not suck water through more than 34 feet, but it could force up the water to any height. In fact he sometimes forced up water to a height of 300 feet. This means that he used high pressure steam up to 10 atmospheres. This was a risky procedure though Papin had shown about 1680, how the risk in using high pressure steam could be minimised by the introduction of the safety valve.

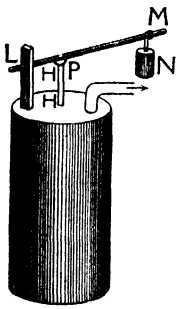


Fig. 2.—Papin's Safety valve.

Papin, a French settler in England, had discovered a method of softening bones by boiling them in a closed vessel under pressure. This, as we know, raises the boiling point of water to about 150°C. and makes the water a very powerful solvent. We are more concerned with the safety valve which he attached to the boiler to prevent his vessel from being blown up by high pressure steam. This is shown in Fig. 2.

The *safety valve* consisted of a rod LM pivoted at L and carrying a weight N at the other end. It pressed down the valve P which exactly fitted the

top of the tube HH leading from the inside of the boiler. Whenever the steam pressure exceeded a certain limit, it forced up the valve P and the excess steam would rush out. By adjusting the weight of N or its distance from L, the maximum steam pressure could be regulated at will.

Papin also proposed a steam engine which did not work.

4. Newcomen's Atmospheric Engine.—The next forward step was the invention of Newcomen's Atmospheric Engine which was designed to pump out water from mines and wells, and was in practical use for more than fifty years. This engine is interesting from the historical point of view since it directly led to the great inventions of James Watt, and it employed for the first time, the cylinder and the piston, which has been a feature of steam engines ever since. Fig. 3 illustrates the Newcomen Engine.

A is the cylinder, T is the piston suspended by a chain from the lever pivoted to masonry works. The other arm of the lever carries the piston rod W of the water pump which goes into the well. There is a counter-weight M to balance the weight of the piston T. The problem is to move the piston T up and down.

This was achieved as follows:—Starting with the piston T at the bottom of A, steam is introduced from the boiler B which forces the piston up till it reaches the top. The steam is shut off by the tap D, and cold water sprayed through F which condenses the steam in the cylinder. Vacuum is produced inside the cylinder and consequently the atmospheric pressure forces down the piston. D is again opened and a fresh cycle begins. The water in the cylinder A drains out through a side pipe.

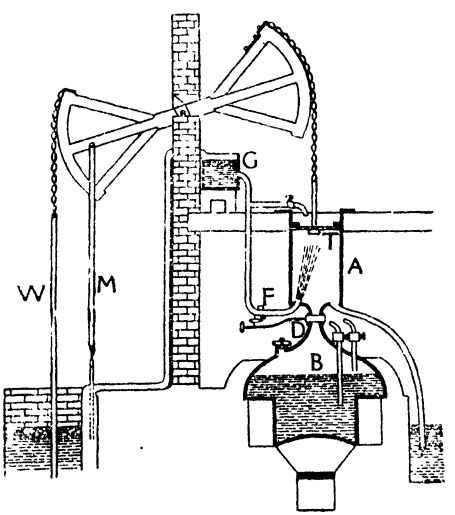


Fig. 3.—Newcomen's Atmospheric Engine.

For closing and opening the valves automatically, a parallel motion guide was provided which carried

mechanism for automatically operating the valves. The story goes that the invention was due to a lazy boy who was employed to close and open the valve by hand, but who tieh a parallel rod to the swinging arm of the lever, and connected it by means of cords to the valves, and leaving this rod to do his work, enjoyed himself all the while in playing. Whatever may be the origin, the parallel guide has been a permanent feature of steam engines ever since.

In the Newcomen Engine, the useful work is done by the atmospheric pressure while steam is only employed to produce vacuum, hence the name *atmospheric engine*. It is easily seen that it is very wasteful of fuel.

5. James Watt.—James Watt is commonly credited with the discovery of the steam engine. The circumstances* which directed his attention to steam engine are pretty well known. He was an ingenious scientific instrument maker at Glasgow, and in 1763 he was asked by the professor of Physics at the Glasgow University to repair a Newcomen Engine belonging to them which had never worked well. While engaged in the repair of this machine, the idea occurred to him that the Newcomen Engine was awfully wasteful of fuel, and being of an inventive temperament, he began to ponder, and experiment on the production of a better type of machine. He was thus led to a series of investigations, and contrivances which gave the steam engine its present form, and rendered it a mighty factor in the onward march of industry and civilisation. We are describing some of his inventions below.

6. Use of a Separate Condenser.—Watt observed that a large part of the expansive power of steam is lost on account of the fact that the cylinder is alternately heated and cooled. The expansive power of steam depends upon its temperature. Now when the steam enters the cylinder, which has been previously cooled to create a vacuum, some heat is taken up by the cylinder in becoming heated and is not converted into useful work. The temperature of steam falls and its expansive power is

* The popular writers generally want to add an element of romance in the story of the great invention by relating that he hit upon the design of steam engines when he was a mere boy, by observing the expansive power of steam in a kettle of boiling water. This story is wrong because Savery's engine and Newcomen's engine had been in use for three-quarters of a century before James Watt began his investigations.

diminished. Another disadvantage in using the cylinder as condenser is that cold water entering the cylinder becomes heated and exerts appreciable vapour pressure, thus preventing the formation of a good vacuum. The problem was to condense the steam without cooling the cylinder. Watt achieved this by the use of a separate condenser.

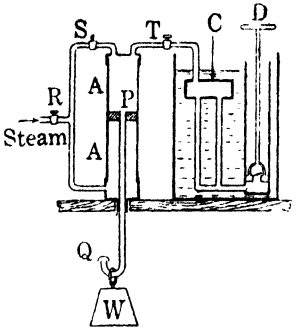


Fig. 4.—Watt's Experimental condenser.

The principle of the separate condenser is illustrated in Fig. 4. AA is the cylinder in which the piston P moves to and fro. The piston is provided with a hollow tube PQ carrying a valve Q at the end such that Q allows steam to go out but is closed by the atmospheric pressure when there is vacuum inside. Starting with the piston P at the bottom of the cylinder, R and S are opened and the part of the cylinder above P is filled with steam, forcing out the air and residual steam through Q. Then S is closed and T opened. The steam is drawn into the condenser C which had been previously evacuated by the pump D, and is there condensed by the cold water surrounding the condenser. Consequently a vacuum is produced above P and steam from below pushes the piston P upwards, doing work on the weight W. Then T is closed, S opened and P is drawn down to the bottom by W and the cycle begins afresh. The pump D serves to remove the air and water produced from steam in C.

To keep the cylinder hot, Watt further surrounded the cylinders by a steam box and wood. Now-a-days the cylinders are jacketted with asbestos or some other badly conducting substance, and then covered with thin metal sheets.

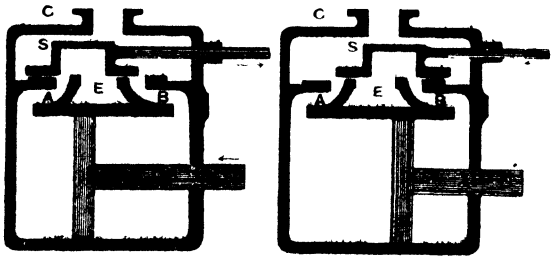


Fig. 5.—Double-acting cylinder with slide valve.

7. The Double-acting Engine.—Shortly afterwards Watt employed steam instead of the atmosphere to push the piston down. The piston was then raised up by the counter-

weight attached to the other arm of the beam. For these things to be possible the upper end of the cylinder must be closed. Watt achieved this by means of a steam-tight *stuffing box* which was kept tightly pressed against the piston. This was the so-called *single-acting engine* of Watt. Watt, however, soon realised that in this engine no work was done by steam during that stroke in which the piston was raised up by the action of the counter-weight. He saw that the power could be approximately doubled if during this useless stroke, steam is admitted to the lower side and the upper side is connected to the condenser. This is achieved in the *double-acting engine*, invented by Watt, with the aid of a number of valves. A modern double-acting cylinder provided with the valves is shown in Fig. 5. The cylinder has ports or holes A, B near its each end and between these lies another port E leading to the exhaust or condenser. To the cylinder is fastened the steam chest C containing the D-*slide valve* S. Steam from the boiler enters the steam chest at the top. In the position (*a*) steam enters the cylinder through the port B and pushes the piston to the left, thereby driving the steam in front through A to the exhaust E. As the piston moves to the left the slide valve moves to the right and closes both the ports A and B for a time, and later when the piston reaches the extreme left position, B is closed and A opened. Steam then enters through A forcing the piston backward and driving the steam in front to the exhaust. This is shown at (*b*). The double-acting engine is now universally employed in all kinds of steam engines.

The timely action of the slide valve is adjusted by means of an eccentric wheel attached to the moving shaft (see Fig. 7). In powerful engines as in locomotives the slide valve is often replaced by a piston valve which is very similar.

8. Expansive Power of Steam.—Watt's another great invention was the so-called expansive working of steam. He saw that if steam is allowed to enter the cylinder all the time the piston is moving outwards, the steam pressure in the cylinder will be the same as in the boiler and though we get a powerful stroke, the expansive power of steam is not utilised. If however the steam is cut off when the piston has moved some distance, the piston would complete its journey by the expansive power of steam, whose pressure will in consequence be reduced to almost that of the

condenser. Thus more work is obtained from the same amount of steam by allowing the steam to expand adiabatically and hence the running of the machine becomes considerably economical. It is thus of great advantage to use high pressure steam.

It was mentioned in the last section that the slide valve closes both the ports A and B when the piston has moved some distance. From this instant to the end of the stroke the steam is allowed to expand adiabatically

9. The Governor and the Throttle Valve.—Another simple but very useful invention of Watt was that of the governor. This is a piece of self-acting machinery which controls the supply of steam from the boiler into the cylinder, and ensures smooth running of the engine at a constant speed.

Watt's governor is shown in Fig. 6. S is a vertical spindle which is made to revolve by means of gearing from the engine shafts. Its speed, therefore, rises or falls with the engine speed. It carries a pair of heavy balls which are fastened to S by rods pivoted at P. The balls rise on account of centrifugal force as the spindle rotates, and as they do so they pull down a collar C which slides smoothly in the spindle S. The collar C fits into one end of a lever L pivoted at Q. The other end is connected to a tap in the steam pipe called the throttle valve.

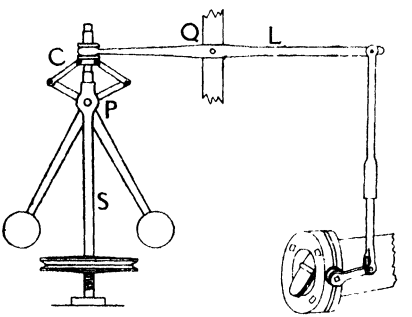


Fig. 6.—Watt's governor with throttle valve.

As C is pulled down, the throttle valve tends to close the tap, the steam supply falls off, and the engine speed falls. If the engine speed is too much diminished, the balls fall down, C is pushed up, and the throttle opens admitting more steam, and the speed goes up. Thus the governor automatically regulates the speed at which the engine runs. Improved forms of governors are now employed in engines.

10. The Crank and the Flywheel.—Watt was the first to convert the to-and-fro motion of the piston into circular motion by means of the connecting rod and the crank. Thus the steam engine can be made to turn wheels in mills, work lathes and drive all kinds of machinery in which a rotary motion is needed.

The connecting-rod R and the crank C are shown in Fig. 7 at (*a*). The crank is a short arm between the connecting-rod and the shaft S. The connecting-rod is attached to the piston-rod and consequently takes up the to-and-fro motion of the latter. As the connecting-rod moves forward it pushes the crank and thereby rotates the shaft S. In the return stroke the circular motion is completed. There are, however, two points in each revolution when the connecting-rod and the crank are in the same line and the piston exerts no turning moment. These are called the 'dead centres.' At two points when the crank is at right angles to the connecting-rod the torque is maximum. To prevent this large variation in the magnitude of the torque from producing variations in the speed of the shaft during a single revolution, a big flywheel F, shown at (*c*), is attached to the shaft. The flywheel on account of its large moment of inertia carries the crank shaft across the dead centres; in fact it absorbs the excess of energy supplied during a part of the half-revolution and yields back the same in the remaining part of the half-revolution when less energy is supplied. Thus the flywheel acts as a reservoir of energy which checks variations during a single stroke, while the governor prevents variation from stroke to stroke.

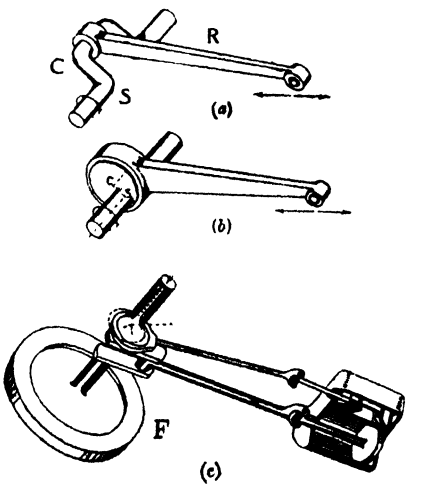


Fig. 7.—Crank, Eccentric and Flywheel.

Another mechanism to convert the to-and-fro motion into circular motion or *vice versa* is the eccentric, shown at (*b*), Fig. 7. It consists of a disc mounted off its centre on the shaft S and surrounded by a smoothly fitting collar to which the rod is attached. The behaviour is as if there was a crank of length SC. Such an eccentric is mounted on the shaft carrying the flywheel (shown at *c*) and works the slide valve. The effects can be properly timed by suitably mounting the eccentric on the shaft.

The essential parts of a simple engine are shown in Fig. 8. They will be easily followed from the figure.

11. Modern Steam Engines.—Since the time of Watt many important innovations have been introduced into the steam engine though the main features remain the same. The innovations were needed in order to suit the circumstances of ever-widening application of steam engines to various purposes. Watt always used steam engines with low steam pressure, and of a static type. He was evidently afraid of explosions. But engines using low pressure steam are comparatively inefficient, as we shall see presently, and in modern times high pressure engines have almost replaced the old Watt engines necessitating the construction of special type of boilers.

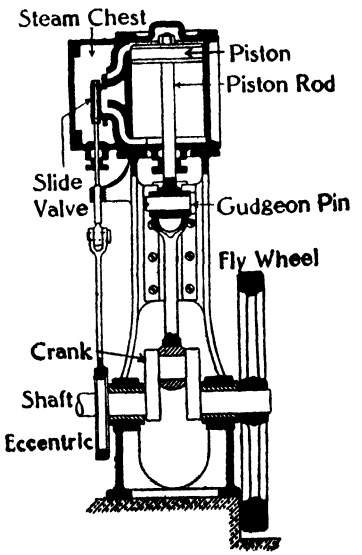


Fig. 8.—Main parts of a Steam Engine.

Condensers in modern engines consist of a number of tubes containing cold water kept in circulation by means of a pump, and are further provided with a pump to remove the air and water produced by steam on condensation.

Again in powerful engines the high pressure steam is not allowed to expand completely in a single cylinder. The steam is partly expanded in one cylinder and passed on to one or more cylinders where the expansion is completed. Such engines are known as *compound engines* and may consist of three or four cylinders.

Richard Trevithick was the first to construct a 'locomotive,' *i.e.*, a steam engine which can draw carriages on rails. But his schemes came to naught, and it was left to George and Robert Stephenson, father and son, to construct the first successful locomotive—the Rocket, and run the first railway train in 1829, between Liverpool and Manchester. Robert Fulton was the first to apply the steam engine to ships in 1812.

12. Efficiency of Engines.—The earlier workers had no idea of the Nature of Heat, and being engineers rather than physicists, they did not make any serious attempt at understanding the physical processes involved in the running of a steam engine. They measured efficiency by finding out the quantity of coal to be burnt per unit of time in order to develop a certain power. This was rather a commercial way of measuring efficiency.

An absolute measurement of efficiency is obtained from the first law of thermodynamics. A heat engine is merely an apparatus for the conversion of heat to work. The heat supplied is obtained by finding out the calorific value of the fuel consumed by burning a sample of the fuel in a bomb calorimeter (p. 70). If Q be the calorific value of the fuel consumed per unit of time, and W the power developed, we can define efficiency as the ratio between Q and W, *viz.*,

$$\eta = \frac{W}{JQ}.$$

η is accordingly the fraction of the total heat converted to work.

For an ideal engine, η should be unity. But actual experience shows that η is a rather small fraction. In Watt's days, it was only 5%; now-a-days even in the best type of steam engines, it is never more than 17%.

The question arises whether this lack of perfectness is to be ascribed to the bad designing of heat engines, or whether there is something in the very nature of things which prevents us from converting the whole amount of heat to work.

This question was pondered over by Sadi Carnot about a hundred years ago. He showed that even with an ideal engine, it is never possible to convert more than a certain percentage of heat to work.

13. The Carnot Engine.—As we have seen, the function of the steam engine is to convert the chemical energy stored in coal to energy of motion by utilising the expansive power of steam.

The machinery necessary for this purpose is however so complicated that one is apt to lose sight of the essential physical principles in the details of mechanical construction. Let us, therefore, discuss the physical principles involved in the running of a heat engine. Three things are apparently necessary, *viz.*, a source of heat, a working substance, and

machines. In the steam engine, the source of heat is the furnace where heat is supplied by the burning of coal. But we may get heat by a variety of other means.* *e.g.*, by burning oil, wood, naphtha, or even directly from the sun (solar engines), or from the inside of volcanoes (as is sometimes done in Italy). We can, therefore, replace the furnace by the general term "reservoir of heat." For steam, we can use the general term "working substance," for any substance which expands on heating can be used for driving heat engines. As a matter of fact, we have got hot air engines in which air is heated by a gas burner or a kerosene lamp, and pushes the piston up and down as steam would do.

In addition to the three requisites mentioned above, we require a fourth one, *viz.*, the possibility of having a temperature difference. This at first is not so apparent, but can easily be made clear. In a hot air engine, the heated air can push the piston outward since the air outside is at a lower temperature. If there were no difference of temperature, no difference of pressure could be created, hence the machine would not work. We, therefore, require not only a source of heat, but also a *sink*, *i.e.*, a heat reservoir at a lower temperature. In steam engines, the surrounding air acts as the sink of heat.

Carnot observed that the function of the machine is to extract a certain quantity of heat Q from the heat reservoir F, convert a part of it to work and transfer the rest to the heat sink G. He also showed how these operations should be carried out so that the efficiency may be maximum.

Since whenever there is a difference of temperature, there is a possibility of converting heat to work, the converse is also true, *i.e.*, if we allow heat to pass from F to G by conduction, we miss our opportunity of getting work. Hence we must extract heat from F in such a way that loss of heat by conduction is reduced to a minimum. Carnot, therefore, thought of the following ideal arrangement.

* Barjot suggested (*Scientific American*, p. 196, March 1930) that the heat of Arctic waters may be utilised as a source of power. The unfrozen water below the frozen surface of the sea is above 0°C. while the atmospheric temperature is below 0°C. He thought out a project by means of which this difference of temperature could be utilised in working a turbine, but the practical utility of the project has yet to be established. The French inventor Claude is reported to be engaged in maturing a project by which the heat of the Gulf Stream can be converted to work.

F is a heat reservoir at temperature T (Fig. 9), G a heat-sink at T′. S is the cylinder of the engine containing a perfect gas instead of steam as the working substance and fitted with a non-conducting piston. The walls of the cylinder are impervious to heat but the bottom is perfectly conducting. The behaviour of the working gas is shown by the indicator diagram showing the pressure and the volume of the gas at any instant. Let the following steps be performed:—

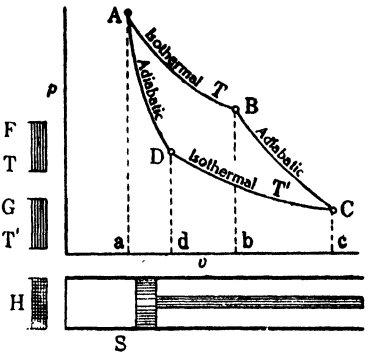


Fig. 9.—The ideal Carnot engine with indicator diagram.

(1) Let the initial temperature of the gas within S be T and let it be placed in contact with F, and the piston moved forward slowly. As the piston moves, the temperature tends to fall, and heat will pass from F to S. The operation is performed very slowly, so that the temperature of the air is always T. The representative point on the indicator diagram moves from A to B, along an isothermal curve. The heat Q extracted in this process is equal to the work done by the piston in free expansion, and is given by

$$w_1 = Q = \int_A^B p\,dv = RT \log_e \frac{v_b}{v_a} = \text{area } Aabb \quad . \quad . \quad (1)$$

(2) F is then removed and H, which is simply a non-conducting cap, is applied to the cylinder, and the piston allowed to move forward (by inertia). Then the gas will describe the adiabatic BC and will fall in temperature. We stop at C when the temperature has fallen to T′. The work done by the gas is given by

$$w_2 = \int_B^C p dv = \int_B^C \frac{K\,dv}{v^\gamma} = \frac{K}{1-\gamma}\left[\frac{1}{v_C^{\gamma-1}} - \frac{1}{v_B^{\gamma-1}}\right]$$

$$= \frac{1}{1-\gamma}[p_C v_C - p_B v_B] = \frac{R(T-T')}{\gamma-1} = \text{area } Bbc C \quad . \quad . \quad (2)$$

where $pv^\gamma = K = p_C v_C^\gamma = p_B v_B^\gamma$.

Since the pressure is now very much diminished, the gas has lost its expansive power, hence it must be brought back to its original condi-

tion. To effect this we compress the gas in two stages: first isothermally along the path CD, and then adiabatically along DA. The point D is obtained by drawing the isothermal T′ through C, and the adiabatic through A.

(3) During the isothermal compression, the cylinder is placed in contact with the sink G at T′. The heat which is developed owing to compression will now pass to the sink. This is equal to the work done on the gas and is equal to

$$w_3 = Q' = \int_D^C p dv = RT' \log_e \frac{v_c}{v_d} = \text{area } CcdD. \quad . \quad . \quad (3)$$

(4) The cylinder S is now placed in contact with H and the gas is compressed adiabatically. The work done on the gas by adiabatic compression is

$$w_4 = \int_D^A p dv = \frac{R}{\gamma - 1}(T - T') = \text{area } Dda A. \quad . \quad . \quad (4)$$

It is thus seen that $w_2 = w_4$.

The net work done by the engine

$$W = w_1 + w_2 - w_3 - w_4 = \text{area ABCD} \quad . \quad . \quad . \quad (5)$$

$$= w_1 - w_3 = Q - Q' \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Since B and C lie on the same adiabatic, we have by equation 24, p. 54.

$$T v_b^{\gamma - 1} = T' v_c^{\gamma - 1}$$

or

$$\frac{v_c}{v_b} = \left(\frac{T}{T'}\right)^{\frac{1}{\gamma - 1}} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Similarly, $\frac{v_d}{v_a} = \left(\frac{T}{T'}\right)^{\frac{1}{\gamma - 1}} = \rho$, the adiabatic expansion ratio.

Hence

$$\frac{v_b}{v_c} = \frac{v_a}{v_d}$$

or

$$\frac{v_b}{v_a} = \frac{v_c}{v_d} = r, \text{ the isothermal expansion ratio.}$$

We have, therefore,

$$Q=RT \log r,\ Q'=RT' \log r$$

and $$W=Q-Q'=R(T-T') \log r \quad . \quad . \quad . \quad . \quad (8)$$

Hence $$\frac{Q}{T}=\frac{Q'}{T'}=\frac{W}{T-T'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

or $$W=Q\left(\frac{T-T'}{T}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Thus the efficiency of the Carnot engine is

$$\eta=\frac{W}{Q}=\frac{T-T'}{T}=1-\frac{T'}{T} \quad . \quad . \quad . \quad . \quad (11)$$

$$=1-\left(\frac{1}{\rho}\right)^{\gamma-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Having analysed the mode of operation of the Carnot cycle, we now proceed to show that (1) it is reversible at each stage. (2) that no engine can be more efficient than the Carnot engine, (3) that the nature of the working substance is immaterial.

14. Reversibility of the Carnot Cycle.—A *reversible* process is one which can be retraced in the opposite direction so that the substance passes through exactly the same states in all respects as in the direct process. Further the thermal and mechanical effects at each stage should be exactly reversed, *i.e.*, the amounts of heat received and of work done in each step should be the same as in the direct process, but with opposite signs. Processes in which this does not take place are called *irreversible*.

Examples of reversible processes are the transfer of heat from one body to another at the same temperature, the gradual stretching of a spring, the process of slowly bringing an elastic substance into a state of stress, balanced expansion of gas, etc. Examples of irreversible processes are sudden unbalanced expansion of a gas, either isothermal or adiabatic, Joule-Thomson expansion, or any process in which friction, electrical resistance in a conductor, thermal conduction, etc. play a part.

It is now important to notice that the Carnot cycle is reversible at each stage, *i.e.*, instead of abstracting the heat Q from a source T and transferring a part Q′ to a sink T′ and converting

the balance $Q-Q'$ to work, we can proceed in such a way that the machine abstracts the heat Q' from the sink at T', then we perform the work W on the machine, and Q is transferred to the source at T. This is done by proceeding along the reverse route ADCBA, *i.e.*, first allowing the gas to expand adiabatically from A to D, then allowing it to expand isothermally from D to C in contact with the sink at T', the heat Q' being extracted in the process. Then we compress the gas adiabatically till we reach the point B (temperature T). Then S is placed in contact with the source, the gas is further compressed isothermally till we reach A, and the heat Q is transferred to the body at the higher temperature T. The machine, therefore, acts as a *refrigerator, i.e.*, by performing the work W on it, we are depriving a colder body T' of the heat Q'.

An engine in which the working substance performs a reversible cycle is called a *reversible engine.* Engines in which the cycle is irreversible are called *irreversible engines.* For the Carnot cycle to be reversible it is essential that the working substance should not differ sensibly in temperature from that of the hot body and the condenser when it is exchanging heat with them. There should be no transfer of heat by conduction in the usual sense, for it would be irreversible. This requires that the isothermal processes AB, CD should be described indefinitely slowly and the source and the condenser must have an indefinitely large capacity for heat so as not to change in temperature during the process.

Again the piston should move very slowly without friction. The changes in volume should be brought about by very small changes in the load on the piston.

It will be thus seen that the Carnot cycle imagines a stationary condition of equilibrium while a process essentially involves a changing state. Consequently the cycle is only ideal and cannot be realised in practice.

15. Carnot's Theorem.—The idea of reversibility is of the greatest importance in thermodynamics for the reason that, working between the same initial and final temperatures, *no engine can be more efficient than a reversible engine.* This is known as Carnot's theorem. We now proceed to prove this important theorem.

Suppose we have two engines R and S, of which R is a reversible engine and S an irreversible engine. If possible, let S be more efficient than R. Suppose S absorbs the heat Q from A, converts a part W' to

work and returns the rest, *viz.*, $Q-W'$ to the condenser. Let S be coupled to R (Fig. 10) and be used to drive R backwards. We are using R as a refrigerator. It thus abstracts a certain amount of heat from B, has the work W performed on it, and returns the same heat Q to the source A. The amount of heat that R abstracts from B must equal $Q-W$. Now since S is assumed to be more efficient than R, $W'>W$ and hence $Q-W>Q-W'$, *viz.*, R abstracts more heat from B than S restores to it. Thus the net result is that the compound engine RS abstracts heat $(W'-W)$ per cycle from B and converts the whole of it to work, while the source is unaffected. We are thus enabled, by a set of machines, to deprive a body continuously of its heat-content and convert the whole of it to work without producing any change in other bodies. It does not violate the first law for we are creating energy out of heat.

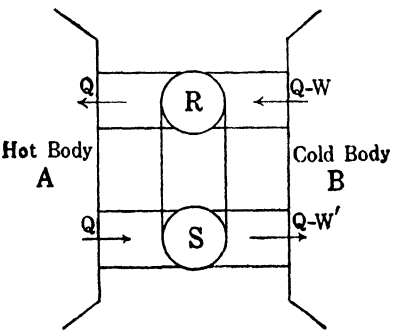


*Fig. 10.—Coupling a reversible and an irreversible engine.

Impossibility of perpetual motion of the second type.—But still the process is quite as good as perpetual motion† of the first kind, for heat is in excess about us, and if the process were feasible, it would give us all essential advantages of a perpetual motion machine, *viz.*, that of getting work without any expenditure, though not without energy. Human experience forbids us to accept such a conclusion.‡ Hence we conclude that no engine can be more efficient than a reversible engine.

Again, if we assume that a reversible engine using a particular working substance is more efficient than another working with a different

* Reproduced from Ewing's Steam Engine by the kind permission of Messrs. MacMillan & Co.

† This was a term in use amongst the medieval philosophers who thought that a machine might be invented some day which will create work out of nothing. For some mechanical contrivances which were intended to produce perpetual motion, see Andrade, *Engines*, page 14. The gradual evolution of the law of Conservation of Energy leading to the first law of thermodynamics showed that the idea is purely chimerical, since energy can never be created out of nothing, but can only be transformed from one form to the other.

‡ This result of human experience is the fundamental basis of the second law of thermodynamics. In fact Kelvin stated the second law in this form. For fuller discussion, see Chap. X.

substance, we arrive by a similar argument at the same absurd result. Hence *the efficiency is the same for all reversible engines and this is the highest limit for the efficiency of any engine that can be constructed or imagined.* This is Carnot's theorem. Thus reversibility is the criterion of perfection in a heat-engine. Hence we see that the efficiency of a reversible engine is maximum and is independent of the nature of the working substance. We chose perfect gas as our working substance, since its equation of state being known, we can easily evaluate η.

NOTE:—It may be mentioned that Carnot was ignorant of the true nature of heat at the time when he published his theorem of efficiency. He followed the old caloric theory in his speculations according to which, the quantity of caloric Q contained in a substance was invariable. When the engine was placed in contact with a high temperature source T_1, its energy was supposed to be raised to QT_1, the temperature being likened to potential. At temperature T_2 the energy dropped to QT_2. Hence the work done was supposed to be proportional to the drop of potential, *viz.*, $Q(T_1-T_2)$. The efficiency naturally came out to be $\frac{Q(T_1-T_2)}{QT_1}=1-\frac{T_2}{T_1}$, being defined as the ratio of the actual work done to the maximum work which might possibly be obtained.

It was Clapeyron who showed that Carnot's arguments and results remained intact when the Kinetic Theory of heat was introduced.

INTERNAL COMBUSTION ENGINES*

16. Historical Introduction.—Like other types of heat engines, the idea of this type also dates from medieval times. Ch. Huygens, the great Dutch physicist, invented in 1680 an engine consisting of a vertical cylinder and piston, in which the piston was thrown upwards by the explosion of a charge of gunpowder. This filled the cylinder with hot gases which eventually cooled, and the piston was forced down by gravity. Each stroke required a fresh charge of gunpowder.

This engine was never used, probably owing to the difficulty of introducing fuel after every explosion but the idea persisted. The discovery of combustible gases (coal gas, producer gas ..) and of mineral oils brought the idea within the range of practical possibilities, as the difficulty of supplying fuel promised solution. But many long years of

* These are called *internal* combustion engines because heat is produced by combustion of fuel *inside* the cylinder in contrast with the steam engine which may be called *external* combustion engine because heat is produced in the boiler. The internal combustion engine is much more efficient than the steam engine because the working substance can be heated to a much higher temperature (2000°C.).

practical and theoretical study were necessary before such engines became commercially possible.

It is not possible to go into the details of these early attempts, and it will suffice to describe and explain the action of the two types* which have survived, *viz.*, (1) the Otto engine in which heat is absorbed at *constant volume*, (2) the Diesel engine in which heat is absorbed at *constant pressure*. Nearly 80 per cent of internal combustion engines today are of the Otto type. We shall compare the action of these engines with that of the ideal Carnot engine in which heat is absorbed at *constant temperature*.

17. The Otto Cycle.—The Otto cycle which we are now going to describe was originally proposed by Beau de Rochas (1862), but the practical difficulties were first overcome by Otto in 1876. The working of the engine will be clear from Fig. 11. The engine consists of the cylinder and the piston, the cylinder being provided with inlet valves for air and gas (if gas is used for combustion), and exhaust valves. The opening and closing of these valves are controlled by the motion of the piston. There are four strokes in a complete cycle:—

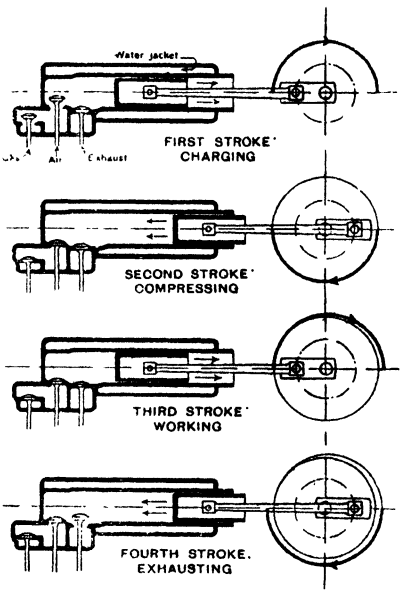


Fig. 11.—The four strokes of the Otto engine.

(*i*) *The Charging Stroke.*—In this the inlet valves are open, and a suitable mixture of air and gas is sucked into the cylinder by the forward motion of the piston.

(*ii*) *The Compression Stroke.*—During this stroke all the valves are closed, and the combustible mixture is compressed adiabatically to about

* Sometimes internal combustion engines are divided into (1) gas engines, (2) oil and petrol engines. It is however more scientific to divide them with regard to the cycles they follow and not with regard to fuel. Hence the engines have been divided into the constant volume, constant pressure and constant temperature type.

$\frac{1}{5}$th of its original volume by the backward motion of the piston. The temperature of the mixture is thereby raised to about 600°C.

At the end of the compression stroke, the mixture is fired by a series of sparks.

(*iii*) *The Working Stroke.*—The piston is now thrown forward with great force, since owing to combustion a large amount of heat is developed which raises the temperature of the gas to about 2000°C. and a corresponding high pressure is developed.

(*iv*) *The Scavenging or the Exhaust Stroke.*—At the end of the third stroke, the cylinder is filled with a mixture of gases which is useless for further work. The exhaust valves are then opened, and the piston moves backward and forces the mixture out. After scavenging is complete, a fresh charge of gas and air is sucked in and a fresh cycle begins.

The thermodynamical behaviour is illustrated in the indicator diagram (Fig. 12).

It should be remembered that air is the working substance in the Otto engine, the function of gas or petrol being merely to heat the air by its combustion. EC represents the suction stroke (gas and air being sucked at atmospheric pressure). CD represents the compression stroke. At D (pressure about 5 atmospheres, temperature about 600°C.) the mixture is fired by a spark. A large amount of heat is liberated, and the representative point shifts to A (temperature 2000°C., pressure about 15 atmospheres), volume remaining constant. AB represents the working stroke. At B the exhaust valve is opened, and the pressure falls to the atmospheric pressure CV_1. CE is the scavenging stroke.

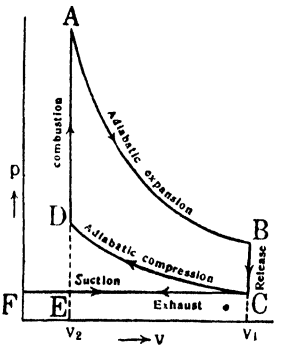


Fig. 12.—Four-stroke Otto cycle.

The *efficiency* of the engine can be very easily worked out. The amount of heat added $= C_v(T_a - T_d)$ where C_v is the specific heat at constant volume. (We suppose that this quantity retains the same value between 600°C. and 2000°C. which is only approximately true.)

$$\text{Heat rejected} = C_v(T_b - T_e).$$

Hence efficiency $\eta = 1 - \dfrac{T_b - T_c}{T_a - T_d}$ . . . . . (13)

From the relation $TV^{\gamma-1} = \text{constant}$ for an adiabatic (see p. 54, equation 24), we obtain

$$\frac{T_a}{T_b} = \left(\frac{V_b}{V_a}\right)^{\gamma-1} = \frac{T_d}{T_c} = \rho^{\gamma-1} \quad . \quad . \quad . \quad . \quad (14)$$

where ρ is the adiabatic expansion ratio.

Hence $$\frac{T_b - T_c}{T_a - T_d} = \left(\frac{1}{\rho}\right)^{\gamma-1}$$

Therefore the efficiency $$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad . \quad . \quad . \quad . \quad (15)$$

We obtain a similar expression for efficiency in terms of the adiabatic compression ratio as we get in a Carnot cycle (see equation 12, p. 219). The question arises: why not try to make the Carnot cycle a practical possibility?

We shall now treat this question in more detail. In designing a machine, other factors have to be taken into consideration besides the mere question of theoretical efficiency. The engine must be, in the first place, quick-acting, *i.e.*, a cycle ought to be completed as quickly as possible. This practically rules out the Carnot engine as it takes up heat at constant temperature, the process is therefore very slow and the engine becomes very bulky and heavy in relation to the power output. In the Otto engine, the absorption of heat is almost instantaneous. But even where quickness is not the deciding factor, there are other weighty arguments against the adoption of the Carnot cycle. Pressure inside the cylinder varies during a cycle, and the machine must be so designed that it can withstand the maximum pressure. Hence practical considerations impose a second condition, *i.e.*, the maximum pressure developed inside the cylinder during a cycle should not be too great. Further we must have a reasonable amount of work per cycle.

Now due to the adiabatic compression in the last stage of the Carnot cycle an enormous pressure is developed. A detailed consideration shows that working between the same two temperatures, say 2040°A and 340°A, the Carnot engine developes a maximum pressure of about 1000 atmos. while in the Otto engine it is only about 27 atmos., though of course the efficiency is reduced from about 83% to about 44%. The Carnot engine

also requires a large volume for the cylinder. These considerations show clearly that the Carnot engine is quite impracticable. It will have to be very bulky and very stout and the power output will be very small compared to its bulk.

In the case of the Diesel cycle which is described in the next section the maximum pressure developed is about 35 atmos. and the efficiency rises to about 55%. It is for this reason that the Diesel engine is employed in cases where we want a large output of work.

18. The Diesel Cycle.—Diesel was dissatisfied with the low efficiency of the Otto engine and began investigations with the idea that the efficiency of the Carnot cycle may be reached by certain other contrivances. He did not succeed in his attempt, but was led to the invention of another engine which, for certain purposes, presents some advantages over the Otto engine.

Now since $\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}$, it is easily seen that if the compression ratio ρ can be still further pushed up, η would substantially increase. But in the Otto engine, ρ cannot be increased beyond a certain value (about 5) otherwise the mixture would be fired during compression before the spark passes.

In the Diesel engine no gas or petrol is introduced during compression. The indicator diagram for the cycle is shown in Fig. 13. In the first stage pure air is sucked in (EC in Fig.) and compressed to about $\frac{1}{17}$th of its volume (CD in Fig.). A valve is then opened, and oil or vapour is forced under pressure. The oil burns spontaneously as the temperature in the cylinder is about 1000°C. and above the ignition point of the fuel. The supply of oil is so regulated that during combustion, as the piston moves forward, the pressure remains constant (DA). At a certain stage, when the temperature has reached the maximum value, about 2000°A, the supply of oil is cut off. The piston is allowed to move forward, describing the adiabatic AB. At B a valve is opened, and the pressure drops to C. CE

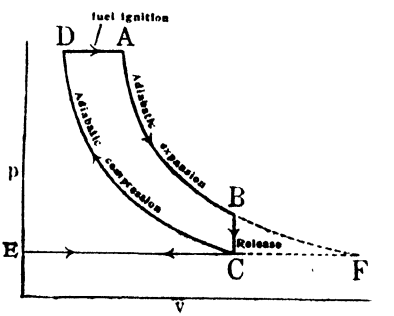


Fig. 13.—The Diesel cycle.

is the scavenging stroke, in which the useless gas mixture is forced out, and the apparatus becomes ready for a fresh cycle.

The Diesel cycle can be performed in a cylinder of the type shown in Fig. 14. The cylinder is provided with the air inlet, the oil supply and the exhaust valves. The action of the cycle will be very clearly followed from the figure.

Instead of opening a valve at B we may allow the gas to expand as far as F where the inside pressure has fallen to atmospheric pressure, and the air mixed with the burnt gas be forced out by a back stroke FC. As this would involve a rather large volume for the cylinder, this procedure is not adopted in actual practice.

We shall now calculate the efficiency of the Diesel engine. Let us first calculate the efficiency for the imaginary cycle AFCD.

Heat taken $= C_p\,(T_a - T_d)$

Heat rejected $= C_p(T_f - T_c)$

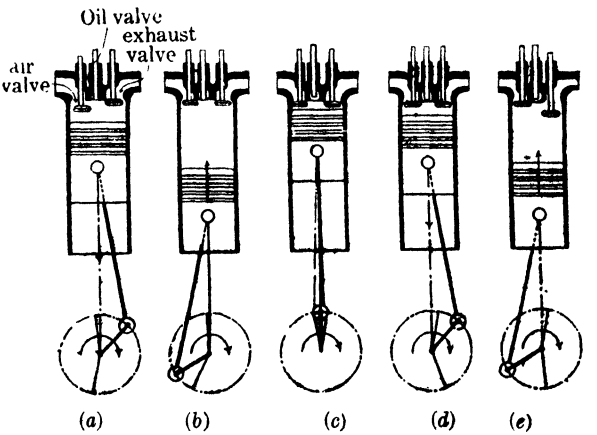


Fig. 14.—Strokes in a Diesel Engine.

(*a*) Beginning of suction stroke : air valve open.
(*b*) Beginning of compression stroke; all valves closed.
(*c*) Beginning of working stroke; oil valve open.
(*d*) Working stroke in progress. End of fuel injection; all valves closed.
(*e*) Beginning of scavenging stroke : exhaust valve open.

From the relation $p = c\,T^{\frac{\gamma}{\gamma-1}}$ (equation 25, p. 54) we have

$$\left(\frac{p_1}{p_2}\right)^{\frac{\gamma-1}{\gamma}} = \frac{T_d}{T_c} = \frac{T_a}{T_f} = \frac{T_a - T_d}{T_f - T_c}$$

$$\therefore \eta = 1 - \frac{T_f - T_c}{T_a - T_d} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

or
$$\eta = 1 - \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} = 1 - \left(\frac{V_a}{V_f}\right)^{\gamma-1}$$

$$= 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

So we have for the efficiency the same formula as for the Carnot or the Otto cycle. But in the Diesel engine the cylinder is designed for a maximum pressure of about 34 atmospheres. This determines the compression ratio because $p_1/p_c = \rho^\gamma = 34$. This gives $\rho = 12{\cdot}6$ and $\eta = 63\%$, which is a substantial improvement on the Otto engine.

But as stated above, we have to take the cycle DABC. Heat is rejected at constant volume. We have

$$\text{Heat rejected} = C_v(T_b - T_c)$$

$$\therefore \eta = 1 - \frac{C_v(T_b - T_c)}{C_p(T_a - T_d)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

which yields a lower value of about 55%.

The Diesel engine therefore consumes less fuel than the Otto engine, but as it has to withstand a higher pressure it must be more robust. Also the mechanical difficulties are much greater, but they have been successfully overcome.

19. Semi-Diesel Engines.—We have seen that in Diesel engines a large compression ratio (12 to 1) is employed and the maximum pressure developed is enormous (35 atmos.); further a costly high-pressure air blast is necessary to force the liquid fuel into the cylinder. To avoid these the semi-Diesel engine, also called the *hot bulb engine*, has been invented. In this the air is compressed to about 15 to 20 atmos. instead of 35 atmos. This air does not yet become hot enough to ignite the oil and is consequently passed through a hot bulb where it is heated by contact with the bulb to the required temperature. The hot bulb is simply a portion of the cylinder which is not cooled by the water jacket. It consequently becomes much heated and serves to heat the compressed air. Next the oil (fuel) is injected into this hot bulb where, by the combined action of the compressed air and the hot bulb, it ignites. For starting the machine the hot bulb must be heated by a separate flame. After a few cycles the bulb becomes hot and begins to function properly.

Then the external flame is removed. The semi-Diesel engines now-a-days are generally two-stroke oil engines without the automatic control valves.

20. The "National" Gas Engine.—We shall now describe a typical Otto engine. Fig. 15 shows a 100 horse power "National" gas engine.

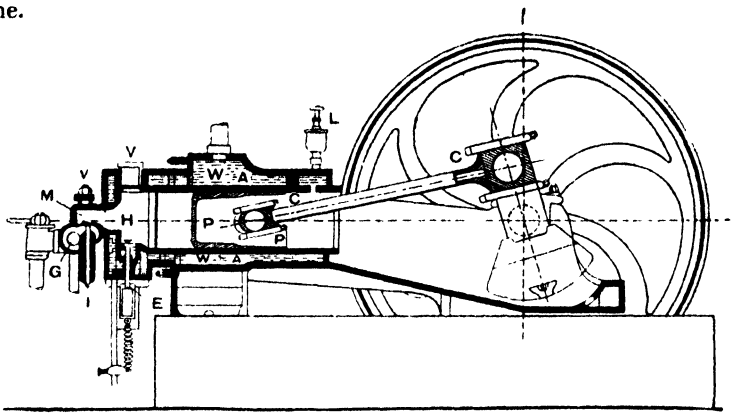


Fig. 15.—The "National" gas engine.

The engine is a stationary horizontal one having a single cylinder AA. The piston PP is attached to the crank shaft by the connecting rod CC and fits gas-tight into the cylinder AA. H is the combustion chamber having the inlet valve I, the gas valve G and the exhaust valve E. The cylinder, the combustion chamber and the valve casings are cooled by the water jacket WW. L is the lubricator, V, V are plugs which may be removed to examine the valves. M is the ignition plug where a spark is produced by the "Magneto" and serves to ignite the charge. The various valves and the magneto are worked by suitable cams mounted on a shaft driven by the crank shaft.

The working of the machine is identical with that indicated in Fig. 11. The machine is started by rotating the fly-wheel so that the piston commences its outward stroke. An explosive mixture is introduced and ignited, and the piston is thrown forward. Then the working follows as indicated on page 223.

21. Diesel Four-Stroke Engines.—These engines employ a cylinder and valves of the type shown in Fig. 14. In constructional design they are not much different from the Otto engine. They are further provided with a high pressure air blast for injecting the liquid fuel.

22. The Fuel.—Some engines employ gaseous fuels the chief of which are coal gas, producer gas, coke-oven gas, blast-furnace gas, water gas and natural gas (chiefly methane). The common liquid fuels are petrol, kerosene oil, crude oil, benzol and alcohol. In the Otto engine, if liquid fuel is used, it must be first vaporised and then admitted. Diesel engines generally employ crude oils and hence their fuel is very cheap.

23. Applications.—During the brief period of fifty years the internal combustion engines have been much developed and employed for a variety of purposes. The steam engine, we have seen, is very wasteful of fuel, but the internal combustion engine is much more economical and has consequently been much employed.

The Otto four-stroke engine is employed in motor cars and aeroplanes. Petrol vapour is used as fuel in both cases. Four-stroke Diesel engines are largely employed in driving ships. Where very large power is necessary, the two-stroke Diesels are in common use. Diesel engine is more efficient and more economical of fuel. Still has combined a steam engine with a Diesel engine and has obtained much greater efficiency in steam locomotives (Still-Kitson locomotives).

STEAM TURBINES

24. The Steam Turbine.—We shall now give a brief description of the engines belonging to the windmill type. Windmills are set in motion by the impact of wind on the vanes of the mill; and at first sight it may appear strange why they should be classed as heat engines. But a little reflection will show that the wind itself is due to the unequal heating of different parts of the earth's surface, hence the designation is justified. But wind-power is rather unreliable, hence steam turbines were invented in which the motive power is supplied by the artificial wind caused by high pressure steam. There are two types of turbines:—(1) the *Impulse Turbine* in which steam issuing with great velocity from properly designed nozzles strikes against the blades set on a turbine wheel and in passing through them has its velocity altered in direction. This gives an impulse to the wheel which is thereby set in rotation. (2) The *Reaction Turbine* is somewhat similar in principle to the Barker's Mill which, as a laboratory toy, has been known to generations of students. In this the wheel is set in rotation in the opposite direction by the reaction produced by a jet of steam issuing out of the blades set in the wheel.

Though the steam turbines are simple in theory, in practice great mechanical and constructional difficulties had to be encountered, but thanks largely to the efforts of De Laval, Curtis and most of all to Sir C. Parsons who may be described as the James Watt of the steam turbine, that the difficulties were successfully overcome. To-day the turbine is a prime mover of great importance and is almost exclusively used as the source of power for all large power land stations for the generation of electricity and propulsion of big ships. Their great advantage lies in the fact that instead of the reciprocating motion of the ordinary steam engine, a uniform rotary motion is produced by a constant torque applied directly to the shaft. They are more efficient than other engines because in them there is no periodic change of temperature in any part and so no heat is wasted. The full expansive power of steam can be utilised under suitable conditions. In America a turbine engine has been constructed which employs mercury vapour in place of steam and it is claimed that about 65% of heat energy is converted to work.

25. The Theory of Steam Jets.—The essential feature of the turbines is that in them the heat energy of steam is first employed to set the steam itself in motion inside the fixed nozzles or bladings (in reaction turbines) and this kinetic energy is utilised in doing work on the blades. The fixed nozzles are so designed as to convert most efficiently the thermal energy of steam into its kinetic energy and produce a constant steam jet. We shall therefore first study the formation of jet under these conditions. We shall find an expression for the kinetic energy imparted to the steam in traversing the fixed nozzle from the region of high pressure B (Fig. 16) to the region of low pressure C.

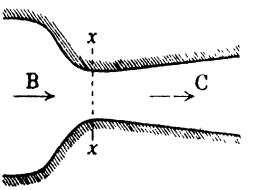


Fig. 16—The fixed nozzle producing the jet.

Let the pressure, volume, internal energy and velocity of steam in B per gram be denoted by p_1, v_1, u_1 and w_1 and the corresponding quantities in C by p_2, v_2, u_2 and w_2. Then the gain in kinetic energy of steam per gram on traversing the nozzle is $(w_2^2-w_1^2)/2J$ calories. The net work done on steam in this process as on p. 150 is $p_1v_1-p_2v_2$, while the loss in internal energy is u_1-u_2. Thus on the assumption that the process is adiabatic we have from the first law of thermodynamics,

$$\frac{1}{2J}(w_2^2-w_1^2)=p_1v_1-p_2v_2+u_1-u_2=i_1-i_2; \qquad (30)$$

i.e., the gain in kinetic energy is equal to the heat drop. Generally the initial velocity is sensibly zero and hence the kinetic energy of the issuing jet is given by the heat drop i_1-i_2.

If we now assume that there is no loss of heat energy through frictio or eddy currents in the nozzle, the heat drop $i_1 - i_2$ is equal to the hea drop from the pressure p_1 to p_2 under isentropic conditions. This can b readily obtained from steam tables and represents under most favourabl conditions the maximum work obtainable from the turbine. Under idea conditions the ordinary steam engine would also yield the same amount o work, *i.e.*, equal to the heat drop. The greater efficiency of steam turbine is however mainly due to the following two causes:—(1) In the turbin there are nowhere any periodic changes in temperature as are found i the cylinder of the steam engine; (2) the turbine is capable of utilisin low pressure steam with full advantage.

26. The De Laval Turbine.—The velocity which is theoretically attainable in a steam jet is therefore enormous, and this causes extra ordinary mechanical difficulties. For if we want to utilise the whole o this energy, by allowing the jet of steam to impinge on the blades o buckets of a turbine wheel, simple mathematical considerations show tha the velocity of the blades should not be short of one-half the velocity o the jet. Thus for maximum efficiency we should require to have a speec of the order of 1000 metres/sec. at the periphery of the wheel whicl carries the blades. The number of revolutions per minute necessary tc produce such peripheral speeds for a wheel of moderate dimensions reache the value of about 30,000 and such speeds are impracticable for twc reasons. First there are no constructional materials which can withstanc such enormous peripheral speeds. The rotating parts would fly to piece on account of the large centrifugal force developed and there would be mechanical vibration of the rotating shaft. Secondly if the shaft is to be coupled to another machine which should usually rotate at a much lower speed, say 2000 r. p. m., the problems of gearing become almost insuperable. These difficulties were first successfully overcome by De Laval for low power turbines. For the gearing down, he used double-helical gear wheels with teeth of specially fine pitch. To enable the requisite peripheral speeds to be obtained with safety, the turbine wheel was made very thick in

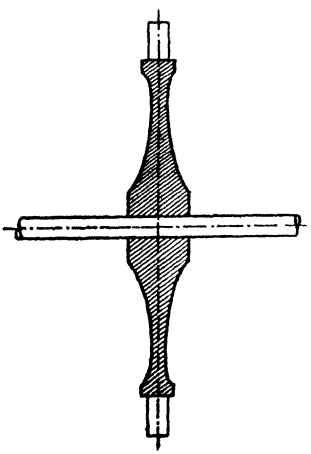


Fig. 17—Vertical section of the wheel of De Laval turbine.

the neighbourhood of the axis (see Fig. 17) so that it can withstand the stresses set up by rotation and further the shaft was made thin.

A De Laval turbine is illustrated in Fig. 18. The steam jet issuing from the fixed nozzles impinges on the blades, has its direction changed by them and thereafter escapes to the exhaust. Due to this action of the steam the blades are set in rotation. These are known as '*impulse turbines*' because the steam in passing through them is not accelerated but has only its direction changed. The interaction of steam with the blades is clearly indicated in Fig. 19. In these turbines the blades are 'parallel,' *i.e.*, a passage

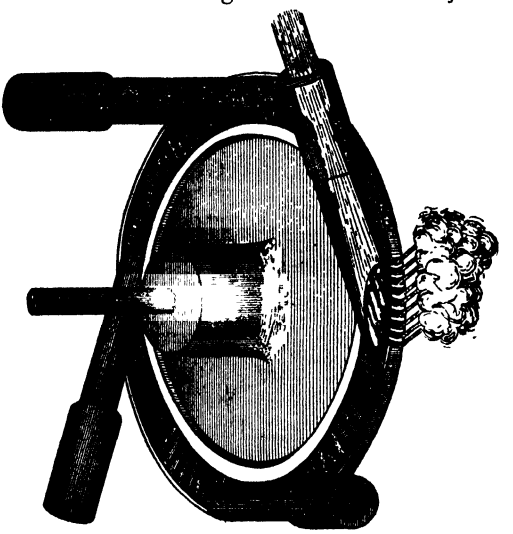


Fig. 18—A De Laval turbine.

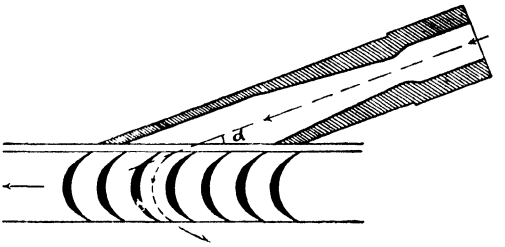


Fig. 19—Action of steam on the blades of a De Laval turbine.

between two blades has nearly the same cross-section everywhere so that the blades offer very little obstruction to the steam jet and hence the pressure of the steam remains practically the same on both sides of the wheel.

27. Division of the Pressure Drop into Stages. Rateau and Zölly Turbines.—As a prime mover, the De Laval turbine is quite efficient for producing low power. For generating high power, super-

heated steam must be used so that the pressure drop in the jet would be enormous, and hence for maximum efficiency the blades must move with very high velocity. Such large velocities are incompatible with safety. For this reason, the entire pressure drop is divided into a number of *stages.* Each stage consists of one set of fixed nozzles and one ring of moving blades mounted on a wheel fixed to the shaft. Across each stage, the pressure drop is small so that the blade velocity necessary for maximum efficiency is considerably reduced and can be easily attained in practice. This principle of *pressure compounding* was first given by Parsons and later adapted by Curtis, Rateau and Zölly to the De Laval type. Rateau turbine has 20 to 30 stages, Zölly has about 10.

28. Reaction Turbines—Parsons' Work.—Parsons began his researches on steam turbine about the same time as De Laval (1884), but he did not accept the latter's solution of the problem, and went on with his own investigations which were completed by about 1897. His researches resulted in the evolution of a completely new type—the so-called *Reaction Turbines.* The mechanism of this type is shown in Fig. 20.

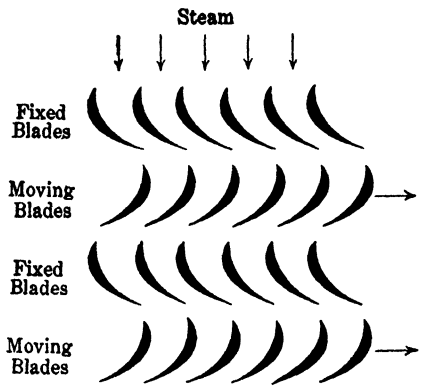


Fig. 20.—The blading system of a reaction turbine.

The essential feature of the Parsons' Turbine is its blading system. This consists of alternate rings of a set of fixed blades mounted on the inside of the cylindrical case or the stator, with a set of moving blades mounted on the shaft or the rotor, arranged between each pair of rings of moving blades as shown in Fig. 20. There are no separate nozzles for producing a jet, but the fixed blades act as nozzles. It will be noticed that the blades have convergent passages, *i.e.,* the cross-section of the passage goes on decreasing towards the exit side.

As the steam passes through the moving blades, there is a drop of pressure in consequence of which the steam jet increases in velocity as it traverses the blade-passage, and as it issues out, a backward *reaction*

is produced on the blades which consequently begin to revolve. The steam then again passes to the next set of fixed blades where it again acquires velocity and enters the next set of moving blades nearly perpendicularly.

The moving blades are secured in grooves on the rotor shaft with their lengths radially outwards and parallel to each other. The fixed blades are secured in grooves in the enclosing cylinder and project inwards almost touching the surface of the spindle. The steam is admitted parallel to the axis of the shaft (axial flow type). One pair of rings of moving and fixed blades is said to form a *stage*, and generally a turbine has a large number of stages.

Pressure Compounding:—On account of the peculiar form of the blade-passage, the pressure goes on falling rather slowly, so that the whole pressure drop is spread over a large number of stages which may amount to 45 or even 100. In consequence of this arrangement, the velocity of the jet is very small compared to that of the De Laval type, and the requisite blade speed is 100 to 300 ft. per sec. This reduction of velocity brought about by the distribution of available pressure over a large number of stages constituted the master-invention of Parsons which was also applied to other turbines with great advantage as already mentioned.

We have stated above that the steam enters the moving blades perpendicularly. In actual practice however the steam enters the moving blades with some relative velocity giving it an impulse as in De Laval's turbine and so the turbine works partly by impulse and partly by reaction. Thus it will be seen that the distinction between 'impulse' and 'reaction' turbines is more popular than scientific and should not be taken too literally. All turbines are driven by 'reaction,' due to the alteration of velocity of the steam jet in magnitude and direction. The real distinction between the two types is that in the 'impulse' turbines the reaction is due to the steam jet being slowed down while in the pure 'reaction' turbine the reaction is produced by the acceleration imparted to the steam in the moving blades themselves on account of the pressure drop. Still however by simply looking at the blades one can say whether the turbine is of the 'impulse' or 'reaction' type, the impulse blading being characterised by parallel passages and the reaction blading by the convergent passages.

Books Recommended.

1. Andrade—*Engines.*

2. Ewing—*Steam Engine and other Heat Engines.*

3. Glazebrook—*A Dictionary of Applied Physics,* Vol. I, Articles on Steam Engine; Engines, Thermodynamics of Internal Combustion; Turbines, development of; Turbines, Physics of; etc.

CHAPTER X

THERMODYNAMICS

1. Scope of Thermodynamics.—The object of the science of Heat is the study of all natural phenomena in which heat plays the leading part. We have hitherto studied a few of these phenomena in a detached way, *viz.*, properties of gases, change of state, variation of heat content of a body (calorimetry). There are other phenomena (*e.g.* Radiation, *i.e.*, the production of light by heated bodies) which have not yet been treated; there are others which, strictly speaking, do not come under Physics, *viz.*, Chemical equilibria, Electro-chemistry, but in which heat plays a very prominent part. The detailed study of all these phenomena is beyond the scope of this volume. The object of this chapter is simply to develop general methods for the study of all such phenomena.

The first requisite for such studies is the definition of the thermal state of a body or system of bodies. Next comes the development of general principles. The studies fall under two headings:—(*i*) the study of energy relationships, (*ii*) the study of the direction in which changes take place. The guiding principles for the two cases are the First and the Second Laws of Thermodynamics.

2. The Thermal State of a Body or System of Bodies.—The thermal state of a simple homogeneous body like a gas or a solid is defined by its temperature T, pressure p or the volume v. These quantities are therefore called *Thermodynamical Variables.* Of the three quantities only two are independent, the third being automatically fixed by the values of the first two. The equation

$$p = f(v, \mathrm{T}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which defines p in terms of v and T is called the 'Equation of State' of the body. The form of (1) is known only for a perfect gas (Chap. IV). But though (1) is generally unknown we can proceed a good deal towards studying the behaviour of a substance under different conditions by using differential expressions.

From equation (1) we have, on differentiation, in the general case

$$dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT \quad . \quad . \quad . \quad . \quad (2)$$

where $\left(\frac{\partial p}{\partial v}\right)_T$ denotes the rate of increase of pressure with increase of volume when the temperature is maintained constant and $\left(\frac{\partial p}{\partial T}\right)_v$ denotes the rate of increase of pressure with increase of temperature when the volume is kept constant. It will thus be readily seen that

$-v\left(\frac{\partial p}{\partial v}\right)_T$ = bulk modulus of elasticity in an isothermal process, or inverse of the coefficient of compressibility,

$\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v$ = coefficient of pressure increase in an isochoric process.

For an *isobaric* or *isopiestic* process, $dp=0$. Hence equation (2) yields

$$\left(\frac{\partial v}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_T}$$

or

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p . \quad . \quad . \quad . \quad (3)$$

Now $\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$ = coefficient of volume expansion in an isobaric process (Chap. VII).

Equation (3) shows that the volume elasticity, the volume coefficient of expansion and the pressure coefficient of expansion are not independent but are inter-related.

As an illustration, consider mercury at 0°C. and atmospheric pressure. For it, the coefficient of volume expansion is $1{\cdot}81\times10^{-4}$ and the coefficient of compressibility in atmospheres is $3{\cdot}9\times10^{-6}$. Hence from (3)

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p}{-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T} = \frac{1{\cdot}81\times10^{-4}}{3{\cdot}9\times10^{-6}} = 46{\cdot}5 \text{ atmos.}$$

and the pressure coefficient

$$\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v = 46{\cdot}5$$

Hence it follows that a pressure of about 46 atmos. is required to keep the volume of mercury constant when its temperature is raised from 0°C. to 1°C.

We may remark however that the thermodynamical system is composed of a very large number of molecules, and the aggregate effect due to these molecules is what we observe. Thermodynamical quantities are therefore statistical quantities, and a particular thermodynamical state can be got at by assigning different sets of values to the molecular parameters.

3. Different Forms of Energy.—As thermodynamics is largely a study of energy-relationships, we must clearly understand the term '*Energy*.' The student must be familiar with the concept of 'Energy' from his study of mechanics. 'Energy' of a body may be defined as its capacity for doing work and is measured in ergs on the C. G. S. system of units.

Everybody must be familiar with the two ordinary forms of energy, *viz.*, the *kinetic energy* and the *potential energy*. A revolving flywheel possesses a large amount of kinetic energy which can be utilised in raising a piece of stone from the ground, *i.e.*, in doing work. In this process the kinetic energy of the flywheel is converted into the potential energy of the mass of stone. The mass of stone also in its raised level possesses energy which we call potential energy and which can also be made to yield work. For when the stone falls down under gravity the flywheel can be coupled to a machine and be made to do work. Thus kinetic and potential energies are mutually convertible and in a conservative system of forces the sum of the kinetic and potential energies is constant throughout the process. All moving bodies possess kinetic energy by virtue of their motion and all bodies placed at a distance from a centre of force possess potential energy by virtue of their position.

There are other forms of energy also with which the student of physics must have become familiar, and which we shall now take up. We have already pointed out that *heat* consists in the motion of molecules and must therefore be a form of energy. The experiments of Joule and Rowland showed that there exists an exact proportionality between

mechanical energy spent and the heat developed. Friction is the chief method of converting mechanical energy into heat. The conversion of heat into work has also been accomplished by the help of steam engines and other heat engines which have been completely described in Chap. IX. Thus it has been fully established that heat is a form of energy.

Energy may be manifested in *electrical* phenomena also in a variety of ways. It is well-known that when two current-carrying coils are placed with their planes parallel to each other, they attract or repel each other depending upon the direction of flow of the current. In this case we are getting motion purely from electrical currents. Or we may take the more familiar example of the tramway. Here electric currents are made to run the carriage. Again a wire carrying a current becomes heated. Thus electricity is also a form of energy which can be easily converted into the mechanical or thermal form.

Energy may also be manifested as *chemical energy*. For we know that a bullet fired from a gun possesses enormous kinetic energy which is derived from the chemical actions that take place when the powder detonates. Further a large amount of heat is evolved during a number of chemical reactions, *viz.*, in the combination of hydrogen and oxygen. Also the chemical actions going on in a voltaic cell produce electrical current. Thus chemical energy can be easily converted into mechanical energy, heat, electrical energy, etc.

There are various other forms of energy, all of which can be converted into some one of the other forms. The important ones are the following:— magnetic energy, radiant energy (Chap. XI), surface energy (surface tension), radioactive energy and energy of gravitation.

4. Laws of Energy Changes.—There are three important laws governing energy transformations:—

(1) *The Transmutation of energy,*
(2) *The Conservation of energy,*
(3) *The Degradation of energy.*

5. The Transmutation of Energy.—This principle states that energy can be converted from one form to another. We have already seen how mechanical energy, electrical energy and chemical energy can be converted into heat. In fact all kinds of energy can be directly

converted into heat. Mechanical energy obtained from a water-fall working a turbine, may be utilised to generate electrical energy by coupling the turbine to a dynamo. The electrical energy may be converted into thermal energy as in electrical furnaces, or into chemical energy as in the charging of secondary cells. Heat energy can be converted into electrical energy as in the phenomena of thermo-electricity, into mechanical energy as in steam engines, and so on. Examples could be multiplied indefinitely.

6. The Conservation of Energy.—This principle states that during a process involving interchanges of energy, the total energy of the system remains constant. In other words energy is indestructible and uncreatable by any process. No formal proof of the law can be given. It is a generalisation based upon human experience and is amply borne out by its consequences. The law arose out of the attempts of earlier philosophers to devise a machine which will do work without expenditure of energy. They however failed in their attempt. Later it was recognized that all the machines invented were simply devices to multiply force and could not multiply energy, and the true function of a machine was to transmit work. Only that much work could be obtained from a machine as was supplied to it, and that too in ideal cases. This shows that energy obeys the law of conservation approximately. In these cases however all energy cannot be recovered as some is dissipated as heat. But heat is also a form of energy, and on equating the work obtained plus the heat developed to the work done, we find that the relation of equality is satisfied. Thus the principle is established for this case and follows from a result of human experience which may be stated in this form:—

"*It is impossible to design a machine which will create energy out of nothing and produce perpetual motion. Energy can only be transformed from one form to another.*"

7. The Dissipation of Energy.—Energy, we have seen, is capable of existing in different forms. In some forms however it is more available to us than in other forms, *i.e.*, we can get more work from energy in one form than in another. For example, mechanical energy is the highest available form while the heat energy of a body at a low temperature is in a much less available form. Now the law of degradation or dissipation of energy says that *energy always tends to pass from a more available to*

a less available form. This is called the degradation or dissipation of energy, and is intimately connected with the Second Law of thermodynamics; it will therefore be taken up later.

FIRST LAW OF THERMODYNAMICS

8. First Law.—We have already enunciated the law of conservation of energy. The First Law of thermodynamics is simply a particular case of this general principle when one of the forms of energy is heat. It may be mathematically stated in the form

$$dQ = dU + dW \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where dQ is the heat absorbed by the system, dU the increase in its internal energy and dW the amount of work done by it. It is essential to note that dQ is here expressed in energy units, and can be found by multiplying the heat added in calories by J, the mechanical equivalent of heat. The value of J is $4{\cdot}18 \times 10^7$ ergs per calorie.

APPLICATIONS OF THE FIRST LAW

9. Specific Heat of a Body.—We shall have first to define the thermal energy of a body. It is easy to see that the total thermal energy of a body or a thermodynamical system depends entirely on its thermal state and is uniquely given by the independent thermodynamical co-ordinates. In the case of a simple body we have, considering a gram-molecule of the substance,

$$U = f(V, T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Now $\left(\frac{\partial U}{\partial T}\right)_v = C_v$, the specific heat at constant volume. For a perfect gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (p. 52); for a gas obeying Van der Waals' equation

$$\frac{\partial U}{\partial V} = \frac{a}{V^2}.$$

If an amount of heat dQ be added to a thermodynamical system, say a perfect gas, part of it goes to increase the internal energy of the gas by dU, while the remainder is spent in doing external work, *e.g.*, when

the gas expands by a volume dV against the pressure p. We have by the first law,

$$dQ = dU + p\frac{dV}{J}$$

or, if dQ, dU are expressed in energy units,

$$dQ = dU + pdV \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If we consider a gram-molecule

$$\frac{dQ}{dT} = \text{molar specific heat } C.$$

Combining (6) and (7) we get

$$C = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V} + p\right)\left(\frac{\partial V}{\partial T}\right)$$

$$\text{or } C - C_v = \left(p + \frac{\partial U}{\partial V}\right)\left(\frac{dV}{dT}\right) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

C will have different values according to varying external conditions. If pressure be kept constant

$$C_p - C_v = \left(p + \frac{\partial U}{\partial V}\right)\left(\frac{\partial V}{\partial T}\right)_p \quad . \quad . \quad . \quad . \quad (9)$$

For a perfect gas, $\frac{\partial U}{\partial V} = 0$, $p\frac{\partial V}{\partial T} = R$ . . . . . (10)

$$\therefore \quad C_p - C_v = R$$

as has been deduced on p. 51. The relation for solids and liquids is complicated (see Sec. 36, Example 1).

It is easy to see that dQ, the heat added, cannot be determined only from the initial and final states of the body, and a knowledge of how the heat has been added is essential. Hence C, the specific heat, has no significance unless the external conditions are prescribed. We have defined C_p and C_v but there may be other processes, *e.g.*, adiabatic, when $dQ = 0$ and $C = 0$.

10. Work Done in Certain Processes.—The following expressions for work done in different processes have been already proved:—

(*a*) Work done by a perfect gas in isothermal expansion is (p. 217)

$$RT \log_e \frac{V_a}{V_b}.$$

(*b*) Work done by a perfect gas in adiabatic expansion in which the temperature falls from T_1 to T_2 is (p. 217)

$$=R\frac{(T_1-T_2)}{\gamma-1}$$

(*c*) In the case of a cyclic process the substance returns to its initial state and hence $dU=0$.

Equation (7) then yields

$$dQ=\frac{pdV}{J}$$

i.e., the heat absorbed by the substance is equal to the external work done by it during the cyclic process. Thus in Carnot's cycle the work done during a cycle is Q_1-Q_2.

11. Discontinuous Changes in Energy—Latent Heat.—When a body is in the condensed state (solid or liquid) and is subjected to increasing temperature, the state may suddenly change from solid to liquid form (fusion), or from liquid to gaseous form (evaporation), or from one crystalline form to another (allotropic modification). In such discontinuous changes the energy also changes discontinuously (phenomena of latent heat). Let us consider the evaporation of 1 gram of water at 100°C. and 1 atmos. pressure. The application of First Law yields

$$L=u_2-u_1+p\ (v_2-v_1) \quad . \quad . \quad . \quad . \quad (11)$$

where u_2, v_2 respectively denote the internal energy and volume of 1 gram of vapour, and u_1, v_1 the corresponding quantities for the liquid.

Equation (11) expresses the fact that the heat added is spent in two stages: (1) in converting 1 gram of water to 1 gram of vapour having the same volume, (2) in doing external work, whereby the vapour produced expands under constant pressure to its specific volume.

u_2-u_1 is sometimes known as internal latent heat and $p(v_2-v_1)$ as the external latent heat. For water at 100°C.

$v_1=1$ c.c., $v_2=1674$ c.c. (specific volume of saturated vapour)

Hence $$p\ (v_2-v_1)=\frac{1{\cdot}013\times10^6\times1673}{4{\cdot}18\times10^7}\text{cal.}$$

$$=40{\cdot}5\text{ cal.}$$

Since $L=538{\cdot}7$, we have $u_2-u_1=498{\cdot}2$ cal.

It is often convenient to denote the different states of aggregation of the same substance according to the following convention. $[H_2O]$, (H_2O), H_2O denote water in the solid, liquid and gaseous states respectively. The quantity taken is always a mol unless otherwise stated. The symbolical equation

$$H_2O = (H_2O) + 10{,}160 \text{ cal.} \quad . \quad . \quad . \quad . \quad (12)$$

expresses the experimentally observed fact that the energy content of a mol of H_2O (gas) at 0°C. exceeds the energy-content of a mol of H_2O (liquid) at 0°C. by 10,160 calories, the change taking place at constant volume.

We have further

$$(H_2O) = [H_2O] + 1{,}430 \text{ cal.} \quad . \quad . \quad . \quad (13)$$

i.e., energy of a mol of liquid H_2O at 0°C. exceeds the energy of a mol of ice at 0°C. by 1,430 cal.

From equations (12) and (13) we have by addition

$$H_2O = [H_2O] + 11{,}600 \text{ cal.} \quad . \quad . \quad . \quad (14)$$

i.e., heat of sublimation of 1 mol of ice at constant volume is 11,600 calories. This is a consequence of the First Law applied to a physical process and can be easily verified.

12. First Law applied to Chemical Reactions—Hess's Law of Constant Heat-summation.—The First Law can be extended to Chemical Reactions. Thus when 2 mols of H_2 and 1 mol of O_2 are exploded together in a bomb calorimeter, 2 mols of (H_2O) are formed, and 136,800 calories of heat are evolved. Allowing for the heat evolved in passing from the gaseous to the liquid state, we obtain from the First Law, since $dQ = -116{,}500$ and $dW = 0$

$$2U_{H_2} + U_{O_2} - 2U_{H_2O} = 116{,}500 \text{ cal.} \quad . \quad . \quad . \quad (15)$$

i.e., the energy of 2 mols of H_2 and 1 mol of O_2 exceeds the energy of 2 mols of H_2O by 116,500 calories.

Hess stated in 1840, before the First Law had been discovered, that if a reaction proceeds directly from state 1 to state 2, and again through a series of intermediate states, then the heat evolved in the direct change is equal to the algebraic sum of the heats of reaction in the intermediate stages. This is an important law in Thermo-chemistry and is known as Hess's Law of Constant Heat Summation.

The law is illustrated by the following examples:—

$$C \text{ (diamond)} + \tfrac{1}{2}O_2 = CO + 26{,}100 \text{ cal.}$$

$$CO + \tfrac{1}{2}O_2 = CO_2 + 68{,}300 \text{ cal.}$$

We have by adding

$$C \text{ (diamond)} + O_2 = CO_2 + 94{,}400 \text{ cal.} \quad . \quad . \quad . \quad (16)$$

This is verified by experiments.

We take another example. Let the symbol $(LiOH)_{aq}$. denote the solution of 1 mol of the substance.

Then take the equations:—

$$2[Li]+2(H_2O)=2(LiOH)_{aq}.+H_2+106{,}400 \quad . \quad . \quad . \quad (17)$$

$$2[LiH]+2(H_2O)=2(LiOH)_{aq}.+2H_2+63{,}200 \quad . \quad . \quad . \quad (18)$$

The energy evolved is very easily determined from solution experiments. If we subtract (18) from (17) we get

$$2[Li]+H_2=2\,[LiH]+43{,}200 \text{ cal.} \quad . \quad . \quad . \quad (19)$$

i.e., the heat of formation of two mols of [LiH] from [Li] and H_2 is 43,200 cal.

THE SECOND LAW OF THERMODYNAMICS AND ENTROPY

13. Scope of the Second Law.—The Second Law of Thermodynamics deals with a question which is not at all covered by the First Law, *i.e.*, the question of the direction in which any physical or chemical process involving energy changes takes place.

A few illustrations will clear the point. Let us consider the thermodynamic process illustrated by the symbolic equation:—

$$2H_2+O_2=2H_2O+U \text{ calories} \quad . \quad . \quad . \quad . \quad (20)$$

The equation tells us that if 2 mols of H_2 gas combine with one mol of O_2, 2 mols of H_2O-vapour are formed and U calories of heat are evolved, or *vice versa*, when 2 mols of H_2O-vapour are decomposed completely into H_2 and O_2, U calories of heat must be absorbed. This result is obtained as a matter of experience from calorimetric experiments, and we interpret the result according to the First Law of Thermodynamics by saying that in the combination of 2 molecules of hydrogen with 1 molecule of oxygen into 2 molecules of H_2O, the diminution in energy amounts to $U/2N$ ergs per molecule. This result can further be utilised in calculating energy relations in other reactions. But the first law cannot tell us in what direction the reaction will take place. If we have a mixture consisting of H_2, O_2 and H_2O-vapour in arbitrary proportions at some definite temperature and pressure, the first law cannot tell us whether some H_2 and O_2 will combine to form H_2O or some H_2O will dissociate into H_2 and O_2, the system thereby passing to a state of greater stability.

Or we can take a physical example. When two bodies, A and B, exchange heat, the first law tells us that the heat lost by one body is equal

to the heat gained by the other. But it does not tell us in which direction the heat will pass. Only experience tells us that the heat will pass from the hotter body to the colder spontaneously, but in speaking of hotter and colder bodies, we are making use of a new physical concept (temperature) which is not at all included within the scope of the first law. For giving us guidance in deciding the question of direction in which a process will take place, we require a new principle and this principle, which arose out of Carnot's speculations about the convertibility of heat to work, is generally known as the Second Law of Thermodynamics.

14. Preliminary Statement of the Second Law.—The problem of convertibility of heat to work has been treated in Chap. IX. It is readily observed that the main question was about the direction of energy transformation. Mechanical energy and heat are only different forms of energy, but while mechanical energy can be completely converted to heat by such processes as friction, it is not possible to convert heat completely to work. Even by using reversible engines which are the most efficient, only a fraction can be converted to work. The conversion is therefore only partial. The question is, why is it so?

An answer to this question has been given already in Chap. IX, *viz.*, if it were possible to design an engine more efficient than a reversible engine, we could continuously convert heat to work, and this will produce perpetual motion of a kind. We may call this *perpetual motion of the second kind.* We are convinced that this is not possible, and we may start from a statement which expresses our conviction just as the first law is based on the conviction that Energy cannot be created, but can only be transformed. We may make the statement in the following form:—

"*It is impossible to construct a Heat Engine which will continuously abstract heat from a single body, and convert the whole of it to work, without leaving changes in the working system.*" This statement is equivalent to Clausius or Lord Kelvin's statement of the Second Law.

Lord Kelvin stated the law in this form:—"*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.*"

Clausius stated it in the form:—"*It is impossible for a self-acting machine, unaided by any external agency to convey heat from one body*

to another at a higher temperature, or heat cannot of itself pass from a colder to a warmer body."

It must be clearly understood that these statements refer to continuous or cyclical processes. For it is always possible to let heat pass from a colder to a hotter body and at the same time the substance to change to a state different from its initial one. As an example consider an isolated system comprised of a cold compressed gas and a hot rarefied gas communicating with each other through a movable piston. When the piston is released, the hot vapour is compressed and heat is thereby transferred from the cold to the hot gas. The state of the two gases however changes as a result of the process.

15. Absolute Scale of Temperature.—Lord Kelvin* showed in 1848 that with the aid of the ideal Carnot engine it was possible to define temperature in terms of energy; and the scale so obtained is independent of the nature of any particular substance. Kelvin started from the result (p. 221) that the efficiency of all reversible engines working between two temperatures is a function of the two temperatures only and is independent of the nature of the working substance. This may be mathematically stated in the form

$$\frac{W}{Q_1} = f(\theta_1, \theta_2) \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where W is the work done by the Carnot engine, Q_1 the heat taken in and θ_1, θ_2† the temperatures between which the engine works.

Now $W = Q_1 - Q_2$ where Q_2 is the heat rejected. Hence

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

or

$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2) \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where F denotes some other function.

It can be easily shown that the ratio $\frac{Q_1}{Q_2}$ can be expressed in the form $\frac{\psi(\theta_1)}{\psi(\theta_2)}$. For if we have reversible engines working between the pairs of

* *Phil. Mag.*, 1848; *Trans. Roy. Soc. Edin.*, 1854.

† These may be measured on any arbitrary scale.

temperatures (θ_1,θ_2), (θ_2,θ_3), (θ_1,θ_3), and the heat absorbed or evolved (as the case may be) at these temperatures be Q_1, Q_2, Q_3, then

$$\frac{Q_1}{Q_2}=F(\theta_1,\theta_2) \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$$\frac{Q_2}{Q_3}=F(\theta_2,\theta_3) \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$\frac{Q_1}{Q_3}=F(\theta_1,\theta_3) \quad . \quad . \quad . \quad . \quad . \quad (25)$$

But by multiplying (23) by (24) we get

$$\frac{Q_1}{Q_3}=F(\theta_1,\theta_2)\times F(\theta_2,\theta_3).$$

Hence the function F must satisfy the relation

$$F(\theta_1,\theta_3)=F(\theta_1,\theta_2)\times F(\theta_2,\theta_3) \quad . \quad . \quad . \quad (26)$$

This will be so only when $F(\theta_1,\theta_2)$ is of the form $\frac{\psi(\theta_1)}{\psi(\theta_2)}$. Therefore for any reversible engine

$$\frac{Q_1}{Q_2}=\frac{\psi(\theta_1)}{\psi(\theta_2)} \quad . \quad . \quad . \quad . \quad . \quad (27)$$

It will be seen that if $\theta_1>\theta_2$, $Q_1>Q_2$ and therefore $\psi(\theta_1)>\psi(\theta_2)$, *i.e.*, $\psi(\theta)$ is a quantity which increases monotonously with θ and may be used to measure temperature. Denote the value of $\psi(\theta)$ by τ.

The relation (27) then becomes

$$\frac{Q_1}{Q_2}=\frac{\tau_1}{\tau_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

(28) is used to define a new scale of temperature τ which is called the absolute or the thermodynamic scale. This scale does not depend upon the properties of any particular substance for equation (28) is universally true. The ratio of any two temperatures on this scale is equal to the ratio of the heat taken in and rejected by an engine working reversibly between the two temperatures.

The zero of this scale ($\tau=0$) is that temperature at which $Q_2=0$ (from 28) and hence $W=Q_1$. Thus all the heat taken by the engine has been converted into work and the efficiency of the engine is unity. τ cannot

be less than this, *i.e.*, negative, for if it were so, the engine could convert more heat to work, than it takes from the source. This is impossible and hence $\tau=0$ is the lowest temperature conceivable. This is the absolute zero of temperature which need not be the temperature at which all molecular motions cease to exist as one might otherwise infer from elementary kinetic theory.

The zero having been determined, let us fix the size of the degree. In conformity with general usage we suppose that the interval between the freezing and the boiling points of water is divided into 100 equal parts on this scale, *viz.*,

$$\frac{Q_{steam}}{Q_{ice}} = \frac{\tau_{ice}+100}{\tau_{ice}} \quad . \quad . \quad . \quad . \quad . \quad (29)$$

The thermodynamic scale has thus been completely defined and fixed. Let us see how this scale can be actually realised in practice.

For this we must investigate the property of some actual substance. A perfect gas is very suitable for this purpose. In fact we have already shown on p. 219 that for a Carnot engine using a perfect gas as the working substance,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where T_1, T_2 are the temperatures measured on the perfect gas scale. Equation (28) combined with (30) yields

$$\frac{\tau_1}{\tau_2} = \frac{T_1}{T_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

i.e., the ratio of any two temperatures on the thermodynamic scale and the perfect gas scale are equal. Thus the absolute zero of the thermodynamic scale coincides with the zero of the perfect gas thermometer, for if $\tau_2=0$, $T_2=0$. Further from (29) and (31) since the interval between the ice point and steam point is 100° on both scales, τ_{ice} and T_{ice} are identical, and in general from (31) other temperatures on the two scales are also identical. Thus the thermodynamic scale is given by the perfect gas thermometer. For the methods of reducing the ordinary gas scale to perfect gas scale see p. 11,

ENTROPY

16. Definition of Entropy.—The formulation of the Second Law, as on p. 247 is not of much use for finding out the direction of change in a chemical or physical process. We want a more general and mathematical formulation which was supplied by Clausius.

Clausius shifted the interest from the problem of convertibility of heat to work, to that of change of thermal state of the working substance, for it is only the working substance which undergoes a thermodynamical change in the process. He observed that when the heat Q is added to it reversibly at temperature T, and Q′ taken away from it reversibly at temperature T′ we have

$$\frac{Q}{T} - \frac{Q'}{T'} = 0 \quad . \quad . \quad . \quad . \quad . \quad (32)$$

This property was utilised in defining an additional thermodynamical function (Entropy) for the gas which proved to be of great importance in the further development of thermodynamics. In the following deduction, we have followed Ewing's treatment.*

Let us take a gas in a definite state A (Fig. 1), and compare this state with another state B, which is obtained by the addition of heat energy. It is easy to see that the amount of heat added from outside may be anything, owing to the variety of ways in which heat can be added. This can be visualised by drawing curves between A and B. There may be an infinite number of curves passing between A and B, corresponding to the infinite number of ways in which heat can be added. It will now be shown that the integral

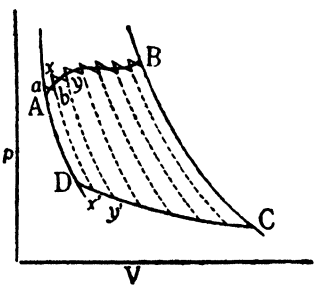


Fig. 1.—The entropy function.

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

does not depend on the path, but only on the coordinates of A and B.

Let us draw two adiabatics through A and B, and draw an isothermal DC at temperature t cutting these adiabatics in D and C respectively. Let

* See Glazebrook, *A Dictionary of Applied Physics*, Vol. 1, p. 271.

us now divide the area ABCD into a number of elementary Carnot cycles $xyy'x'$ as in Fig. 1 (xy, $x'y'$, isothermals, and xx', yy' adiabatics).

Let dQ be the amount of heat absorbed at temperature T while the point shifts from x to y and dq be the amount given up while it shifts from y' to x'. Then we have

$$\frac{dQ}{T} = \frac{dq}{t}.$$

Adding up for all the Carnot cycles between A and B, we have

$$\Sigma \frac{dQ}{T} = \Sigma \frac{dq}{t} = \frac{1}{t} \Sigma dq \quad . \quad . \quad . \quad . \quad (33)$$

This is the value of $\int \frac{dQ}{T}$ along the zigzag path $Aabxy$, for the value of the integral along the adiabatics is 0.

In the limiting case when the Carnot cycles are infinitely small the zigzag path $Aabxy$ coincides with AB. Hence

$$\int_A^B \frac{dQ}{T} = \Sigma \frac{dQ}{T} = \frac{1}{t} \Sigma dq \quad . \quad . \quad . \quad . \quad (34)$$

The value of the integral $\int_A^B \frac{dQ}{T}$ is now seen to be equal to $\frac{1}{t} \Sigma dq$, and hence it is independent of the path between A and B.

Instead of taking the particular isothermal DC we may draw any other isothermal cutting AD and BC, the value of the integral cannot be thereby changed, for if we construct a number of Carnot cycles between the first and the second isothermal we have

$$\frac{1}{t} \Sigma dq = \frac{1}{t'} \Sigma dq'.$$

The points A and B may be taken anywhere on the adiabatics AD and BC respectively, the value of the integral will remain the same, for $\int \frac{dQ}{T}$ along an adiabatic is zero since $dQ = 0$. Hence it follows that if we pass from one adiabatic to another the expression $\int_1^2 \frac{dQ}{T}$ denotes a quantity which increases by a constant amount independent of the manner of transformation. If we start from some zero state and denote the value

of the integral $\int_0^A \frac{dQ}{T}$ by s_A, it follows that s_A is a function of the coordinates of A alone. Clausius called it the *entropy* of the substance. Now since we are not familiar with the zero state of the body when it will be deprived of all its heat, we cannot find the absolute value* of the entropy in any state. We are however generally concerned with changes in entropy and hence we can measure from any arbitrary zero as is done in the case of energy. To measure the entropy in any state we have to take the substance along any reversible process to its zero state and find the value of $\Sigma dq/t$ along this process. The entropy, though conveniently measured with respect to a reversible process, has nothing to do with it and exists quite independent of it.

The above treatment is perfectly general and will hold whatever substance is taken as the working substance provided, of course, if the only work done by the substance is by expanding against a uniform external pressure. In that case from the first law we have $dQ=du+pdv$. Hence we may more generally define† entropy by the integral

$$s=\int^{T} \frac{du+pdv}{T} \quad . \quad . \quad . \quad . \quad . \quad (35)$$

It is easily seen that entropy is proportional to the mass of the substance taken, for if we take M grams of the substance $dU=Mdu$, $dV=Mdv$ and hence $S=Ms$. We shall now establish some important theorems concerning the entropy function.

17. Entropy of a System.—In the last section it was shown that if the entropy per unit mass of a substance is s the entropy of m grams of the substance is ms. It can be shown in a similar way that if we have a system of bodies in *thermodynamical equilibrium* with different thermodynamical variables and having masses m_1, m_2 . . . and specific entropies s_1, s_2 . . . ., the entropy of the whole system is

$$S=m_1s_1+m_2s_2+\ldots \quad . \quad . \quad . \quad . \quad . \quad (36)$$

* This has been calculated theoretically only for gases.

† This definition however does not include the case of diffusion. A more general definition is the following : If from any cause whatever, the unavailable energy of a system with reference to another system at T_0 undergoes an increase $\triangle E$, then $\frac{\triangle E}{T_0}$ measures the increase of entropy of the system.

18. Entropy remains Constant in Reversible Processes.—The sum of the entropies of all systems taking part in a *reversible* process remains constant. Considering the Carnot cycle we notice that the working substance has the same entropy at the end of the cycle as at the beginning since it returns to the same state. The loss in entropy of the source is $\frac{Q_1}{T_1}$, the gain by the condenser is $\frac{Q_2}{T_2}$, and hence the net gain in the entropy of the system is

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0 \quad . \quad . \quad . \quad . \quad (37)$$

Thus the entropy of the whole system remains constant.

In the *isothermal expansion* of the working substance in the first part of the Carnot cycle the increase in entropy of the working substance is $\frac{Q_1}{T_1}$, the loss by the source is $\frac{Q_1}{T_1}$ and hence the total entropy remains constant. This holds for any reversible transformation.

Working out as on p. 217 we see that the increase in entropy of a gram-molecule of perfect gas in isothermal expansion from volume V_1 to V_2 at temperature T is

$$\Delta S = \int_{V_1}^{V_2} \frac{dU + pdV}{T} = \frac{1}{T}\int_{V_1}^{V_2} pdV$$

$$= R\, ln^* \frac{V_2}{V_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

The change in entropy during a *reversible adiabatic compression or expansion* is zero. For in such a process the external work done is $\int pdV$ and change in entropy is $\Delta S = \int \frac{dU + pdV}{T}$, but by the condition of the process $dU + pdV = dQ = 0$.

19. Entropy Increases in Irreversible Processes.—The entropy of a system increases in all irreversible processes. As examples of such processes we may mention the conduction or radiation of heat, the rushing of a gas into a vacuum, the mutual diffusion of two gases, the development of heat by friction, flow of electricity in conductors, etc. We shall prove the theorem here for a few cases.

* *ln* denotes natural logarithm.

(*i*) *Increase of Entropy during Conduction or Radiation of Heat.*— Suppose a quantity of heat dQ is conducted away from a body A at temperature T_1 to another body B at temperature T_2 $(T_1>T_2)$, then A loses entropy equal to $\frac{dQ}{T_1}$ while B gains entropy by an amount $\frac{dQ}{T_2}$. Thus the total gain in entropy of the two bodies is

$$\triangle S=dQ\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \quad . \quad . \quad . \quad . \quad . \quad (39)$$

which is positive since $T_1>T_2$. Hence the entropy of the system as a whole increases during thermal conduction. Similarly in the case of radiation, if a quantity of heat dQ is radiated from the body A to the body B, the gain in entropy is given by the same expression. Thus increase of entropy is always produced by the equalisation of temperature.

(*ii*) *Gas rushing into a vacuum.*—Consider a perfect gas in a vessel rushing into an evacuated vessel and let the whole system be isolated. Since the gas is perfect the temperature does not change in the process. The gain in entropy may be obtained by finding the value of $\int\frac{dQ}{T}$ along any reversible path connecting the initial and final states. The reversible process most convenient for this purpose is an isothermal expansion of the gas against a pressure which is always just less than the pressure of the gas.

$$\therefore \int\frac{dQ}{T}=\frac{1}{T}\int dQ=\frac{Q}{T}=\frac{W}{T},$$

where W is the work done by the gas in the isothermal expansion. Hence the gain in entropy

$$\triangle S=\frac{W}{T}=\frac{1}{T}\int pdV=R\,ln\,\frac{V_2}{V_1} \quad . \quad . \quad . \quad . \quad (40)$$

where V_1, V_2 denote the initial and final volumes of the gas.

Hence the entropy of the system increases in this irreversible process.

20. The Entropy of a Perfect Gas.—Let us take m grams of a perfect gas having the temperature T and occupying the volume v. The entropy is given by

$$ms=\int^{T}\frac{du+pdv}{T}.$$

Since $du = mc_v dT$, $p = \frac{mRT}{Mv}$, we have

$$ms = m\left(c_v \ln T + \frac{R}{M} \ln v\right) + \text{const.} \quad . \quad . \quad . \quad (41)$$

We can also express ms in terms of pressure. From the relation

$$c_p = c_v + \frac{R}{M}$$

we get

$$ms = m\left(c_p \ln T - \frac{R}{M} \ln p\right) + \text{const.} \quad . \quad . \quad . \quad (42)$$

21. General Statement of Second Law of Thermodynamics.—We have shown above for a few irreversible processes that increase of entropy takes place during such a process. This result is however very general and holds for any process occurring of itself. We shall not attempt to prove* here this general statement, but only enunciate it in the following words:—*Every physical or chemical process in nature takes place in such a way that the sum of entropies of all bodies taking part in the process increases. In the limiting case of a reversible process the sum of entropies remains constant.* This is the most general statement of the Second Law of Thermodynamics and is identical with the *Principle of Increase of Entropy*, viz., the entropy of a system of bodies tends to increase in all processes occurring in nature, if we include in the system all bodies affected by the change.

Clausius summed up the First Law by saying that *the energy of the world remains constant* and the Second Law by saying that *the entropy of the world tends to a maximum.* Though the terms 'energy of the world' and 'entropy of the world' are rather vague; still, if properly interpreted, these two statements sum up the two laws remarkably well.

22. Supposed Violation of the Second Law.—Maxwell invented an ingenious contrivance which violates the Second Law as enunciated above. Following Boltzmann's idea, he imagined an extraordinary being who could discriminate between the individual molecules. Suppose such a creature, usually known as Maxwell's demon, stands at the gate in a

* For a proof see the Authors' *Treatise on Heat*, pp. 458—461.

partition separating two volumes of the same gas at the same temperature and pressure and, by opening and shutting the gate at the proper moment, allows only the faster moving molecules to enter one enclosure and the slower molecules enter the other enclosure. The result will be that the gas in one enclosure will be at a higher temperature than in the other and the entropy of the whole system thereby decreases, though no work has been done. This apparently violates the Second Law.

We observe however that to Maxwell's demon the gas does not appear as a homogeneous mass but as a system composed of discreet molecules. The law of entropy does not hold for individual molecules, but is a *statistical law* and has no meaning unless we apply it to matter in bulk.

23. Entropy and Unavailable Energy.—Consider a source at temperature T_1 and suppose it yields a quantity of heat Q to a working substance. If the lowest available temperature for the condenser of the Carnot cycle is T_0 the amount of heat rejected is $Q\frac{T_0}{T_1}$, $Q\left(1-\frac{T_0}{T_1}\right)$ is called the available energy. Now suppose a quantity of heat Q passes by conduction from a body at temperature T_2 to another at temperature T_3 the gain in unavailable energy is $Q\left(\frac{1}{T_3}-\frac{1}{T_2}\right)T_0$, T_0 being the lowest available temperature. Hence the increase of unavailable energy is equal to the increase of entropy multiplied by the lowest temperature available. Thus entropy is a measure of the unavailability of energy, and the law of increase of entropy implies that the available energy in the world tends to zero, *i.e.*, tends to pass from a more available form to a less available form. This is the law of degradation or dissipation of energy mentioned on p. 241, and is thus seen to be equivalent to the Second Law. It follows as a corollary that all transformations, physical or chemical, involving changes of energy will cease when all the energy of the world is run down to its lowest form.

24. Physical Concept of Entropy.—The entropy of a substance is a real physical quantity. It is a definite function of the state of the body like the temperature, pressure, volume or internal energy. It is difficult to form a tangible conception of entropy because there is nothing physical to represent it; it cannot be felt like temperature or pressure. It is a statistical property of the system and is intimately connected with the

probability of that state. Growth of entropy implies a transition from a more to less available energy, from a less probable to a more probable state, from an ordered to a less ordered state of affairs. The idea of entropy is necessitated by the existence of irreversible processes.

Entropy may be measured in terms of calorie or ergs per degree. As an example, we shall calculate the quantity of entropy absorbed by 10 grams of water when its temperature is raised from 0°C. to 1°C. Here

$$\Delta Q = 10 \times 1 \text{ cal.}$$

$$T = 273{\cdot}5^\circ \text{ (mean value)}$$

$$\therefore \Delta s = \frac{10}{273{\cdot}5} = {\cdot}0365 \text{ cal. per degree.}$$

The above calculation is however only approximate as the temperature is gradually increasing. More accurately, we must find out over a short interval and integrate. Thus

$$ds = \frac{10.1.dT}{T}$$

where T is the temperature (absolute), dT the rise in temperature and the specific heat has been assumed unity.

$$\therefore s = 10 \log_e T + c,$$

where c is a constant. Thus for the above case

$$\Delta s = 10 \log_e \frac{274}{273} = {\cdot}0366 \text{ calories per degree.}$$

It is in this way that the entropy tables for water are calculated, taking the entropy at 0°C.=0

APPLICATIONS OF THE TWO LAWS OF THERMODYNAMICS

25. General Considerations.—In order to make frequent use of the Second Law we must put it in a convenient form. For this purpose a mathematical formulation is more desirable and was supplied by Clausius, *viz.* (p. 252).

$$dQ = T ds^* \quad . \quad . \quad . \quad . \quad . \quad (43)$$

* The results deduced from this equation in the following pages and their confirmation by experiments may be taken as direct verification of this equation and therefore of the Second Law.

where dQ is the heat absorbed during a reversible process connecting the two states. Hence from the first law

$$dQ = du + pdv \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where p denotes the intrinsic pressure of the substance and is given by its equation of state. Combining these two equations we get

$$du + pdv = Tds \quad . \quad . \quad . \quad . \quad . \quad (44)$$

Let us further investigate into the nature of the variations du, dv and ds. As already stated in Chap. IV and also on p. 237, the state of every substance is fixed if we know any two of the variables p, v, T, u . . . . For example, the internal energy $u = f(v, T)$ is uniquely defined if v and T are given. Thus if we represent the internal energy u of the substance on the coordinate system v, T, the value of u for every point is fixed and does not depend upon the path along which we bring the substance to that point (state), *i.e.*, it is independent of the variations with respect to v or T. Mathematically, this means that u is a single-valued function of the coordinates of the point, or that du is a perfect differential. In books on Calculus it is shown that the property of such a function is that

$$\frac{\partial^2 u}{\partial x \partial y} = \frac{\partial^2 u}{\partial y \partial x} \quad . \quad . \quad . \quad . \quad . \quad (45)$$

The entropy function was shown on p. 252 to be such that its value does not depend upon the path of transformation, *i.e.*, s is also single-valued function of the coordinates. Similar is the case with the volume function.

As a contrast and for clearer understanding, it may be mentioned that pdv and $dQ = du + pdv$ are not perfect differentials for their values depend upon the path of transformation. This may be easily seen as $\int pdv$ represents the area of the indicator diagram and has different values for different values of p.

We now proceed to make use of the above ideas to the further development of equation (44).

26. The Thermodynamical Relationships (Maxwell).—Equation (44) may be written as

$$du = Tds - pdv \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Now if x and y are any two independent variables, we have since u, s, and v are expressible in terms of x and y,

$$ds = \frac{\partial s}{\partial x}dx + \frac{\partial s}{\partial y}dy$$

$$dv = \frac{\partial v}{\partial x}dx + \frac{\partial v}{\partial y}dy$$

and

$$du = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy.$$

Substituting the values of ds, dv, du in (46) and equating the coefficients of dx, dy, we get

$$\frac{\partial u}{\partial x} = \mathrm{T}\frac{\partial s}{\partial x} - p\frac{\partial v}{\partial x}$$

$$\frac{\partial u}{\partial y} = \mathrm{T}\frac{\partial s}{\partial y} - p\frac{\partial v}{\partial y}.$$

Now since du is a perfect differential

$$\frac{\partial^2 u}{\partial x \partial y} = \frac{\partial^2 u}{\partial y \partial x}$$

$$\text{or } \frac{\partial}{\partial x}\left(\mathrm{T}\frac{\partial s}{\partial y} - p\frac{\partial v}{\partial y}\right) = \frac{\partial}{\partial y}\left(\mathrm{T}\frac{\partial s}{\partial x} - p\frac{\partial v}{\partial x}\right)$$

Expanding out and remembering that $\frac{\partial^2 v}{\partial x \partial y} = \frac{\partial^2 v}{\partial y \partial x}$, and $\frac{\partial^2 s}{\partial x \partial y} = \frac{\partial^2 s}{\partial y \partial x}$, we get

$$\frac{\partial \mathrm{T}}{\partial x}\cdot\frac{\partial s}{\partial y} - \frac{\partial \mathrm{T}}{\partial y}\cdot\frac{\partial s}{\partial x} = \frac{\partial p}{\partial x}\cdot\frac{\partial v}{\partial y} - \frac{\partial p}{\partial y}\cdot\frac{\partial v}{\partial x} \quad . \quad . \quad (47)$$

which when geometrically interpreted means that the corresponding elements of area whether represented on T, s or p, v coordinates are equal. This relation will hold for a simple homogeneous substance.

For convenience of remembering we may write (47) as

$$\frac{\partial(\mathrm{T}, s)}{\partial(x, y)} = \frac{\partial(p, v)}{\partial(x, y)}$$

where $\frac{\partial(\mathrm{T}, s)}{\partial(x, y)}$ stands for the determinant

$$\begin{vmatrix} \frac{\partial \mathrm{T}}{\partial x} & \frac{\partial \mathrm{T}}{\partial y} \\ \frac{\partial s}{\partial x} & \frac{\partial s}{\partial y} \end{vmatrix}$$

Any two of the four quantities T, s, p, v can be chosen as x, y. This can be done in six different ways and correspondingly, we have six thermodynamical relationships, though all of them are not independent.

27. First Relation.—Let us take the temperature and the volume as independent variables, and put $x=\mathrm{T}$, $y=v$ in (47). Then

$$\frac{\partial \mathrm{T}}{\partial x}=1, \quad \frac{\partial v}{\partial y}=1$$

and

$$\frac{\partial \mathrm{T}}{\partial y}=\frac{\partial \mathrm{T}}{\partial v}=0; \quad \frac{\partial v}{\partial x}=0$$

since T and v are independent. Hence we have

$$\left(\frac{\partial s}{\partial v}\right)_{\mathrm{T}}=\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{v} \quad . \quad . \quad . \quad . \quad . \quad (48)$$

which implies that the increase of entropy per unit increase of volume at constant temperature is equal to the increase of pressure per unit increase of temperature when the volume is kept constant. We can apply equation (48) to the equilibrium between two states of the same substance. Multiplying both sides by T

$$\left(\frac{\partial \mathrm{Q}}{\partial v}\right)_{\mathrm{T}}=\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{v} \quad . \quad . \quad . \quad . \quad . \quad (49)$$

which means that the latent heat of isothermal expansion is equal to the product of the absolute temperature and the rate of increase of pressure with temperature at constant volume. Thus if a body changes its state at T° and absorbs the latent heat L, and the specific volume in the first and the second states are v_1, v_2, equation (49) yields

$$\frac{\mathrm{L}}{v_2-v_1}=\mathrm{T}\frac{\partial p}{\partial \mathrm{T}}$$

or

$$\frac{\partial p}{\partial \mathrm{T}}=\frac{\mathrm{L}}{\mathrm{T}(v_2-v_1)} \quad . \quad . \quad . \quad . \quad . \quad (50)$$

This is Clapeyron's equation and is one of the most remarkable formulæ in thermodynamics. A more rigorous proof of this will be given in sec. 37.

Let us first employ (50) to find the change in the freezing point of a substance by pressure. In the case of water at 0°C.

$$L = 79{\cdot}6 \times 4{\cdot}18 \times 10^7 \text{ ergs (latent heat of fusion)}$$

$$T = 273$$

$v_2 = 1{\cdot}000$ c.c. (specific volume of water at 0°C.)

$v_1 = 1{\cdot}091$ c.c. („ „ „ ice at 0°C.)

$$\therefore \frac{\partial p}{\partial T} = \frac{79{\cdot}6 \times 4{\cdot}186 \times 10^7}{273 \times (1 - 1{\cdot}091)}$$

Now if $\delta p = 1$ atmosphere $= 1{\cdot}013 \times 10^6$ dynes

$$\delta T = -0{\cdot}0075°$$

This shows that the melting point of ice is lowered by increase of pressure, the lowering per atmosphere being 0·0075°. The pressure necessary to lower the melting point by 1°C. is $\frac{1}{{\cdot}0075}$ = about 130 atmos. This accounts for the phenomenon of Regelation of ice and the experiment of Tyndall (p. 122).

These results have been quantitatively verified by Kelvin. His experimental results are given in Table 1.

Table 1.—Depression of freezing point with increase of pressure.

Increase of pressure.	Depression of freezing point in °C.	
	observed.	calculated.
8·1 atmos.	0·0580	0·0607
18·6 „	0·1289	0·1260

For substances which contract on solidification the melting point will be increased by pressure. Thus for acetic acid whose melting point is 16·5°C., de Visser found experimentally that an increase of pressure by 1 atmosphere increases the melting point by 0·02432°C., while equation (50) gave 0·02421°C. This verifies relation (50).

Equation (50) will also hold in the case of fusion of metals. With its help the change in melting point of any substance with pressure can be easily calculated. The values so calculated, together with the experimentally observed values, for a few metals are given in Table 2.* The agreement is fairly satisfactory.

Table 2.—Change in melting point with pressure.

Metal.	Melting point.	Latent heat.	$v_l - v_s$ per gm.	δT per 1000 atmos. (calc.)	δT per 1000 atmos. (obs.)
Sn ...	231·0	14·25	0·003894	+3·34	+3·28
Cd ...	320·4	13·7	0·00564	+5·91	+6·29
Pb ...	326·7	5·37	0·003076	+8·32	+8·03
Bi ...	270·7	12·6	−0·00342	−3·56	−3·55

Equation (50) may also be employed to calculate the latent heat. For the vaporization of water at 100°C. we have the following data:—

$$T=373,\ v_1=1 \text{ c.c.},\ v_2=1674 \text{ c.c.}$$

$$\frac{dp}{dT}=27{\cdot}12 \text{ mm. of mercury}$$

$$\therefore L=\frac{373\times(1674-1)\times 27{\cdot}12\times 1{\cdot}013\times 10^6}{760\times 4{\cdot}186\times 10^7}$$

$$=539 \text{ cal.}$$

The accurate experiments of Henning give L=538·7 cal. at 100°C. which is very close to the calculated value. We can also calculate the latent heat of evaporation of water at various temperatures from (50) if we know the values of v_2 and $\frac{\partial p}{\partial T}$ at these temperatures. The values of L so calculated are given in Table 3, together with the observed values. The agreement is seen to be very close.

* Taken from Jellinek, *Lehrbuch der Physikalischen Chemie*, Vol. 2, p. 517 (1930 edition).

Table 3.—Latent heat of steam at different temperatures.

$t°C.$	$\frac{dp}{dT}$ in mm. of Hg.	v_2 in c.c.	L. (calc)	L. (obs.) Henning.
100	27·12	1674	539·5	538·7
110	36·10	1211	533·4	532 1
120	47·16	892·2	526·6	525·3
130	60·60	669 0	520·1	518·2
140	76 67	509 1	512·9	510 9
150	95·66	393·1	505·7	503 8
160	117·7	307·3	497 5	496 6
170	143·4	243·0	489·8	489·4
180	172·7	194·3	481·8	482·2

28. Application to a liquid film.—Equation (48) may also be applied to the case of a liquid film. If such a film is stretched, its volume remaining constant, the energy equation for this case is

$$(dQ)_v = du - 2H dA,$$

for the work done by the film is $-2H dA$, where H is the surface tension and dA the increase in area of the film. The usual term $p\,dv$ on the right has disappeared since the total volume remains constant. Hence corresponding to p and dv we have in this case $-2H$ and dA respectively. Therefore equation (49) yields

$$\left(\frac{\partial Q}{\partial A}\right)_{T,v} = -2T\left(\frac{\partial H}{\partial T}\right)_v$$

and for a finite change,

$$\delta Q = -2T\left(\frac{\partial H}{\partial T}\right)_v dA \quad . \quad . \quad . \quad . \quad (51)$$

For a liquid the surface tension decreases with temperature, therefore $\frac{\partial H}{\partial T}$ is negative and δQ is positive. Hence an amount of heat must be supplied to the film when it is stretched in order that its temperature may remain constant. In an adiabatic stretching the temperature will fall by an amount

$$\delta T = \frac{2T}{C_A}\left(\frac{\partial H}{\partial T}\right)_v dA \quad . \quad . \quad . \quad . \quad (52)$$

where C_A is the heat capacity of the film.

29. Second Relation.—Another important application of the thermodynamic formulæ consists in its application to some adiabatic changes such as the sudden compression of a liquid or sudden stretching of a rod. For this case let us put $x=\mathrm{T}$, $y=p$.

Equation (47) then reduces to

$$\left(\frac{\partial s}{\partial p}\right)_{\mathrm{T}} = -\left(\frac{\partial v}{\partial \mathrm{T}}\right)_{p} \quad . \quad . \quad . \quad . \quad (53)$$

which means that the decrease of entropy per unit increase of pressure during an isothermal transformation is equal to the increase of volume per unit increase of temperature.

Multiplying both sides by T we have

$$\left(\frac{\partial \mathrm{Q}}{\partial p}\right)_{\mathrm{T}} = -\mathrm{T}\left(\frac{\partial v}{\partial \mathrm{T}}\right)_{p} = -\mathrm{T}v\alpha \quad . \quad . \quad (54)$$

where α is the coefficient of volume expansion at constant pressure.

From this relation it follows that if α is positive, *i.e.*, the substance expands on heating, $\left(\frac{\partial \mathrm{Q}}{\partial p}\right)_{\mathrm{T}}$ is negative, and hence in this case an amount of heat must be taken away from the substance when the pressure is increased, in order that the temperature may remain constant. That is, heat is generated when a substance which expands on heating is compressed. For substances which contract on heating, a cooling should take place.

These conclusions were verified experimentally by Joule who worked with fish-oil and water. The liquid was contained in a vessel closed at the top by a piston and the pressure was suddenly increased by placing weights upon the piston. The change in temperature was measured by a thermopile. From (54) we have,* for a finite change,

$$\Delta\mathrm{T} = \frac{\mathrm{T}v\alpha}{c_p}\,\Delta p \quad . \quad . \quad . \quad . \quad . \quad (55)$$

where c_p is the specific heat of the substance and v its specific volume. We have assumed that $v\alpha/c_p$ is independent of pressure, and then integrated for a finite change in p. Joule's results with water are very interesting and are quoted below.

* We may directly deduce this result from equation (58).

Table 4.—Increase in temperature of water by sudden increase of pressure.

Δp in kg per cm.^{2}	Initial temp. in °C.	ΔT obs.	ΔT calc.
26·19	1·20	−0·0083	−0·0071
26·19	5·00	+0·0044	+0·0027
26·19	11·69	0·0205	0·0197
26·19	18·38	0·0314	0·0340
26·19	30·00	0·0541	0·0563
26·17	31·17	0·0394	0·0353
26·17	40·40	0·0450	0·0476

The agreement between the observed and the calculated values is seen to be very close. This proves the essential correctness of the theory; in fact these results formed one of the earliest experimental verifications of the second law. Thus the thermodynamic theory explains the remarkable fact that water below 4°C. cools by adiabatic compression in spite of the fact that the internal energy is increased.

Another series of experiments consist in the adiabatic stretching of wires. The best results were obtained by Haga.* The change in temperature of the stretched wire was measured by means of a thermopile formed by the wire itself and another thin wire wound round it. It will be seen that tension means a negative pressure and hence wires of substances which expand on heating should show a cooling when stretched adiabatically. In this case the work done is not pdv but $-\mathrm{F}dl$, hence $\frac{\partial v}{\partial \mathrm{T}}$ must be replaced by $-\frac{\partial l}{\partial \mathrm{T}}$ where l is the length of the wire. Hence in place of (55) we get

$$\Delta \mathrm{T} = -\frac{\mathrm{T}}{C}\left(\frac{\partial l}{\partial \mathrm{T}}\right)_p \Delta \mathrm{F} = -\frac{\mathrm{T}\beta}{wc_p}\Delta \mathrm{F} \quad . \quad . \quad (56)$$

where β is the coefficient of linear expansion, w the mass per unit length of the wire, c_p, its specific heat in mechanical units and C the heat capacity of the wire.

For a German silver wire of diameter 0·105 mm. at room temperature, Haga found the mean value $\Delta \mathrm{T} = -0{\cdot}1063$ for a tension of 13·05 kgm. and $\Delta \mathrm{T} = -0{\cdot}1725$ for 21·13 kgm. tension, giving a mean value of 0·00813 per kgm. If we substitute the values of w, c_p, β in equation (56) and use the value $\mathrm{J} = 4{\cdot}18 \times 10^7$ ergs, we get $\Delta \mathrm{T} = -0{\cdot}00810$ in close agreement with the experimental value.

* *Wied. Ann.*, Vol. 15 (1882).

India-rubber when moderately stretched has a negative expansion coefficient. This should show a heating effect when further stretched adiabatically, which is found to be true experimentally and may be felt even by the lips.

30. Third and Fourth Relations.—Besides the above two, there are other less important relations. Thus putting $x=s$, $y=v$ in (47) we get

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \quad . \quad . \quad . \quad . \quad . \quad (57)$$

Again putting $x=s$, $y=p$ we get

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \quad . \quad . \quad . \quad . \quad . \quad (58)$$

The interpretation of these results is left to the reader.

31. Fifth and Sixth Relations.—The above relations are known as Maxwell's four thermodynamic relations. Besides these, there are two more relations which may be obtained by taking p, v, or T, s, as the pair of independent variables. They are

$$\left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial s}{\partial v}\right)_p - \left(\frac{\partial T}{\partial v}\right)_p \left(\frac{\partial s}{\partial p}\right)_v = 1 \quad . \quad . \quad . \quad (59)$$

$$\left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial v}{\partial s}\right)_T - \left(\frac{\partial p}{\partial s}\right)_T \left(\frac{\partial v}{\partial T}\right)_s = 1 \quad . \quad . \quad . \quad (60)$$

32. Variation of Intrinsic Energy with Volume.—From the relation $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$ we find easily, substituting $\frac{du+pdv}{T}$ for ds, that

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \quad . \quad . \quad . \quad . \quad (61)$$

This equation enables us to calculate the variation of intrinsic energy with volume.

For perfect gases $p=\frac{RT}{V}$, hence $\frac{\partial U}{\partial V}=0$ (Joule's Law, p. 52). For gases obeying the Van der Waals' law $p=\frac{RT}{(V-b)}-\frac{a}{V^2}$ it can be easily seen by substituting in (61) that

$$\frac{\partial U}{\partial V} = \frac{a}{V^2} \quad . \quad . \quad . \quad . \quad . \quad (62)$$

For general systems, we can transform (61) to a form which allows us to calculate $\frac{\partial u}{\partial v}$ from experimental results. This follows from equation (3) of page 238 where it is shown that

$$\left(\frac{\partial p}{\partial \mathrm{T}}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_\mathrm{T} \cdot \left(\frac{\partial v}{\partial \mathrm{T}}\right)_p . \quad . \quad . \quad . \quad (63)$$

Hence
$$\left(\frac{\partial u}{\partial v}\right)_\mathrm{T} = -\mathrm{T}\left(\frac{\partial p}{\partial v}\right)_\mathrm{T}\left(\frac{\partial v}{\partial \mathrm{T}}\right)_p - p$$

$$= \mathrm{TE}\alpha - p, \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

where E = bulk modulus, α = coefficient of volume expansion.

We shall compare the ratio $\frac{\partial u}{\partial v} : p$ for a typical liquid, *viz.*, mercury. For mercury at 0°C. and atmospheric presure we have as on p. 238

$$\left(\frac{\partial p}{\partial \mathrm{T}}\right)_v = 46{\cdot}5 \text{ atmos.}$$

Hence
$$\frac{1}{p}\left(\frac{\partial u}{\partial v}\right)_\mathrm{T} = 46{\cdot}5 \times 273{\cdot}2 - 1$$

$$= 12700.$$

Now $\frac{\partial u}{\partial v}$ is sometimes known as the internal pressure, the idea being that the visible pressure is equal to the force per sq. cm. with which the particles bombard a layer inside the liquid minus the internal pressure, *i.e.*, force/cm^2 with which they are drawn inwards due to forces of cohesion. The above comparison shows that for ordinary liquids, this force is very great but when we increase the temperature, the ratio diminishes till it vanishes when the perfect gas stage is reached.

33. The Joule-Thomson Effect.—In Chapter VI, we have proved that in the Joule-Thomson expansion $u+pv$ remains constant while the pressure changes on the two sides of the throttle valve. Let us calculate the consequent change in temperature. We have by the conditions of the process

$$\delta(u+pv) = 0 \quad . \quad . \quad . \quad . \quad . \quad (65)$$

Since from the two laws of thermodynamics $\delta u + p\delta v = \mathrm{T}\,\delta s$, we have from (65)

$$\mathrm{T}\,\delta s + v\delta p = 0 \quad . \quad . \quad . \quad . \quad . \quad (66)$$

or $$T\left(\frac{\partial s}{\partial T}\right)_p \delta T + T\left(\frac{\partial s}{\partial p}\right)_T \delta p + v\delta p = 0$$

Now $$T\left(\frac{\partial s}{\partial T}\right)_p = c_p\,;\ \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

Hence $$c_p\,\delta T = \left(T\,\frac{\partial v}{\partial T} - v\right)\delta p$$

or $$\frac{\delta T}{\delta p} = \frac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{c_p} \qquad . \quad (67)$$

This gives the Joule-Thomson effect.

For a perfect gas, $T\left(\frac{\partial V}{\partial T}\right)_p - V$ is easily seen to be zero and the Joule-Thomson effect vanishes. The porous plug experiment therefore provides a very decisive test of finding whether a gas is perfect or not.

For a gas obeying Van der Waals' law it can be proved that

$$\frac{\delta T}{\delta p} = \frac{2a(V-b)^2 - bV^2RT}{RTV^3 - 2a(V-b)^2} \cdot \frac{V}{C_p}$$

$$= \frac{1}{C_p}\left(\frac{2a}{RT} - b\right) \text{approx.} \qquad . \quad . \quad (68)$$

Hence $\frac{\delta T}{\delta p}$ is positive, *i.e.*, when δp is negative there is cooling as long as

$$T \text{ is } < \frac{2a}{bR}.$$

At T greater than $\frac{2a}{bR}$ the gas becomes heated on suffering Joule-Thomson expansion. The temperature given by $T_i = \frac{2a}{bR}$ is called the temperature of inversion since on passing this temperature the Joule-Thomson effect changes its sign. It will be easily seen that $\frac{2a}{bR} = \frac{27}{4} T_c$ approximately where T_c is the critical temperature of the gas. We have already dwelt upon this point in Chap. VI. These results have been approximately verified by experiments.

34. We will analyse the Joule-Thomson effect in another way which perhaps gives a better insight into the mechanism of the phenomena.

We have

$$c_p \frac{\delta T}{\delta p} = T\left(\frac{\partial v}{\partial T}\right)_p - v$$

$$= -T\left(\frac{\partial s}{\partial p}\right)_T - v$$

Now $$Tds = du + pdv$$

$$\therefore \quad c_p \frac{\delta T}{\delta p} = -\left(\frac{\partial u}{\partial p}\right)_T - \left(\frac{\partial (pv)}{\partial p}\right)_T \quad . \quad . \quad . \quad . \quad (69)$$

The first term on the right measures deviation from Joule's law while the second gives the deviation from Boyle's law, and the Joule-Thomson effect is the resultant effect due to deviations from both these laws.

Now $\left(\frac{\partial u}{\partial p}\right)_T$ is always negative, for that part of the internal energy which is due to molecular attractions always decreases with decrease of volume, *i.e.*, increase of pressure. Hence due to deviations from Joule's law alone the Joule-Thomson effect will be a cooling effect. Upon this will be superposed the effect due to deviations from Boyle's law which is a cooling effect, if $\frac{\partial (pv)}{\partial p}$ is negative (*i.e.*, before the bend in Fig. 6, p. 109) and a heating effect if $\frac{\partial (pv)}{\partial p}$ is positive.

35. Correction of Gas Thermometer.—From the relation (67) we find that

$$T \frac{\partial v}{\partial T} = c_p \frac{\delta T}{\delta p} + v$$

or

$$\frac{dT}{T} = \frac{dv}{v + c_p \frac{\delta T}{\delta p}}$$

If we assume c_p constant we have on integration, supposing* $\frac{\delta T}{\delta p}$ to be constant,

$$\log T = \log\left(v + c_p \frac{\delta T}{\delta p}\right) + \text{const.}$$

or

$$T = a\left(v + c_p \frac{\delta T}{\delta p}\right) \quad . \quad . \quad . \quad . \quad . \quad (70)$$

* More accurately, however, we have to integrate over short intervals when the right-hand term is put in a more convenient form.

Thus the thermodynamic temperature T is related to the volume of the gas in this complicated way and not only as $T \propto v$ as in the case of perfect gases. Let the thermodynamic temperatures corresponding to melting point of ice and boiling point of water be T_0 and T_{100} and the corresponding volumes of the gas be v_0 and v_{100}. Then

$$\frac{T_0}{T_{100}-T_0} = \frac{T_0}{100} = \frac{v_0 + c_p \frac{\delta T}{\delta p}}{v_{100}-v_0}$$

Let $\alpha = \frac{v_{100}-v_0}{100\, v_0}$ = volume coefficient of expansion, then

$$T_0 = \frac{1}{\alpha}\left(1 + \frac{c_p}{r_0}\frac{\delta T}{\delta p}\right) . \quad . \quad . \quad . \quad . \quad (71)$$

This gives the temperature of the melting point of ice on the thermodynamic scale. The quantities on the right-hand side in (71) must be measured on the thermodynamic scale. It will be seen however that $c_p \frac{\delta T}{\delta p} = c_p' \frac{\delta \theta}{\delta p}$, where c_p', $\delta\theta$ are measured on any other scale (mercury or gas scale), for

$$c_p' = c_p \frac{dT}{d\theta}, \quad \frac{\delta\theta}{\delta p} = \frac{\delta T}{\delta p}\frac{d\theta}{dT}$$

where θ denotes the practical scale. Hence the observed value of $c_p' \frac{\delta\theta}{\delta p}$ may be substituted in (71).

The results for a few gases have been calculated and are given in Table 5. For hydrogen the Joule-Thomson cooling is $-0{\cdot}039°$C. per atmos. $Mc_p = 6{\cdot}86 \times 4{\cdot}18 \times 10^7$ ergs, $Mv_0 = 22{\cdot}4 \times 10^3$ c.c. and $\alpha = {\cdot}0036613$.

Table 5.—Joule-Thomson correction to the gas thermometer.

Gas.	Volume coefficient of expansion α.	Mean Joule-Thomson cooling per atmos.	Uncorrected temperature of melting ice $\theta_0 = \frac{1}{\alpha}$.	Correction term $\frac{c_p}{\alpha v_0}\frac{\delta T}{\delta p}$	Thermodynamic temperature T_0.
H_2	·0036613	−0·039°C.	273·13	−0·13	273·0
Air	·0036706	+0·208	272·44	+0·70	273·14
CO_2	·0037100	+1·005	269·5	+4·4	273·9

$$\therefore T_0 = 273{\cdot}13\left(1 - \frac{{\cdot}039\times 6{\cdot}86\times 4{\cdot}18\times 10^7}{10^6\times 22{\cdot}4\times 10^3}\right)$$
$$= 273{\cdot}13\ (1 - {\cdot}00050) = 273{\cdot}0$$

For air the data are most reliable and yield the value $T_0 = 273{\cdot}14$. It will be seen that though for the various gases the melting point on the uncorrected gas thermometer ($\theta_0 = \frac{1}{\alpha}$ in column 4) is much different, the melting point corrected by making use of the Joule-Thomson effect comes to about 273°.

To find the correction at other temperatures to be applied to the gas thermometer we must employ (70). Thus comparing (70) and (71), we have $a = \frac{1}{v_0\alpha}$. Then any temperature T_1 is easily found if we measure the corresponding specific volume and the Joule-Thomson effect, for

$$T_1 = \frac{1}{v_0\alpha}\left[v_1 + c_p\frac{\delta T}{\delta p}\right] \quad . \quad . \quad . \quad . \quad (72)$$

The gas thermometer temperature is $\theta_1 = \frac{v_1}{v_0}\cdot\frac{1}{\alpha}$, and the correction term is $\frac{c_p}{v_0\alpha}\cdot\frac{\delta T}{\delta p}$. But as already mentioned on p. 11 the existing data on Joule-Thomson effect are not sufficient, and the corrections are calculated from the deviations from Boyle's law.

36. Examples.—We shall now give a few examples which will illustrate the utility of the foregoing thermodynamic formulæ and will give some practice in applying them.

1. Prove that $c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$
$$= TE\alpha^2 v$$
where E is the bulk modulus of elasticity, α the coefficient of volume expansion and v the specific volume.

[We have $c_p = T\left(\frac{\partial s}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_v + T\left(\frac{\partial s}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p$

and $T\left(\frac{\partial s}{\partial T}\right)_v = c_v,\ \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

$$\therefore c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$$

Further from p. 238, $\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$

$$\therefore c_p - c_v = -T\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p^2 = TE\alpha^2 v.]$$

2. Prove that $\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$

[We have $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$. Differentiating partially with respect to T we get $\frac{\partial^2 s}{\partial T \partial v} = \frac{\partial^2 p}{\partial T^2}$. Now $c_v = T\left(\frac{\partial s}{\partial T}\right)_v$ and therefore

$\left(\frac{\partial c_v}{\partial v}\right)_T = T\frac{\partial^2 s}{\partial v \partial T} = T\frac{\partial^2 s}{\partial T \partial v} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$.]

3. Prove that $\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$

[Start from $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$ and proceed as above.]

37. Clapeyron's deduction of the Clausius-Clapeyron Relation.—This equation was deduced on pp. 261-262 but the method employed there is open to objection because the thermodynamic relations hold rigorously for a homogeneous substance and their extrapolation to discontinuous changes is open to question. As however the relation is important, a more rigorous deduction is given below which is due to Clapeyron.

Let ABCD, EFGH (Fig. 2) represent two consecutive isothermals at temperatures T and T+dT. From F and G draw adiabatics meeting the second isothermal at M and N. We can suppose a unit mass of the substance to be taken through the reversible Carnot cycle FGNM, for instance, by allowing it to expand isothermally along FG, adiabatically along GN and compressing it along NM isothermally and then adiabatically along MF. The substance at F is in the liquid state and at G in the form of vapour. The amount of heat taken during the cycle is therefore L+dL at temperature T+dT. Therefore the work done during the cycle is by the second law

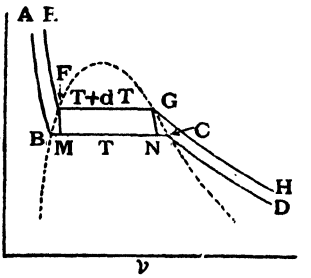


Fig. 2.—Clapeyron's deduction of the Clausius-Clapeyron relation.

$$(L+dL)\left(1-\frac{T}{T+dT}\right) = \frac{L\,dT}{T} \text{ to the first order.}$$

Again the work done during the cycle = area of the parallelogram FGNM which is in the limit equal to FG multiplied by the perpendicular distance between FG and MN, *i.e.*, dp, the increase in pressure due to increase in temperature by dT. Now FG is the change in volume due to evaporation of 1 gram of liquid and therefore equal to $v_2 - v_1$ where v_2, v_1 denote the specific volumes of the vapour and the liquid respectively. Hence the area of the cycle is

$$(v_2 - v_1)\, dp.$$

Equating the two expressions for the area we get

$$(v_2 - v_1)\, dp = \frac{L}{T}\, dT$$

or

$$\frac{dp}{dT} = \frac{L}{T\,(v_2 - v_1)} \quad . \quad . \quad . \quad . \quad (50)$$

38. Specific Heat of Saturated Vapour.—A simple expression for the specific heat of saturated vapour may be deduced with the help of Fig. 2. Consider the cycle represented by the curve BFGC. The amount of heat taken by the substance during its passage from B to F is $c_{s_1}\, dT$, that during the path FG is $L + dL$. On the other hand the substance gives back heat equal to $c_{s_2}\, dT$ during the path GC and equal to L during the path CB. c_{s_1} denotes the specific heat of the liquid in contact with vapour, and c_{s_2}, the specific heat of the vapour in contact with liquid (specific heat of saturated vapour). The total amount of heat taken during the cycle BFGC is

$$c_{s_1}\, dT + L + dL - c_{s_2}\, dT - L$$

and this must in the limit be equal to the area FGNM, which is equal to $\frac{L\,dT}{T}$ as proved in the last section

$$\therefore c_{s_1}\, dT + L + dL - c_{s_2}\, dT - L = \frac{L\,dT}{T}$$

or

$$\frac{dL}{dT} - \frac{L}{T} = c_{s_2} - c_{s_1} \quad . \quad . \quad . \quad . \quad (73)$$

This is the latent heat equation of Clausius.

It may be noted that c_{s_1} is neither the specific heat at constant pressure nor the specific heat at constant volume. Here the liquid and the vapour always remain in contact and therefore the vapour always remains saturated. Both the pressure and the volume are so varied that the condition of saturation is always satisfied. It is easily seen that c_{s_1} does not appreciably differ from c_{p_l}, the specific heat at constant pressure, for the effect of

pressure is too small to bring about any considerable change in the state of the liquid. c_{s_1} can therefore be put equal to c_{p_1}. We can now calculate the value of c_{s_2} from equation (73). For water at 100°C.

$$\frac{dL}{T} = -0{\cdot}64;\ L = 539 \text{ cal.},$$

$$T = 373°;\ c_{p_1} = 1{\cdot}01$$

$$\therefore c_{s_2} = 1{\cdot}01 - 0{\cdot}64 - \frac{539}{373} = -1{\cdot}07$$

Thus the specific heat of saturated water vapour at 100°C. comes out to be a negative quantity. This is rather a paradoxical result but at the same time perfectly true. In Chapter II we have seen that the specific heat may vary from $+\infty$ to $-\infty$ depending entirely upon the external conditions. In the present case the condition of saturation has to be always satisfied. Now saturated water vapour has a pressure of 760 mm. at 100°C. and 787·6 mm. at 101°C., *i.e.*, the specific volume of saturated water vapour decreases as the temperature rises. This is so with all vapours. Hence when saturated water vapour at 100°C. is heated to 101°C. at constant pressure it becomes unsaturated, but since the condition of saturation has to be satisfied it must be compressed till the pressure becomes 787·6 mm. This compression generates heat, and in the case of water at 100°C., the heat generated is so great that some of it must be withdrawn in order that the temperature may not rise above 101°. The net result in this case is that heat must be withdrawn from and not added to the system during the whole operation. Thus we explain physically why the specific heat of saturated vapour sometimes becomes negative.

From these considerations it will be seen that saturated steam must become superheated by adiabatic compression, *e.g.*, water vapour at 100°C. and 760 mm. pressure, when compressed suddenly to 787 mm. would be heated by 2·1°C., and hence become superheated; conversely when it is allowed to expand adiabatically, say from 787 mm. to 760 mm., the temperature would fall by 2·1°C., *i.e.*, to 98·9°, and hence would be supercooled, and partial condensation may occur. For certain vapours however the work done in compressing the substance is not so great and the specific heat is positive. These become superheated by adiabatic expansion. Even in the case of water, the value of c_{s_2} varies with temperature, and gradually increases as T is raised because now L falls very rapidly. At about 150°C., $c_{s_2} = 0$ and above this point it becomes positive.

These conclusions were experimentally verified by Hirn in 1862. He allowed steam from boilers at a pressure of five atmospheres to enter a long cylinder fitted with glass plates at its ends. When the cylinder had attained the temperature of the steam, the supply and the exit tubes were closed, and the vapour when viewed from the ends looked quite transparent. The exit tube was next suddenly opened and the vapour expanded adiabatically and a dense cloud was observed inside the cylinder, thereby confirming the results from theory.

39. The Triple Point.—If we now plot the saturation value of p against T we get a curve OA (Fig. 3) the slope at every point of which will be given by

$$\frac{dp}{dT} = \frac{L_1}{T(v_g - v_l)}$$

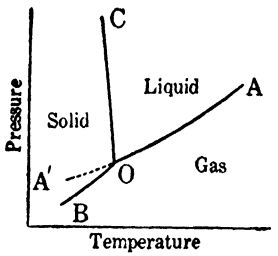


Fig. 3.—The triple point.

where L_1 is the latent heat of vaporisation, and v_g, v_l denote the specific volumes at the temperature considered.

To fix our ideas let us consider the case of water. When the temperature is reduced to 0°C. the water freezes and we get ice. But ice has also definite vapour pressure which has been measured. The vapour pressure curve of ice may be represented by the line OB, the slope at every point of which will be given by

$$\frac{dp}{dT} = \frac{L_2}{T(v_g - v_s)}$$

where L_2 is the latent heat of sublimation.

Similarly for the phenomenon of melting, the curve OC represents the relation between pressure and temperature, and the slope at any point is given by

$$\frac{dp}{dT} = \frac{L_3}{T(v_l - v_s)}$$

where L_3 is the latent heat of fusion. We have already seen on p. 262 that for ice $\frac{dp}{dT} = 130 \times 10^6$, *i.e.*, the curve should be almost vertical.

It can be shown purely from thermodynamic considerations that these curves must meet in a point which is known as the Triple point. For

water it is nearly but not exactly at 0°C. and can easily be calculated from the consideration that at this point, the vapour tension of water is equal to the melting pressure of ice.

At 0°C. the vapour pressure of water is 4·58 mm. while the melting pressure of ice is 760 mm. If we increase the temperature by a very small amount, the vapour pressure does not appreciably change, but the melting pressure changes rapidly. We have to find out the temperature at which the melting pressure reduces to 4·58 mm. From the calculations on p. 262 we have $dT = ·0075$°C. approximately.

The coordinates of the triple point are therefore T = ·0075°C., $p = 4·58$ mm. At this point the three phases (solid, liquid and vapour) co-exist.

It was formerly supposed that the curves OA, OB are continuous. It was first proved by Kirchhoff that this is not so, for according to (50)

$$\frac{dp}{dT} \text{ for OA at } 0°\text{C.} = \frac{L}{T(v_2 - v_1)}$$

$$= \frac{607 \times 4·18 \times 10^7 \times 760}{273 \times 21 \times 10^4 \times 10^6}$$

$$= 0·337 \text{ mm. per degree.}$$

$$\frac{dp}{dT} \text{ for OB (sublimation)} = \frac{687 \times 4·18 \times 10^7 \times 760}{273 \times 21 \times 10^4 \times 10^6}$$

$$= 0·376 \text{ mm. per degree.}$$

The dotted curve OA′ is merely the continuation of OA. It presents the vapour pressure of supercooled liquid. At −1°C. we have vapour pressure of liquid − vapour pressure of solid = ·04 mm. of mercury. This has been verified by the experiments of Holborn, Scheel and Henning.

40. Calculation of Electromotive Force of Reversible Cells.— As is well known, voltaic cells are a convenient source of supplying continuous electrical energy, which is obtained from the chemical actions going on in the cell. The cell is simply a contrivance for converting chemical energy into electrical energy. In fact, with the aid of thermodynamical principles, we can calculate the E. M. F. developed by a reversible cell if we have a knowledge of the heat developed by the chemical reaction going on in the cell. We shall now deduce the relation giving the E. M. F. in terms of the heat of reaction.

Let the cell constituents react at temperature T producing an E. M. F. = E volts. In the ordinary Daniell cell this consists in Zn being dissolved

in dilute H_2SO_4 and copper being deposited from the solution on the positive pole. The work done by the cell is $A = EB.n \times 10^7$ ergs where B is the charge carried by a gram-equivalent of the ion and n, the valency of the ion. From the first law the heat absorbed by the cell $Q = A - U$ where U is the heat of reaction. Let this heat be allowed* to flow to a lower temperature $T - dT$ by any reversible process. Then the work obtained is, from the second law,

$$dA = \frac{Q}{T} dT = (A - U)\frac{dT}{T}$$

Or putting for A the value $EBn \times 10^7$ ergs, we have

$$E - T\frac{dE}{dT} = \frac{U}{Bn \times 10^7} = \frac{U \times 4{\cdot}2 \times 10^7}{96450 \times n \times 10^7}$$

$$= \frac{U}{23050 \times n}$$

where U is expressed in calories. This is the equation for the E. M. F. of reversible galvanic cells.

As an illustration let us consider the Daniell cell. It consists of a glass vessel (Fig. 4) with a copper plate in the centre which dips in copper sulphate solution. On the outer side is a Zn-plate dipping in zinc sulphate solution. The two are separated by a porous clay vessel, the function of which is to prevent quick mixing of the two salts.

When the two plates are connected by a wire a current passes from Cu to Zn through the wire outside the cell, and from Zn to Cu inside the cell. The E.M.F. is found to be 1·09 volts. The passage of the current is attended with chemical reactions:—Zn goes into solution When 96450 coulombs pass, ½ gm.-atoms When 96450 coulombs pass, ½ gm-atoms (32·5 gm.) of Zn go into solution, and ½ gm.-atoms (31·5 gm.) of copper get deposited. The reaction is of the type

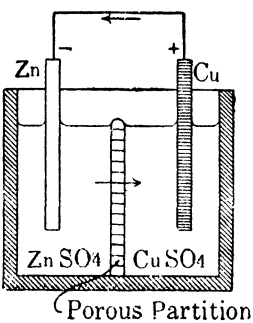


Fig. 4.—Schematic diagram of the Daniell cell.

$$Cu \mid CuSO_4 \text{ aq.} \mid \text{aq. } ZnSO_4 \mid Zn.$$

* The actions taking place in the cell are reversible. The reversible cycle can be completed as follows :—Let the cell be allowed to lose heat by an amount sdT so that its temperature falls to $T - dT$, and the corresponding E.M.F. becomes $E - dE$. Next pass the charge Bn through the cell in the direction opposite to discharging. Cu will go into solution and Zn will get deposited on the negative pole. The heat evolved by the cell in this process is from first law $= A - dA - (U - dU)$. Next allow the cell to heat up and rise to T°, and thereby return to its initial state. The work done by the cell is dA while an amount of heat $A - U$ passes from T° to $T - dT$. $\therefore dA = (A - U)\frac{dT}{T}$ from second law. We have neglected the heats in stages (2) and (4).

The net chemical reaction is

$$[Zn] + (CuSO_4) = [Cu] + (ZnSO_4)$$

In this process, chemical energy is being converted to electrical energy. The chemical energy evolved in the process can be worked out from the following two equations:—

$$[Zn] + (H_2SO_4) = (ZnSO_4) + H_2 + 248500 \text{ cal.}$$

$$[Cu] + (H_2SO_4) = (CuSO_4) + H_2 + 197370 \text{ cal.}$$

Combining the above two we get

$$[Zn] + (CuSO_4) = [Cu] + (ZnSO_4) + 51130 \text{ cal.}$$

More accurate experiments of Jahn however show that at 0°C.

$$U = 50110 \text{ cal.}$$

and $$\frac{dE}{dT} = 3{\cdot}4 \times 10^{-5} \frac{\text{volt}}{\text{degree}}$$

$$\therefore E - T\frac{dE}{dT} = \frac{50110}{23050 \times 2} = 1{\cdot}087 \text{ volts.}$$

$$\therefore E = 1{\cdot}087 + 273{\cdot}2 \times {\cdot}000034$$

$$= 1{\cdot}0963 \text{ volts approximately}$$

while the experimental value is 1·096 volts. Similarly we can calculate the E. M. F. of other reversible cells.

The application of the principles of thermodynamics to radiation is discussed in the next chapter.

41. General Conditions of Physical or Chemical Equilibria.— In sec. 21 we have stated that for all changes taking place in a system, the entropy of the entire system taken as a whole increases or remains constant provided we include in the system all bodies affected by the change. Hence the condition necessary for any change to take place in the system is $\delta S \geqq 0$ where S is the entropy of the entire system affected by the change. Now if the system is in such a state that this condition cannot be satisfied, *i.e.*, for it $\delta S \leqq 0$, then no change will take place. That is, the system will be in equilibrium. This is the most general condition of equilibrium. δ here denotes a virtual change.

In most cases however any virtual change consistent with the external conditions can be reversed if the sign of all the variations be changed. Hence if the change $\delta S < 0$ is possible, the change $\delta S > 0$ is also possible and the system will not be in equilibrium. Hence the condition for equilibrium reduces to

$$\delta S = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (74)$$

Thus the states of equilibrium are given by the condition that the entropy is a maximum.

In the above, S denotes the entropy of the entire system affected by the change, *i.e.*, the reaction system together with the surroundings. For adiabatic processes there is no exchange of energy between the system and the surroundings, and therefore the condition for equilibrium becomes $\delta S=0$ where S denotes the entropy of the reaction system. In a general case however we must put (74) in a more suitable form. For this the Authors' *Treatise on Heat* should be consulted.

Book Recommended.

Planck, *Treatise on Thermodynamics.*

CHAPTER XI

RADIATION

1. Introduction.—Even when a heated body is placed in vacuum, it loses heat. In this case no heat can be lost by conduction or convection since matter, which is absolutely essential for both these processes, is absent. In such cases we say that heat is lost by 'Radiation.' To differentiate this process from conduction, it is enough to note that copper and wood, which are so much different in their conducting powers, cut off radiation equally well when placed between the hot body and the observer.

Now heat has been shown to be a form of energy, and the propagation of heat by radiation consists merely in a transference of energy. But the radiant energy in the process of transference does not make itself evident unless it falls on matter. When it falls on matter and is absorbed, it is converted to heat and can be thereby detected.

Let us now study some of the properties of radiant energy. For this purpose we require a source of heat as radiator and some instrument to measure the emitted radiation. As emitter Leslie employed a hollow metal cube filled with hot water, whose sides could be coated with different substances. The cube is so made that it can be rotated about a vertical axis. Such a cube is called a Leslie cube and is shown in Fig. 1. For measuring the radiation the early experimenters employed a differential air-thermometer or a thermopile which are described in the next section.

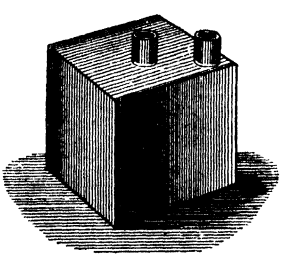


Fig. 1.—Leslie cube

2. Some Simple Instruments for Measuring Radiation.—Leslie, one of the earliest workers, used a *differential air-thermometer* which is now only of historical interest. This consists of two equal bulbs A and B (Fig. 2) containing air and communicating with each other through a narrow tube bent twice at right angles and containing some non-volatile liquid like sulphuric acid. When the bulbs are at the same temperature the liquid stands at the same height in both the columns C and D, but if one of the bulbs A is heated the level of the liquid falls in the column C and rises in the column D. By noting the difference in level of the two columns the difference in temperature of the bulbs can be easily calculated.

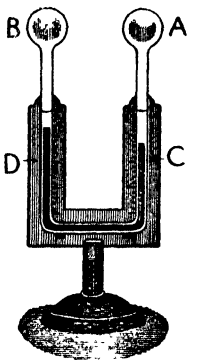


Fig. 2.—Leslie differential air-thermometer.

Melloni was the first to introduce *thermopiles* for the measurement of radiant energy. In its original form, Melloni's thermopile consisted of a number of bismuth and antimony rods, placed alternately with their ends joined, as indicated in Fig. 3. The left face forms the hot junction, and the right the cold junction. The antimony bars are shaded and the bismuth bars are left clear. The current flows across the hot junction from bismuth to antimony.

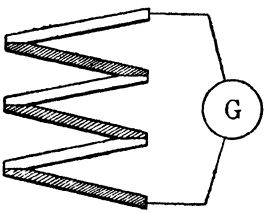


Fig. 3.—Principle of the thermopile.

In an actual thermopile a large number of pairs is employed. The bars are arranged in the form of a cube such that all the hot junctions are at one face and the cold junctions at the opposite face. Such a cube is shown in Fig. 4. The near face is the hot junction and is coated black. The thick lines denote the insulating material, generally mica, between the different layers, and the thin lines denote the soldered junctions. The current enters at A, flows across the soldered junction at the near face into the antimony bar, and

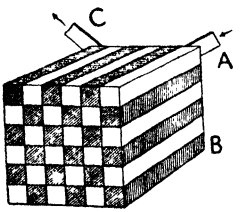


Fig. 4.—The thermopile.

so on. It enters the next layer at B on the cold face and so on. Finally the current leaves the thermopile at C. A thermopile mounted for use is shown in Fig. 5. The blackened face is provided with a conical protector to protect it from stray radiations, while the cold face is covered with a metallic cap. Another cap serves to prevent the hot junction when not in use.

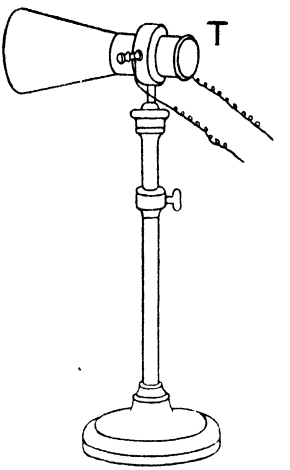


Fig. 5.—The thermopile (mounted).

Other types of radiometers are described in sections 21—24.

3. Properties and Nature of Radiant Energy.—With the aid of these simple apparatus it can be demonstrated that Radiant Energy and Light obey identical laws and have identical properties. We mention some of the points of resemblance:

(*i*) *Radiant energy, like light, can travel through vacuum,* for we are able to receive heat from a hot electric glow lamp though it is highly evacuated. Even when a feeble current passes through the filament which is not sufficient to make the filament glow, the thermal radiation coming from the latter can be detected by a sensitive thermopile.

(*ii*) *Radiation, like light, travels in straight lines.*—This can be easily seen for the heat coming from a flame can be easily cut off by interposing a screen just sufficient to prevent the light coming from it. On replacing the flame by a hot non-luminous source, no heating effect can be detected by a thermopile. The exact geometrical shape of the image can be verified by cutting out a cross from the screen and holding close to it a piece of wood coated with paraffin wax. The wax will melt in the shape of a cross.

(*iii*) *Radiation travels with the velocity of light.*—This follows from the observation that the obstruction of the radiation from the sun during a total solar eclipse is immediately accompanied by a fall of temperature.

(*iv*) *Radiant energy follows the law of inverse square like light.*—This may be experimentally proved by the simple arrangement

shown in Fig. 6. A is a vessel containing hot water and having one surface B plane and coated with lamp-black. S is a thermopile. It will be found that if we move the thermopile to another position S′ (say double the previous distance), the deflection of the galvanometer connected to it will be unchanged. Now the area of the surface of B from which radiation can reach the thermopile is increased four times, and as the amount of radiation reaching the pile remains the same, the intensity of radiation must be reduced to $\frac{1}{4}$th, *i.e.*, the intensity of radiation varies inversely as the square of the distance.

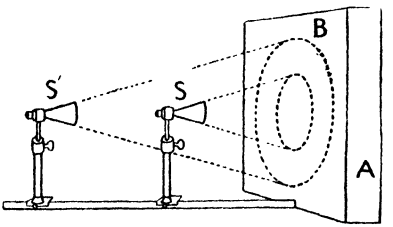


Fig. 6.—Verification of inverse square law.

(*v*) *Radiation obeys the laws of reflection of light.*—This can be easily verified by placing two parabolic mirrors A and B at some distance apart with their axes in the same line (Fig. 7). A luminous source placed at the focus of A produces an image at the focus of B.

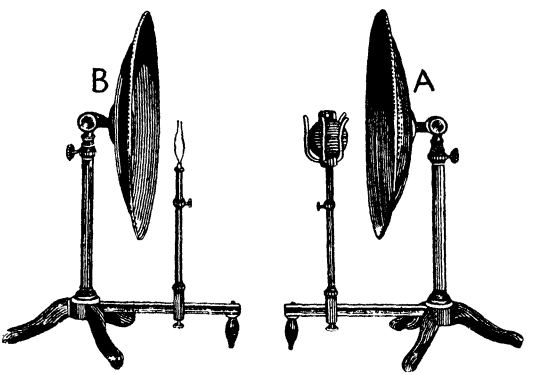


Fig. 7.—Verification of laws of reflection for radiation.

If we replace the luminous source by a hot non-luminous one say a Leslie cube and put a piece of tinder at the other focus, the tinder is ignited. This shows that heat and light travel along the same path and hence obey identical laws. In fact all the laws and results of geometrical optics are applicable to it.

(*vi*) *Radiant energy suffers refraction, like light.* A spectrum may be obtained by refraction through a prism (Sec. 29).

(*vii*) *Thermal radiation can also be polarised* in the same way as light by transmission through a tourmaline plate. This can be shown by the following experiment:—Arrange that light from an incandescent lamp traverses two similar plates of tourmaline. On rotating one of the

plates the image will be found to vanish. Replace the lamp by a Leslie cube. Now a thermopile placed in the position occupied by the image will record no deflection; if however one of the plates be rotated, a deflection will be observed.

4. Identity of Radiant Energy and Light—Continuity of Spectrum.—All these observations lead us to the conclusion that radiant energy is identical with light. As we shall see presently, Radiation or Radiant Energy is the general and more expressive term; light (or rather visible light) being only a kind of radiant energy which has the distinctive power of affecting the retina of the human eye, and thus producing the sensation of colour. But like other kinds of radiant energy, light is also converted to heat when it is absorbed by matter.

The identity of light and radiant energy can further be seen from the following experiments:—

(*i*) When we produce a spectrum of the sun by means of a prism, it is terminated on one side by the red, and on the other side by the violet. But it can be easily seen that these limits are only apparent, and are due to the fact that the human eye is a very imperfect instrument for the detection of radiation. W. Herschel (1800) placed a blackened thermometer bulb in the invisible part beyond the red, and found that the thermometer recorded a rise in temperature. The rise in temperature was observed also when the thermometer was placed in the visible region. Thus W. Herschel discovered the infra-red part of the solar spectrum, and showed that it was continuous with the visible spectrum.

The source of radiation in this case is the sun, which may be regarded as an intensely hot body. But it may be substituted by any sufficiently hot substance, say a piece of burning coal, the positive crater of the arc, or a glowing platinum wire. Only in these cases the intensity of radiation is not great, and the spectrum does not extend so far towards the violet.

(*ii*) *Production of Light by Heating.*—A very simple experiment will suffice to bring out the point which has been just mentioned. Suppose we take a piece of blackened platinum wire and pass through it a continuously increasing current. The function of the current is simply to heat the wire. We find that it becomes warm, and sends out radiant energy. If a thermopile be held near it, the galvanometer connected to it will show a deflexion. When some more current is passed, the wire begins to glow

with a dull red light. This shows that the wire is just emitting red radiation of sufficient intensity to affect the human eye. Accurate observations show that this takes place at about 525°C. (Draper point). With increasing temperature, the colour of the emitted radiation changes from dull red to cherry red (900°C.), to orange red (1100°C.), to yellow (1250°C.), until at about 1600°C. it becomes white. The temperature of a luminous body can be estimated from its colour. Such a colour scale of temperature is given in the chart on pp. 27-28. This shows that *shorter waves are emitted by a heated body in sufficient intensity only with increasing temperatures.* Vice versa, we may argue that when the temperature of the wire is below the Draper point, it is emitting longer waves than the red, but these waves can be detected only by their heating effect.

Radiant Energy or Radiation is thus a more general name for Light. It can be of any wavelength from 0 to ∞ as illustrated in the chart on the following pages. Light forms less than ¾ths of an octave on the scale.

Explanation of the Chart.—We are using here the logarithmic scale. *i.e.*, log λ is plotted along the vertical line. Thus (-5) on the scale indicates that the wavelength is 10^{-5} cm., (2) indicates that $\lambda = 10^2$ cm. As shown in the chart visible light extends from 7×10^{-5} cm. (red) to about 4×10^{-5} cm. (violet). The infra-red part was discovered by W. Herschel and the extension towards the longer wavelength side is chiefly due to the *rest-strahlen* method of Rubens and Nichols. These rays are detected chiefly by the thermopile, for ordinary photographic plates are not sensitive beyond the green. Above green, pan-chromatic plates may be used, but they are also not sensitive beyond 8000 Å.U. Beyond this, plates dipped in dycyanine or neocyanine may be used up to 10000 Å.U.

The Hertzian waves are produced by purely electromagnetic methods (due to oscillation of current in an inductance-capacity circuit) and were first discovered by Hertz in 1887. Marconi applied them for wireless transmission (1894). Waves used for this purpose are generally 20—500 metres in length, though waves of about 10 km. length have been used in the past. These long electromagnetic waves differ from the light waves only in their wavelength, and attempts have been made to get shorter and shorter rays by purely electromagnetic methods so that one can pass continuously to the long infra-red rays. The limits successively reached are due to Lebedew, Lampa, Sir J. C. Bose (4 mm.) and the gap between electromagnetic waves and heat waves have been completely bridged by the recent work of Nichols and Tear, Arcadiewa, and others.

The ultraviolet part (rays shorter than the last visible $\lambda = 3800$) was discovered by W. Ritter in 1802. He found that a photographic plate was affected even beyond the visible limit. Glass spectrographs usually give lines as far as $\lambda = 3400$, after which either uviol glass (limit $\lambda = 2800$), or quartz prisms should be used. At about $\lambda = 2200$, the gelatine used in

ELECTROMAGNETIC WAVES

Wavelength	Log λ	Radiation	Generation	Detection and Analysis	Discoveror
cms					
10^{-11} Siegbahn unit	-11	Cosmic rays	Conversion of matter to Radiant Energy	Measurement of absorption coefficient	Kolhörster (1913) Millikan etc (1923)
	-10	γ-rays	Radioactive Disintegration	Photo-electric method	
·06A.U.	-9	X-rays Hard	Bombardment of metal targets by electrons	Crystals & Photography or Ionisation chamber	Röntgen (1895) Laue (1912)
10^{-8} Ångstrom unit	-8	Medium		Fluorescence	
	-7	Soft		Glass / Quartz / Fluorite / Vacuum grating / Reflection Grating (vacuum)	Compton (1925) Thibaud (1926)
136 A.U.	-6		Vacuum Spark	Photography	Millikan (1919) & Lyman (1906)
$1{\cdot}0\times10^{-5}$	-5	Ultra-violet		Prisms	Schumann (1890)
4×10^{-5}			Spark. Arc Flame		Ritter (1802)
8×10^{-5} μ	-4	VISIBLE Violet / Red			NEWTON Herschel (1840)
	-3	Infra-red	Heating	Wire gratings & Thermo-couples	
1 mm	-2			Residual ray Method	Rubens & Nichols (1898)
·4 mm		Hertzian waves		Focal Isolation	Wood (1912) Nichols & Tears (1924)
	-1	(Short)	Spark gap	Coherer	
4 mm	0				Bose (1902)

ELECTROMAGNETIC WAVES (Contd.)

Wavelength	Log λ	Radiation	Generation	Detection and Analysis	Discoveror
cms	−1				
	0		Spark gap discharge		
	+1	Hertzian waves	Triode valve Oscillator	Coherer	
1 metre	+2			Crystal rectifier	Hertz (1887)
	3	Short-wave Broadcasting		Triode valve	
100 metres	4				
	5	Long-wave Broadcasting			
10^4 metres	6	Hertzian waves ↓			
	7	No upper limit			
	8				

the photographic plates begins to absorb. Schumann was the first to prepare plates without gelatine and open up what is called the Schumann region. Below $\lambda = 1850$ Å.U. quartz begins to absorb heavily, and Schumann therefore used fluorite spectroscopes. Beyond $\lambda = 1400$, air absorbs heavily, and the whole operation of producing light and photographing the spectrum must be done in vacuum. The pioneer in this field was Th. Lyman of Harvard, who was able to photograph lines as far as $\lambda = 600$. In this region gratings have to be used for producing the spectrum.

X-rays were shown by M. Laue in 1912 to be light waves of extremely short wavelength 10^{-8} cm., *i.e.*, about 1000 times shorter than ordinary light. He used a crystal as a diffraction grating. The shortest X-ray measured by the crystal method has the wavelength $\lambda = 05$ Å.U. γ-rays, obtained in radioactive disintegration, are still shorter, *viz.*, from 10^{-9} to 10^{-10} cm. in wavelength. Cosmic rays, which are supposed to come from stars and interstellar space about us, are believed to be of still shorter wavelength (10^{-13} to 10^{-14} cm.).

The gap between the Lyman region (600 Å.U.) and the soft X-ray region (about 20 A.U.) has been gradually bridged by the works of Millikan and Bowen, Compton, Thibaud and others. Millikan and Bowen used ordinary vacuum spectrographs with diffraction gratings. Their source of light was condensed vacuum spark. For wavelength in this region, crystal gratings have their grating spaces too small, while the ruled gratings have their spaces too large. Compton instituted the method of obtaining spectra in this region with the aid of coarse gratings at glancing angle (see Saha and Saha, *Treatise on Modern Physics*, Vol. I, p. 273).

Since radiant heat and light are identical, all the laws and theorems of Optics and Spectroscopy can be applied to the study of radiation. But in this chapter, we shall deal with the subject only as far as it is connected with heat. We shall first enter into a preliminary discussion regarding the passage of radiation through matter.

5. Fundamental Radiation Processes.—Every hot body emits radiation from its surface which depends upon the nature of the surface, its size and the nature of the surroundings. This is known as *emission.* When the emitted radiation falls on matter, a part is *reflected* regularly or irregularly (diffuse), another part is *absorbed* while the remainder is *transmitted.* The coefficients of reflection, absorption and transmission are connected by the relation

$$r + a + t = 1$$

where

r = fraction of total energy reflected
a = „ „ „ „ absorbed
t = „ „ „ „ transmitted.

From our common experience, we can define certain substances with limiting properties as regards their behaviour towards radiant energy.

Perfectly Black Bodies.—For such bodies, $r=0$, $t=0$, $a=1$. Lampblack is the nearest approach to such a body. Apparently, it neither reflects nor transmits the light which falls on it, absorbs all, and hence appears black. But the perfectly black body is only an ideal conception, for even lampblack is found to transmit light of long wavelength. It absorbs about 96% of visible light, platinum black absorbs about 98%.

6. Theory of Exchanges (Prevost—1792).—Prior to 1792, the ideas regarding radiant energy were very much confused. People used to talk of hot radiations and cold radiations. A block of ice was supposed to emit cold radiations because it produced a sensation of cold. Prevost of Geneva was the first to recognise that this was a loose way of talking. He taught that substances at all temperatures emit 'radiant energy,' but the amount increased with the temperature and is not affected by the presence of surrounding bodies. The rise or fall of temperature which is observed in a body is due to its exchange of radiant energy with surrounding bodies. This is known as *Prevost's Theory of Exchanges.*

Thus when we stand near a fire, we feel the sensation of warmth, because our body, *which is also a radiator,* is receiving more energy from the fire than it is losing by its own radiation. When we stand near a block of ice, we feel a sensation of cold because our body being at about 37°C. loses more energy by radiation than it receives from the ice, which is at a much lower temperature, *i.e.*, 0°C. These considerations are quite general, and may be applied to all similar phenomena.

A body will cease to emit radiation only when it is at the absolute zero of temperature (−273°C.).

7. Laws of Cooling.—When we have clearly recognised that every substance emits radiation by virtue of its temperature, it becomes necessary to investigate how this emission varies with temperature and the nature of the surface. In this section we shall confine our attention to the effect of temperature, both of the substance and the surroundings. Newton was the first to study systematically the loss or gain of heat by a body placed in a given surrounding. The experiments can be most simply performed by heating a large-bulbed mercury thermometer and enclosing the bulb in an evacuated flask, the walls of which are blackened inside and are further maintained at a fixed temperature by means of a suitable bath. The rate

of fall of temperature of the thermometer gives the rate of cooling. It was found that if we plot the rate of cooling $-\frac{d\theta}{dt}$ as ordinate against the excess of temperature as abscissa, the curve is a straight line, or in other words,

$$-\frac{d\theta}{dt}=k(\theta-\theta_0) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where θ_0 is the temperature of the enclosure, *i.e.*, the rate of cooling is proportional to the excess of temperature of the substance above the surroundings. This is *Newton's law of cooling.*

The law holds when the temperature difference is not large. Even the earlier experiments showed considerable deviations from the law when the temperature difference exceeded 40°C.

In order to find out a law which will hold for all differences of temperature, an elaborate series of experiments were performed by Dulong and Petit who found that their results were given by a formula of the form

$$-\frac{d(\theta-\theta_0)}{dt}=k\,(a^{\theta}-a^{\theta_0}) \quad . \quad . \quad . \quad . \quad (2)$$

where a is a constant and k depends upon the nature of the emitting surface, and θ, θ_0 denote respectively the temperatures of the emitting surface and the surroundings.

Stefan showed later that the results of Dulong and Petit may be represented by the equation

$$-\frac{d\mathrm{T}}{dt}=a(\mathrm{T}_1^4-\mathrm{T}_0^4) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where a is a universal constant and T the absolute temperature; or in other words, the emissive power of a substance varies as the fourth power of the absolute temperature. This is Stefan's law and can be deduced from theoretical considerations (*vide* sec. 26). It is therefore the correct law of cooling for black bodies.

8. Emissive Power of Different Substances—Preliminary Experiments.—Having made an experimental study of how the emissive power varies with temperature, let us find how the emissive power varies with the nature of the surface of the emitting body. For this purpose we require a Leslie cube and a thermopile. One face of the cube is coated

with lampblack while another face is coated with the substance whose emissivity is to be found. The radiation from both these surfaces can be allowed to fall alternately on a thermopile placed at some distance. The ratio of the deflections recorded by the thermopile in the two cases gives the ratio of the emissive powers of the two substances. In this way the relative emissivities of different substances were determined. The experiments were performed by Leslie, Melloni and others.

9. Reflecting Power.—The reflecting power of different substances can be very simply found by allowing the radiation from a Leslie cube to fall on a reflecting surface and the reflected radiation to fall on a thermopile. Next the thermopile is placed at the position occupied by the reflecting surface. The ratio of the deflections in the two cases gives the reflecting power. This however varies with the wavelength of radiation employed, and as the earlier workers did not employ monochromatic radiation, their results are not of much value.

10. Diathermancy.—Diathermancy with regard to heat is analogous to transparency in the case of light. Substances which allow radiation to pass through them are called diathermanous, while those which do not, are called athermanous. The early experiments in this direction were performed by Melloni and Tyndall. Direct radiation from a Leslie cube fell on a thermopile producing deflection; next the experimental substance was introduced and the deflection observed. The ratio of the two deflections gives the diathermancy or transmission coefficient of the substance. Solids, liquids and gases were treated in this way. The best diathermanous solids are rocksalt (NaCl), sylvine (KCl), quartz, fluorite and certain other crystals. Pure air is highly diathermanous, but water vapour and carbon dioxide show marked absorption.

11. Absorption.—For studying the absorption of solids Melloni took a copper disc and coated one face with lampblack and the other face with the experimental substance. The copper disc was placed between the Leslie cube and the thermopile, the lampblacked surface facing the thermopile. The plate will assume a steady temperature T. The heat radiated per unit area of plate is

$$H = (E + E')T$$

where E and E′ denote the emissivity of lampblack and of the substance. Now this must equal the radiation which it absorbs. The thermopile

reading gives ET and therefore E. Knowing E′ we get H, the energy absorbed. In this way the absorptive power of different substances could be compared. For gases a sensitive arrangement was employed.

The terms diathermanous or athermanous lack in scientific precision. Every substance ought to be defined, so far as its transmitting or absorbing properties are concerned, with respect to a particular wavelength. In the above experiments monochromatic radiations were not employed. The whole subject is now studied as a branch of physical optics under the head 'dispersion and reflection' with which it is intimately connected.

12. Relations existing between the Different Radiation Quantities.—The foregoing experiments however show that at the same temperature a lampblacked surface emits the maximum energy while a polished surface emits very little energy. It was further found that radiating and absorbing powers vary together; that good radiators are good absorbers and poor reflectors, while poor radiators are poor absorbers. Lampblack is opaque to radiation but allows radiation of very long wavelength to pass through it.

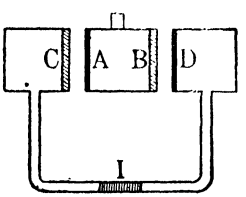


Fig. 8.—Ritchie's experiment.

A very simple experiment devised by Ritchie* demonstrates vividly the relation between emissive and absorptive powers of a body. A Leslie cube AB, which is a hollow metallic vessel and can be filled with liquid at any temperature, is placed between the two bulbs of a differential air thermometer (Fig. 8). The face A of the cube and the bulb D are coated with lampblack while the face B and the bulb C can be coated with a layer of the substance whose emissivity is to be investigated, say powdered cinnabar. By filling the cube with a hot liquid the index was not found to move, and hence the amounts of energy received by C and D are equal. If e denotes the amount of heat emitted by the substance and a its absorptive power, while E and I denote the corresponding quantities for lampblack, we have

$$e = a\mathrm{E}$$

$$\text{or} \quad \frac{e}{\mathrm{E}} = a \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

* *Pogg. Ann.*, Vol. 28, p. 378 (1833).

Now $\frac{e}{E}$ may be called the coefficient of emission of the substance, and hence the relation shows that the coefficient of emission is equal to the absorptive power. It will be seen that the effect of temperature upon the coefficient of emission has been neglected here. Anyway, the experiment shows at least qualitatively that the coefficient of emission and absorption vary in the same manner from one substance to another.

These ideas were further developed and made more precise by Kirchhoff and Balfour Stewart. Before proceeding further it is however necessary to define the concepts used in Radiation with more rigour. We now proceed to do this in the next section.

13. Fundamental Definitions.—If a body is heated it radiates heat from its surface in all directions, which comprises waves of all lengths. The nature of radiation depends on the physical properties of the body. We denote by $e_\lambda\, d\lambda$ the amount of radiation (measured in ergs) emitted normally per unit solid angle per second within the wavelengths λ and $\lambda+d\lambda$. We shall call e_λ the emissive power of the body. Similarly if dQ_λ be the amount of radiant energy falling on the body in the form of radiation (λ to $\lambda+d\lambda$) and a fraction $a_\lambda\, dQ_\lambda$ of it is absorbed by the body and converted into heat, then a_λ is called the absorptive power of the body for these rays (λ to $\lambda+d\lambda$). For black bodies $a_\lambda=1$ for all wavelengths, but for other substances a_λ depends on the physical nature of the body.

14. Kirchhoff's Law.—In sec. 12 we saw that emission and absorption vary together. In 1859, Kirchhoff deduced an important law which may be stated as follows:—

At a given temperature the ratio of the emissive power to the absorptive power is the same for all substances and is equal to the emissive power of a perfectly black body.

Though this law was first recognised by Balfour Stewart, Kirchhoff was the first to deduce it from thermodynamical principles, and apply it in all directions. It is therefore usually known as Kirchhoff's law.

We have here considered the total emission regardless of wavelength but the same relation holds for each wavelength separately. Thus for radiations of the same wavelength and the same temperature, the ratio of

the emissive and absorptive powers for all bodies is the same and equal to the emissive power of a perfectly black body. This also holds for each plane-polarised component of any ray.

Kirchhoff's own proof of the law is however very complicated and has somewhat fallen into disuse. We shall give in sec. 19 a much simplified proof of the law. But before doing so let us consider its applications.

15. Applications of Kirchhoff's Law.—The law embodies two distinct relations, a qualitative and a quantitative one. Qualitatively, it implies that if a body is capable of emitting certain radiations it will absorb them when they fall on it. Quantitatively, it signifies that the ratio is the same for all bodies.

Various experimental proofs and observations may be cited in support of the qualitative relation. If a piece of decorated china is heated in a furnace to about 1000°C. and then taken out suddenly in a dark room, the decorations appear much brighter than the white china, because they, being better absorbers, emit also much greater light. If we take a polished metal ball and have a black spot on it by coating it with platinum black, then on heating the ball to about 1000°C. and suddenly taking it out in a dark room, it will be found that the black spot is shining much more brilliantly than the polished surface. Again take the case of a coloured glass. We know that green glass looks green because it absorbs red light strongly and reflects the green (red and green being complementary colours). Hence when a piece of green glass is heated in a furnace and then taken out, it is found to glow with a red light. Similarly a piece of red glass is found to glow with a green light. A more decisive example illustrating selective action is that of erbium oxide, didymium oxide, etc., which when heated emit certain bright bands in addition to the continuous spectrum. If now a solution of these oxides is made and continuous light is passed through it, the very same bands appear in absorption.

16. Application to Astrophysics.—Besides these applications Kirchhoff's law was in a sense responsible for the birth of two entirely new branches of Science, *viz.*, Astrophysics (Physics of the sun and the stars) and Spectroscopy. We shall recount here briefly how these developments grew out of Kirchhoff's law. Newton had shown in 1680 that the sunlight can be decomposed by means of a prism into the seven colours of the rainbow, but Fraunhofer, who repeated the experiment in 1801 with better

instruments, found to his surprise that the spectrum was not continuous, but crossed by dark lines. Their number is at present known to be 20000, but Fraunhofer noticed about 500 of them, and denoted the more prominent bands by the letters of the alphabet:—A, B, C. . . . Such a solar absorption spectrum is shown in Fig. 9 (*c*) together with a continuous prismatic (*a*) and continuous grating spectrum (*b*).

Fraunhofer never understood how these dark lines originated, neither did any of his contemporaries. But he realized their great importance, measured them, and catalogued their wavelengths. He examined the light from stars, and showed that their spectra were also crossed by dark lines just as in the case of the sun. A typical stellar spectra is shown in Fig. 9 (*e*).

In the meantime, however, other sources of light were examined by the spectroscope and some knowledge was obtained of their spectra. It was found that a glowing solid gives a continuous spectrum, but a flame tinged with NaCl gives a pair of intense yellow lines on a dark background. It was found that if an electric discharge was passed through a glass tube containing gas at low pressure, a large number of emission lines were obtained on a dark background. For hydrogen these are shown in Fig. 9 (*d*).

But still the dark lines of Fraunhofer remained unexplained. Some physicists, notably Fizeau, observed that if the spectrum of the sun is examined side by side with the spectrum from a sodium flame, the yellow lines appear in the same place as the D-band of the Fraunhofer spectrum. Similar is the case with the hydrogen spectrum. In Fig. 9 (*c*) and (*d*) we see the emission spectrum of hydrogen side by side with the Fraunhofer spectrum. It is clearly seen that some of the dark lines in the latter occur in the same place as the bright lines in the former.

The explanation given by Kirchhoff not only completely solved the problem, but was far-reaching and extremely fruitful in its consequences. He supposed that the central body of the sun consists of a glowing mass which emits a continuous spectrum without black lines. But this light has to pass through a cooler atmosphere surrounding the central mass. In this atmosphere all the elements like Na, Cu . . . , etc., are present in the gaseous form in addition to ordinary gases like H_2, N_2, O_2, etc.

We have seen how the early workers studied the phenomenon of radiation with simple apparatus and had arrived at some very general laws. Every substance when heated emits radiation, *i.e.*, light. Every substance has again got the power of absorbing light. Kirchhoff arrived at the same law from thermodynamic reasoning (sec. 19) and applied it to explain the dark lines. Sodium can emit the D-lines when it is excited; hence when white light falls on it, it can absorb also the same light, and allows other light to pass through it unmolested. The gases in the outer cooler mantle round the sun therefore deprive the continuous spectrum from the central mass of the lines they themselves can emit, and give rise to the black lines. The D-bands therefore prove that there is sodium in the sun's atmosphere. Similarly the other dark lines testify to the presence of their respective elements in the atmosphere of the sun.

To face p. 296

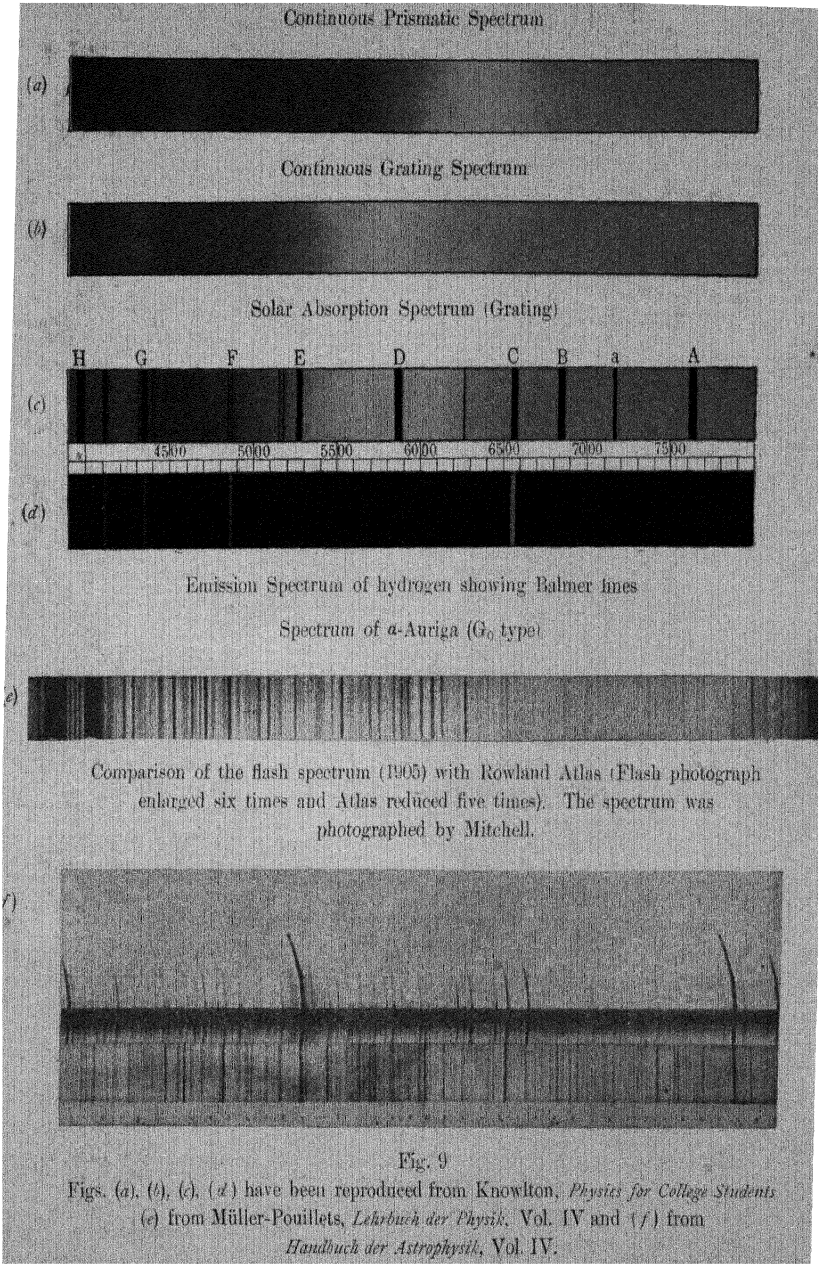


Fig. 9

Figs. (*a*), (*b*), (*c*), (*d*) have been reproduced from Knowlton, *Physics for College Students* (*e*) from Müller-Pouillets, *Lehrbuch der Physik*, Vol. IV and (*f*) from *Handbuch der Astrophysik*, Vol. IV.

The correctness of Kirchhoff's explanation is seen further from flash spectrum results. We have supposed that the atmosphere of the sun contains Na. Now if we could observe the spectrum of the atmosphere apart from that of the central glowing core (the photosphere), the lines would appear bright. We cannot ordinarily do it because the solar atmosphere is so thin that we cannot cover up the disc properly, leaving the atmosphere bare; the scattered sky-light completely obscures the spectrum outside of the disc. But during a total solar eclipse, the solar disc is completely covered, and the sky-light is also reduced by the moon's shadow. To any one observing the sun through a spectroscope, the solar atmosphere will be laid bare at the time of totality and the dark lines will flash out as bright lines. This was found actually to be the case by Prof. Young in 1872. Fig. 9 (*f*) shows a flash spectrum of 1905 Eclipse which is placed side by side with Rowland Atlas for the sake of comparison. The lines of the flash spectrum are thus found to be due to the elements in the sun's atmosphere.

But Kirchhoff's discovery is of much more far-reaching importance than the mere success in explaining the Fraunhofer bands would indicate. It clearly asserted for the first time, *that every different type of atom, when it is properly excited, emits light of definite wavelength which is characteristic of the atom.* Just as a man is known by his voice, or a musical instrument by the quality of its note, so each atom can be recognised by the particular lines it emits. Thus was born the subject of Spectrum Analysis, which aims at identifying elements by their characteristic lines, and forty new elements were added with its aid to the list already known. The different atoms are regarded as so many different types of instruments, each capable of producing its own characteristic ætherial music.

APPLICATION OF THERMODYNAMICS TO RADIATION

17. Temperature Radiation.—Since material substances at all temperatures are found to emit radiation, it becomes possible to apply the laws of thermodynamics to the problems of temperature radiation. The expression "Temperature Radiation" should be clearly understood, for matter can be made to emit radiant energy in many other ways, *e.g.*, by discharge of electricity (as in a Geissler tube), by phosphorescence, fluorescence, or by chemical action as in flames. But Kirchhoff's law holds only for temperature radiation. For radiation produced by other methods the law cannot be applied.

18. Exchange of Energy between Radiation and Matter in a Hollow Enclosure.—Let us suppose that there is an enclosure with its walls, which are impervious to external radiation, maintained at a constant temperature. We shall study what takes place when we place substances having widely different physical properties within this enclosure.

In the first place, the whole space is filled with radiation which is being emitted by the walls. This radiation arises out of the heat energy of the walls, and should therefore be regarded as a part of this heat energy. If we now place a material body A inside the enclosure, it is easy to see that whatever the initial temperature of A might have been, *it will ultimately acquire the same temperature as the walls.** This can be proved by the method of *reductio ad absurdum*, for suppose that in the equilibrium state the temperature is different. Then a Carnot engine may be used to transfer heat reversibly from the walls to A until A had the same temperature as the walls. During this process a certain amount of heat will be converted to work. But again A would be reduced automatically to a different temperature, as according to our assumption, this is the stable state of affairs. Hence again the difference of temperature can be utilized for the conversion of heat to work. We thus see that if the body were to assume a temperature different from that of the walls, we have at our disposal a means of continuously converting the heat of a single body to work without maintaining a second body at a lower temperature. This is against the second law, and hence we conclude that all material bodies placed in the enclosure would ultimately assume the temperature of the walls.

Let us now suppose that a body made up of different substances is placed within the enclosure. Then the different parts of the body have different emissive and absorptive powers. The total energy absorbed by the body will be equal to the energy it emits, since its temperature remains constant in the equilibrium state. Hence the total energy absorbed by the body will be the same whatever be the position or the orientation of the body with respect to the enclosure. And as the different surfaces of the body have different coefficients of absorption, this can be the case only when the radiation emitted by the enclosure is the same in all directions.

We shall now prove that the radiation inside the hollow enclosure is *independent of the nature or the geometrical shape of the walls of the enclosure* or of any body placed inside it. Let us suppose that we have two enclosures A and B having walls of different shape and material and communicating with each other through a screen which allows radiation of wavelength lying between λ and $\lambda + d\lambda$ to pass through it. Now the

* This may be easily seen for in the equilibrium state the entropy will be maximum and this can occur only when all temperature differences cease to exist.

walls of both A and B are maintained at the same temperature T. If in the steady state the intensity of radiation of the wavelength λ be greater in A than in B, some radiation will pass through the screen from A to B and the density of radiation will increase in B and decrease in A. The screen is then closed. The excess radiation will be absorbed by the walls of B and raise its temperature to T′, while the temperature of the walls of A will fall. Now a Carnot engine may be worked between T′ and T yielding a certain amount of work and lowering thereby the temperature of B and increasing that of A till the two are brought to the same temperature. The process can be repeated and thus we can get an indefinite amount of work while the entire system (AB) will go on becoming colder. Thus in effect we are getting work indefinitely by using the heat of a single body. This is impossible by the second law of thermodynamics. Hence the intensity of radiation for every wavelength must be the same in the two enclosures, *i.e.*, the quality and intensity of radiation depends only upon the temperature and on nothing else.

If we now place a black body inside the enclosure, it will emit an energy of the same quality and intensity as it absorbs. Hence it follows that the radiation inside the enclosure is identical in every respect with the radiation emitted by a black body at the same temperature as the walls of the enclosure. These conclusions were arrived at by Kirchhoff in 1858.

19. Deduction of Kirchhoff's Law.—Suppose we have a uniformly heated enclosure containing some substance whose emissive and absorptive powers for radiation of wavelengths lying between λ and $\lambda+d\lambda$ are e_λ and a_λ respectively. We have already shown in the previous section that the amount of radiation dQ falling on the substance from the walls does not depend upon the nature or the shape of the walls. Of this a portion $a_\lambda\, dQ$ is absorbed by the substance while the remainder $(1-a_\lambda)\,dQ$ is reflected or transmitted. Further the substance will emit radiation equal to $e_\lambda\, d\lambda$ in virtue of its temperature. Equating the energy absorbed to the energy emitted we have

$$e_\lambda d\lambda = a_\lambda\, dQ \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In the case of a perfectly black body of emissivity E_λ we have (since $a_\lambda=1$)

$$E_\lambda\, d\lambda = dQ \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Combining (5) with (6) we get

$$\frac{e_\lambda}{a_\lambda} = E_\lambda \quad . \quad . \quad . \quad . \quad . \quad (7)$$

i.e., at any temperature the ratio of the emissive power to the absorptive power of a substance is constant and equal to the emissive power of a perfectly black body. This is the thermodynamic proof of Kirchhoff's law. We have proved the law here for bodies inside the enclosure. Now since the emissive and absorptive powers depend only upon the physical nature of the body and not upon its surroundings, it follows that the law will hold for all bodies under all conditions for pure temperature radiations.

20. The Black Body.—The considerations put forward in sec. 18 enable us to design a perfectly black body for experimental purposes. For if the enclosure maintained at a constant temperature be filled with radiation characteristic of a perfectly black body, and if we make a small hole in the wall and examine the radiation coming out of it, this diffuse radiation will be identical with radiation from a perfectly black emissive surface. The smaller the hole, the more completely black the emitted radiation is. Generally a correction has to be applied for the lack of blackness due to the finite size of the hole, since some of the radiation coming from the wall is able to escape out and the state of thermodynamic equilibrium as postulated in section 18 does not hold. This is avoided in the particular type of black body due to Fery (Fig. 11). So we see that the uniformly heated enclosure with a small cavity behaves as a black body towards emission.

Again such an enclosure behaves as a perfectly black body* towards incident radiation also. For any ray passing into the hole will be reflected internally within the enclosure and will be unable to escape outside. This may be further improved by blackening the inside. Hence the enclosure is a perfect absorber and behaves as a perfectly black body.

Though Kirchhoff had proved in 1858 that the radiation inside a uniformly heated enclosure is perfectly black it was long afterwards in 1895 that Wien and Lummer could utilise this conception to obtain a black body for experimental purposes.

* Kirchhoff defines a black body as one " which has the property of allowing all incident rays to enter without reflection and not allowing them to leave again." See Planck, *Wärmestrahlung*.

The black body of Wien consists of a hollow cylindrical metallic chamber C (Fig. 10) blackened* inside and made of brass or platinum,

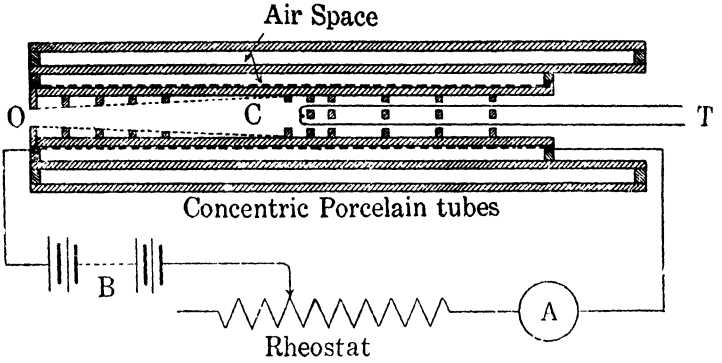


Fig. 10.—Black body of Wien.

depending upon the temperature that it has to stand. The cylinder is heated by an electric current passing through thin platinum foil as indicated by thick dashes. The radiation then passes through a number of limiting diaphragms and emerges out of the hole O. The cylinder is surrounded by concentric porcelain tubes. The temperature of the black body is given by the thermo-element T. This is the type of black body now commonly used.

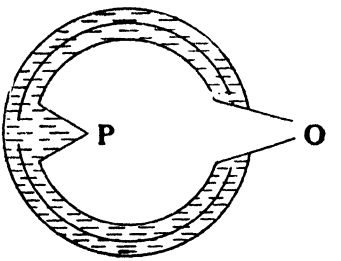


Fig. 11.—Black body of Fery.

Another type due to Fery is shown in Fig. 11. Note the conical projection P opposite the hole O. This is to avoid direct radiation from the surface opposite the hole which would otherwise make the body not perfectly black.

A striking property of such an enclosure is that if we place any substance inside it, the radiation emitted from it is also black and independent of the nature of the body. Thus all bodies inside the enclosure lose their distinctive properties. For a mirror placed inside will reflect the black radiation from the wall and hence the emitted radiation is black. Any substance if it absorbs any radiation transmitted from

* The walls however need not be black. Blackening merely enables the equilibrium state to be reached quickly.

behind must emit the same radiation in consequence of Kirchhoff's law and the total radiation leaving it must become identical with that from the walls, *i.e.*, of a black body.

RADIOMETERS

21. Sensitiveness of the Thermopile.—We shall now describe the instruments which are used for the measurement of radiation. The differential air thermometer, which was employed by Leslie and the earlier workers, has already been described in sec. 2, but is now only of historical interest.

Among the modern instruments, the thermopile has been described in sec. 2. Special care however has to be taken in order to make it sensitive as we have sometimes to measure very small amounts of energy. In the design of thermopiles, the following considerations have to be borne in mind:—(1) metals used should give large thermo-E. M. F.; (2) junctions should be as thin as possible; (3) connecting wires should be thin so as to minimise the loss of heat by conduction; (4) the junction should be coated with lampblack so that all the heat falling on it may be absorbed; (5) it should be mounted in vacuum, so that there is no loss of heat by convection, and the deflections remain steady; a rocksalt window is then provided to let in the incident radiation.

The sensitiveness also depends upon the number of thermo-junctions but this cannot be increased indefinitely as the external resistance will increase. The best procedure is to have the piles as light as possible and to choose a number so that the total resistance of the thermopile is equal to the galvanometer resistance.

The galvanometer to which the thermopile is connected should be of low resistance type with high voltage sensitiveness. For ordinary work the suspended coil type galvanometers are generally employed but are not sufficiently sensitive on account of their high resistance. For accurate work the suspended magnet (astatic) type of galvanometers are generally employed, namely, the Broca, the Paschen and the Thompson galvanometers. These are however very much susceptible to external magnetic disturbances and can be successfully used only by skilled workers.

The Linear Thermopile.—The extreme sensitiveness of the galvanometers mentioned above, enables us to work with only a few pairs of

thermo-elements. The hot junctions are all arranged in a vertical line. The wires are very fine and are wound on a small frame. This is called the linear thermopile and is used in investigating the lines of the infra-red spectrum.

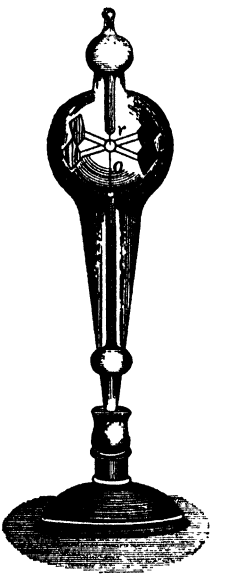


Fig. 12.—Crookes' radiometer.

22. Crookes' Radiometer.—This consists of a number of thin vertical vanes of mica suspended at the ends of a light aluminium rod *r* inside an evacuated glass vessel (Fig. 12). Two such rods fixed at right angles are shown in the figure. They are suspended in such a way that they can rotate about the vertical axis *a*. The outer face of the vanes is coated with lampblack, while the inner faces are left clear. When radiation (thermal or light) falls on the blackened face the vanes begin to revolve in such a direction that the blackened face continually recedes away from the source of radiation.

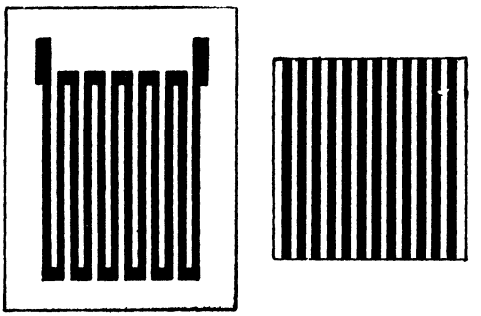
The cause of this motion is easily understood. The blackened face absorbs the incident radiation and thereby its temperature is raised, while the clear face remains at a lower temperature. The molecules bombarding the blackened face therefore become more heated than the molecules bombarding the other side of the vane and consequently they exert greater pressure on the vanes. The result is that there is a net effective force repelling the vanes away from the incident radiation. This is known as the *radiometer effect* and is essentially due to the presence of molecules. It is obvious that the velocity of revolution will be a measure of the intensity of radiation.

By suspending the vanes by means of a quartz fibre as in galvanometers we can measure the intensity of radiation if we observe the steady deflection produced. Such a radiometer has been employed by some investigators for measuring the intensity of radiation.

23. The Bolometer.—The bolometer is now rather rarely used, being superseded by modern types of thermopile. It was invented by S. P. Langley and depends for its action on the change of resistance of platinum strips or wires when heated.

The sensitiveness of the bolometer depends (1) on the sensitiveness of the galvanometer; (2) on the thinness of the strips, because the thinner the strips the larger will be the rise in temperature and the increase in resistance for a given amount of incident radiation.

Two types of bolometers have been used in radiation measurements: (1) the surface bolometer for total radiation measurements, (2) the linear bolometer for measurement of distribution of energy in the spectrum of a black body.



Figs. 13 & 14.—The Surface Bolometer.

The surface bolometer consists of exceedingly thin strips of platinum, 1 to 2×10^{-3} mm. thick, joined together in series. The method of constructing such a thin conductor is as follows:—A sheet of platinum is welded to a thick sheet of silver and the composite sheet is rolled. The sheet is then punched out as shown in Fig. 13 and attached to a hollow frame of slate. The silver is then dissolved off in nitric acid, the end joints being protected by a coating of varnish. The strips are then coated with platinum black. Fig. 14 shows a front view of such a grid. A grid so constructed has a resistance of about 60 ohms.

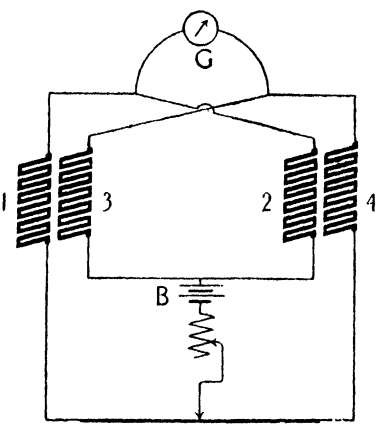


Fig. 15.—Connections of the Bolometer.

For experimental purposes four such grids, similar in all respects to each other, are connected in the form of a Wheatstone bridge. The method of connecting the grids is shown in Fig. 15. The grids 1 and 3 are in opposite arms of the Wheatstone bridge and are so arranged that the strips in 3 receive the radiation passing between the strips in 1 and so the effect is doubled. 2 and 4 are similarly

arranged but are protected from radiation. The whole is enclosed in a box. In the absence of incident radiation the galvanometer shows no deflection. When radiation is incident on grids 1 and 3 a deflection is produced.

In the linear bolometer a single narrow and thin strip of platinum is used.

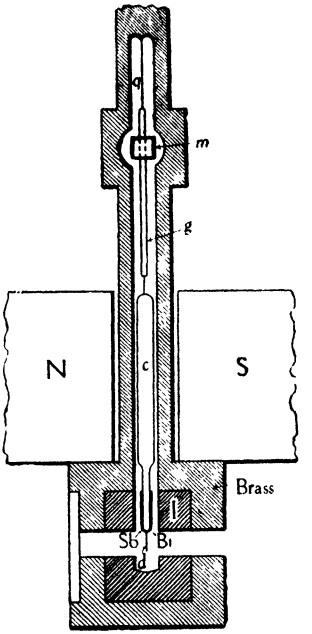


Fig. 16.*—Boys' Radiomicrometer.

24. The Radiomicrometer.—This was invented by Boys and is essentially a thermocouple without an external galvanometer. A single loop Cu of fine copper or silver wire is suspended (Fig. 16) between the poles of a strong permanent magnet NS as in a suspended coil galvanometer. To the lower ends of the copper wire two thin bars of antimony Sb and bismuth Bi are attached, and the lower ends of these are again attached to a thin disc or narrow strip *d* of blackened copper. To the upper end of the copper loop is attached a thin glass rod *g* carrying a light galvanometer mirror *m* for measuring deflection, the glass rod itself being attached to a fine quartz suspension *q*. The whole system is extremely light. Radiation, falling horizontally on the copper disc, heats the junction of antimony and bismuth and an electric current flows through the copper coil causing a deflection which depends upon the intensity of the energy received by the copper disc. To prevent disturbances due to diamagnetism of bismuth, the rods of the thermocouple are surrounded by a mass of soft iron. The whole suspended system is enclosed in brass (shown shaded in the diagram).

25. Pressure of Radiation.—As radiation has been shown to be identical with light, it possesses all the properties which is ascribed to light. One of the properties of light most important for our present

* Reproduced from ' The Theory of Heat ' by Preston by the kind permission of Messrs. Macmillan & Co.

purpose is that it exerts a small but finite pressure on surfaces on which it is incident. This had been suspected by philosophers for a long time since the days of Kepler, who observed that as the comets approach the sun, the tail of the comet continuously veers round, so as to be always opposite the sun (Fig. 17). This he tried to explain on the assumption that light exerts pressure on all material bodies on which it is incident, but the pressure increases in importance only when the size of the particle is reduced. Though painstaking experimental investigations failed to show the existence of pressure of light, Maxwell propounded in 1870 his Electromagnetic Theory of light, and showed that Light should exert a pressure, but this is very small being equal to the energy density of light.

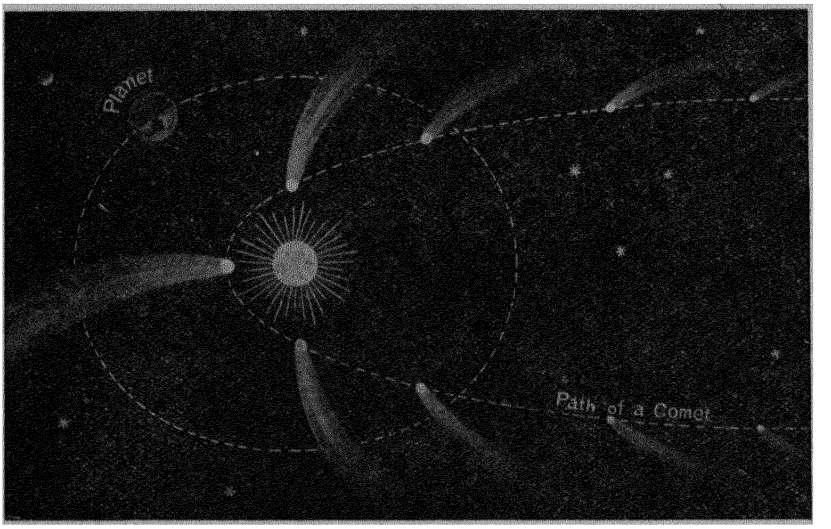


Fig. 17.—Tail of the comet.

Bartoli also showed from thermodynamic considerations that radiation should exert some finite pressure. The pressure of radiation is however so small that for a long time it baffled all attempts to measure it. The difficulties were overcome only in 1900 when Lebedew, and a little later, Nichols and Hull demonstrated experimentally its existence and were able to measure it. They confirmed the theoretical conclusion that pressure is equal to energy density of radiation.

When the radiation is diffuse, it can be shown that pressure is equal to one-third the energy density of radiation.

The fact that radiation exerts a finite pressure, however small it may be, is of great importance in the theory of black-body radiation. It shows that black radiation is just like a gas, for it exerts pressure and possesses energy. In fact we can regard the black radiation as a thermodynamic system and calculate its energy and entropy, and apply the thermodynamic laws and formulæ. We shall make use of these ideas in the next section.

26. Total Radiation from a Black Body.—The Stefan-Boltzmann Law.—As already mentioned in sec. 7, J. Stefan, in 1879, deduced empirically from the experimental data of Dulong and Petit that the total radiation from any heated body is proportional to the fourth power of its absolute temperature. In 1884 Boltzmann gave a theoretical proof of the law based on thermodynamical considerations. He showed that the law applies strictly to emission from a black body. The law is therefore generally known as the Stefan-Boltzmann law, and may be formally enunciated as follows:—*If a black body at absolute temperature T be surrounded by another black body at absolute temperature T_0 the amount of energy E lost per second per square centimetre of the former is*

$$E=\sigma(T^4-T_0^4) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For proving this law, we consider radiation in a black-body chamber and apply the thermodynamical laws to the radiation as mentioned in the previous section. Let u denote the energy density of radiation inside the enclosure, V its volume and p the pressure of radiation. Then both u and p are simply functions of the absolute temperature T. We have further the total energy U of radiation equal to uV. Applying* equation (61) of p. 267 we get

$$\frac{\partial U}{\partial V}=T\frac{\partial p}{\partial T}-p \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

* Boltzmann deduced the law by imagining the radiation to perform a Carnot cycle. He utilized the conceptions of Bartoli. This is however unnecessary here for we have shown black radiation to be analogous to a gas and can therefore proceed directly to apply the general thermodynamical laws to radiation.

and $$\frac{\partial U}{\partial V}=u,\ p=\frac{u}{3}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

since the radiation is diffuse (sec. 25). Hence equation (9) reduces to

$$u=\frac{T}{3}\frac{\partial u}{\partial T}-\frac{u}{3}$$

or $$\frac{du}{u}=4\frac{dT}{T}$$

or $$u=aT^4 \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where 'a' is a constant independent of the properties of the body. Hence the total energy lost on one side by emission will also be proportional to the fourth power of the absolute temperature. This is the Stefan-Boltzmann law.

27. Experimental Verification of Stefan's Law.—The law was subjected to experimental test by various investigators. Lummer and Pringsheim investigated the emission from a black body over the range of temperatures 100°C. to 1260°C. and found the law to hold true within experimental errors. We give below a brief account of their apparatus and arrangement.

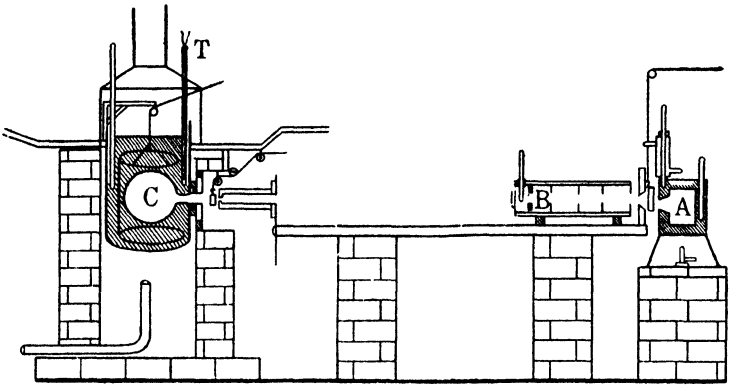


Fig. 18.—Lummer and Pringsheim's apparatus for verifying Stefan's law.

A is a hollow vessel containing boiling water (Fig. 18) which acts as the standard source of radiation for calibrating the bolometer from

time to time. The black body C employed for the range of temperatures 200° to 600°C. consisted of a hollow copper sphere blackened inside with platinum-black, and placed in a bath of a mixture of sodium and potassium nitrates which melts at 219°C. This salt bath could be maintained at any desired temperature. The temperature could be measured with a thermo-element T.

For temperatures between 900°C. and 1300°C. the black body shown in Fig. 19 was employed. D is an iron cylinder coated inside with platinum-black and enclosed in a double-walled gas furnace. The temperature inside the iron cylinder was obtained by a thermo-element enclosed in a porcelain tube passing through the furnace.

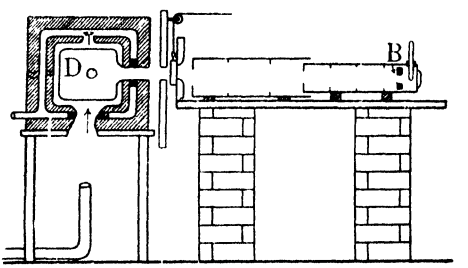


Fig. 19.—Black body for 900° to 1300°C.

The measuring instrument shown at B was the surface bolometer of Lummer and Kurlbaum. A description of this as well as the method of connecting it has been already given in sec. 23. Besides there are a number of water-cooled shutters so that the radiation can be stopped or allowed to fall at will.

The procedure adopted was as follows:—The bath was heated up to the desired temperature and maintained steady, and then the shutter was raised to allow radiation from C to fall on the bolometer, and the maximum deflection registered by the galvanometer noted. The bolometer was kept at different distances from the black body and the inverse square law verified. Next observations were taken with the black body at different temperatures. The observations were all reduced to a common arbitrary unit depending on the radiation from the black body A at 100°C. and kept at a distance of 633 mm. If d represents the deviation of the galvanometer needle, T the absolute temperature of the black body, 290° the temperature of the shutter protecting the bolometer, then

$$d=\alpha\,(T^4-290^4) \quad . \quad . \quad . \quad . \quad . \quad (12)$$

from Stefan's law. α was found to be constant. Hence the truth of Stefan's law is established.

DISTRIBUTION OF ENERGY IN THE SPECTRUM OF A BLACK BODY

28. Laws of Distribution of Energy in Blackbody Spectrum.—From a study of the colour of radiation given on p. 27 in the chart it will be obvious that as the temperature of a body is raised, the colour emitted by it becomes more and more rich in waves of shorter wavelength. Some of the stars shine with a bluish white light which indicates that their temperature must be very high. In fact the wavelength for which the intensity of emission is maximum shifts towards the shorter wavelength side as the temperature is raised. These results were also arrived at by Wien in 1893 from thermodynamic considerations of black radiation inside a hollow reflecting chamber. He showed that $E_\lambda\, d\lambda$ the amount of energy contained in the spectral region included within the wavelengths λ and $\lambda + d\lambda$ emitted by a black body at temperature T is of the form

$$E_\lambda\, d\lambda = \frac{A}{\lambda^5} f(\lambda T)\, d\lambda \quad . \quad . \quad . \quad . \quad . \quad (13)$$

and further if λ_m denote the wavelength corresponding to maximum emission of energy and E_m the maximum energy emitted

$$\lambda_m T = b \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$E_m T^{-5} = m \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where m and b are constants. In other words if the temperature of radiation is altered, the wavelength of maximum emission is altered in an inverse ratio. Equation (13) is known as *Wien's Displacement Law.*

A further step forward in developing the theory was taken by Planck who showed from very novel considerations (which developed into the modern quantum theory) that the energy density of radiation inside the enclosure is given by

$$u_\lambda d\lambda = \frac{C_1}{e^{c_2/\lambda T} - 1}\, d\lambda \quad . \quad . \quad . \quad . \quad (16)$$

where $C_1 = \frac{8\pi hc}{\lambda^5}$ (h being a constant) and $c_2 = 4{\cdot}96\, b$ approximately. This is known as *Planck's law.* We shall now consider how the spectra can be obtained experimentally and the foregoing results verified.

29. Experimental Study of the Blackbody Spectrum.—The first systematic study of the infra-red spectrum was undertaken by Langley who illuminated the slit of a spectrometer by means of sunlight and produced the spectrum by a prism of rocksalt. The rays were focussed by a lens on a bolometer which was arranged in a Wheatstone bridge adjusted for no deflection. The radiation heated the bolometer whose resistance altered and a deflection of the galvanometer was produced which was recorded on a moving photographic plate. The prism could be rotated by a clockwork and so different portions of the spectrum fell on the bolometer and were recorded.

The spectrum can also be produced by a Rowland grating but on account of the considerable overlapping prisms have been generally employed. Lenses of quartz or fluorite are generally used. It is however better to use a concave mirror for focussing radiation.

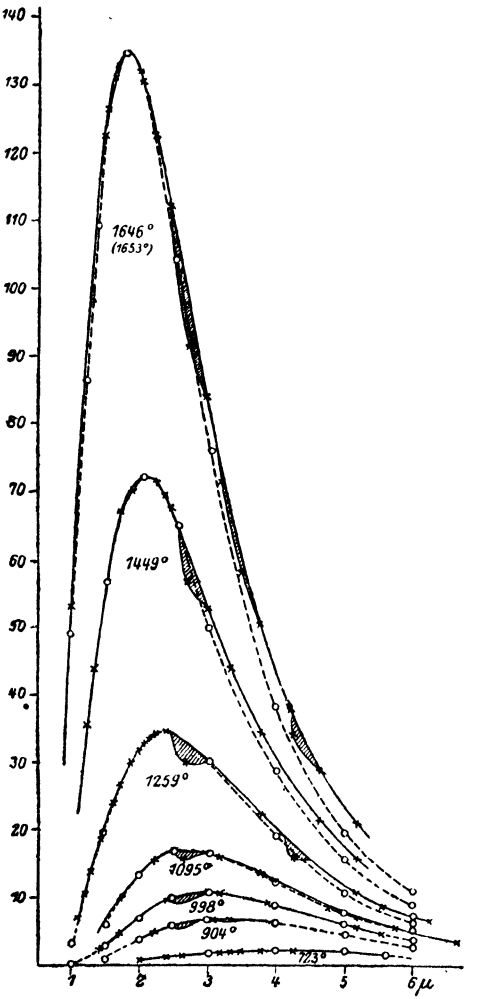


Fig. 20.—Distribution of energy in the blackbody spectrum.

Wien's displacement law was subjected to a series of experimental tests by Paschen, Lummer and Pringsheim, Rubens and Kurlbaum. We give below a short description of the experiment and results of Lummer and Pringsheim (1899). They used radiation from an electrically heated carbon tube and produced the spectrum by refraction

through a fluorspar prism. The distribution of energy was measured by means of a linear bolometer which was enclosed in an air-tight case to diminish the absorption due to water vapour and carbon dioxide. Corrections were applied to convert the prismatic spectrum into a normal one by means of the known dispersion curve of fluorspar. The distribution of energy in the spectrum for various temperatures between 621° and 1646°A was obtained and curves plotted (Fig. 20). The ordinates represent emissive powers and the abscissæ wavelengths. The full lines denote the curves obtained experimentally while the dotted lines represent the curves calculated from a semi-empirical law given by Wien. The total radiation at a temperature is represented by the area enclosed between the curve and the x-axis. The wavelength of maximum emission shifts towards the origin as the temperature rises. From these curves the values of E_λ and λ_m could be read. The experimental data are given in the following table.

Table 1.—Experimental Verification of Wien's Displacement Law.

Temp. °A	λ_m in μ's	E_m.	$\lambda_m T$ in micron-degrees	$E_m T^{-5} \times 10^{17}$
1646	1·78	270·6	2928	2246
1460·4	2·04	145·0	2979	2184
1259·0	2·35	68·8	2959	2176
1094·5	2·71	34·0	2966	2164
998·5	2·96	21·5	2956	2166
908·5	3·28	13·66	2980	2208
723·0	4·08	4·28	2950	2166
621·2	4·53	2·026	2814	2190
			Mean = 2940	2188

The table shows clearly the validity of equations (14) and (15). Knowing the value of b or m these laws enable us to determine the temperature of any substance (assumed to be a black body) if λ_m or E_m be found out. The value of b is seen to be ·294 cm.×degree, and of m to be $2{\cdot}188 \times 10^{-14}$ ergs×degree.

This furnishes us with a simple method of determining the temperature of the heavenly bodies. Thus for the moon $\lambda_m = 14\mu$ and hence

$$T = \frac{\cdot 294}{14 \times 10^{-4}} = 200^\circ \text{ A}$$

Similarly we can calculate the temperature of the sun (sec. 42).

PYROMETRY

30. Gas Pyrometers.—In Chapter I we have already described the constant volume hydrogen thermometer having a platinum-iridium bulb. For temperatures above 500°C, hydrogen cannot be used as the thermometric gas because the platinum bulb is permeable to it, hence nitrogen is invariably employed. As regards the material of the bulb Jena glass can be used to about 500°C. while quartz glass can stand up to about 1300°C. but is attacked by traces of alkali from hand, etc. Ordinary porcelain is porous and permeable to the thermometric gas but glazed porcelain was formerly employed up to about 1000°C. above which however the glazing softens and breaks; also its expansion is not regular. Platinum alloys are now invariably used. An alloy of platinum and iridium was employed by Holborn and Valentiner up to 1600°C. Iridium however distils and also makes the bulb brittle. Holborn and Day found the alloy of 80Pt-20Rh best for the purpose and used a modified form of bulb of this material to about 1600°C. They performed experiments with great care and took into account 25 possible sources of error so that their values are regarded as standard at high temperatures. The correction however becomes enormous, the uncertainty being about 2° at the melting point of palladium.

31. Resistance Pyrometer.—The platinum resistance pyrometer has been described in Chapter I. It can be used to about 1200°C. though the melting point of platinum is 1770°. If used above 1200° the platinum becomes changed and does not return to its initial zero and has to be re-standardised. The mica insulation also sometimes breaks due to moisture getting inside. Up to about 1000°C. it is the most sensitive and useful pyrometer.

32. Thermo-electric Pyrometers.—The thermo-electric pyrometers have been almost completely described in Chapter I. It is shown

there that for temperatures up to 600°C. the base couples Cu-constantan, nickel-silver are most sensitive. The Pt, 90Pt-10Rh couple is however best for all high temperature work and can be used to about 1750°. It is free from parasitic disturbances and any change in composition, and is the most sensitive pyrometer in the range 1000° to 1600°. In the lower range however it can be replaced by Ni, 90Ni-10Cr couple up to 1300°C. when the latter is much more sensitive. A couple of Ir, 90Ir-10Ru can be used to about 2100°C. while thermocouples of tungsten and an alloy of tungsten with molybdenum have been used upto 3000°C. Above 1600° however radiation pyrometers are preferred.

Radiation Pyrometry.

33. Temperature from Radiation Measurements.—In the foregoing pages we have seen that the radiation emitted by a black body depends upon its temperature and upon nothing else. Hence if we measure the radiation emitted by the body with the help of some instrument we can find its temperature. We may either measure the total radiation emitted by the body and deduce the temperature by making use of Stefan's Law (equation 8). These are called Total Radiation Pyrometers. Or we may measure the energy $E_\lambda d\lambda$ emitted in a particular portion of the spectrum and make use of Planck's Law (equation 16) of distribution of energy in the spectrum. These are called Spectral or Optical pyrometers.

Radiation pyrometers possess the great advantage that they can be employed to measure any temperature however high that may be or wherever the object may be. The pyrometer itself has not to be raised to that temperature nor need it be placed in contact with the hot body.

Further there is no extrapolation difficulty as the radiation formulæ have been found to hold rigorously for all temperatures. But the radiation pyrometer suffers from a serious drawback. It can measure accurately the temperature of black bodies only.

It is however generally employed to measure the temperature of any hot source. In that case it gives that temperature at which a perfectly black body would have the same intensity of emission (total or spectral) as the body whose temperature is being measured. It is called the black-body temperature of the substance and is consequently lower in all cases than its actual temperature. The greater the departure from perfect blackness the greater is the error involved. The lower practical limit for

radiation pyrometers is about 600°C, for then the emission from the body becomes too small to be measured accurately. Still however with certain devices it can be used to measure much lower temperatures as that of the moon.

34. Total Radiation Pyrometers.—Féry was the first to devise a radiation pyrometer based on Stefan's Law. These pyrometers are merely thermopiles so arranged that the readings are independent of the distance between the hot body and the pyrometer. We shall describe Féry mirror pyrometer which is typical of this class. Fig. 21 shows a modern type of instrument. Radiation incident from the right side falls on the concave mirror M which can be moved backwards and forwards for the purpose of focussing the radiation on the receiver S to which the hot junction of the thermocouple is attached. The cold junction of the thermocouple is protected from radiation by the tongue T and is further surrounded by the box B which also contains the thermocouple receiver, and a small opening just in front of S. The electromotive force

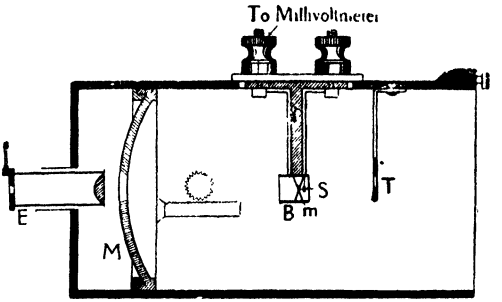


Fig. 21.—Fery radiation pyrometer.

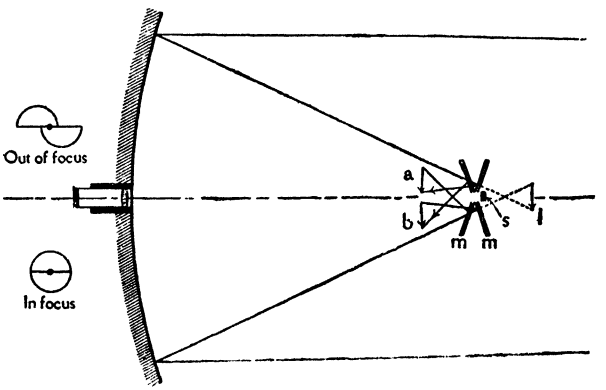


Fig. 22.—The focussing device.

developed is read on a millivoltmeter connected as indicated. The instrument possesses no lag, the steady state being reached in about a minute.

To enable the observer to focus the radiation accurately on the thermocouple, Féry employed two semi-circular mirrors, inclined to each other at an angle of about 5° and placed immediately in front of S, an opening of about 1·5 mm. being left at the centre of the mirror to allow the incident radiation to pass. Now if the image of a straight line formed by the concave mirror does not lie in the plane of the inclined mirrors they will form two images separated by a distance (see Fig. 22) and the line will appear broken when seen through the eyepiece. The concave mirror is moved till this relative displacement of the two-halves of the image disappears, and then the apparatus becomes adjusted. It will be easily seen that so long as the heat image formed by the concave mirror is larger than the hole, the thermocouple measures the intensity of the heat image and not the total radiation.

The E. M. F. of the couple in these cases is given by the relation

$$V = a(T^b + T_0{}^b) \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where T is the temperature of the black-body to be measured, T_0 the temperature of the receiver S and b a constant which varies from 3·8 to 4·2 depending upon the instrument. Generally T_0 can be neglected in comparison with T. This departure from the index value of 4 is due to various causes.

It is for this reason that the pyrometer has to be calibrated by actual comparison with a standard thermometer using radiation from a black-body chamber or heated strip.

35. Optical Pyrometers.—In these, the intensity of radiation from a black body in a small width of the spectrum lying between λ and $\lambda + d\lambda$ is compared with the intensity of emission of the same colour from a standard lamp. The formulæ required for this case can be easily worked out by assuming Planck's law. There are two types of optical pyrometers:—(1) the Disappearing Filament type, (2) the Polarising type. We now proceed to describe these instruments.

36. The Disappearing Filament Type.—This type of pyrometer was first introduced by Morse in America. It was later improved by Holborn and Kurlbaum, and by Mendenhall and Forsythe. A pyrometer of this type is shown in Fig. 23, and is essentially a telescope having a lamp

at the position usually occupied by the cross-wires. C is a metal tube containing the filament of a lamp L which is heated by the battery B and the current can be adjusted to any amount by varying the rheostat R. A is the source whose temperature is to be measured. Radiation from this is focussed by the lens D on the lamp L where a heat image is formed. The lamp is viewed through the eyepiece E in front of which is placed a red filter glass. Besides there are a number of limiting diaphragms.

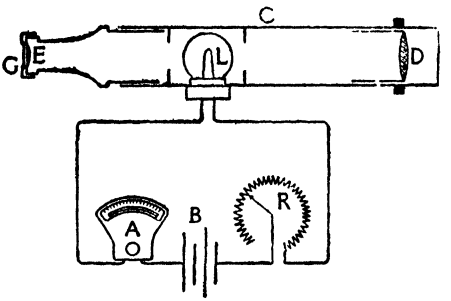


Fig. 23.—Disappearing Filament Pyrometer.

In making an experiment the observer looks through E and varies the current in the lamp till the filament becomes invisible against the image of the source. If the current is too strong the filament stands out brightly while if the current is too small, the filament looks black. The filter glass enables this matching to be done for approximately monochromatic radiation. The instrument is calibrated by direct comparison with a standard thermocouple and then extrapolated by the use of rotating sectors. Thus from the strength of the current required to match the radiation the temperature of the incident radiation can be deduced. Sometimes the ammeter is directly calibrated in degrees.

37. Polarising Type.—In 1901 Wanner constructed another pyrometer in which the comparison was made by the aid of a polarising device.

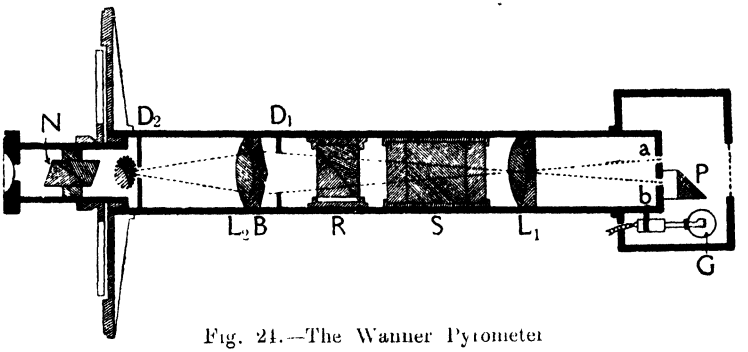


Fig. 24.—The Wanner Pyrometer

Here the ray of a particular colour from the source is compared with a ray of the same colour obtained from a standard electric lamp. A diagram illustrating the essential parts of the instrument is given in Fig. 24. *a*, *b* are two circular holes arranged symmetrically about the optical axis of the system. Radiation from the hot source enters the system through *a* while the comparison beam is supplied by the electric lamp D which illuminates the right-angled prism P and the latter directs the light on to *b*. Both beams are rendered parallel by means of an achromatic lens L_1, which is placed at a distance from the slit equal to its focal length. The parallel beams are dispersed by the direct vision spectroscope S and then pass through the polarising Rochon prism R which separates each beam into two beams polarised in orthogonal planes. B is a biprism placed in contact with a second achromatic lens L_2 which focusses the two beams on the slit S. The biprism produces in the two beams deviations of such amount that one image from each source is brought into juxtaposition. Since the holes *a*, *b* are at the focus of the lens A, the images produced by the second lens are also circular but the biprism splits them into semicircles. Six out of the eight images are stopped out while the remaining two are observed through the nicol N.

If the two beams are of equal intensity a uniformly illuminated disc with a diametrical line is observed if the plane of polarisation of the nicol prism makes an angle of 45° with the plane of polarisation of each component. Rotating the nicol in either direction diminishes the brightness of one image and augments that of the other. If the two beams are of unequal intensity matching is affected by rotating the nicol prism in either direction. A graduated circle is attached to the analyser to observe the angle of rotation.

Let the angle at which radiation from any source matches the lamp be ϕ. Then it can be shown that

$$\ln \tan \phi = a + \frac{b}{T} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where T is the absolute temperature and *a*, *b* are constants. If we determine two values of ϕ corresponding to two values of T we get a straight line from which the temperature for any value of ϕ can be read. In practice the pyrometer is calibrated by a direct comparison with a standard thermometer, and the disc is directly graduated in degrees.

RADIATION FROM THE SUN

38. The Solar Constant.—The sun emits radiant energy continuously in space of which an insignificant part reaches the earth. But even this is heavily absorbed by the earth's atmosphere, the total absorption varying from 20 to 40% depending upon the time of the day and the season of the year, and the different parts of the spectrum are absorbed to a different degree. We naturally seek for a more constant quantity which is furnishd by the rate at which solar radiations are received by 1 sq. cm. of black surface held at right angles to the sun's rays and placed at the mean distance of the earth provided there were no absorption in the atmosphere or provided the atmosphere were not present. This is called the *solar constant* and is generally expressed in calories per minute. We shall now give a method of determining the solar constant.

39. Determination of Solar Constant.—The Absolute Pyrheliometer.—Among the early workers who attempted to measure the solar constant were Pouillet, Langley and Wilson. The instruments with which the solar radiations are measured are called pyrheliometers. We

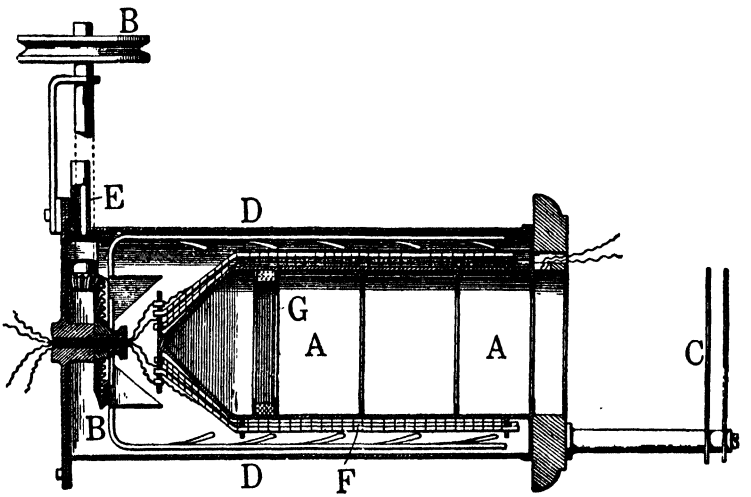


Fig. 25.—The Water-stir Pyrheliometer.

shall describe the *Water-stir pyrheliometer* employed in the Astrophysical Observatory of the Smithsonian Institution, Washington, U. S. A. Fig. 25

gives a cross-sectional view of the apparatus. AA is the black-body chamber for the reception of solar radiation. which is further protected from air currents by a vestibule, not shown. This is simply a hollow cylinder placed in front of AA. The chamber is blackened inside and has its rear end of conical shape, and is surrounded by water contained in the calorimeter DD which is stirred vigorously by means of a stirring arrangement BB run by an electric motor from outside. C is a diaphragm of known aperture for admitting the solar radiation. The incident radiation is completely absorbed by the chamber producing a rise in temperature of the water contained in the calorimeter. This rise is measured by the platinum resistance thermometer F whose wire is carefully wound upon an insulating frame round AA. At E is inserted a mercury thermometer. The calorimeter DD is carefully insulated from thermal effects occurring outside.

For calibrating the instrument, a known amount of electrical energy is supplied to the manganin resistance wire G and the rise in temperature noted. Thus the heat obtained by solar radiation can be compared with the heat generated electrically.

Another type of pyrheliometer is called the *water-flow pyrheliometer.* In these a steady stream of water flows past the absorption chamber and the temperature difference between the incoming and outgoing water is observed.

The above instruments are called absolute pyrheliometers since they measure the energy directly. For most purposes it is more convenient to employ secondary pyrheliometers in which the radiation is absorbed by a blackened silver disc. They are previously calibrated by comparison with an absolute pyrheliometer.

We are thus able to measure the radiation received per minute from which we must calculate the solar constant. The radiation received varies with the time of the day, depending upon the zenith distance of the sun. If we assume the absorption by the atmosphere to be homogeneous. then applying Biot's law, we have

$$I = I_0 e^{-k_1 d} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where d is the thickness of the medium traversed, I_0, I the intensity of the beam just at the beginning and end of the medium. This holds strictly for a monochromatic ray. We shall however apply it to the total radiation

notwithstanding the fact that k_1 varies widely with the wavelength. Now since d refers to a thickness of variable density and k_1 also is not known, it is more convenient to write the above equation in the form

$$S = S_0 a^{\sec z} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where z is the sun's zenith distance, S_0, S represent the true and the observed solar constant respectively, a is a constant called the *transmission coefficient*. Then taking logarithms

$$\log S = \log S_0 + \sec z \log a \quad . \quad . \quad . \quad . \quad (21)$$

Plotting the values of log S as ordinates and the corresponding values of sec z as abscissæ we obtain a straight line whose intercept on the ordinate axis will give log S_0, whence S_0 is found.

Accurate experiments give the mean value of the constant to be 1·937 calories per minute. The constant is found to fluctuate with the eleven-year cycle of the sun.

40. Temperature of the Sun.—The sun consists of a central hot core terminating in a surface called the photosphere. By the expression 'temperature of the sun' we generally mean the temperature of the photosphere. The temperature inside the central core is however much greater than this. We shall now give some simple methods for determining the temperature of the sun.

41. Temperature from Total Radiation.—According to careful observations by Abbot and others the solar constant is 1·937 cal. per minute. We can now find out what would be the temperature of a black surface free from any atmosphere and having dimensions and position of the sun which would emit the same total radiation at the distance of the earth. This naturally gives us the minimum value for the temperature of the photosphere.

Let the radius of the sun be r then the amount of heat lost by the sun per second

$$H = 4\pi r^2 \sigma T^4$$

where T is the temperature of the sun. If we now describe a sphere of radius R concentric with the sun (R being the distance of the earth), then

the energy will be spread over the surface $4\pi R^2$, and hence the amount received per unit surface of the earth is

$$S = \frac{4\pi r^2}{4\pi R^2}\sigma T^4$$

or

$$T^4 = \left(\frac{R}{r}\right)^2 \frac{S}{\sigma} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Now $\frac{r}{R}$ = mean angular radius of the sun

$= 959'' = 4{\cdot}649 \times 10^{-3}$ radians

$\sigma = 5{\cdot}77 \times 10^{-5}$ ergs. sec.$^{-1}$ cm.$^{-2}$ degree^{-4}

$S = 1{\cdot}937$ cal. cm.$^{-2}$ min.$^{-1}$

We obtain after substituting values in (22) that

$$T = 5732° \text{ A}$$

42. Temperature from Wavelength of Maximum Emission.—Wien's displacement law $\lambda_m T = {\cdot}2884$ cm. $\times$ degrees (equation 14) may also be employed to determine the temperature of the sun. Abbot's investigations show that $\lambda_m = 4753$, whence $T = 6059°$A. This temperature is about 300° higher than the temperature deduced from total radiation. This divergence is easily understood if we remember the fact that the sun does not actually behave like a black body.

43. Temperature of Stars.—The stars are so many suns, only they are at enormous distances compared to the sun. The determination of their temperature is subject to the same uncertainties as in the case of the sun, and the methods followed are almost identical except that here the total radiation method fails as it is often not possible to determine the diameter of stars. The temperatures are deduced from the distribution of intensity in their emission spectrum by the application of equation (14).

Books Recommended.

1. Glazebrook, *A Dictionary of Applied Physics*, Vol. 4, article by Coblentz.
2. Planck, *Wärmestrahlung* or English translation by Masius.
3. E. Griffiths, *Methods of Measuring Temperature.*
4. Burgess and Le Chatelier, *The Measurement of High Temperature.*
5. Abbot, *The Sun.*

EXAMPLES

I

1. Discuss the advantages of using one of the permanent gases as a thermometric substance for defining a scale of temperature. Describe some convenient and accurate form of gas thermometer, explain its mode of use and show how the temperature is calculated from the observations made with it. (Madras, B.Sc. 1925).

2. Explain carefully the method of determining the pressure coefficient of a gas by means of a constant volume thermometer. If in this method 1 per cent of the volume is exposed to a temperature of 30°C. throughout the observations, find what correction must be applied to the observed pressures at 0°C. and 100°C. (Madras, B.Sc. 1924).

3. Explain clearly the meaning of absolute temperature on the air thermometer scale. A gram of air is heated from 25°C. to 70°C. under a constant pressure of 75 cm. of mercury. Calculate the external work done in the expansion given that the density of air at N. T. P. is 0·001293.

4. What is an air thermometer? Explain the method of measuring temperature by Callendar's compensated air thermometer. Describe a method for measuring very high temperatures. (A. U., B.Sc. 1927).

5. Describe briefly the methods of standardisation and the range of usefulness of platinum resistance thermometers, and discuss some of the difficulties of precise resistance measurement and the precautions to be taken to avoid or correct for these. (A. U., B.Sc. Hons. 1929).

6. Describe various methods of measuring or estimating high temperatures. (A. U., B. Sc. 1931, 1932).

7. Give a short account of the methods in use for the measurement of low temperatures. Describe how standard temperatures below 0°C. have been fixed. (A. U., B.Sc. Hons. 1927).

II

1. Enunciate Newton's law of cooling and show how corrections can be made for the heat lost by radiation during calorimetric experiments. Establish a relation for finding the specific heat of liquids by the method of cooling. (Nagpur, B.Sc. 1930).

2. Describe the steam calorimeter. Explain how it may be used to determine (*i*) the specific heat of a gas at constant volume, (*ii*) the specific heat of a small solid. (A. U., B.Sc. 1929).

3. Describe a method of determining the specific heat of a gas at constant volume, giving a neat diagram of the arrangement of the apparatus necessary. Why is the specific heat at constant pressure greater than that at constant volume? (Dacca, B.Sc. 1930).

4. Describe the constant flow method of Callendar and Barnes for the measurement of the mechanical equivalent of heat. In an experiment using this method, when the rate of flow of water was 11 gm. per minute, the heating current 2 amperes and the difference of potential between the ends of the heating wire 1 volt, the rise of temperature of the water was 2·5°C. On increasing the rate of flow to 25·4 gm. per minute, the heating current to 3 amperes and the potential difference between the ends of the heating wire to 1·51 volts, the rise of temperature of the water was still 2·5°C. Deduce the value of the mechanical equivalent of heat. (A. U., B.Sc. 1931).

5. Describe Nernst vacuum calorimeter and indicate briefly how it has been used for measuring specific heats at low temperatures. (A. U., M.Sc. 1925).

6. Write an essay on the determination of the specific heat of a substance. (Dacca, B.Sc. 1930).

7. A quantity of air at normal temperature is compressed (*a*) slowly, (*b*) suddenly, to $\frac{1}{10}$ of its volume. Find the rise of temperature, if any, in each case.

[Ratio of the two specific heats of air = 1·4, log 2·73 = ·4362; log 6·858 = ·8362].

Deduce the formula used for (*b*). (A. U., B.Sc. 1928).

8. Discuss the relation between specific heat of a substance and its atomic and molecular weight. (Bombay, B.Sc. 1924).

9. Describe a method of determining the ratio of the specific heats of a gas at constant pressure and constant volume. How has the mechanical equivalent of heat been calculated from a knowledge of this ratio? (A. U., B.Sc. 1929).

10. Explain how the mechanical equivalent of heat can be deduced from a knowledge of the specific heats of air at constant pressure and constant volume. State clearly any assumptions made in your reasoning and describe experiments, if any, which afford justification for such assumption. (Madras, B.Sc. 1925).

11. Describe a method of determining the ratio of the two specific heats of a gas. Show that it follows from the kinetic theory of gases that the ratio of the two specific heats in the case of a monatomic gas is 1·66. (Madras, B.Sc. 1924).

12. Find the ratio of the specific heats of a gas from the following data:—A flask of 10 litres capacity weighs, when exhausted, 160 gm.; filled with the gas at a pressure of 75 cm. of mercury it weighs 168 gm. The column of the gas which when confined in a tube closed at one end and maintained at the same temperature as the gas in the flask, responds best to a fork of 223·6 vibrations per second, is 50 cm.

III

1. Give the outlines of the methods by which the mechanical equivalent of heat can be determined. Assuming that for air at constant pressure the coefficient of expansion is $\frac{1}{273}$, the density at 0°C. and atmospheric pressure is 0·001293, the specific heat $c_p = 0{\cdot}2389$ and the ratio $c_p/c_v = 1{\cdot}405$, calculate the mechanical equivalent of heat. Suppose that there is inappreciable cohesion between the molecules. (Bombay, B.Sc. 1924).

2. Define the mechanical equivalent of heat. If the kinetic energy contained in an iron ball, having fallen from rest through 21 metres is sufficient to raise its temperature through 0·5°C. calculate a value for the mechanical equivalent of heat (given $g = 980$ cm. per sec. per sec. and specific heat of iron $= 0{\cdot}1$).

3. Show how the method of electrical heating has been adopted in the determination of the mechanical equivalent of heat. One gram of water at 100°C. is converted into saturated vapour at the same temperature. Calculate the heat equivalent of the external work done during the change Density of water at 100°C. $= 0{\cdot}958$ gms. per c.c.; density of saturated steam at 100°C. $= 0{\cdot}000598$ gms. per c.c.

4. Explain what is meant by the "velocity of mean square" of the molecules of a gas and their "mean free path." Show how these two quantities can be found. (Bombay, B.Sc. 1924).

5. Show that pressure of a gas is equal to two-thirds of the kinetic energy per unit volume. Calculate the kinetic energy of hydrogen per gram-molecule at 0°C. (A. U., B.Sc. 1930).

6. Deduce Boyle's and Avogadro's laws from the kinetic theory of gases. What interpretation of temperature is given according to this theory? (A. U., B.Sc. 1928).

7. Deduce an expression for the conductivity of a gas from the kinetic theory. How would you actually proceed to determine the conductivity of any particular gas? (A. U., B.Sc. Hons. 1931).

8. State the law of equipartition of energy. Prove that for a monatomic gas, the value of gamma, the ratio between the specific heats is 5/3 and for a diatomic gas it is 7/5. (A. U., B.Sc. 1932).

IV

1. How has van der Waals modified the isothermal equation for a gas? Calculate the values of the critical pressure, volume and temperature in terms of the constants of his equation. How do the theoretically derived results tally with experiments? (A. U., B.Sc. 1931).

2. Define critical temperature, pressure, and volume of a vapour, and give some account of the behaviour of a substance near the critical point. (A. U., B.Sc. 1927).

3. Draw diagrams showing the general form of the isothermals and show which portion of the diagram corresponds to the liquid, the saturated

vapour and the coexistence of the liquid and vapour. (Bombay, B.Sc. 1926).

4. Give an account of the properties of fluids in the neighbourhood of the critical point. Describe how you would determine the critical constants of a substance. (A. U., B.Sc. Hons. 1928).

V

1. How would you determine the vapour pressure of a liquid above its normal boiling point? Explain how clouds are formed by the mixing of warm moist air with cold moist air. (A. U., B.Sc. 1927).

2. Describe a method of determining the vapour density of a volatile liquid, and explain the theory of your method. (Dacca, B.Sc. 1928).

3. Give an account of a method which has been adopted for the determination of the pressure of saturated vapour between 100°C. and 120°C. Explain clearly what is meant by the statement that the specific heat of saturated vapour at 100°C. is negative. (Madras, B.Sc. 1924).

VI

1. Write an essay on 'artificial production of cold.' (A. U., B.Sc Hons. 1930).

2. Describe the manufacture of liquid air. (A. U., B.Sc. 1930).

3. Discuss theoretically the production of cold by expansion of gases through porous plugs. How has this principle been applied in machines for liquefying air? (A. U., B.Sc. Hons. 1931).

4. Write a short essay on the liquefaction of the so-called permanent gases. (Dacca, B.Sc. 1928).

5. Describe a method of liquefying hydrogen, and explain the principle involved in the process. (A. U., B.Sc. 1928).

6. Write an essay on the liquefaction of hydrogen. (A. U., M.Sc. 1926).

VII

1. Describe, in full detail, the method by which the expansion of crystals when heated may be studied experimentally. (A. U., B.Sc. Hons. 1927).

2. Describe a method by which the cubical expansion of a liquid can be accurately determined by weighing a solid of known expansion in it at two known temperatures.

A solid is found to weigh 29·9 gms. in a liquid of specific gravity 1·21 at 10°C. its weight in air being 45·6 gms. It weighs 30·4 gms. in the same liquid at 25°C. when its specific gravity is 1·17. Calculate the coefficient of cubical expansion of the solid.

3. (*a*) Describe Regnault's method for the determination of the coefficient of absolute expansion of mercury. Indicate briefly the precautions adopted by Regnault to avoid errors.

(*b*) If the coefficient of cubical expansion of glass and mercury are $2{\cdot}5\times10^{-5}$ and $1{\cdot}8\times10^{-4}$ respectively, what fraction of the whole volume of a glass vessel should be filled with mercury in order that the volume of the empty part should remain constant when glass and mercury are heated to the same temperature. (Dacca, B.Sc. 1928).

VIII

1. By what processes does hot water in an open vessel lose heat? Describe experiments by which the several causes of loss may be shown to exist. (Dacca, B.Sc. 1928).

2. Define the thermal conductivity of a substance and describe some way of finding it.

An iron boiler $\frac{5}{8}$ inch in thickness exposes 60 square feet of surface to furnace and 600 lbs. of steam at atmospheric pressure are produced per hour. The thermal conductivity of iron in inch-lb-sec. units is 0·0012 and the latent heat of steam is 536. Find the temperature of the underside of the heating surface. Explain why this is not the temperature of the furnace (Dacca, B.Sc. 1929).

3. Explain the difference between the thermal conductivity and the diffusivity of a substance.

The two sides of a metal plate 1·5 square metres in area and 0·4 cm. in thickness are maintained at 100°C. and 30°C. respectively. If the thermal conductivity of the metal be 0·12 C.G.S. units find the total amount of heat that will pass from one side to the other in one hour. (Dacca, B.Sc. 1928).

4. Define the terms conductivity and diffusivity as used in the theory of heat conduction. Describe a method of comparing the conductivity of two metal bars. Account for the fact that the evaporation of liquid air is greatly reduced when kept in a Dewar vacuum vessel. (Madras, B.Sc. 1924).

5. Define conductivity. Deduce an expression for the flow of heat in a long bar when it has acquired a steady state. (B. H. U., B.Sc. 1931).

6. Define the coefficient of heat conductivity of a substance and give details of some method of determining this constant for iron. (A. U., B.Sc. 1931).

7. Describe Ingen-Hausz's experiment, and prove from the mathematical theory that the conductivities of different bars vary as the square of the length up to which wax is melted. (A. U., B.Sc. 1932).

8. Describe Forbes' method of determining the thermal conductivity of a metallic bar, and explain the formulæ used. (A. U., B.Sc. 1928).

9. Define thermal conductivity. A steady stream of water flowing at the rate of 500 grams a minute through a glass tube 30 cms. long, 1 cm. in external diameter and 8 mm. in bore, the outside of which is surrounded by steam at a pressure of 760 mm., is raised in temperature from 20°C. to

30°C. as it passes through the tube. Find the conductivity of glass (Nagpur, B.Sc. 1930).

10. Define thermal conductivity. Describe a method you have adopted in experimentally finding this constant for a good conductor. Find the coefficient of conductivity of a badly conducting material upon which the following experiment was made:—A very thin-walled hollow silver cylinder 40 cm. in diameter and 50 cm. in length is covered all over its external surface including the ends by a layer of the material 0·33 cm. in thickness. Steam at a temperature of 100°C. is passed through the cylinder and the external temperature is 20°C. Water is found to accumulate within the cylinder at the rate of 3 gm. per minute. The latent heat of vaporization of water at 100°C. is 537 cal. per gram and cross-sections of the steam inlet and outlet are each 10 square centimetres. (Madras, B.Sc. 1925).

11. Define conductivity and diffusivity of heat. When steam is passed through a circular tube of length l and having the internal and external diameters a and b respectively, prove that the radial flow of heat outwards is given by

$$2\pi \mathrm{K}l(\theta_1-\theta_2)\log_e \frac{b}{a}$$

where K is conductivity and θ_1, θ_2 the temperatures inside and outside the tube. How will you determine the conductivity of india-rubber? (A. U., B.Sc. Hons. 1930).

12. Prove that if a long bar is periodically heated at one end, the law of propagation of heat is given by the equation

$$\frac{d\theta}{dt} = h^2 \frac{d^2\theta}{dx^2}$$

Obtain a solution of this equation and show how with its aid the diurnal and annual variation of temperature at some depth below the surface of the earth can be explained. (A. U., M.Sc. 1926).

IX

1. What do you understand by a reversible cycle as opposed to an irreversible one? Give instances of each. (A. U., B.Sc. 1931).

2. Explain what is meant by a reversible cycle. Shew that no engine working between a given source and refrigerator has a greater efficiency than a reversible engine. Explain why the efficiency of all heat engines in practice are much below that of a reversible engine. (A. U., B.Sc. 1929).

3. Describe with diagrams an Otto engine and deduce an expression for its efficiency. (A. U., B.Sc. 1932).

4. Describe some kind of internal combustion engine and explain fully how heat is thereby converted into work.

Describe its uses and applications and dwell upon its advantages over the steam engine. (A. U., B.Sc. 1927).

5. Describe the cyclical process of a steam engine and compare its efficiency with that of an internal combustion engine. Explain (1) why steam engine is preferred in railways, and (2) why petrol engine is used in aeroplanes. (A. U., B.Sc. 1930).

6. Write an essay on 'Heat engines.' (Dacca, B.Sc. 1929).

7. Explain the indicator diagram and apply it to Carnot's cycle. Explain the conditions for reversible working and show that in general for reversible cycles $\int \frac{dQ}{\theta} = 0$. (Bombay, B.Sc. 1924).

X

1. Show that when a body expands, the external work performed is given by the expression

$$\int_{v_1}^{v_2} p\, dv$$

From the following data calculate what fraction of the specific heat of copper is due to the external work done in expansion in an atmosphere at a pressure of 76 cms. of mercury:—

Specific heat of copper = 0·093.

Specific gravity of copper = 8·3, of mercury = 13·6.

Coefficient of linear expansion of copper 0·000016, $J = 4{\cdot}2 \times 10^7$ ergs per calorie. (A. U., B.Sc. 1929).

2. Explain external and internal work. Discuss the changes in the kinetic energy of the molecules of a gas when heated and hence show that the ratio of the specific heats for a monatomic gas is 5/3.

3. Write an essay on the transformation into heat of other forms of energy. (Cal., B.Sc. 1928).

4. In what sense can the second law of thermodynamics be regarded as furnishing an absolute scale of temperature? How can readings of gas thermometers be reduced to this particular scale? (A. U., B.Sc. Hons. 1931).

5. Show that temperatures measured on Lord Kelvin's scale of absolute temperatures will agree with those measured by the aid of a perfect gas thermometer. (Madras, B.Sc. 1924).

6. Write notes on one of the following:—

(*a*) Lord Kelvin's absolute scale of temperature,

(*b*) Joule and Kelvin's porous plug experiment. (Nagpur, B.Sc. 1930).

7. Derive an expression for the entropy of a perfect gas in terms of its pressure, volume and specific heats. (Bombay, B.Sc. 1926).

8. Prove that the increase of entropy per unit increase of volume under constant pressure is equal to the increase of pressure per unit increase of temperature during an adiabatic change. (Bombay, B.Sc. 1926).

9. State the second law of thermodynamics and apply it to the determination of the effect of pressure on the melting point of a solid. (A. U., B.Sc. 1928).

10. Prove the thermodynamic relation

$$\left(\frac{d\phi}{dv}\right)_\theta = \left(\frac{dp}{d\theta}\right)_v$$

and hence prove

$$L = \theta \frac{dp}{d\theta}\left(v_2 - v_1\right)$$

(B. H. U., B.Sc. 1931).

11. Deduce the latent heat equation

$$d\theta = \frac{\theta(v_2 - v_1)}{L} dp.$$

Calculate the depression of the melting point of ice per atmospheric increase of pressure, given

$$\frac{\text{Density of ice at } 0°C}{\text{Density of water at } 0°C} = \frac{10}{11}$$ (Nagpur, B.Sc. 1930).

12. Prove that

$$\frac{dp}{d\theta} = \frac{L}{\theta(v_1 - v_2)}$$

One gram of water-vapour at 100°C. and atmospheric pressure occupies a volume of 1640 c.c. and L=536 calories. Prove that the vapour pressure of water at 99°C. is about 733 mm. of mercury. (A.U., M.Sc. 1926).

13. Show, on thermodynamic principles, that when a liquid film is suddenly expanded, it must fall in temperature, and find an expression for the heat that must be supplied to keep it constant. (A. U., B.Sc. Hons. 1927).

14. Deduce an expression for the specific heat of saturated vapour and prove that in the case of water at 100°C. it is negative. How do you explain the paradox 'negative specific heat.' (A. U., B.Sc. Hons. 1931).

15. Define the triple point. Describe the successive changes observed in a system containing water at its various states when pressure is changed at a constant temperature (*a*) when the temperature is above the triple point, (*b*) when the temperature is below it. (Dacca, B.Sc. 1930).

XI

1. State Newton's law of cooling. A copper calorimeter weighing 15 gms. is filled first with water and then with a liquid. The times taken in the two cases to cool from 65°C. to 60°C. are 170 sec. and 150 sec. respectively. The weight of the water is 11 gms. and that of the liquid is 13 gms. Calculate the specific heat of the liquid. The specific heat of copper is 0·1. (Cal., B.Sc. 1928).

2. State Stefan's law and discuss in the light of the same (1) Newton's law of cooling, (2) the temperature of the sun, and (3) the temperature of a tungsten arc. (A. U., B.Sc. 1932).

3. Describe any furnace and explain how you would measure its temperature. (A. U., B.Sc. 1930).

4. Discuss the principles underlying the measurement of temperatures by means of optical pyrometers, and show how the value of the temperature is estimated. Describe fully and clearly a practical form of apparatus of this type. (A. U., B.Sc. Hons. 1930).

5. Write a short and critical account of the methods in use for the determination of the solar constant and its fluctuations. How can you derive from it the temperature of the photosphere of the sun? (A. U., B.Sc. Hons. 1929).

6. Under what conditions may a thermodynamic investigation of the radiation within an enclosure be carried out?

Show that under these conditions the radiation varies as the fourth power of the temperature. (A. U., B.Sc. Hons. 1928).

PHYSICAL CONSTANTS*

The Gas Constant	R	$= 8{\cdot}314 \times 10^7$ ergs per gm. molecule
		$= 1{\cdot}986$ calories.
Coefficient of expansion α for perfect gas at 0°C		$= 0{\cdot}0036604$ per °C.
Volume of one gram-molecule at N. T. P.		$= 22{\cdot}414$ litres.
Avogadro number	N	$= (6{\cdot}064 \pm 0{\cdot}006) \times 10^{23}$.
Number of molecules per c.c. at N. T. P.		$= 2{\cdot}705 \times 10^{19}$.
Mass of the H-atom	M	$= 1{\cdot}662 \times 10^{-24}$ gm.
Density of mercury at N. T. P.		$= 13{\cdot}5951$ gm. cm^{-3}.
Pressure of 1 atmosphere		$= 1{\cdot}01325 \times 10^6$ dynes cm^{-2}. (for $g = 980{\cdot}665$ cm. sec.$^{-2}$).
Mechanical equivalent of heat	J	$= 4{\cdot}1860 \times 10^7$ ergs. cal^{-1}.
Boltzmann's constant	k	$= (1{\cdot}3709 \pm 0{\cdot}0014) \times 10^{-16}$ erg. °C^{-1}.
Stefan-Boltzmann constant	σ	$= 5{\cdot}767 \times 10^{-12}$ watt. cm^{-2} °C^{-4}.
Wien's constant	b	$= 0{\cdot}2884$ cm. degree.
Planck's constant	h	$= (6{\cdot}547 \pm 0{\cdot}008) \times 10^{-27}$ erg. sec.
Velocity of light in vacuum	c	$= (2{\cdot}99796 \pm 0{\cdot}00004) \times 10^{10}$ cm. sec.$^{-1}$.
Electronic charge	e	$= (4{\cdot}7668 \pm 0{\cdot}0038) \times 10^{-10}$ e. s. u.
		$= (1{\cdot}5900 \pm 0{\cdot}0013) \times 10^{-20}$ e. m. u.
Faraday number	F	$= 96494 \pm 5$ int. coulombs. per gm. equiv.
Mass of the electron	m	$= (9{\cdot}038 \pm 0{\cdot}010) \times 10^{-28}$ gm.
The ratio of charge to the mass for the electron	e/m	$= (1{\cdot}7592 \pm 0{\cdot}0011) \times 10^7$ e. m. u./gm.
Gravitation constant	G	$= 6{\cdot}664 \times 10^{-8}$ cm.^{3} gm.$^{-1}$ sec.$^{-2}$.

* Adopted from the following sources:—Compilations of R. T. Birge, *Phys. Rev. Suppl.*, **1**, 1, 1929; and those of F. Göpel, F. Henning, W. Jaeger and others in *Handbuch der Physik*, **2**, 1926; W. H. J. Child's book on *Physical Constants*; and some other sources.

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