THE PROPERTIES OF MATTER

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BY

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"Opinionum commenta delet dies, naturæ judicia confirmat."
—Cicero.

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PREFACE.

THIS Text-book is based upon a course of a hundred lectures delivered at His Exalted Highness The Nizam's College, Hyderabâd, to students working for the B.A. Degree Examination of the University of Madras.

The order followed is the reverse of that adopted in most Text-books dealing with the Properties of Matter.

Commencing with the First Law of Thermodynamics, an extension is made to the more general Principle of the Conservation of Energy, and hence to the metaphysical conception of the Identity of Energy throughout its various transformations.

Since our knowledge of mechanical systems is, in general, more complete than that relating to other modes of energy, a logical sequence leads to the study of the Kinetic Theory of Matter, the consequences of which can be most fully developed when applied to matter in the gaseous state.

The Properties of Gases are, therefore, next investigated from the standpoint of the Kinetic Theory, and the continuity of the gaseous and liquid states supplies the natural transition to a detailed study of liquids. The Properties of Solids are dealt with last.

It is thought that this method of treatment is simpler, and follows a more natural sequence than is attained by commencing with a study of the Properties of Matter in the solid state—and proceeding, in the reverse order, to a consideration of Liquids and Gases. Particular emphasis has been laid upon the experimental treatment of the subject, without which most of the time spent in the study of any branch of Physical Science is wasted. Use has been made, whenever possible, of original papers. In addition I wish to acknowledge my indebtedness to the following works: Jean's *Dynamical Theory of Gases*, Preston's *Heat*, Meyer's *Kinetic Theory of Gases*, Poynting and Thomson's *Heat*, and *Properties of Matter*, Travers' *Study of Gases*, Edser's *Heat*, and *General Physics*, Young's *Stoichiometry*, Lewis' *Physical Chemistry*, Findlay's *Phase Rule*, Darling's *Liquid Drops and Globules*, Boys' *Soap-bubbles.*

I am also indebted to Messrs. F. E. Becker & Co., Hatton Wall, London, E.C. 1, for their courtesy in lending a number of blocks for printing illustrations—the remaining diagrams have been reproduced from original drawings.

My best thanks are also due to my sister, Miss Veronica McEwen, for kindly revising the proofs.

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CHAPTER I.

THE FIRST LAW OF THERMODYNAMICS.

1. The Nature of Heat.—It has been known from antiquity that two bodies when rubbed together become warmer. Passing over the earlier theories as to the material or quasi-material nature of heat—which have, now, but an historic interest—and recognising heat as one of the forms of energy, we may express the above-mentioned phenomenon in scientific language by stating that: "Whenever work is done against friction, heat is produced." Further, the researches which are described in this chapter will be found to show that the amount of heat produced always bears a fixed ratio to the amount of work that has been transformed.

2. Mayer's Researches.—The rate of exchange between mechanical energy and heat energy—or the "Mechanical equivalent of heat"—was first determined by J. R. Mayer, of Heilbronn, in 1842, by calculation from the specific heats of air at constant pressure and constant volume.

Experiment shows that the specific heat of any gas at constant pressure exceeds its specific heat at constant volume. On the assumption that the excess of heat energy required in the former case is entirely used in doing the work of pushing out the surrounding atmosphere during expansion, and that none is absorbed in doing work against internal cohesive forces, we can calculate the mechanical equivalent of heat by equating the external work done during the expansion to the difference between the two specific heats. Now the molecular volume of any gas—that is, the volume occupied by the molecular weight of the gas expressed in grammes—is, approximately, 22,380 c.cs. at 0° C. and 76 cms.

If the coefficient of expansion of the gas at constant pressure be taken at the mean value of 0·003665 (Regnault), then, on raising the temperature to 1° C. the molecular volume will become

$$22{,}380(1 + 0{\cdot}003665) \text{ c.cs., i.e. } 22{,}462 \text{ c.cs.}$$

Hence the expansion is 82 c.cs.

Since a pressure of 76 cms. of mercury is equal to $76 \times 13{\cdot}596 \times 981$ dynes per sq. cm. (i.e. 1,013,800 dynes/cm.^{2}), the work done by the gas in expanding against this pressure $= 82 \times 1{,}013{,}800$ ergs
$= 8{\cdot}31 \times 10^7$ ergs.

Applying this result to air, we may, according to Witkowski, take the specific heat of air at constant pressure, C_p, as 0·2372. This number expresses the heat in calories required to raise 1 gm. of air 1° C. at constant pressure (*vide* Cap. III.). The specific heat of air at constant volume, C_V—which also refers to unit mass of the air—may be determined from a knowledge of the ratio of the specific heats, or directly by means of Joly's steam calorimeter (*vide* Cap. III.). We shall take the value $C_V = 0·1715$ obtained by Joly's direct determination.

Multiplying these results by 28·88—the molecular weight of air—we obtain the values of the molecular heats at constant pressure, Cm_p, and constant volume, Cm_V respectively.

Thus $Cm_p = 0·2372 \times 28·88 = 6·85$ cals.
and $Cm_V = 0·1715 \times 28·88 = 4·95$ cals.

Therefore the difference between the molecular heats $\Delta = 1·90$ cals.

Or $Cm_p - Cm_V = 1·90$ cals.

Now this quantity of heat is equivalent to the external work done by the molecular volume of air during its expansion, i.e. to $8·31 \times 10^7$ ergs.

Therefore the mechanical equivalent of 1 calorie $= \dfrac{8·31 \times 10^7}{1·90}$ ergs
$= 4·2 \times 10^7$ ergs.

The actual value found by Mayer, making use of the data available in 1842, was 36,500 cm.-gms., which corresponds to $3·6 \times 10^7$ ergs.

It is clear, as already stated, that this method of calculating the mechanical equivalent of heat is only permissible on the assumption that no energy is absorbed in doing work against internal molecular cohesion, or, at any rate, on the assumption that the quantity of energy so absorbed is negligibly small. In 1845 Mayer published a second paper in which he quoted an experiment by Gay-Lussac to justify this assumption. Gay-Lussac, in this experiment, allowed air at atmospheric pressure to expand from a globe into another equal globe which had previously been exhausted, and he found that the cooling produced in the first globe was equal to the heating effect observed in the second globe. Mayer pointed out that the cooling in the first vessel was due to the work done by the remaining gas in compressing the gas into the second vessel, and that the heating produced in the second vessel was due to the work done on the gas that had entered during its subsequent compression. Since the heat gained in the second vessel equalled the heat lost in the first, Mayer concluded that the mere expansion of air, without doing external work, does not produce any change of temperature—and, consequently, that no heat energy is absorbed during the expansion in doing work against internal cohesive forces.

The later researches of Joule and Thomson (Lord Kelvin), on the passage of a gas through a porous plug have, however, shown that some work is done against internal forces in the separation of the molecules, or that there is a change in the intrinsic energy of a gas on mere expansion, and that, therefore, Mayer's assumption is only an approximation (*vide* Appendix A). But the magnitude of the cohesive forces in a gas at the ordinary density is so small that the accuracy of the calculation of the mechanical equivalent of heat from the external work done by the gas during expansion at atmospheric pressure is not sensibly affected. When a gas, however, is subjected to the combined influence of high pressure and low temperature it must be noted that a large proportion of the molecules are brought close together—and that, consequently, considerable cohesive forces will be exerted—in which case Mayer's assumption ceases to be justified. Under such conditions, if expansion occur, heat energy must be absorbed to do the work of separating the molecules against their cohesive forces, and, in general, a marked cooling of the gas results.

3. Joule's Researches.—Dr. Joule's researches on the rate of exchange between mechanical energy and heat energy were commenced in 1840, and in 1843 he published an account of his first experiments on the mechanical equivalent of heat. It should be noted that Mayer's second paper, in which he justified his method of calculation from the specific heats of air, did not appear until 1845, i.e. two years later.

In 1844 Joule announced some further results, obtained from experiments on the compression of air, in which he compared the heat gained or lost with the work done on or by the air when compressed or allowed to expand. Since the validity of these results depended upon the absence of cohesive forces, Joule carried out an investigation similar in many respects to that of Gay-Lussac's. In this investigation air was compressed to several atmospheres in a thin copper vessel, which was connected to a similar copper vessel. The latter vessel was exhausted, and both vessels were placed in water in the same calorimeter. When a steady temperature had been attained, a stopcock between the two vessels was opened, and, on stirring up the water in the calorimeter, it was found that practically no change of temperature had occurred as a result of the expansion. Joule also found that if the two vessels were placed in separate calorimeters the cooling produced in the first calorimeter was approximately equal to the heating produced in the second calorimeter.

Owing to the large capacity for heat of the calorimeters and vessels, compared with that of the enclosed air, these experiments were not susceptible of very great accuracy.

In 1845 Joule first described a method by which water in a calorimeter was churned up—the mechanical energy being derived from falling weights—and, subsequently, he greatly improved this direct method of ascertaining the mechanical equivalent of heat.

In the earlier experiments, a weighed quantity of water was placed in a specially constructed copper calorimeter, A (Fig. I.). This calorimeter was fitted inside with fixed radial vanes or baffles, and was closed with a lid provided with two openings. Through the central opening in the lid passed a spindle to which were attached paddles of such a size that they could just pass through openings cut in the fixed vanes. The object of the fixed radial vanes was to prevent the circulation of the water as a whole—the water being merely churned up by the paddles, and its kinetic energy converted (through viscosity), into heat energy. The second opening in the lid, not shown in the figure, served for the insertion of a very sensitive thermometer. The spindle was connected to a drum, B, from which strings passed horizontally to the wheels of two equal "wheels and axles," and equal masses were suspended by strings from the axles. The temperature of the water in A having been noted, the masses were released and the paddles thereby set in motion. On the masses reaching the floor, the drum, B, was detached from the spindle, by removing the pin, C, and the masses were again wound up, without rotating the paddles, by turning the handle at the top of the drum. The pin, C, was then re-inserted and the masses allowed to fall again, causing the paddles to rotate. This was repeated twenty times in succession in each experiment, and the rise in temperature of the water and the calorimeter noted. The total heat generated was then equated to the total mechanical energy lost by the falling masses, after making the necessary corrections for (i) the terminal velocity of the masses on reaching the floor; (ii) friction in the systems of the falling masses; (iii) radiation from the calorimeter; (iv) elasticity of the strings,[1] and (v) the loss of energy by the sound vibrations given out by the apparatus. The magnitude of these corrections was determined by means of subsidiary experiments. Joule thus found that 772 ft.-lbs. at Manchester would, on being transformed into heat, raise the temperature of 1 lb. of water from 60° F. to 61° F.

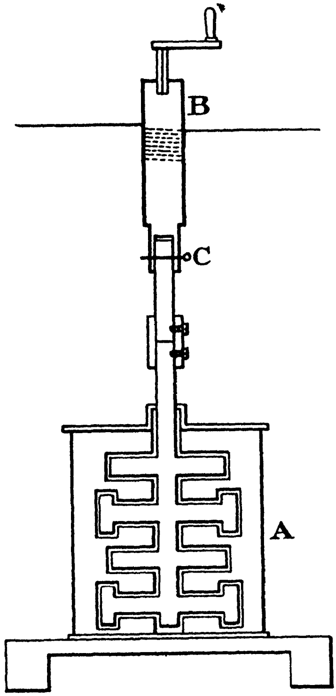

FIG. I.—Joule's Calorimeter.

In later determinations of the mechanical equivalent of heat Joule somewhat modified the details of the above method, the paddles being

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[1] The strings, being initially stretched, contracted when the masses reached the ground and thus produced a further rotation of the paddles.

rotated at a uniform rate by means of a handle, while the calorimeter was prevented from rotating by means of an applied couple. This couple was, of course, equal and opposite to that exerted by the paddles. Hence the total work transformed into heat = the moment of the applied couple (G) × 2π × n, where n = the number of complete revolutions.

For the work, w, done by the couple during a very small rotation, $\delta\theta$, is given by—

$$w = 2\mathrm{F}s = 2\mathrm{F}a\delta\theta = \mathrm{G}\,.\,\delta\theta \text{ (Fig. II.)}.$$

Therefore, the total work, W, done by the couple during n revolutions is given by—

$$\mathrm{W} = \int \mathrm{G}\,.\,d\theta, \text{ and, if the couple be } \textit{constant}\text{—}$$

$$\mathrm{W} = \mathrm{G}\int d\theta = \mathrm{G} \times 2\pi \times n.$$

The value finally obtained by Joule was that 772·5 ft.-lbs. at Manchester were equivalent to the heat required to raise the temperature of 1 lb. of water from 60° F. to 61° F. Expressed in C.G.S. units this becomes $4{\cdot}16 \times 10^7$ ergs per gm. of water per 1° C. at 15° C. Subsequent determinations of the mechanical equivalent of heat have been made by various investigators, with results in substantial agreement with the value obtained by Dr. Joule. A number of the more important of these determinations will now be briefly considered.

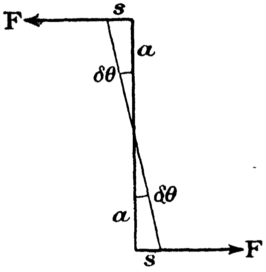

FIG. II.

4. Rowland's Investigation.—Professor Rowland of Baltimore repeated Joule's experiment on a larger scale, employing a steam engine as his source of mechanical energy, and obtaining a much greater rise in temperature during each determination than had been secured by Joule. The temperatures were read on a mercury thermometer which was standardised by comparison with an air thermometer.

Rowland found that the amount of mechanical energy which must be transformed in order to raise the temperature of 1 gm. of water 1° C. varied appreciably at different temperatures—indicating a variation in the specific heat of water with temperature—with a minimum value at 29° C. He confirmed this result by means of calorimetric determinations.

The value for the mechanical equivalent obtained by Rowland was $4{\cdot}19 \times 10^7$ ergs per gm. of water per 1° C. at 15° C.

5. The Investigation of Reynolds and Morby.—Reynolds and Morby, using 100 horse-power engine with a hydraulic brake, obtained a value of $4{\cdot}18 \times 10^7$ ergs per mean calorie. In their determinations ice-cold water was passed into the brake and the rate of flow so adjusted that the issuing water was not far short of the boiling-point. By measuring the rise in temperature and the quantity of water flowing through in a given time, the amount of heat generated could be calculated, and this was equated to the work done in that time.

6. Griffiths' Investigation.—Griffiths, in 1883, employed an electrical method of generating heat for the determination of the rate of exchange between mechanical energy and heat energy.

If the potential of two points in an electric circuit be V_1 and V_2 respectively, the work done in transferring unit quantity of electricity from one point to the other is equal to $V_1 - V_2$.

If W represents the work done when a quantity of electricity, Q, is transferred, we have the equation

$$V_1 - V_2 = \frac{W}{Q}.$$

$$\therefore W = (V_1 - V_2)Q.$$

Now, if the strength of a current C be constant, it is represented by the equation

$$C = \frac{Q}{t},$$

where Q is the quantity of electricity which traverses any section of the circuit in t seconds.

Hence—

$$W = (V_1 - V_2) \,.\, C \,.\, t.$$

Further, if the energy of an electric current is not utilised in performing mechanical work, or in chemical action within the circuit, it will appear as heat in the conductor.

$\therefore$ J.H. $= W = (V_1 - V_2) \,.\, C \,.\, t$, where J is the mechanical equivalent of heat. It should be noted that if the difference of potential be measured in volts, the current strength in ampères, and the time in seconds, then—since 1 volt $= 10^8$ C.G.S. electromagnetic units, and 1 amp. $= 10^{-1}$ C.G.S. electromagnetic units—W must be expressed in Joules; (1 Joule $= 10^7$ ergs).

Since in accordance with Ohm's Law, $V_1 - V_2 = C \,.\, R$, where R is the resistance of a conductor, $V_1 - V_2$ the difference of potential between its ends, and C the strength of the resultant current, we may write—

$$\text{J.H.} = W = (V_1 - V_2) \,.\, C \,.\, t = C^2 \,.\, R \,.\, t = \frac{(V_1 - V_2)^2}{R} \,.\, t.$$

If, as before, $V_1 - V_2$ be measured in volts, and C in amps., R must be measured in ohms; (1 ohm $= 10^9$ C.G.S. electromagnetic units).

In Griffiths' experiment a coil of resistance wire, attached to heavy copper leads, was immersed in water in a calorimeter. A steady current was passed through the coil, and the difference of potential between its ends was determined by comparison with standard Clark's cells. The resistance of the coil being known, it was only necessary to measure the heat developed in any given time to obtain J from the equation $J.H. = \frac{(V_1 - V_2)^2}{R} . t$.

Griffiths thus found $4{\cdot}2 \times 10^7$ ergs per gm. of water at 15° C. per 1° of the hydrogen scale.

It was observed that a small amount of electrolysis of the water in the calorimeter occurred, but the amount of energy so absorbed was found to be negligible provided that the resistance, R, of the immersed spiral and the potential difference, $V_1 - V_2$, between its ends were not too great. To obtain accordant results it was found necessary to keep the water in the calorimeter very thoroughly stirred, making due allowance for the heat developed by the stirring alone. The amount of heat so developed was ascertained in a separate investigation. Very special precautions were also taken to regulate the temperature, so that accurate correction could be made for the loss of heat by radiation during any experiment.

7. The Investigation of Schuster and Gannon.—Schuster and Gannon also employed an electrical method of heating, and determined the mechanical equivalent of heat by passing a current through a coil in a calorimeter, and using the relation $J.H. = (V_1 - V_2) . C . t$.

The difference of potential, $V_1 - V_2$, between the ends of the resistance coil was determined by comparison with standard Clark's cells, and the quantity $C . t$ was directly obtained—from the known electro-chemical equivalent of silver—by passing the current through a silver voltameter.

Schuster and Gannon's resulting value was $4{\cdot}19 \times 10^7$ ergs per gm. of water per 1° C. of the nitrogen thermometer at 15° C.

8. The Investigation of Callendar and Barnes.—More recently Callendar and Barnes have employed a modification of the electrical heating method. In their determinations water was allowed to flow steadily through a fine glass tube, and was heated by means of a platinum wire conveying an electric current. The water entered the tube at one constant temperature, and flowed out at another constant temperature, the difference in temperature being measured by means of a pair of differential platinum thermometers. By using a fine tube and employing a suitable rate of flow for the water it was found that no stirring was necessary. The heat generated in calories was obtained by multiplying the mass of water which passed through the tube by the difference in temperature of the water on entering and flowing out, and by the mean specific heat of water between these two temperatures. This product when multiplied by J, and divided by the time of flow in seconds, gave the rate of generation of heat in Joules per second, and this was equated to the electrical energy transformed in unit time, viz. $(V_1 - V_2)C$. The difference of potential, $V_1 - V_2$, between the ends of the resistance wire was determined in terms of a Clark cell by means of a potentiometer, which was also used to measure the current strength C, by observing the difference of potential on a standard resistance which was included in the circuit. The usual correction for the loss of heat by radiation was applied when measuring the total heat generated. The value of the mechanical equivalent of heat in Joules per calorie was thus obtained; expressed in ergs per gm. of water per 1° C. of the hydrogen thermometer, at 15° C., this value was found to be $4 \cdot 19 \times 10^7$.

It should be noted that the results of all the electrical methods depend upon the value assumed for the E.M.F. of the Clark cell.

9. Hirn's Investigation.—A determination involving the reverse process, viz.—the transformation of heat into work—has also been carried out by Hirn. From observations of the work done by a steam-engine, and the heat energy used up in performing it, he obtained a fair value for the mechanical equivalent of heat. The method is not susceptible, however, of any great accuracy.

10. Experimental Determination of the Mechanical Equivalent of Heat.—Two convenient methods by which the mechanical equivalent of heat may be rapidly estimated in the laboratory will now be described.

Experiment I.—Determination of the Mechanical Equivalent of Heat by the Fall of Mercury in a Tube.—Take the temperature of some mercury in a small beaker. About 50 c.cs. of mercury should be employed. Pour the mercury into a glass tube, about 1 metre in length, and 3 to 4 cms. internal diameter, one end of the tube being closed. Quickly cork up the other opening with a rubber cork, and invert the tube repeatedly, holding the tube vertically at each inversion, and resting its lower end on a table. The mercury will remain at the end of the tube while it is being rotated, but will fall as soon as the tube is held stationary in a vertical position. The rotation should be repeated forty or fifty times to secure an adequate rise in temperature. Pour out the mercury quickly into the beaker and again observe the temperature.

If m = the mass of mercury, s = the specific heat of mercury, and $\delta\theta$ = the rise in temperature, and if it be assumed that no heat has been lost, then

$$\text{Heat generated, H,} = m \times s \times \delta\theta \text{ calories.}$$

Also, if l = the vertical distance through which the centre of gravity of the mercury falls at each inversion of the tube, and n = the number of times the fall is repeated, then

Kinetic energy transformed, W, $= m \times g \times l \times n$ ergs.

Hence, the mechanical equivalent of heat, J, can now be obtained by employing the relation

$$W = J.H.$$
$$\therefore J = \frac{W}{H} = \frac{m \,.\, g \,.\, l \,.\, n}{m \,.\, s \,.\, \delta\theta} = \frac{g \,.\, l \,.\, n}{s \,.\, \delta\theta}.$$

It should be noted that l is less than the length between the end of the tube and the inner surface of the cork by an amount equal to the depth of the mercury when measured in the tube.

Although the value of J is independent of the mass, m, of the mercury, yet a moderately large quantity of mercury should be employed so that the heat used in warming the tube and beaker may be very small in comparison with that used in warming the mercury.

The determination described above, although possessing the advantage of simplicity, is not susceptible of any great accuracy.

A much more accurate method of determining the value of the mechanical equivalent is described in the following experiment:—

Experiment II.—Determination of the Mechanical Equivalent of Heat by means of Callendar's Apparatus.—A general view of Professor Callendar's apparatus is given in Fig. III. It comprises a thin cylindrical brass calorimeter, C, mounted so as to rotate about a horizontal axis, B, and containing a known weight of water. A mass, F, of several kilogrammes, is suspended by means of two parallel and highly flexible silk ribbons which pass round the curved surface of the calorimeter. The ends of the silk ribbons are connected to an ebonite cross-piece, to the centre of which another silk ribbon is also attached. The latter silk ribbon also passes round the curved surface of the calorimeter, lying between the other ribbons, the whole thus forming a silk friction belt which makes one and a half complete turns round the calorimeter. A framework, carrying a load, E, of a few hundred grammes, is fastened to the free end of the single silk ribbon, and this framework is also attached to a light spring balance, D, the upper end of the spring being secured to the rigid frame, P, of the apparatus. Any extension of the spring will thus act in opposition to the weight of the framework and its load.

On rotating the calorimeter at a moderate speed, by means of the electric motor, M, frictional forces are called into play between the calorimeter and the silk ribbons, and the direction of rotation is made such that these frictional forces tend to support the weight of the larger mass, F, attached to the two silk ribbons.

The weights are adjusted to suit approximately the friction of the belt, and the final adjustment is effected automatically by means of the spring balance. For if at any instant the tension in the silk belt were too great, and with it the frictional forces called into play, the effect would be to raise the heavier mass and lower the lighter mass, and this would result in more of the weight of lighter mass being supported by the spring balance, with a consequent slackening of the tension in the belt. A revolution counter, N, records the number of turns made by the calorimeter.

Let n be the number of revolutions of the calorimeter in a given experiment, m_1 and m_2 the larger and smaller masses (including their respective connecting hook and framework), m_3 the mean reading of the spring balance, and d the diameter of the calorimeter.

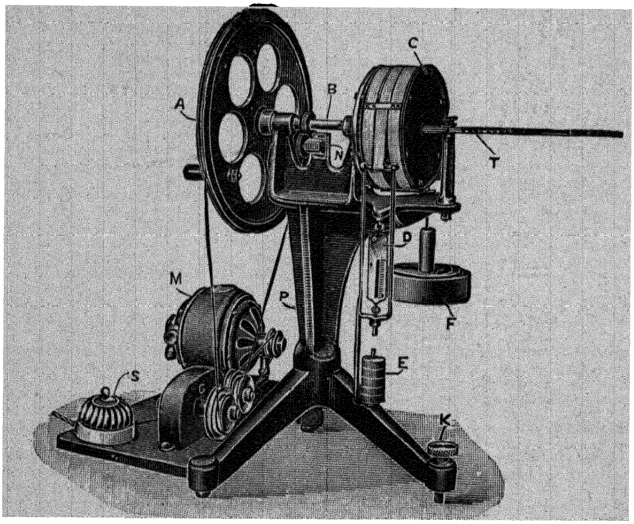

FIG. III.—Callendar's Apparatus.

Then, the mechanical energy, W, transformed into heat is given by the equation—

$$W = (m_1 - m_2 + m_3) \times g \times \pi d \times n.$$

The rise of temperature of the water in the calorimeter is read by means of a sensitive thermometer, T, inserted through a central opening, as shown in the figure, and bent so that its bulb lies near the curved periphery of the calorimeter. Since the thermometer is stationary, the rotation of the calorimeter keeps the water thoroughly stirred. The heat generated, H, is equal to the product of the mass of water plus the water equivalent of the brass calorimeter ($m + g$), the rise in temperature, $\delta\theta$, and the mean specific heat of water, s, between the initial and final temperatures.

Thus,
$$H = (m + g) \times \delta\theta \times s.$$
$$\therefore\ J = \frac{W}{H} = \frac{(m_1 - m_2 + m_3) \times g \times \pi d \times n}{(m + g) \times \delta\theta \times s}.$$

Loss of heat due to radiation and conduction can be eliminated by arranging that the initial temperature of the water in the calorimeter is as much below the room temperature as the final temperature is above it.

If the specific heat of water be treated as constant, a number of experiments may be carried out concurrently, the temperature indicated by the thermometer being read after every 100 or 200 revolutions of the calorimeter. It will be found that the rise in temperature for a given number of revolutions is approximately constant. Under these conditions, however, a correction for loss of heat must be applied to each experiment.

11. The First Law of Thermodynamics.—It is clear from the investigations which have been described that, when work is expended in the generation of heat, there is a constant ratio between the work transformed and the heat generated. The constancy of this ratio is known as the First Law of Thermodynamics.

The First Law of Thermodynamics may be expressed, algebraically, by means of the equation $W = J.H.$, which states that J units of work are equivalent to one unit of heat.

Taking the unit of work as 1 erg., and the unit of heat as that required to raise 1 gm. of water 1° C. of the hydrogen scale, at 15° C., J may be taken as having the value $4{\cdot}19 \times 10^7$.

It should be noted that it has been tacitly assumed that *all* the work expended was transformed into heat in the calorimeter, after making due allowance for the loss of mechanical energy in certain obvious ways, such as from the friction of pulleys, or friction wheels; the terminal velocity of falling masses; the radiation of sound waves. It is probable that other phenomena may also occur—such as the electrification of the two bodies rubbed together—but the constancy of the value found for J by different observers—using varying methods—may be taken to indicate that the quantity of work expended in the production of such phenomena is practically negligible.

12. The Principle of the Conservation of Energy.—All known forms of energy, other than kinetic energy and heat energy, can be measured on their transformation into one of these two latter forms—and there is sufficient evidence that the rate of transformation in each particular case is also constant. Thus we are led to regard the First Law of Thermodynamics as merely a particular case of a wider generalisation known as the Principle of the Conservation of Energy. This principle may be stated, formally, as follows:—

The total amount of energy in the universe is invariable throughout all its changing modes of manifestation.

When transformation of one form into some other form, or forms, occurs, such transformation always takes place according to rates of exchange which are quantitatively constant in each case.

13. The Identity of Energy.—It will be observed that the preceding statement of the principle of the conservation of energy involves an assumption as to the "Identity of Energy" throughout its various manifestations. It is usual to make this metaphysical assumption, and to regard the exchange of one form of energy for another not merely as a "*replacement,*" but as a true "*transformation*" of one identical thing—*energy*—which only differs in the manner in which it affects our senses.

CHAPTER II.

THE KINETIC THEORY OF MATTER, AND ITS APPLICATION TO THE GASEOUS STATE.

14. The Kinetic Theory of Matter.—Our knowledge of the energy transactions in mechanical systems, where only changes of kinetic and potential energy need be considered, is, in general, more complete than that relating to systems where the transformation of other forms of energy is involved.

Consequently. the assumption as to the "identity of energy" throughout its various modes of manifestation naturally leads to an attempt to express the various forms of energy in mechanical terms—and, further, since the material universe is only made known to our senses through energy transactions, we may logically attempt an explanation of the varied properties of matter from a mechanical standpoint.

Such an attempt is, in fact, the basis of the Kinetic Theory of Matter, and, in applying this theory, we adopt the hypothesis that all matter is possessed of an atomic or molecular structure. This idea of the atomic structure of matter is to be found in the writings of the Greek philosophers, and furnishes a simple explanation of such varied phenomena as, for example, compression, diffusion, evaporation, and solution: phenomena which are incapable of explanation if it be assumed that matter is continuous in nature,—i.e. without "structure"—and therefore susceptible, theoretically at any rate, of infinite division without arriving at any ultimate constituent particles.

The atomic hypothesis was revised by John Dalton at the commencement of the nineteenth century, and utilised by him to explain the quantitative laws of chemical combination. The hypothesis, as presented by Dalton, may be expressed in the following form:—

All compound bodies consist of atoms of elements united with each other. An atom is an excessively small indivisible particle, and the atom of each element has its own definite mass.

This hypothesis was further developed by Amadeo Avogadro, who differentiated between the smallest ultimate particle of an element capable of entering into chemical combination, and the smallest particle of an element or a compound which existed independently in a free state: the former he termed an atom, and the latter a molecule. In .the case of a compound body the molecule must consist of an aggregate of two or more atoms. The molecule of an elementary substance may consist of a single atom, or of two or more such atoms grouped together.

Thus, a given mass of an element, or a compound, contains a definite number of similar molecules, and since work is necessary both to effect the chemical decomposition of the molecules and also to alter the distance between them—(for work is, in general, necessary to alter the volume of any substance)—it follows that forces exist both between the atoms in the molecule and between the molecules themselves.

Matter may therefore be regarded as possessing a store of energy in virtue of the kinetic energy possessed by atoms and molecules in motion, and the potential energy possessed by atoms with regard to each other, and molecules with regard to each other.

Recent researches in radioactivity have further demonstrated that the elementary atom is no longer to be regarded as the ultimate indivisible particle of matter, but that it is, itself, a store-house of the kinetic and potential energies of the electrons of which it is composed. Theories, such as Langmuir's, have also been developed indicating that the various properties of different substances are merely functions of the arrangements of the electrons within the atoms and molecules.

The kinetic theory can be most fully developed when applied to matter in the gaseous state, for whereas in solids and liquids the molecules are close together and exert considerable cohesive forces—as is shown, for example, by the elasticity of solids, and the resistance offered by liquids to compression—the molecules in a gas are, on the average, much farther apart, and, consequently, exhibit an almost entire absence of cohesion.[1]

It will be remembered that, as already explained, the validity of Mayer's method of calculating the mechanical equivalent of heat depends upon the fact that the magnitude of the cohesive forces in a gas at the ordinary density is extremely small.

Now, a gas may be regarded as composed of an enormous number of minute molecules, and the rapidity of gaseous diffusion shows that these molecules must be in a state of very rapid motion. Consequently, frequent collisions will occur between the molecules—but, in a gas under average conditions of temperature and pressure, the time occupied by these collisions will only bear a very small ratio to the time during which the molecules are moving freely about, as, otherwise, the gas would exhibit marked cohesion. The fact that only a small time is occupied in the collisions, although the molecules are

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[1] As an example of the increased distance between the molecules in the case of a vapour it may be mentioned that 1 c.c. of water at 100° C. forms, approximately, 1700 c.cs. of steam at 100° C. and 76 cms. The molecules of the steam are, therefore, about 12 times as far apart as those of the water The fact that water is an "associated" liquid has here been neglected.

very numerous, indicates that the molecules are very small compared with their distance apart.

15. The Pressure Exerted by a Perfect Gas.—In order to make an elementary mathematical analysis of the problem, we may consider an ideal or " Perfect " gas as composed of an enormous number of identical spherical molecules, negligibly small compared with their distance apart—perfectly smooth and elastic, and moving about with extreme rapidity. The collisions of these molecules instantly change their velocities and directions of motion, the time occupied by such collisions thus being infinitely small. Consequently a perfect gas exhibits no cohesion.

The pressure exerted by such a gas on the walls of any containing vessel is due to the momentum imparted by the molecules when they collide with the walls.

Since we have an enormous number of very minute molecules moving about extremely rapidly in all directions, the average momentum imparted in unit time to any sensible area of the wall may be regarded as constant, and the pressure exerted will, therefore, be uniform. In such a perfect gas the momentum imparted per second to unit area of the wall must vary as the number of molecules colliding per second, and, consequently, varies directly as the gaseous density. The pressure of a perfect gas will thus be proportional to its density, and, therefore, reciprocally proportional to its volume.

Consider a small hollow cube, the interior of which measures l cms. in each direction, and let this cube be filled with the ideal gas. Consider a molecule of the ideal gas moving with velocity C in any direction, and striking against one of the interior faces of the cube. We can resolve the velocity C into three components along the axes of the cube—i.e. into components which are respectively perpendicular to the three opposite pairs of faces of the cube.

Let these three components be u, v, and w respectively.

Then $$C^2 = u^2 + v^2 + w^2.$$

Now, we cannot assume that the velocity of any particular molecule remains constant, but since—if the gas and the faces of the cube are at the same temperature—the average energy of the gas is unchanged by the impacts between its molecules and the cube, we are justified in assuming that, *on the average*, the velocities of the molecules are unchanged by such impacts. This assumption is confirmed by the fact that, in a real gas the pressure is found to remain constant. We may, therefore, suppose that when a molecule strikes against one of the interior faces of the cube, its component of velocity perpendicular to that face is completely reversed, the other two components being unaffected.

If the mass of a molecule of the ideal gas be m, and its component of velocity perpendicular to a pair of opposite faces of the cube be u, then its corresponding component of momentum is mu. The momentum given up by the molecule on striking against one of these faces and rebounding will, therefore, be $2mu$, since the component of velocity perpendicular to the face has changed from u to $-u$. The component of velocity, u, thus gives rise to a pressure on one pair of opposite faces of the cube. Since the interior of the cube measures, as already stated, l cms. in each direction, there will be $\frac{u}{2l}$ impacts per second at *each* of these opposite faces—i.e. $\frac{u}{l}$ impacts per second on the pair of faces.[1]

Thus the momentum given up in unit time to this pair of faces $= 2mu \times \frac{u}{l} = \frac{2mu^2}{l}$, and this is the same as the force exerted on this pair of faces, for—by Newton's Second Law of Motion—*Force* is measured by the change of momentum produced per second.

Similarly, for the other two pairs of opposite faces of the cube, the force exerted is equal to $2\frac{mv^2}{l}$ and $2\frac{mw^2}{l}$, respectively.

If there be n molecules of the ideal gas inside the cube, the total force exerted

$$= 2\frac{m}{l}(u_1^2 + u_2^2 + \ldots + u_n^2) + 2\frac{m}{l}(v_1^2 + v_2^2 + \ldots + v_n^2)$$
$$+ 2\frac{m}{l}(w_1^2 + w_2^2 + \ldots + w_n^2).$$

Now, the force exerted on unit area is the same as pressure, and since in the small cube that we are investigating the molecules are moving freely in all directions, we may conclude, from considerations of symmetry, that the force exerted on each face of the cube is equal, and hence that the pressure on all the faces is equal. This conclusion is, moreover, confirmed by the experimental evidence that the pressure exerted by a real gas on the walls of a small containing vessel is uniform.

Therefore, the pressure, P, exerted by the ideal gas—i e. the total force exerted by all the molecules on unit area—is given by—

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[1] Although owing to collisions no actual molecule can be considered to move backwards and forwards uninterruptedly between opposite faces, yet the effect produced will be the same as if, in fact, no collisions occurred. For since the molecules of the ideal gas are of equal mass, and are perfectly smooth and elastic, and since the collisions of these molecules instantly change their velocities and directions of motion, it follows that a change in the velocity of a molecule, due to a collision, must instantly result in an equal and opposite change in the velocity of the molecule with which it has collided—the latter molecule acquiring the velocity lost by the former, and moving on in its place. Moreover, since the dimensions of the molecules themselves may be treated as negligible, the distance to be travelled between successive impacts at opposite faces of the cube will not be affected by molecular collisions.

$$P=\frac{2\frac{m}{l}\{(u_1^2+u_2^2+\ldots+u_n^2)+(v_1^2+v_2^2+\ldots+v_n^2)+(w_1^2+w_2^2+\ldots+w_n^2)\}}{6l^2}$$

$$=\frac{2\frac{m}{l}\{(u_1^2+v_1^2+w_1^2)+(u_2^2+v_2^2+w_2^2)+\ldots+(u_n^2+v_n^2+w_n^2)\}}{6l^2}$$

$$=\frac{2\frac{m}{l}\{C_1^2+C_2^2+\ldots+C_n^2\}}{6l^2}.$$

Let $n.\bar{C}^2 = C_1^2 + C_2^2 + \ldots + C_n^2.$

$$\therefore P = \frac{2mn\bar{C}^2}{6l^3},$$

$$= \frac{1}{3}\cdot\frac{mn\bar{C}^2}{V},$$

where V = the volume occupied by the ideal gas.

$$\therefore P.V. = \tfrac{1}{3}.m.n.\bar{C}^2.$$

Since $\bar{C}^2 = \frac{C_1^2 + C_2^2 + \ldots + C_n^2}{n}$, it is the mean of the squares of the velocities of the molecules. It must be noted that $\sqrt{\bar{C}^2}$, i.e. $\bar{C}$ is *not* the average, or mean molecular velocity, but the square root of the mean of the squares of the velocities. $\bar{C}$ is termed "the velocity of mean square," or "the root mean square velocity."

We have already seen that, if the ideal gas and the faces of the cube are at the same temperature, the average energy of the gas is unchanged by the impacts between its molecules and the cube. Further, the ideal gas exhibits no cohesion, and all its molecules thus possess the potential energy of complete separation from one another. Consequently a mere change in volume, when no external work is done, does not produce any change in the kinetic energy—and, therefore, none in the temperature—of the gas, since no work is done against, or by, internal molecular cohesive forces.[1]

Since, therefore, the ideal gas exhibits no cohesive forces, the total kinetic energy possessed by the molecules in virtue of their translatory motions through space must remain constant as long as the temperature is constant. Now, the total kinetic energy possessed by all the molecules in the small cube

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[1] In the case of a real gas, the fact that mere expansion at the ordinary density, without doing external work, only produces a very small change in temperature has already been used to show that practically no work is done against internal forces acting between the molecules.

$$\begin{aligned} &= \tfrac{1}{2}mC_1^2 + \tfrac{1}{2}mC_2^2 + \ldots + \tfrac{1}{2}mC_n^2, \\ &= \tfrac{1}{2}m(C_1^2 + C_2^2 + \ldots + C_n^2), \\ &= \tfrac{1}{2}m \,.\, n \,.\, \overline{C}^2. \end{aligned}$$

The average kinetic energy possessed by a single molecule

$$= \tfrac{1}{2}\, m \,.\, \overline{C}^2.$$

Thus $\overline{C}^2$ is proportional to the kinetic energy possessed by the molecules, and is therefore constant if the temperature is constant.

Consider, now, the equation $P.V. = \frac{1}{3} \,.\, m \,.\, n \,.\, \overline{C}^2$.

All the terms on the right-hand side are constant when the temperature is constant.

$\therefore$ P.V. = constant, when the temperature is constant.

This relationship between the pressure and the volume of a given mass of an ideal gas, at constant temperature, is in agreement with the experimental results obtained by R. Boyle in the case of actual gases subjected to moderate degrees of pressure, and is usually called Boyle's Law.[1]

16. The Temperature of a Gas, and its relation to the Molecular Velocity.—Let us next consider the relation between the temperature of a gas and the mean of the squares of the velocities of its molecules.

When temperatures are measured by means of a gas thermometer, we have the equation $P.V. = R \,.\, \theta$ for the isothermals of a gas which obeys Boyle's Law and Charles' Law—R being a constant, and θ the absolute temperature of the gas.

Thus, $P.V. = R \,.\, \theta = \frac{1}{3} \,.\, m \,.\, n \,.\, \overline{C}^2$, the gas being considered as perfect.

$$\therefore \theta \propto \overline{C}^2.$$

Hence the absolute temperature of such a gas is proportional to the mean of the squares of the velocities of its molecules, and so is proportional to the energy of translation of its molecules. Consequently the absolute zero of temperature on a gas thermometer must correspond to the condition when the molecules of the gas have lost all their kinetic energy and have all come to rest.

If we imagine the gas to be at the absolute zero of temperature, and we add heat, then, since in a perfect gas internal cohesive forces are absent, it follows that any addition of heat must result in a corresponding gain of kinetic energy by the molecules, provided no external work be done by the gas. Thus the addition of equal quantities of heat will produce equal increments of kinetic energy, i.e. equal increments in the value of $\overline{C}^2$, and consequently, since $P.V. = \frac{1}{3} \,.\, m \,.\, n \,.\, \overline{C}^2$,

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[1] We have considered merely the case of a small cube—but the argument can be easily extended to any small irregularly shaped vessel by considering the latter to be built up of a very large number of smaller cubes. The pressures on the common sides of the cubes will then be in equilibrium.

will produce equal increases of pressure if the volume be constant, and equal increases of volume if the pressure be constant. The addition of equal quantities of heat will thus produce equal rises in the absolute temperature of the gas as measured on a gas thermometer.

It must be noted that this relation between the *temperature* and the quantity of heat added only holds good for gases which obey Charles' Law, i.e. for gases whose coefficients of increase of pressure at constant volume—or whose coefficients of expansion at constant pressure—are all equal, and of the approximate value 0·00367. For it is only on account of this equality that we can make the same absolute scale of temperature applicable to them all. If we take two gases with different coefficients of increase of pressure, and heat them, while their volumes are kept constant, it is obvious that at any higher temperature, which is the same for each, the two gases will be exerting different pressures, and must, therefore, have received unequal quantities of heat. However, we shall see later, from other considerations, that all perfect gases *must* have the same coefficient of increase of pressure at constant volume—or coefficient of expansion at constant pressure. In other words, that they must obey Charles' Law.

17. Equipartition of Energy.—Now, we saw that the absolute temperature of the gas under consideration in the previous paragraph was proportional to the mean of the squares of the velocities of its molecules, and, therefore, to the energy of translation of its molecules. We also saw (§ 15) that the *average* kinetic energy possessed by each molecule of the gas was equal to $\frac{1}{2}m\overline{C}^2$. Let us consider the case of two different gases at the same absolute temperature. In accordance with the theorem of the equipartition of energy in a system of molecules of different masses which was enunciated by Waterston in 1821, we may state that—"In mixed media, the mean square molecular velocity is inversely proportional to the specific weight of the molecule." This theorem was enunciated independently by Maxwell, who also arrived at the conclusion that the average kinetic energy of a single molecule is the same for molecules of different gases when the gases are at the same temperature. Maxwell's conclusion has been confirmed by the theoretical investigations of Professors Bryan and Boltzmann and Professor J. J. Thomson.

If, therefore, m_1 and m_2 represent the masses of the molecules of the two different gases, and if $\overline{C}_1^2$ and $\overline{C}_2^2$ be, respectively, the mean of the squares of the velocities of these molecules, we may state, in accordance with Maxwell's conclusion, that—

$$\frac{1}{2}m_1\overline{C}_1^2 = \frac{1}{2}m_2\overline{C}_2^2,$$

since, as already premised, the two gases are at the same absolute temperature.

If, also, we consider equal volumes, V, of the two different gases, at equal pressure, P, we have—

$$P.V. = \tfrac{1}{3} m_1 n_1 \bar{C}_1^2 = \tfrac{1}{3} m_2 n_2 \bar{C}_2^2,$$

where n_1 and n_2 are the numbers of molecules of the respective gases in the volume V, the gases being considered perfect.

Combining these equations we have—

$$n_1 = n_2.$$

Thus, equal volumes of different gases at the same temperature and pressure contain the same number of molecules. This generalization is known as Avogadro's Law.

If ρ_1 and ρ_2 be the densities of the respective gases, then—

$$\rho_1 = \frac{m_1 n_1}{V} \text{ and } \rho_2 = \frac{m_2 n_2}{V}.$$

$$\therefore \frac{\rho_1}{\rho_2} = \frac{m_1}{m_2}.$$

Hence, at the same temperature and pressure, the densities of different gases are proportional to their molecular masses: the latter are commonly referred to as molecular weights.

It has been seen how Avogadro's Law of the equality of the molecular density of two gases at the same temperature and pressure can be deduced, in the case of a perfect gas, from Maxwell's conclusion that the average kinetic energy of a single molecule is the same for different gases at the same temperature. Consequently, the total kinetic energy possessed by all the molecules in a volume V is the same for two different gases at the same temperature and pressure, so that we have—

$$\text{Total kinetic energy} = \tfrac{1}{2} m_1 n_1 \bar{C}_1^2 = \tfrac{1}{2} m_2 n_2 \bar{C}_2^2.$$

If, therefore, we take equal volumes of two different gases at the same temperature and pressure, and add to each of them an equal quantity of heat, then, provided that internal cohesive forces are absent and that no external work is done, each gas will gain an equal amount of kinetic energy, which will give rise to equal increases of pressure if the volumes be kept constant.

But since equal quantities of kinetic energy have been gained, the total kinetic energy of each gas has been increased an equal amount, and the average kinetic energy of a single molecule is again equal for the different gases. Therefore, according to Maxwell, the two gases must have been raised to the same temperature by equal additions of heat. Thus we arrive at the conclusion that, for perfect gases, equal rises in temperature will produce equal increases in pressure when the volume is kept unchanged, i.e. all perfect gases have the same coefficient of increase of pressure, at constant volume, with rise in temperature. Similarly, for perfect gases, the coefficient of expansion at constant pressure is the same. The preceding argument may be expressed in a mathematical form as follows :—

Consider equal volumes, V, of two different gases at the same centigrade temperature, $t°$ C., and the same pressure, P. Let m_1 and m_2 represent the molecular masses of the two different gases, and n_1 and n_2 the number of molecules of each in the volume V, and let $\overline{C_1}^2$ and $\overline{C_2}^2$ be the respective means of the squares of the velocities of the molecules. Then, according to Maxwell—

$$\tfrac{1}{2}m_1\overline{C_1}^2 = \tfrac{1}{2}m_2\overline{C_2}^2.$$

Also $$\text{P.V.} = \tfrac{1}{3}m_1n_1\overline{C_1}^2 = \tfrac{1}{3}m_2n_2\overline{C_2}^2,$$

if the gases be considered perfect.

$$\therefore\ n_1 = n_2.$$

Let equal quantities of heat be added to each gas, the volumes remaining unchanged.

Then $\tfrac{1}{2}m_1\overline{\mathfrak{C}_1}^2 = \tfrac{1}{2}m_2\overline{\mathfrak{C}_2}^2$ where $\overline{\mathfrak{C}_1}^2$ and $\overline{\mathfrak{C}_2}^2$ are the new means of the squares of the velocities of the molecules.

Therefore, according to Maxwell, the two gases have both reached the same temperature, $t'°$ C., since the average kinetic energy of a single molecule of each gas is the same.

Also $$\tfrac{1}{3}m_1n_1\overline{\mathfrak{C}_1}^2 = \tfrac{1}{3}m_2n_2\overline{\mathfrak{C}_2}^2, \text{ since } n_1 = n_2.$$

Then, if P'_1 and P'_2 be the new pressures of the two gases, we have, since the volumes have been kept unchanged,

$$P'_1.V. = P'_2.V.$$
$$\therefore\ P'_1. = P'_2 = P'.$$

Thus the two gases have the same coefficient of increase of pressure at constant volume, and, applying Boyle's Law, it follows that they must also have the same coefficient of expansion at constant pressure. This agrees with the experimental results obtained by Charles, Gay-Lussac, Regnault, and others, for the so-called "permanent gases."

Let $p\,.\,v = K$ be the equation to the isothermal of a perfect gas at 0° C., K being a constant. Consider a mass M of such a perfect gas, occupying a volume v_0 at pressure p_0 and temperature 0° C. Let the gas be heated, at constant volume, to $t°$ C., and let the pressure consequently rise to P_t. Then, if β be the coefficient of increase of pressure at constant volume, we have—

$$\frac{P_t - p_0}{p_0 \cdot t} = \beta.$$
$$\therefore P_t = p_0(1 + \beta t).$$
$$\therefore P_t \cdot v_0 = p_0 v_0 \cdot (1 + \beta t)$$
$$= K \cdot (1 + \beta t).$$

If, therefore, P and V represent any corresponding pressure and volume of this mass of the gas at the higher temperature $t°$ C., we have—

$$P.V. = P_t \cdot v_0 = K \cdot (1 + \beta t).$$

Taking the experimental value of β found for the so-called "permanent gases" as approximately 0·00366, or $\frac{1}{273}$, we have—

$$P.V. = K\left(1 + \frac{t}{273}\right),$$
$$= \frac{K}{273}(273 + t),$$
$$= R(273 + t),$$

R being a constant and equal to $\frac{K}{273}$.

Now 273 + t is the absolute temperature of the gas as measured on a gas thermometer.

Let $273 + t = \theta$.

Then $$P.V. = R \cdot \theta.$$

This is the general equation to the isothermal of a perfect gas at an absolute temperature θ.

We may write this equation in the following form :—

$$P = \frac{R \cdot \theta}{V} = \frac{R \cdot \theta \cdot \rho}{M}, \text{ where } \rho \text{ is the density.}$$

Consequently, if the temperature of a given mass of gas be constant, the pressure varies as the density, and if the density be constant, the pressure varies as the temperature. The combined laws of Boyle and Charles are thus contained in the equation P.V. = R . θ.

18. The Numerical Value of the Molecular Velocity of a Gas.—Let us next calculate the numerical value of the velocity of mean square of the molecules of a particular gas at any fixed temperature. Take, for example, the case of oxygen at a temperature of 0° C.

Then, since $$P.V. = \tfrac{1}{3}m \cdot n \cdot \overline{C}^2,$$
$$\overline{C}^2 = \frac{3 \cdot P \cdot V}{m \cdot n}.$$
$$\therefore \overline{C} = \sqrt{\frac{3 \cdot P \cdot V}{m \cdot n}}.$$

Now 1 gm. of oxygen at 0° C. and 76 cms. pressure occupies 699·4 c.cs. Therefore, substituting in the last equation, we have—

$$\bar{C} = \sqrt{\frac{3 \times 76 \times 13{\cdot}596 \times 981 \times 699{\cdot}4}{1}},$$

the pressure, of course, being expressed in dynes per sq. cm.

Whence $\bar{C} = 4{\cdot}61 \times 10^4$ cms./sec., i.e. about one-third of a mile per second.

It must again be noted that $\bar{C}$ is *not* the mean molecular velocity. It can be shown that the mean molecular velocity, Ω, is approximately $= {\cdot}921 \times \bar{C}$, and, therefore, in the case of oxygen at 0° C., has the approximate value $4{\cdot}25 \times 10^4$ cms./sec.

19. Graham's Law.—For a perfect gas $P.V. = \frac{1}{3}m\,.\,n\,.\,\bar{C}^2$, and $\frac{m\,.\,n}{V} = \rho$, where ρ is the density of the gas.

$$\therefore\ P = \tfrac{1}{3}\,.\,\rho\,.\,\bar{C}^2$$

$$\text{whence } \bar{C} = \sqrt{\frac{3\,.\,P}{\rho}}.$$

Also we have seen previously that $\bar{C} \propto \sqrt{\theta}$, where θ is the absolute temperature of the gas. Thus $\bar{C}$ is directly proportional to the square root of the absolute temperature of a gas, and, for different gases at the same pressure, the respective velocities of mean square of the molecules are inversely proportional to the square roots of the gaseous densities. If $\bar{C}_1$ and $\bar{C}_2$ be the respective velocities of mean square of the molecules of two different gases, then since, if the two gases be at the same temperature and pressure, their densities are proportional to their molecular masses, or

$$\frac{\rho_1}{\rho_2} = \frac{m_1}{m_2},$$

we have the relation—

$$\frac{\bar{C}_1}{\bar{C}_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{m_2}{m_1}}.$$

Hence at a given temperature, the velocities of mean square of the molecules of two different gases are inversely proportional to the square roots of the molecular masses. It will be noted that the equation

$$\frac{\bar{C}_1}{\bar{C}_2} = \sqrt{\frac{m_2}{m_1}}$$

is independent of the pressure of either gas.

This relationship could have been deduced at once from Maxwell's theorem that $\frac{1}{2}m_1\overline{C}_1^2 = \frac{1}{2}m_2\overline{C}_2^2$ when two gases are at the same temperature. If we take the mean molecular velocity, Ω, to be equal to $\cdot 921 \times \overline{C}$, i.e. equal to $K \times \overline{C}$, where K is a constant, then this same relationship will apply to it as well as to $\overline{C}$. This agrees with the experimental results obtained by Graham relative to the diffusion of real gases through fine pores, such as occur in biscuit-ware. For, provided the pores are sufficiently fine, the molecules will pass through without colliding with other molecules, and thus the rate at which the molecules pass through the porous partition will be proportional to the mean molecular velocity, and, consequently, will vary directly as the square root of the absolute temperature, and inversely as the square root of the molecular mass of the particular gas. If, then, the temperature be kept constant, different gases will pass through such a porous partition with velocities which vary inversely as the square roots of their respective molecular masses—and this was the conclusion reached experimentally by Graham.[1]

20. Thermal Transpiration.—Consider, next, the case of a vessel divided into two portions by means of a porous partition, and filled with a given gas. Let the pressure of the gas be the same on each side of the partition, but let the absolute temperatures on the two sides be maintained at θ_1 and θ_2 respectively where θ is greater than θ_2.

Now $\overline{C}_{\theta 1} = \sqrt{\frac{3P}{\rho_{\theta 1}}}$, and $\overline{C}_{\theta 2} = \sqrt{\frac{3P}{\rho_{\theta 2}}}$, the suffix indicating the particular temperature to which $\overline{C}$ and ρ relate.

$$\therefore \frac{\overline{C}_{\theta 1}}{\overline{C}_{\theta 2}} = \sqrt{\frac{\rho_{\theta 2}}{\rho_{\theta 1}}}.$$

Also
$$\frac{\overline{C}_{\theta 1}}{\overline{C}_{\theta 2}} = \sqrt{\frac{\theta_1}{\theta_2}}.$$

Therefore, since the mass of gas passing through a porous partition, in any given time, is proportional to the product of the velocity and the density, we have the following relation between the masses, $M_{\theta 1}$ and $M_{\theta 2}$, of the gas flowing across the partition from the hot side to the cold side, and vice versâ, in the same time:—

$$\frac{M_{\theta 1}}{M_{\theta 2}} = \frac{\overline{C}_{\theta 1} \cdot \rho_{\theta 1}}{\overline{C}_{\theta 2} \cdot \rho_{\theta 2}} = \frac{\overline{C}_{\theta 2}}{\overline{C}_{\theta 1}} = \sqrt{\frac{\theta_2}{\theta_1}}.$$

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[1] The rate or velocity with which a gas passes through a porous partition must be carefully distinguished from the number of molecules—and hence the mass of the gas—passing in a given time, the latter being proportional to the *product* of the *velocity* and the *density*.

Thus, $M_{\theta_1} < M_{\theta_2}$—for $\theta_1 > \theta_2$,—and consequently there will be a flow of gas on the whole across the partition from the cold side to the hot, and the pressure of the gas on the latter side will rise. This phenomenon has been realized experimentally, and is called *Thermal Transpiration.*

Equilibrium will be established when $M_{\theta_1} = M_{\theta_2}$, i.e. when—

$$\bar{C}_{\theta_1} \cdot \rho_{\theta_1} = \bar{C}_{\theta_2} \cdot \rho_{\theta_2},$$

or, when $$\sqrt{\frac{3 \,.\, P_{\theta_1} \cdot \rho_{\theta_1}{}^2}{\rho_{\theta_1}}} = \sqrt{\frac{3 \,.\, P_{\theta_2} \cdot \rho_{\theta_2}{}^2}{\rho_{\theta_2}}},$$

or, when $$P_{\theta_1} \cdot \rho_{\theta_1} = P_{\theta_2} \cdot \rho_{\theta_2}.$$

Since $$\frac{P_{\theta_1}}{P_{\theta_2}} = \frac{\bar{C}_{\theta_1}{}^2 \cdot \rho_{\theta_1}}{\bar{C}_{\theta_2}{}^2 \cdot \rho_{\theta_2}} = \frac{\theta_1 \cdot \rho_{\theta_1}}{\theta_2 \cdot \rho_{\theta_2}},$$

equilibrium will be attained when

$$\frac{P_{\theta_1}}{P_{\theta_2}} = \frac{\theta_1 \cdot \rho_{\theta_1}}{\theta_2 \cdot \rho_{\theta_2}} = \frac{\theta_1 \,.\, P_{\theta_2}}{\theta_2 \,.\, P_{\theta_1}};$$

i.e. when $$\frac{P_{\theta_1}}{P_{\theta_2}} = \sqrt{\frac{\theta_1}{\theta_2}}.$$

A condition of equilibrium is thus reached when the pressures on the two sides vary directly as the square roots of the absolute temperatures.

CHAPTER III.

ISOTHERMAL AND ADIABATIC TRANSFORMATIONS, AND THE SPECIFIC HEATS OF GASES.

21. The Specific Heats of Gases.—The preceding investigation of the behaviour of a perfect gas has shown that—

$$P.V. = \tfrac{1}{3} . m . n . \overline{C}^2 = R . \theta,$$

or

$$P = \tfrac{1}{3} . \rho . \overline{C}^2 = \frac{R . \theta . \rho}{M},$$

where ρ is the density, and M the mass of the gas.

If we consider unit mass of the gas, we have—

$$P = \tfrac{1}{3} . \rho . \overline{C}^2 = R . \theta . \rho,$$

or

$$\frac{P}{\rho} = \tfrac{1}{3} . \overline{C}^2 = R . \theta.$$

Let K_m be the kinetic energy per unit mass.

Then

$$K_m = \tfrac{1}{2} . \overline{C}^2 = \frac{3P}{2\rho} = \tfrac{3}{2} . R . \theta.$$

There is, of course, no potential energy arising from intermolecular forces—as the latter are absent in a perfect gas—and any potential energy which may be due to external influences, such as gravitation, may be neglected. There is thus no *intrinsic* potential energy.

Hence K_m is the total intrinsic energy per unit mass.

If K_V be the kinetic energy (and, consequently, the total intrinsic energy) per unit volume, then—

$$K_V = \tfrac{1}{2}\rho\overline{C}^2 = \frac{3P}{2} = \tfrac{3}{2} . R . \theta . \rho.$$

In the following investigation we shall, unless otherwise stated, deal with *unit mass* of the gas, and we shall assume that all quantities of heat are expressed in mechanical units to avoid the use in our equations of the Mechanical Equivalent, J.

Now we have seen that the total intrinsic energy per unit mass is given by the relation

$$K_m = \tfrac{3}{2} . R . \theta,$$

and, consequently, is directly proportional to the absolute temperature.

Suppose a change of energy occur, merely due to the admission of heat, no external work being performed. In this case the volume must be kept constant, or the gas would expand and do external work.

Now, in consequence of the admission of heat, the temperature of the gas will rise, and the amount of heat corresponding to unit mass and unit rise in temperature is the specific heat at constant volume. Therefore, if H units of heat be added, we have—

$$H = C_V(\theta_2 - \theta_1),$$

where C_V is the specific heat of the gas at constant volume.

But, since the absolute temperature has risen from θ_1 to θ_2, the kinetic energy per unit mass, K_m, has increased from $\frac{3}{2} . R . \theta_1$ to $\frac{3}{2} . R . \theta_2$, i.e. by an amount equal to $\frac{3}{2}R(\theta_2 - \theta_1)$.

Hence it follows from the Principle of the Conservation of Energy that—

$$H = C_V(\theta_2 - \theta_1) = \tfrac{3}{2}R(\theta_2 - \theta_1).$$
$$\therefore \underline{C_V = \tfrac{3}{2}R}, \text{ i.e. it is constant.}$$

Let us next consider the more general case when external work is performed.

Let U = the internal or intrinsic energy of unit mass of the gas,
Q = the quantity of heat added (expressed in mechanical units),
and W = the work done by the gas.

Then, if energy, in the form of heat, be added, we know from the Principle of the Conservation of Energy that—

$$\delta U = \delta Q - \delta W,$$

employing the usual notation to represent the corresponding small changes in the quantities U, Q, and W,

$$\text{i.e.} \quad \delta Q = \delta U + \delta W,$$
$$= C_V . \delta\theta + P . \delta V.$$

For if we imagine, for simplicity, that the gas, at pressure P, is enclosed in a cylinder of cross-section A, and that, on expansion, it pushes up a frictionless piston through a small distance δh (Fig. IV.), then—

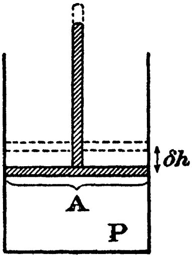

FIG. IV.

The work done, δW = Force × Displacement,
$= P . A . \delta h,$
$= P . \delta V$, where δV is the small change in volume.

The equation $\delta Q = C_V . \delta\theta + P . \delta V$ will be only *necessarily* true when the change in volume, δV, is infinitely small, for it is only in that case that P can be *assumed* to be constant throughout the expansion.

Since
$$P.V. = R . \theta.$$
$$\therefore\ \delta(P.V.) = R . \delta\theta.$$

$\therefore\ P . \delta V + V . \delta P = R . \delta\theta$, neglecting the term $\theta P . \delta V$,—which occurs on the left-hand side of the equation,—as negligibly small.

Hence $P . \delta V = R . \delta\theta - V . \delta P$.

$$\begin{aligned}\therefore\ \delta Q &= C_V . \delta\theta + R . \delta\theta - V . \delta P,\\ &= (C_V + R) . \delta\theta - V . \delta P,\\ &= C_p . \delta\theta - V . \delta P,\end{aligned}$$
where C_p is a constant, and is equal to $C_V + R$.

Let us take the case when there is no change in pressure, and when the rise in temperature of the gas is unity, i.e.—

when
$$\delta P = 0, \text{ and } \delta\theta = 1.$$
Then
$$\delta Q = C_p.$$

Hence C_p is the amount of heat required to raise the temperature of unit mass of the gas 1° Absolute—(or 1° C)—when the pressure is constant, i.e. it is the specific heat at constant pressure.

Thus the specific heat at constant pressure, C_p, is constant, and equal to $C_V + R$, i.e. $= \frac{5}{2} . R$.

22. Isothermal and Adiabatic Transformations.—As previously stated, the equation $\delta Q = C_V . \delta\theta + P . \delta V$ is only necessarily true when δV is infinitely small.

In the case of finite changes we may write the equation in the following form, employing the usual notation of the infinitesimal calculus:—

$$\int dQ = C_V \int d\theta + \int P . dV.$$

Now, $\int_{Q_1}^{Q_2} dQ = Q_2 - Q_1$, and $C_V \int_{\theta_1}^{\theta_2} d\theta = C_V(\theta_2 - \theta_1)$. Consequently these terms merely depend upon the initial and final values of Q and θ respectively. In the case of the last term, however, P may depend upon V, and we cannot necessarily express $\int_{V_1}^{V_2} P . dV$ in terms of the initial and final volumes.

Consequently we cannot obtain the value of $\int_{V_1}^{V_2} P \, . \, dV$ without further information as to the interdependence of P and V.

Suppose, for example, that the point A, in Fig. V., corresponds to the pressure and volume of unit mass of the gas at any particular temperature, and suppose that, after the addition of a certain quantity of heat, the condition of the gas is represented by the point B. Let the continuous line joining A and B represent the path of transformation followed by the gas in passing from A to B. If the change in volume, δV, between any two points, such as C and D, be sufficiently small, we can regard the corresponding pressure, P, as constant throughout the small change, and, consequently, the work done in passing from C to D as equal to $P \, . \, \delta V$—the area of the rectangle differing but little from that of the black curvilinear figure. If C and D be infinitely close together, the work done will, of course, be strictly equal to $P \, . \, dV$, where dV is infinitely small; in which case, by integrating between A and B, we get—

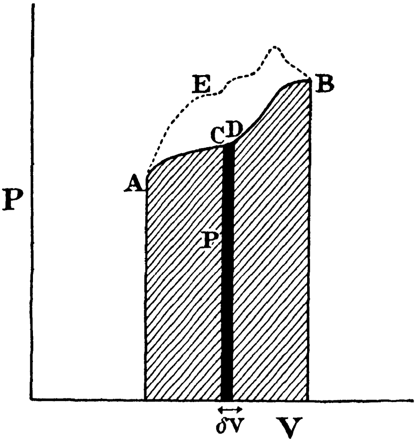

FIG. V.

$$\int_A^B P \, . \, dV = \text{the whole shaded area below the curve.}$$

This shaded curvilinear figure thus represents the work done in passing from A to B along the part ACDB.

Now the path of transformation between A and B can vary, and if the gas had followed, for example, the path AEB it is clear that the area under the dotted curve would have been different from the shaded area. Hence the work done is *not* independent of the path along which the change takes place, and consequently we cannot integrate $P \, . \, dV$ unless we know the curve followed during the transformation. Let us take the case where the transformation is along an isothermal (Fig. VI.).

$$\int dQ = C_V \int d\theta + \int P \, . \, dV.$$

$$\therefore Q_2 - Q_1 = \int_{\text{isothermal}} P \,.\, dV, \quad \text{since } d\theta = 0 \text{ along an isothermal.}^1$$

$$= \int_{\text{isothermal}} \frac{R\theta}{V} \,.\, dV,$$

$$= R \,.\, \theta \,.\, \int_{V_1}^{V_2} \frac{dV}{V},$$

$$= R \,.\, \theta \,.\, \log_e \frac{V_2}{V_1}.$$

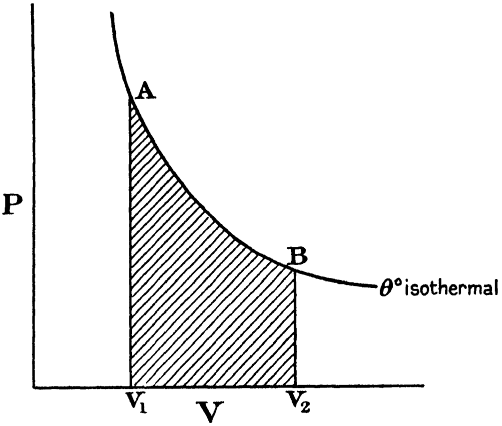

FIG. VI.

This may also be written :—

$$Q_2 - Q_1 = R \,.\, \theta \,.\, \log_e \frac{P_1}{P_2}, \text{ since } \frac{V_2}{V_1} = \frac{P_1}{P_2}, \text{ when } \theta \text{ is constant.}$$

Let us next consider the case where the transformation is along an adiabatic (Fig. VII.), i.e. where heat is neither admitted to, nor abstracted from, the gas.

$$\int dQ = C_V \int d\theta + \int P \,.\, dV.$$

---

[1] This equation states that in order to keep the temperature constant, whilst external work is being done, heat must be added equal in amount to the work done.

$$\therefore \int_{\text{adiabatic}} P\,.\,dV = -C_V\int d\theta, \quad \text{since } dQ = 0 \text{ along an adiabatic.}$$

$$= -C_V(\theta_2 - \theta_1),$$

$= C_V(\theta_1 - \theta_2)$, where θ_1 and θ_2 are, respectively, the initial and final temperatures of the gas.

Again $$\delta Q = C_V\,.\,\delta\theta + P\,.\,\delta V,$$

$$= \frac{C_V}{R}\,.\,(P\,.\,\delta V + V\,.\,\delta P) + P\,.\,\delta V,$$

ubstituting for $\delta\theta$ the value given by the equation

$$P\,.\,\delta V + V\,.\,\delta P = R\,.\,\delta\theta.$$

$$\therefore\ \delta Q = \left(\frac{C_V}{R} + 1\right).\,P\,.\,\delta V + \frac{C_V}{R}\,.\,V\,.\,\delta P,$$

$$= \frac{C_p\,.\,P\,.\,\delta V + C_V\,.\,V\,.\,\delta P}{R}, \text{ since } C_p = C_V + R.$$

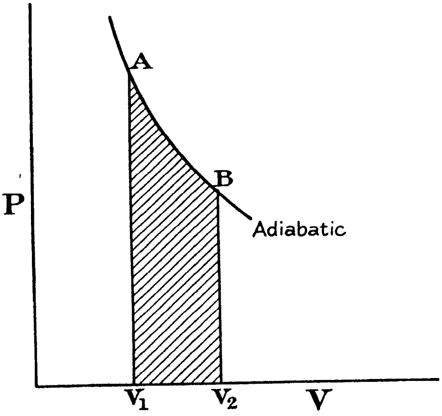

FIG. VII.

Now, since no heat enters, or leaves, at any stage of the transformation, $\delta Q = 0$.

$$\therefore\ C_p\,.\,P\,.\,\delta V + C_V\,.\,V\,.\,\delta P = 0.$$

Multiplying by $\frac{1}{P.V.}$, and integrating, we have—

$$C_p\int\frac{dV}{V} + C_V\int\frac{dP}{P} = 0.$$

$$\therefore\ C_p\,.\,\log_e\frac{V_2}{V_1} + C_V\log_e\frac{P_2}{P_1} = 0.$$

$$\therefore\ \frac{C_p}{C_V}\,.\,\log_e\frac{V_2}{V_1} + \log_e\frac{P_2}{P_1} = 0.$$

Let
$$\frac{C_p}{C_V} = \gamma.$$

Then
$$\gamma \, . \log_e \frac{V_2}{V_1} + \log_e \frac{P_2}{P_1} = 0.$$
$$\therefore \log_e \left(\frac{P_2 \, . \, V_2{}^\gamma}{P_1 \, . \, V_1{}^\gamma} \right) = 0.$$

But $\log_e 1 = 0$.
$$\therefore P_1 \, . \, V_1{}^\gamma = P_2 \, . \, V_2{}^\gamma = B,$$ where B is a *constant.*

We can now calculate the work done during an adiabatic expansion by *directly* integrating P . *d*V.

For
$$\int_{\text{adiabatic}} P \, . \, dV = \int \frac{B \, . \, dV}{V^\gamma},$$
since $P \, . \, V^\gamma = B$, along an adiabatic curve,
$$= B \int \frac{dV}{V^\gamma},$$
$$= \frac{-B}{\gamma - 1} \, . \left\{ \frac{1}{V_2{}^{\gamma - 1}} - \frac{1}{V_1{}^{\gamma - 1}} \right\},$$
$$= -\frac{1}{\gamma - 1} \{P_2 V_2 - P_1 V_1\},$$
since $B = P_1 \, . \, V_1{}^\gamma = P_2 \, . \, V_2{}^\gamma$,
$$= -\frac{R}{\gamma - 1} \{\theta_2 - \theta_1\}$$
since $R = \dfrac{P_1 V_1}{\theta_1} = \dfrac{P_2 V_2}{\theta_2}$,
$$= C_V(\theta_1 - \theta_2),$$
since $\dfrac{R}{\gamma - 1} = \dfrac{C_p - C_V}{\dfrac{C_p}{C_V} - 1} = C_V$.

This is, of course, the equation previously obtained.

Now, for an isothermal transformation, $P.V. = R \, . \, \theta = A$, where A is a constant.
$$\therefore P = \frac{A}{V}.$$

Hence, the slope of the isothermal curve at any point is given by the relation—
$$\frac{dP}{dV} = -\frac{A}{V^2} = -\frac{P}{V}.$$

Again, for an adiabatic transformation, $P . V^{\gamma} = B$, where B is a constant.

$$\therefore P = \frac{B}{V^{\gamma}}.$$

Hence, the slope of the adiabatic curve at any point is given by the relation—

$$\frac{dP}{dV} = -\frac{\gamma . B}{V^{\gamma+1}} = -\frac{\gamma . P}{V}.$$

Thus the slope of the adiabatic curve at any given point is γ times steeper than the slope of the isothermal curve at the same point.

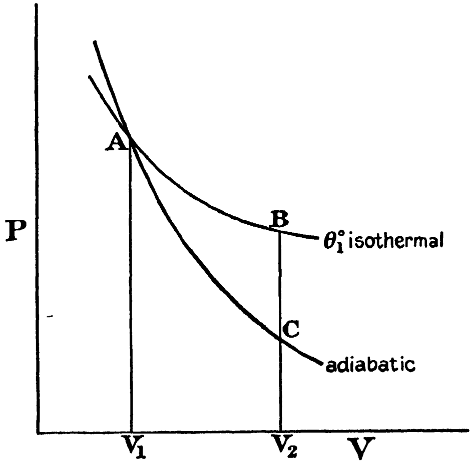

FIG. VIII.

If the point A, in Fig. VIII., correspond to the pressure and volume of unit mass of the gas, at temperature θ_1, then, if the gas expand isothermally, the curve of transformation will be AB, but if the expansion be adiabatic the transformation will follow the steeper curve AC. The work, W, performed by the gas in each case—in expanding from V_1 to V_2—is given by the respective equations,

$$W_{\text{iso.}} = R . \theta_1 . \log_e \frac{V_2}{V_1} = P_1 . V_1 . \log_e \frac{V_2}{V_1},$$

where P_1 is the pressure when the volume is V_1;

$$W_{\text{adia.}} = C_V(\theta_1 - \theta_2),$$

where θ_2 is the final temperature of the gas, i.e. the temperature of the isothermal curve which would pass through the point C.

We have seen that the relation between the pressure and the volume of a perfect gas during an adiabatic transformation is given by the equation $P.V^\gamma. = B$—where B is a constant. By combining this with the equation $P.V. = R.\theta$, we can readily deduce the adiabatic relations which obtain between the pressure and the temperature, and the volume and the temperature, respectively.

For, since

$$P.V. = R.\theta$$
$$\therefore P^\gamma.V^\gamma. = R^\gamma.\theta^\gamma.$$

But, for an adiabatic change

$$P.V^\gamma. = B.$$
$$\therefore \frac{P.V^\gamma.}{P^\gamma.V^\gamma.} = \frac{B}{R^\gamma.\theta^\gamma}.$$
$$\therefore \frac{\theta^\gamma}{P^{\gamma-1}} = \frac{B}{R^\gamma} = \text{constant}.$$

Again:

$$P.V. = R.\theta$$

and

$$P.V^\gamma = B.$$
$$\therefore V^{\gamma-1} = \frac{B}{R.\theta}$$
$$\therefore \theta.V^{\gamma-1}. = \frac{B}{R} = \text{constant}.$$

We shall see, subsequently, that the value of γ for any gas is always greater than unity, and in no case does its value exceed $1\frac{2}{3}$. Thus the quantity $\gamma - 1$ is always positive. Consequently, it follows from the equations we have obtained that, for an adiabatic transformation, θ increases when P increases, or, what comes to the same thing, θ increases when V diminishes.

Experiment III.—The rise in temperature produced when a gas is compressed under approximately adiabatic conditions is employed in the pneumatic fire syringe, shown in Fig. IX. On suddenly plunging down the piston the temperature of the compressed air rises sufficiently to ignite a small piece of cotton moistened with ether which is placed in a cavity at the end of the piston. Or, if the glass tube contains a mixture of air and carbon disulphide vapour, on suddenly pressing down the piston the mixture will be seen to be ignited.

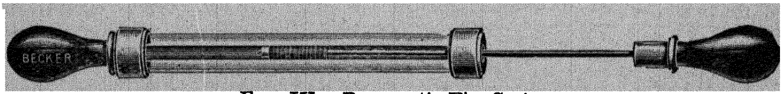

FIG. IX.—Pneumatic Fire Syringe.

Anticipating the experimental results which are given later in this chapter, we may take the value of γ as $1\frac{2}{3}$ for monatomic gases, and $1\frac{2}{5}$ for diatomic gases.

If, therefore, a monatomic gas at a temperature of, say, 300° A. (27° C.) have its volume reduced adiabatically to one-eighth of the initial volume, the resultant temperature will be 1200° A. (927° C).

For
$$\theta_1 . V_1^{\frac{2}{3}} = \theta_2 . V_2^{\frac{2}{3}}.$$
$$\therefore \frac{\theta_2}{\theta_1} = \left(\frac{V_1}{V_2}\right)^{\frac{2}{3}} = (8)^{\frac{2}{3}} = 4.$$
$$\therefore \theta_2 = 4 . \theta_1.$$

In the case of air, $(\gamma = 1\frac{2}{5})$, we should have to compress it adiabatically to one thirty-second of its initial volume to produce the same rise in temperature.

Now, at each stage of the compression the gas must be infinitely near its normal equilibrium state. Otherwise we must introduce an additional term, K, into our fundamental equation to allow for kinetic energy due to the motion of the gas *as a whole*.

We then have—
$$\delta Q = C_V . \delta\theta + P . \delta V + K$$
and this equation, with the additional term K, is now an irreversible one.

Consequently the conditions assumed in the above numerical calculations cannot be realised in practice—for the only way to prevent loss of heat is to compress the gas quickly, and this introduces the additional term K.

Experiment IV.—If the air inside a flask be rendered smoky with a piece of burning phosphorus, and be then rarefied to, say, one-fourth of the atmospheric pressure, the production of eddies on suddenly admitting air, and raising the pressure to atmospheric, will be clearly visible. Or the air may be initially compressed inside the flask to a few atmospheres pressure, after introducing a quantity of smoke from a piece of burning phosphorus, and the formation of eddies inside the flask on sudden expansion to the atmospheric pressure observed. Provided the changes of pressure be sufficiently small, however, very little motion of the gas as a whole is produced, and, in such cases, the term K may be neglected, and the transformation regarded as truly adiabatic.

23. The Numerical Value of γ for a Perfect Gas—It has already been shown that, for a perfect gas—
$$C_V = \tfrac{3}{2} . R$$
and
$$C_p = C_V + R = \tfrac{5}{2} . R.$$
$$\therefore \gamma = \frac{C_p}{C_V} = \tfrac{5}{3} = 1{\cdot}667.$$

This value of the ratio between the specific heats agrees almost exactly with the experimental values obtained for γ in the case of certain elementary gases, when the latter are far removed from their liquefying points—and in no case does the ratio exceed this value. Before discussing more fully, however, the causes which, in a real gas, may contribute towards a diminution in the value of γ, it will be convenient to consider a number of experimental methods for determining the ratio of the specific heats.

24. Clément and Desormes' Method of Determining γ.—*Experiment V.*—A simple form of Clément and Desormes' apparatus is shown in Fig. X. It consists of a thick-walled glass flask, fitted with a side tube, and provided with a large stop-cock. The flask, which should be of considerable capacity, stands on a ring of cork, or other badly conducting material, and the side tube is bent at right angles, and dips below the surface of some Fleuss[1] pump oil in a suitable container, thus serving as a manometer.

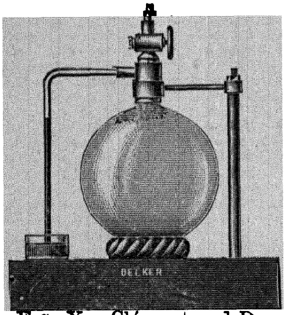

FIG. X.—Clément and Desormes' Apparatus.

A small quantity of concentrated sulphuric acid is introduced into the flask in order to completely dry the enclosed air. To perform an experiment, the air contained in the flask is partially exhausted—as indicated by the rise of the oil in the manometer—and the stop-cock is then closed. Since this rarefaction cools the air which remains in the flask, it will be observed that the level of the oil in the manometer falls as the enclosed air gradually acquires the temperature of the surroundings. When a steady state has been attained, the pressure indicated by the manometer is read. The large stop-cock is now opened for a few seconds, to equalise the internal and external pressures, and is then closed again. The contained air is thus compressed, and, provided the glass flask be large, it may be assumed that a relatively negligible amount of the heat developed by this compression has been communicated to the surroundings during the short time the stop-cock remained open. Hence the compression may be considered as adiabatic. After standing for some time the enclosed air will again acquire its original temperature, and the manometer—which at the moment the stop-cock was closed indicated atmospheric pressure—will now show a diminished pressure within the flask. When the pressure has become steady, a second reading of the level of the oil in the manometer is taken.

---

[1] Fleuss pump oil constitutes a very suitable manometric liquid, since its relative density is low and its vapour pressure, at ordinary temperatures, practically negligible.

If the heights of the oil in the manometer before and after the adiabatic compression were respectively h_1 and h_2, then, provided the actual pressure changes were exceedingly small, we can prove that—

$$\gamma = \frac{h_1}{h_1 - h_2}.$$

For, let the point A, Fig. XI, correspond to the pressure and volume of unit mass of the rarefied air within the flask at the temperature of the surroundings. On opening the stop-cock, this air is compressed adiabatically, the pressure rising to atmospheric. The path of transformation is thus along the adiabatic curve AB. At B the stop-cock is closed, and the air now cools, at approximately constant volume, to its original temperature—i.e. it passes along a vertical line from B to C—C being on the isothermal curve drawn through A. It should be noted that the volume does not remain absolutely constant in passing from B to C, as there is a small diminution owing to the rise of the oil in the manometer tube, but since the volume of air in the manometer is very small compared with the volume of the air within the flask, the diminution in volume thus produced may be neglected. Let the pressures corresponding to A, B, and C be respectively, P_A, P_B, and P_C.

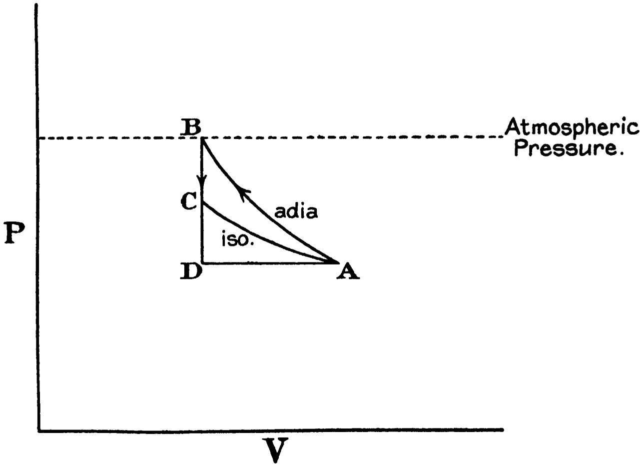

FIG. XI.

Now, provided the changes in pressure are exceedingly small, the arcs AB and AC will be very small portions of the respective adiabatic and isothermal curves through A, and may be regarded as approximately straight lines. Draw through A a straight line AD parallel to the axis of volume, and meeting BC produced in D. Let the angle

DAB = ϕ, and the angle DAC = θ, these being the angles the adiabatic and isothermal curves, respectively, make at A with the horizontal line DA. Then, since the slope of the adiabatic curve at any point is γ times steeper than the slope of the isothermal curve at the same point, we have—

$$\gamma = \frac{\tan \phi}{\tan \theta} = \frac{\dfrac{\text{BD}}{\text{AD}}}{\dfrac{\text{CD}}{\text{AD}}} = \frac{\text{BD}}{\text{CD}} = \frac{\text{P}_\text{B} - \text{P}_\text{A}}{\text{P}_\text{C} - \text{P}_\text{A}}.$$

Now $\text{P}_\text{B} - \text{P}_\text{A}$ is the difference between the atmospheric pressure and the initial pressure of the rarefied gas. Consequently, if ρ be the density of the Fleuss pump oil in the manometer, we have $\text{P}_\text{B} - \text{P}_\text{A} = h_1\rho$, the difference of pressure being expressed in centimetres of water if h_1 be measured in centimetres.

Similarly $\text{P}_\text{C} - \text{P}_\text{A} = (\text{P}_\text{B} - \text{P}_\text{A}) - (\text{P}_\text{B} - \text{P}_\text{C}) = h_1\rho - h_2\rho$.

$$\therefore \gamma = \frac{h_1\rho}{(h_1 - h_2) \,.\, \rho} = \frac{h_1}{h_1 - h_2}.$$

If the manometer tube be fairly short in length (say, 20 to 30 cms.), and if an oil of low density be employed as the manometric substance, the pressure changes cannot be other than small, and the above equation may be employed with sufficient accuracy to calculate the value of γ. With a longer manometer tube, or using a denser liquid such as mercury, the pressure changes may be too great to justify the assumption that the arcs AB and AC are approximately rectilinear. Under these conditions, the value of γ may be calculated in the following manner.

Let the volumes corresponding to A and B (Fig. XI.) be respectively V_A and V_B.

Then, since A and B are on an adiabatic—

$$\text{P}_\text{A} \,.\, \text{V}_\text{A}{}^\gamma = \text{P}_\text{B} \,.\, \text{V}_\text{B}{}^\gamma.$$

$$\therefore \left(\frac{\text{V}_\text{A}}{\text{V}_\text{B}}\right)^\gamma = \frac{\text{P}_\text{C}}{\text{P}_\text{A}}.$$

Also, since A and C are on an isothermal—

$$\text{P}_\text{A} \,.\, \text{V}_\text{A} = \text{P}_\text{C} \,.\, \text{V}_\text{B}.$$

$$\therefore \frac{\text{V}_\text{A}}{\text{V}_\text{B}} = \frac{\text{P}_\text{C}}{\text{P}_\text{A}}.$$

$$\therefore \frac{\text{P}_\text{B}}{\text{P}_\text{A}} = \left(\frac{\text{P}_\text{C}}{\text{P}_\text{A}}\right)^\gamma.$$

Therefore, taking logarithms of both sides of this last equation, we have—

$$\gamma = \frac{\log \frac{P_B}{P_A}}{\log \frac{P_C}{P_A}}.$$

Here, as before, P_B is the atmospheric pressure, expressed in centimetres of water, and $P_A = P_B - h_1\rho$, and $P_C = P_B - h_2\rho$.

If the side tube be bent so as to form a manometer of the ordinary "U" shape, the same apparatus may be employed for determining γ when the enclosed air is initially at a greater pressure than the atmospheric. This method was first employed by Gay-Lussac and Welter. In this case, on opening the stop-cock the pressure falls adiabatically to the atmospheric pressure and the air becomes cooled by the expansion. On standing, the original temperature is attained, and the pressure of the enclosed air rises. The value of γ is then calculated in a manner essentially similar to that already described.

The air inside the flask may now be completely displaced by another gas, the latter being pumped in until the pressure slightly exceeds atmospheric. The stop-cock is then closed, and the experiment carried out as before.[1] The gas must, of course, be thoroughly dried by means of sulphuric acid or other suitable desiccating agent. Using a modification of this method, Röntgen obtained the following values for γ, for air and carbon-dioxide, respectively :—

$$\begin{cases} \gamma_{air} = 1{\cdot}405. \\ \gamma_{CO_2} = 1{\cdot}305. \end{cases}$$

It should be noted that if the enclosed air be initially at a lower pressure than atmospheric an error arises from the fact that the air which enters, on opening the stop-cock, has not the same temperature immediately after entering as the air which was previously in the flask, but is somewhat cooler. Hence, after again closing the stop-cock, the enclosed air will not all cool down equally, and the fall in pressure observed will be too small. Consequently, the value of γ obtained will be slightly too low. This source of error is avoided when the enclosed air is initially above atmospheric pressure, but there still remains a small error arising from the momentum produced in the issuing air—to which we have already referred in § 22. Also, owing to the momentum acquired by the issuing air, there is an excessive outrush of air, on opening the stop-cock, followed by an inrush, and oscillations are set up, which may cause the pressure inside the flask to be either greater or less than the atmospheric at

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[1] If a cylinder containing liquid carbon-dioxide, or a syphon of liquid sulphur dioxide be available, the flask may conveniently be filled with one of these gases.

the moment the stop-cock is closed. This difficulty may be largely avoided by using a very wide stop-cock, or by employing the improved form of Clément and Desormes' apparatus shown in Fig. XII. Here the gas at atmospheric pressure is slightly compressed by raising the mercury reservoir to the upper shelf and opening the pinchcock, thus allowing the mercury to flow into the flask. The highest reading given by the manometer is then noted. After standing for some time the gas, which was heated by the compression, again acquires the temperature of the surroundings, and the pressure becomes steady at a lower value, which is also read. Then, if the pressure corresponding to the point A in Fig. XI. be now taken as the atmospheric, we have—

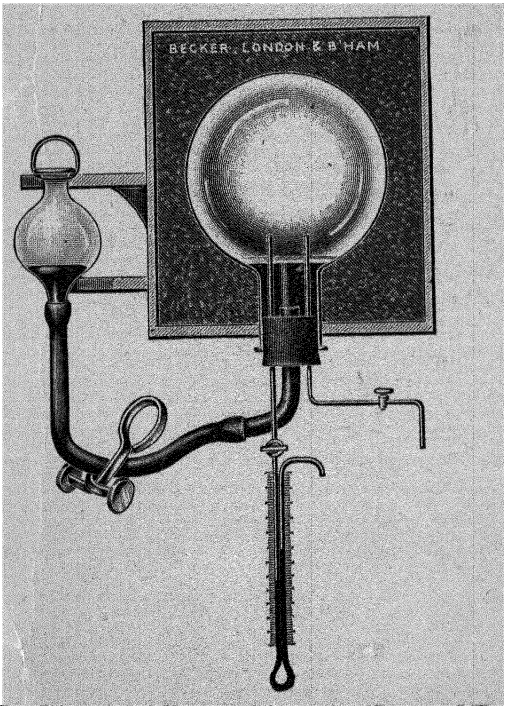

FIG. XII.—Clément and Desormes' Apparatus (Improved Form).

$$\gamma = \frac{P_B - P_A}{P_C - P_A} = \text{(approximately) } \frac{h_1}{h_2},$$

where h_1 and h_2 are the respective heights of the oil in the manometer *immediately* after the adiabetic compression, and after a steady state has been attained.

To prevent as far as possible loss of heat during the compression, the flask is placed inside a wooden box and is packed round with badly conducting material. A layer of concentrated sulphuric acid on the surface of the mercury is generally employed to dry the enclosed gas, but if, for chemical reasons, its use is inadmissible, the gas should be carefully dried with some other desiccating agent before being introduced into the flask. The quantity of mercury taken must be sufficient to completely cover the cork even when the reservoir is on the lower side shelf.

An initial experiment should always be performed to find, approximately, the maximum reading, h_1, given by the manometer. The tap on the manometer is then closed when at this maximum, and is only opened in the subsequent experiment when nearly all the mercury has run into the flask. In this manner the correct maximum reading can be obtained without oscillations being set up. The experiment may be varied by having the gas initially compressed, and allowing it to expand adiabatically.

25. Lummer and Pringsheim's Method of Determining γ. — A variation of Clément and Desormes' method—in which both the change of pressure and temperature were measured—was employed by Lummer and Pringsheim. The dry gas was initially compressed, or rarefied, to a pressure P_0—and the temperature θ_0 read when a steady state had been attained. On opening the stop-cock, the pressure changed to the atmospheric pressure, P_1, and the temperature to a new value, θ_1, the temperature being determined by means of a very sensitive electrical resistance thermometer. It has been seen previously that, for an adiabatic change, $\frac{\theta^\gamma}{P^{\gamma-1}}$ is constant.

$$\therefore \frac{\theta_0^{\gamma}}{P_0^{\gamma-1}} = \frac{\theta_1^{\gamma}}{P_1^{\gamma-1}}.$$

Whence—

$$\gamma = \frac{\log \frac{P_1}{P_0}}{\log \frac{P_1}{P_0} - \log \frac{\theta_1}{\theta_0}}.$$

Lummer and Pringsheim thus obtained the values 1·402 and 1·299 for γ for air and carbon-dioxide, respectively.

26. Determination of γ from the Velocity of Sound.—It was shown by Newton that the velocity, V, of sound in any medium was given by the equation—

$$V = \sqrt{\frac{\text{elasticity}}{\text{density}}}.$$

Newton imagined that the elasticity was the *isothermal* elasticity of the medium. Laplace subsequently showed that it was the *adiabatic* elasticity which should be employed in the above equation. For during the propagation of the sound waves each compression causes a rise—and each rarefaction a fall—in the temperature, but the alternations of compression and rarefaction are so rapid that practically no heat is conducted out of the compressions or into the rarefactions.

We shall prove, later, that in the case of a gas which obeys Boyle's Law its isothermal elasticity is equal to its pressure, and its adiabatic elasticity is equal to γ times its pressure.

Thus, for such a gas, we may write—

$$V = \sqrt{\frac{\gamma \cdot P}{\rho}}.$$

If, for example, we take the velocity of sound in dry air at 0° C. and 76 cms. pressure as $3{\cdot}32 \times 10^4$ cms./sec., and the density of the air as 0·001293 gm /c.c., then—

$$3{\cdot}32 \times 10^4 = \sqrt{\frac{\gamma \times 76 \times 13{\cdot}596 \times 981}{0{\cdot}001293}}.$$

Whence $\gamma = 1{\cdot}406.$

Experiment VI.—Comparison of the Values of γ from the Relative Velocities of Sound in Different Gases—Take a Kundt's apparatus (Fig. XIII.), and scatter some lycopodium powder inside the glass tube. By rubbing the rod it can be thrown into stationary longitudinal undulation, and by adjusting the position of the tightly fitting piston, and hence the length of the enclosed air column, the latter will be also thrown into stationary undulation, as shown by the pattern formed by the lycopodium. Measure the distance between consecutive nodes, as indicated by the powder. Next fill the tube with a different gas and repeat the experiment. The relative velocities of sound in the two gases are proportional to the spaces between consecutive nodes in each case—these spaces being the half wave-length in the gas of the frequency of the vibrations of the rod.

Thus $$\frac{V_1}{V_2} = \frac{\lambda_1}{\lambda_2},$$

where λ_1 and λ_2 are the respective wave-lengths in the two different gases.

But $$\frac{V_1}{V_2} = \sqrt{\frac{\gamma_1 \cdot \rho_2}{\gamma_2 \cdot \rho_1}},$$

the pressure being the atmospheric in each case.

$$\therefore \frac{\lambda_1^2}{\lambda_2^2} = \frac{\gamma_1 \cdot \rho_2}{\gamma_2 \cdot \rho_1}$$

$$\therefore \gamma_1 = \frac{\gamma_2 \cdot \rho_1 \cdot \lambda_1^2}{\rho_2 \cdot \lambda_2^2} = \frac{\gamma_2 \cdot m_1 \cdot \lambda_1^2}{m_2 \lambda_2^2},$$

m_1 and m_2 being the respective molecular masses.

If the second gas be air, we may substitute the values ascertained for γ_2 and m_2, and write the above equation—

$$\gamma_1 = \frac{1{\cdot}406 \,.\, m_1 \lambda_1^2}{28{\cdot}88 \,.\, \lambda_2^2}.$$

The value of γ may thus be deduced for any other gas the molecular mass of which is known.

27. Determination of γ by the Direct Comparison of the Specific Heats at Constant Pressure and Constant Volume.—Numerous determinations of the specific heats of gases at constant pressure have been made by calorimetric methods, in which, in general, a stream of the heated gas is allowed to flow, at constant pressure, through a spiral tube contained in a calorimeter filled with water, the rise in temperature of the calorimeter and its contents being duly noted.

The results obtained by the researches of Regnault, Wiedemann, Lussana, Witkowski, and others for the specific heats of different gases are in close agreement. It was found that the specific heats of actual gases at constant pressure varied appreciably with the pressure and with the temperature, although Witkowski found that, in the case of air at constant atmospheric pressure, the specific heat was practically independent of the temperature.

In the case of a perfect gas, of course, no such variations would exist, and we may suppose that in a real gas the variations are due to molecular aggregation or dissociation. Only one method has been devised for directly determining the values of the specific heats of gases at constant volume, namely, by the use of Dr. Joly's Differential Steam Calorimeter. In this method two hollow spheres, of thin

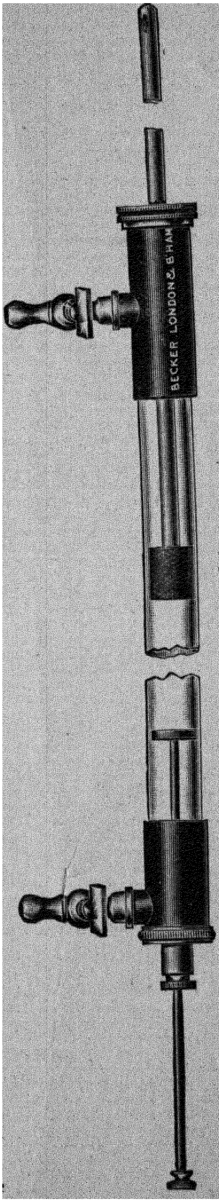

FIG. XIII.—Kundt's Apparatus.

copper, are suspended by means of fine platinum wires from the two ends of a balance beam. The two spheres are constructed of equal thermal capacities, and hang freely inside a chamber which can be filled with dry steam. Small light trays are suspended beneath the spheres to catch any drops of water that may fall down during an experiment. One sphere is exhausted, or else contains a gas at the atmospheric pressure, whilst the other is filled with the gas at a high pressure, the equilibrium of the balance being restored by the addition of the necessary weights. When the temperature is steady it is read, and dry steam is then admitted to the chamber. The excess of steam condensed on the sphere containing the highly compressed gas is directly determined by weighing. The excess of condensed steam is, of course, due to the excess weight of the gas which has been heated at approximately constant volume. Hence the specific heat at constant volume can be deduced. A small correction should be made for the expansion of the copper vessel due to the rise of temperature and the increase of internal pressure.

Joly found that the specific heat at constant volume alters appreciably with the density of the gas.

In the case of air we may, according to Witkowski, take the specific heat at constant pressure, C_p, as 0·2372, at 0° C. and 76 cms., whereas the specific heat at constant volume, C_V, was found by Joly to be 0·1715 at 0° C. and 76 cms.

Hence
$$\gamma = \frac{C_p}{C_V} = \frac{0{\cdot}2372}{0{\cdot}1715} = 1{\cdot}383.$$

28. Jamin and Richard's Method of Determining γ.—MM. Jamin and Richard determined the value of γ by communicating a certain quantity of heat to a gas both at constant pressure and constant volume, the gas being contained in a large vessel, and being heated by means of a platinum spiral conveying a steady electric current. The current was run for the same time in each experiment, and since in each case the loss of heat by radiation from the wire was the same, it followed that the same quantity of heat remained, and was imparted to the gas. In the first experiment the gas was heated at constant pressure and the increase in volume was measured; in the second experiment the gas was heated at constant volume and the increase in pressure was observed.

Let m be the mass of the gas, at an initial pressure, P_0, volume V_0, and temperature θ_0.

When a quantity of heat, Q, is added, at constant pressure, let the temperature rise to θ_1, and the volume increase to V_1, and when the same quantity of heat is added, at constant volume, let the temperature become θ' and the pressure P'.

Then we have—

$$Q = m \, . \, C_p \, . \, (\theta_1 - \theta_0) = m \, . \, C_V \, . \, (\theta' - \theta_0).$$

$$\therefore \frac{C_p}{C_V} = \frac{\theta' - \theta_0}{\theta_1 - \theta_0}.$$

But, for a perfect gas—

$$P_0V_0 = R\theta_0, \; P_0V_1 = R\theta_1, \text{ and } P'V_0 = R\theta'.$$

$$\therefore \frac{\theta' - \theta_0}{\theta_1 - \theta_0} = \frac{(P' - P_0) \, . \, V_0}{(V_1 - V_0) \, . \, P_0}.$$

Whence
$$\gamma = \frac{C_p}{C_V} = \frac{(P' - P_0) \, . \, V_0}{(V_1 - V_0) \, . \, P_0}.$$

For any real gas we have, as before—

$$\frac{C_p}{C_V} = \frac{\theta' - \theta_0}{\theta_1 - \theta_0}.$$

Let a be the coefficient of expansion of the gas at constant pressure, and β the coefficient of increase of pressure at constant volume. Then—

$$V_1 - V_0 = V_0 \, . \, a \, . \, (\theta_1 - \theta_0), \text{ and } P' - P_0 = P_0 \, . \, \beta \, . \, (\theta' - \theta_0).$$

$$\therefore \gamma = \frac{C_p}{C_V} = \frac{\theta' - \theta_0}{\theta_1 - \theta_0} = \frac{(P' - P_0) \, . \, V_0 \, . \, a}{(V_1 - V_0) \, . \, P_0 \, . \, \beta}.$$

MM. Jamin and Richard thus obtained the values 1·41, 1·29, and 1·41 for γ for air, carbon-dioxide, and hydrogen, respectively.

29. The Value of γ in the Case of Real Gases.—In the case of a perfect gas we have seen that *all* its intrinsic energy is the energy of translation of its molecules—the total intrinsic energy per unit mass being $\frac{1}{2}\bar{C}^2$, or $\frac{3}{2}R \, . \, \theta$, and the total intrinsic energy per unit volume being $\frac{1}{2} \, . \, \rho \, . \, \bar{C}^2$, or $\frac{3}{2}R \, . \, \theta \, . \, \rho$.

Such a perfect gas was considered to be composed of an enormous number of identical spherical molecules, negligibly small compared with their distance apart, and perfectly smooth and elastic. In the case of any real gas, however, we can no longer necessarily regard the molecules as thus approximating to moving points. For each particular gas the molecules will, in general, possess a characteristic configuration depending upon the number and chemical nature of the atoms within the molecule. Nor can all the molecules be regarded as identical—for the gas may be partially in a state of dissociation or of molecular aggregation.

Consequently, if a change of energy occur in any real gas, due to the admission of heat, some of the heat may be used in increasing the translatory energy of the molecules, some in external work, and some in increasing the internal energy—the latter arising from the rotatory and vibratory energy of the molecules and their constituent atoms, and also from work done against internal molecular cohesive forces during the separation of the molecules which occurs both in expansion and dissociation. Since we have seen that the magnitude of the cohesive forces in a gas at the ordinary density is very small, we may, in the present discussion, neglect the energy arising from such internal molecular cohesive forces.

Let us consider any gas when in a steady state, and let its *total* energy—i.e. its total *kinetic* energy—equal β times its translatory energy.

Therefore the total intrinsic kinetic energy per unit mass is $\frac{1}{2}\beta\overline{C^2}$, or $\frac{3}{2} . \beta . R . \theta$, and per unit volume $\frac{1}{2}\beta . \rho . \overline{C^2}$, or $\frac{3}{2}\beta . R . \theta . \rho$.

If we assume that the total intrinsic kinetic energy is zero at the absolute zero of temperature, then, since it is found experimentally that for many gases C_p and C_V are approximately independent of the temperature, it follows that, to the same degree of approximation, the total molecular kinetic energy must bear a constant ratio to the translatory energy—i.e. β is constant.

For, as in § 21, if H units of heat be added at constant volume, we have—

$$H = C_V(\theta_2 - \theta_1) = \tfrac{3}{2}R(\beta_2\theta_2 - \beta_1\theta_1), \text{ where } \tfrac{3}{2}R\beta_1\theta_1 \text{ and } \tfrac{3}{2}R\beta_2\theta_2$$

represent the total intrinsic energy per unit mass of the gas at θ_1 and θ_2 respectively.

Taking $\theta_1 = 0$, this gives $C_V\theta_2 = \frac{3}{2}R\beta_2\theta_2$—i.e. $C_V = \frac{3}{2}R\beta_2$.

If, therefore, we may assume that C_V is constant, β_2 must also be constant.

Hence[1] $C_V = \frac{3}{2}\beta R$.

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[1] If, however, we suppose that only the *translatory* energy of the molecules has become zero at the absolute zero of temperature, the total intrinsic energy of the gas at the absolute zero may still be represented by some finite quantity ϵ.

In this case, let $\frac{3}{2}R\beta_1\theta_1 + \epsilon$ and $\frac{3}{2}R\beta_2\theta_2 + \epsilon$ be the total intrinsic energy per unit mass of the gas at θ_1 and θ_2, respectively.

$$\therefore H = C_V(\theta_2 - \theta_1) = (\tfrac{3}{2}R\beta_2\theta_2 + \epsilon) - (\tfrac{3}{2}R\beta_1\theta_1 + \epsilon) = \tfrac{3}{2}R\beta_2\theta_2 - \tfrac{3}{2}R\beta_1\theta_1.$$

Taking $\theta_1 = 0$, this gives $C_V\theta_2 = \frac{3}{2}R\beta_2\theta_2$; i.e. $C_V = \frac{3}{2}R\beta_2$.

If, then, C_V be assumed constant, β_2 must also be constant.

Whence, as before, we have—

$$C_V = \tfrac{3}{2}\beta . R.$$

It must be carefully noted, however, that in this case it is no longer the total kinetic energy, but the *excess* of the latter over its value at the absolute zero of temperature, which equals β times the translatory energy. This distinction, which is not always observed, is of importance, for a knowledge of the conditions governing the transfer of energy between the translatory and the internal molecular energies is necessary before the assumption that the *total intrinsic kinetic energy* of a gas becomes zero at the absolute zero of temperature can be justified.

Neglecting internal cohesive forces, we have, as in § 21—

$$\begin{aligned} C_p &= C_V + R, \\ &= \tfrac{3}{2}\beta R + R, \\ &= (\tfrac{3}{2}\beta + 1)R. \end{aligned}$$

$$\therefore \gamma = \frac{C_p}{C_V} = \frac{\frac{3}{2}\beta + 1}{\frac{3}{2}\beta} = 1 + \frac{2}{3\beta}.$$

On the assumption that the only energy possessed by the molecules is the *kinetic energy of translation*, $\beta = 1$, and $\gamma = 1\frac{2}{3}$.

This was the value of γ previously calculated for a perfect gas.

Now in the case of certain elementary gases, at the ordinary density, γ is found experimentally to possess almost exactly this value. Thus Kundt and Warburg in 1876 determined the ratio of the specific heats for mercury, from the velocity of sound in a tube containing gasified mercury, and obtained the value 1·666 (at 310° C.). Sir William Ramsay found the values 1·66 and 1·65 for Argon and Helium, respectively. Niemeyer obtained 1·667 for γ for Argon. For Neon, Krypton, and Xenon, γ has also been found to have the approximate value 1·66.

Consequently for these gases we must regard practically the whole of the molecular energy as translatory, and therefore the molecules must be very approximately spherical, and also spherically symmetrical with respect to their internal structure. Otherwise a sensible amount of translatory energy would be transformed into rotatory energy at each collision—and this rotatory energy if only slowly dissipated would lead to the molecules possessing energy other than the kinetic energy of translation (which would be inconsistent with the value $1\frac{2}{3}$ found for γ), and if rapidly dissipated would be contrary to the extremely slow rate at which the gas, as a whole, is observed to lose energy. Therefore, since these gases are composed of spherical, symmetrical molecules, we conclude that they are monatomic. Indeed the presence of two or more atoms within the molecule would be inconsistent with the absence of rotatory and vibratory energy.

Since, however, all the gases enumerated above give, when incandescent, very complex spectra consisting of thousands of lines, and since the molecules in each individual gas are considered to be identical, it follows that each molecule must be able to execute vibrations of thousands of distinct periods. Consequently the existence of such spectra show that vibratory energy must be possessed by the molecules—but, in view of the fact that γ has the value $1\frac{2}{3}$, we must conclude that the amount of vibratory energy is negligibly small compared with the kinetic energy of translation.

Now, it can be shown that in a conservative dynamical system, where the total energy is constant, the kinetic energy is equally divided amongst all the modes of motion, or "degrees of freedom," when the system is in a steady state. This is usually referred to as the Law of Equipartition of Kinetic Energy. It is, however, clear that the Law of Equipartition of Kinetic Energy amongst the possible modes of motion, or "degrees of freedom," does not apply to the vibratory energy which gives rise to the spectral lines referred to above. Nor would the law be expected to apply, for the emission of energy in the form of spectral lines is in itself proof that the system is *not* dynamically conservative.

The conclusion that the molecules in mercury vapour are monatomic is of fundamental importance in the theory of chemistry. Amadeo Avogadro, in 1811, in applying his famous generalisation to the case of the formation of steam from the combination of hydrogen and oxygen was led to infer that the molecules of hydrogen and oxygen were diatomic, and those of steam triatomic. For two volumes of hydrogen with one volume of oxygen to form two volumes of steam, and this is consistent with the supposition that $2n.$ molecules of hydrogen have united with $n.$ molecules of oxygen to form $2n.$ molecules of steam, if the above inference be made as to the atomicity of the molecules in each case.

Starting then from the assumption that the molecule of hydrogen is diatomic, and taking the relative density of any gas as the number of times that gas is heavier than an equal volume of hydrogen, measured at the same temperature and pressure, it is clear that by doubling the relative density we at once obtain the molecular weight of the gas, for the molecular weight is referred to the weight of an *atom* of hydrogen as the unit[1]—and we have seen (§ 17) that

$$\frac{\rho_1}{\rho_2} = \frac{m_1}{m_2}.$$

Now, the relative density of mercury vapour has been determined with respect to hydrogen, and has been found to have the value 100. Therefore the molecular weight of mercury vapour is 200. But the atomic weight of mercury—which can be deduced from a knowledge of its "equivalent weight" and its specific heat, by applying the Law of Dulong and Petit—is also found to have the value 200.

Hence the molecules in mercury vapour should be monatomic—and the value obtained for γ by Kundt and Warburg proves that such is actually the case.

Consequently the value found for γ for mercury vapour is a proof of the legitimacy of the assumption that mercury vapour is monatomic—and, therefore, that the molecule of hydrogen is diatomic, (and not, for example, H_4), and so is confirmatory of the whole of chemical formulæ.

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[1] More strictly the atomic weight of hydrogen may be taken as 1·008, oxygen being now adopted as the standard, with an atomic weight of 16.

In the case of the inert gases no chemical evidence can be obtained as to their atomic weights, but since, for all of them, γ has the approximate value 1·66, we are justified in regarding them as monatomic, and in taking their molecular weights—as found from their gaseous densities—as identical with their atomic weights. When we come to diatomic gases such as hydrogen, oxygen, nitrogen, (air), etc., we find that γ has an approximately constant value of $1\frac{2}{5}$. Thus Lummer and Pringsheim obtained the values 1·402, 1·408, and 1·400 for γ for air, hydrogen, and oxygen, respectively, the temperature in each case being about 10° C.; Cazin found 1·41 for nitrogen; Leduc 1·401 for carbon-monoxide; Masson 1·394 for nitric oxide.

In the case of triatomic gases the value of γ approximates to $1\frac{2}{7}$. For example, Makower found 1·305 for water vapour, and Lummer and Pringsheim 1·299 for carbon dioxide.

For polyatomic gases it is found that the value of γ approximates more and more nearly to unity as the number of atoms within the molecule increases. Thus for chloroform ($CHCl_3$), ethyl alcohol (C_2H_5OH), and ether ($(C_2H_5)_2O$), γ has the respective values of 1·15, 1·13 and 1·03.

Hence in the equation $\gamma = 1 + \dfrac{2}{3\beta}$ we see that, to the same degree of approximation, $\beta = 1$ for monatomic gases, $\beta = \frac{5}{3}$ for diatomic gases, and $\beta = \frac{7}{3}$ for triatomic gases, and that as the molecular complexity increases γ tends to unity, and β to infinity.

Now, in the case of monatomic gases, we can see that it follows from considerations of symmetry, and from the experimental evidence of the uniformity of the pressure exerted on the walls of a small containing vessel, that the kinetic energy of the molecules—(which is all translatory energy)—must be equally divided in the three directions of motion, i.e. amongst the three degrees of freedom, corresponding to the three components of the velocity of the centre of mass of each molecule along the three axes of space.

In accordance with the Law of Equipartition of Kinetic Energy originally developed by Maxwell and Boltzmann the division of the kinetic energy of the molecules is equal however many degrees of freedom exist when the distribution of internal energy has acquired a permanent state.

Consequently we should conclude that diatomic gases were possessed of five degrees of freedom, since the total energy of such gases equals $\frac{5}{3}$ times their translatory energy—this translatory energy, of course, having three degrees of freedom.

Similarly triatomic gases should possess seven degrees of freedom, and the number of degrees of freedom would increase progressively with the molecular complexity.

If, however, a molecule possess rotatory energy we should anticipate the existence of at least *six* degrees of freedom, the three extra degrees corresponding to rotation about the three axes of space. It has been suggested that the molecules of diatomic gases, for example, might be regarded as pairs of atoms, rigidly attached together, so that the distance between the atoms remained invariable—each atom being itself symmetrical about an axis and being so attached that the two axes of symmetry were coincident with the axis of the molecule. The whole molecule would thus possess symmetry about one axis, and rotation about this axis of symmetry could be ignored, thus giving rise to five degrees of freedom.

Such a theory is, however, untenable, for it requires the assumption of an infinite force between the atoms in order that they may be absolutely fixed relatively to one another, and, moreover, the existence of spectral lines clearly indicates that vibrations of the atoms actually exist. An explanation of the difficulty has been given by J. H. Jeans, and has already been indicated in referring to the existence of spectral lines in the case of monatomic gases.

Jeans pointed out that the Maxwell-Boltzmann theorem of equipartition of energy is based upon a definite assumption, namely, that there is no interaction between matter and æther—in other words, that it is only applicable to conservative dynamical systems. For such systems, when in a state of equilibrium, the Maxwell-Boltzmann theorem holds good. Now an actual gas, in nature, is *never* in a state of conservative equilibrium for a finite time. Unless a gas could be enclosed in an "adiabatic space" for a sufficient length of time, the Maxwell-Boltzmann theorem could not be expected to apply. In other words, actual molecular systems are dynamically non-conservative, for energy is being continually dissipated into the æther.[1]

Jeans further showed that the normal state for a non-conservative gas corresponds to the condition that the rate of dissipation of energy is very slow, and that when in this normal state the law of equipartition of energy will not apply. This condition is satisfied by actual gases under ordinary circumstances, since they are not radiating an appreciable amount of energy. For such gases, when in this normal state, practically all the energy is shared amongst a few of the degrees of freedom—the internal degrees of freedom receiving, in general, far less energy than the three translational degrees. Thus we have seen that the vibratory energy corresponding to the spectral lines must generally represent a practically negligible amount of energy, for such spectral lines are frequently very numerous, and if the vibratory degrees of freedom each received the share of energy indicated by the law of equipartition it is clear that the value of γ would differ inappreciably from unity.

To summarise this portion of the discussion: We have seen that the total kinetic energy of a molecule may consist of translatory,

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[1] It is, of course, only through the dissipation of energy, in the form of light-waves, that we become aware of the existence of the internal degrees of freedom.

rotatory, and vibratory energy. If the molecules of a gas be perfectly smooth, elastic, and spherically symmetrical, no amount of interaction can alter their rotatory energy, and the latter may, therefore, be ignored. If the molecules very approximately, but not perfectly, satisfy these conditions, then collisions will give rise to only very small rotations. Consequently, if the rotatory energy undergo dissipation, such dissipation must be extremely slow.

Further, it can be shown that the gain of vibratory energy due to collisions is also very small, as is the dissipation of energy which arises therefrom.

Such gases are monatomic and practically all their molecular energy is translatory. For such gases β is approximately unity and $\gamma = 1{\cdot}667$.

For polyatomic gases we must imagine that the molecules are no longer spherically symmetrical, and consequently an appreciable transfer of energy from translatory to rotatory will in general occur at a collision. Here also, if dissipation of rotatory energy occur, it must be extremely small, for otherwise dissipation of energy from the gas as a whole would rapidly take place, and this is contrary to all experimental evidence.

In the case, then, of such polyatomic gases an appreciable amount of the molecular energy will be rotatory, and β will have a value greater than unity, whilst the value of γ will be less than 1·667. The greater the molecular complexity of the gas, the greater, in general, will probably be the spherical asymmetry, and consequently the greater the rapidity with which the transference of energy between the translatory and rotatory forms will take place. Also, since for highly complex gases the value of γ approximates closely to unity, with a correspondingly large value for β, it is clear that their molecules cannot be regarded as rigid, but must possess considerable internal vibratory energy in addition to their rotatory and translatory energy.

In general, we may state that for certain of the degrees of freedom an appreciable transfer of energy from the translatory form may take place during molecular collisions, whereas for the remaining degrees of freedom the transference of energy is extremely small.

Consequently, on adding energy in the form of heat to a gas, some of the (approximate) equilibrium states for some of the degrees of freedom are rapidly brought about, whereas for the other degrees of freedom the transference of energy is so extremely slow that the attainment of the (approximate) states of equilibrium requires an exceedingly long time. The equilibrium states are only approximate, for the gas is never in a condition of conservative equilibrium.

For monatomic gases equilibrium amongst the three translatory degrees of freedom is very rapidly attained, but since the molecules may be regarded as nearly perfectly smooth symmetrical spheres it is clear that the rotatory energy would be altered only exceedingly slowly by any increase in the translatory energy due to an addition of heat to the gas.

In the case of diatomic gases apparently five of the degrees of freedom rapidly acquire a state of equilibrium, and for triatomic gases seven degrees of freedom behave similarly.

The values experimentally found for γ (and hence for β) for different gases only correspond approximately, and not exactly, to an integral number of degrees of freedom in each case. The probable explanation of this divergence is to be found in a lack of homogeneity in actual gases, due to partial dissociation or molecular aggregation, for it is obvious that dissociation into molecules of a simpler nature will raise the value of γ, and that aggregation into more complex molecules will lower its value.

30. The Molecular Heats of Different Gases.—We may conveniently conclude this chapter by calculating the numerical values of the molecular heats at constant pressure, and at constant volume, for different gases. The molecular volume of any gas is, approximately, 22,380 c.cs. at 0° C. and 76 cms. of mercury. Substituting, therefore, in the equation $P.V. = R.\theta$, we have—

$$\begin{aligned} R_m &= \frac{76 \times 13{\cdot}596 \times 981 \times 22{,}380}{273} \text{ ergs/degrees absolute,} \\ &= 8{\cdot}31 \times 10^7 \text{ ergs/degrees absolute,} \\ &= \frac{8{\cdot}31}{4{\cdot}19} \text{ calories per degree,} \\ &= 1{\cdot}98 \text{ calories per degree, where } R_m \text{ refers to the molecular} \end{aligned}$$

weight of the gas.

Now for a perfect gas, $C_V = \frac{3}{2}R$,

$$C_p = C_V + R = \tfrac{5}{2}R,$$

$$\text{and } \gamma = 1\tfrac{2}{3}.$$

Consequently, in the case of monatomic gases, we should anticipate that the molecular heat at constant pressure, Cm_p, would equal $\frac{5}{2} \times 1{\cdot}98$; i.e. 4·95 cals., and the molecular heat at constant volume, Cm_V, would equal $\frac{3}{2} \times 1{\cdot}98$; i.e. 2·97 cals.

For diatomic gases, $\gamma = \dfrac{Cm_p}{Cm_V} = 1\frac{2}{5}$, but $Cm_p - Cm_V$ will still equal 1·98 cals., provided internal cohesive forces can be neglected—for then, as we have seen in Chapter I., the difference between the specific heats merely represents the external work done during expansion.

Hence $\qquad Cm_p = 6{\cdot}93$ cals., and $Cm_V = 4{\cdot}95$ cals.

For triatomic gases, $\gamma = \dfrac{Cm_p}{Cm_V} = 1\frac{2}{7}$, and $Cm_p - Cm_V = 1{\cdot}98$ cals.

Whence $\qquad Cm_p = 8{\cdot}91$ cals., and $Cm_V = 6{\cdot}93$ cals.

The molecular heats at constant pressure, and constant volume, as obtained by direct observations on a number of gases, are given in the following table :—

Gas.	Molecular Weight.	C_p.	Cv.	Cm_p.	Cmv.
Argon . .	39·88	0·123	0·0746	4·91	2·97
Hydrogen . .	2·02	3·402	2·402	6·86	4·84
Nitrogen . .	28·02	0·244	0·175	6·83	4·90
Air	28·88	0·237	0·1715	6·85	4·95
Carbon Dioxide .	44·00	0·202	0·1650	8·88	7·26
Water Vapour .	18·02	0·465	0·340	8·38	6·13

The agreement is fairly good except for the last mentioned. The specific heats of water vapour are those at 100° C., the pressure being atmospheric in the case of C_p. Since at this temperature and pressure the water vapour is at its liquefying point, a very large proportion of the molecules must be close together and exerting cohesive forces, and the difference between the specific heats will no longer correspond only to the external work performed owing to expansion.

CHAPTER IV.

THE ELASTICITY OF GASES, AND THE CONTINUITY OF THE LIQUID AND GASEOUS STATES.

31. Boyle's Law.—In Chapter II. we deduced a number of relationships which apply to a perfect gas.

It will now be convenient to consider, in greater detail, how far these theoretical conclusions are in agreement with the experimental results obtained for actual gases.

One of the most distinguishing characteristics of a gas is its compressibility, and, accordingly, we shall commence with a discussion of the relations obtained between the pressure and the volume of any gas, both when the temperature is constant and no change of state occurs, and also when liquefaction takes place.

Robert Boyle, in a paper communicated to the Royal Society in 1661, first stated the relation which obtains between the pressure and the volume of a given mass of gas when the temperature is constant and no change of state occurs. He compressed air in a bent tube by means of mercury, and found that the pressures and volumes were in reciprocal proportions. In 1662 Boyle published a full account of his experiments in a book entitled "The Defence of the Doctrine Touching the Spring and Weight of Air."

In accordance with Boyle's results, we may state that the volume of a given mass varies inversely as the pressure to which it is subjected, or that the density of a gas varies directly as its pressure.

Thus if V be the volume of a given mass of gas, and P the pressure to which it is subjected, we have, in accordance with Boyle's Law—

$$\text{P.V.} = \text{constant, when the temperature is constant.}$$

It follows that if ρ be the density of a gas, under pressure P,

$$\frac{\text{P}}{\rho} = \text{constant, when the temperature is constant.}$$

If we plot Boyle's results, taking the pressure as ordinates and the volumes as abscissæ, we obtain the rectangular hyperbola, A, shown in Fig. XIV.; by plotting the pressures against the reciprocals of the volumes we obtain the straight line, B, in the same figure.

Boyle's Law was discovered independently by Mariotte in 1676, and is, therefore, sometimes known as Mariotte's Law.

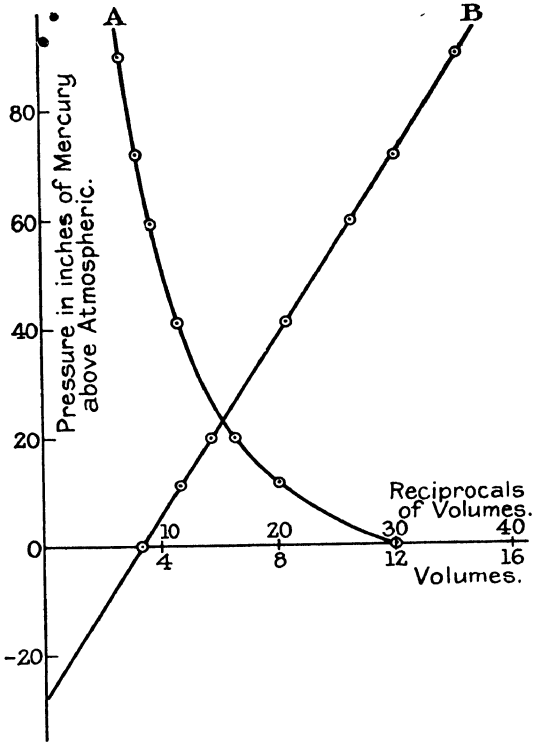

Fig. XIV.

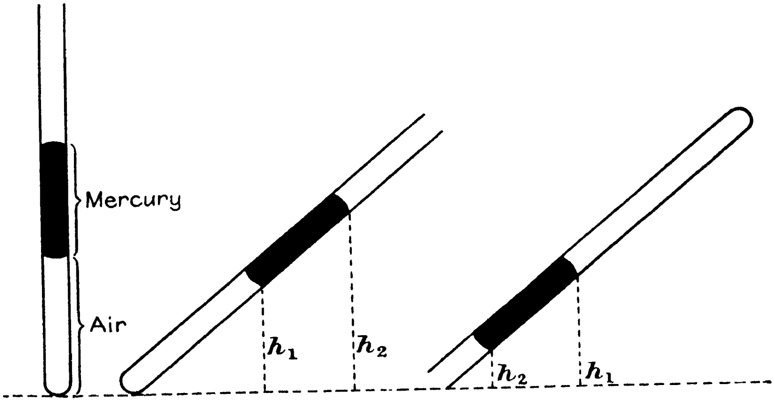

Fig. XV.—Boyle's Law Apparatus.

Experiment VII.—A simple form of apparatus for experiments on Boyle's Law consists of a long narrow glass tube, sealed at one end, and containing a column of air enclosed by means of a mercury column (Fig. XV.). The tube is held in a vertical position, and the lengths of the enclosed air column and of the mercury column are read. Some of the mercury is then ipped out, by slightly inclining the ube, and the latter is then restored o the vertical position, and the lengths of the air and mercury columns are again read. This procedure is repeated ill no more mercury will run out. Readings are then obtained with the ube in inclined positions, in which cases the differences in vertical heights $h_2 - h_1$) must be taken as the readngs for the mercury column. Pressures less than atmospheric may be obtained by having the closed end of he glass tube uppermost. Provided he glass tube be of uniform bore, he volume of enclosed air is proporional to the length of the air column, and its pressure is obtained by adding o the atmospheric pressure the corresponding reading ($h_2 - h_1$) of the mercury column. The product P.V. will be found to be approximately constant, and by plotting P. against V. a rectangular hyperbola will be obtained, as n Fig. XIVA.

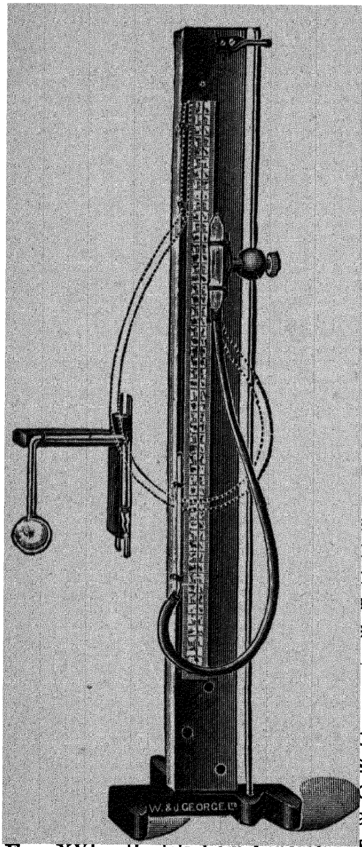

FIG. XVI.—Boyle's Law Apparatus (with Jolly's Air-bulb Attachment).

Experiment VIII.—Determinations of the relationship between the pressure and the volume of a given mass of gas, at constant temperature, may also be made by using the more convenient form of apparatus shown in Fig. XVI. The air bulb attachment enables the same apparatus to be used as Jolly's constant volume air thermometer, which will be referred to in the next chapter.

Both in Experiments VII. and VIII. the air, or other gas, should be carefully dried by connecting the containing tube to a tube containing calcium chloride, or other suitable drying agent, for some time previously to performing an experiment.

32. Compressibility, and the Bulk Modulus of Elasticity.—Now, in accordance with the kinetic theory, we may regard matter as built up of numerous small particles separated by interspaces, and, consequently, on compression these particles are brought closer together. We define the compressibility of any fluid, whether gaseous or liquid, in the following manner:—

Consider a volume, V, of the fluid subjected to a pressure, P. Let δV and δP be corresponding small increments in the volume and pressure, δV being, of course, negative if δP is positive.

Then $\frac{-\delta V}{V}$ is termed the compression, and $\frac{-\delta V}{V.\delta P}$ is termed the compressibility.

The reciprocal of the compressibility is defined as the bulk modulus of elasticity, E.

That is $$E = \frac{-V.\delta P}{\delta V}.$$

It should be noted that the compression, compressibility, and elasticity are *not* constant quantities, but depend upon the initial values of V. and P.

For a gas which obeys Boyle's Law, we have—

$$P.V. = (P + \delta P)(V + \delta V),$$

if the temperature be constant.

$$\therefore P.V. = P.V. + P.\delta V. + V.\delta P. + \delta P.\delta V.$$
$$\therefore P.\delta V = -V.\delta P,$$

since $\delta P.\delta V.$ is negligible when the change is made sufficiently small.

Whence $$E_{iso.} = \frac{-V.\delta P.}{\delta V} = P.$$

Hence if a gas obeying Boyle's Law be compressed isothermally, its isothermal elasticity is equal to its pressure.

If, however, the gas be compressed adiabatically, the relation between its pressure and its volume is given by the equation—

$$P.V^{\gamma}. = \text{constant}.$$
$$\therefore P.V^{\gamma}. = (P + \delta P)(V + \delta V)^{\gamma},$$
$$= (P + \delta P)(V^{\gamma} + \gamma.V^{\gamma-1}.\delta V + \text{negligible terms}).$$
$$\therefore \gamma.P.V^{\gamma-1}.\delta V. = -V^{\gamma}.\delta P, \text{ the term } \gamma.V^{\gamma-1}.\delta P.\delta V. \text{ being negligible.}$$
$$\therefore \gamma.P. = \frac{-V.\delta P.}{\delta V}$$

Whence $$E_{adia.} = \frac{-V.\delta P.}{\delta V} = \gamma.P,$$

Thus the adiabatic elasticity of the gas is equal to γ times its pressure. This was the result previously employed in determining the value of γ from the velocity of sound in a gas (§ 26).

The values of the isothermal and adiabatic elasticities may be more readily obtained as follows :—

For an isothermal compression, P.V. = constant.

$$\therefore \log . P + \log . V = \text{constant}.$$

Differentiating, we have—

$$\frac{dP}{P} + \frac{dV}{V} = 0.$$

$$\therefore E_{\text{iso.}} = -\frac{V . dP}{dV} = P.$$

For an adiabatic compression, $P.V^{\gamma}.$ = constant.

$$\therefore \log . P + \gamma . \log . V = \text{constant}.$$

Differentiating, we have—

$$\frac{dP}{P} + \frac{\gamma . dV}{V} = 0.$$

$$\therefore E_{\text{adia.}} = -\frac{V . dP}{dV} = \gamma . P.$$

33. Deviations from Boyle's Law.—Despretz, in 1827, first showed that for certain gases Boyle's Law was only approximately true. He compressed several different gases in barometer tubes of equal length—standing in the same reservoir of mercury—by enclosing the apparatus in a large vessel full of water and applying pressure by means of a screw. The level of the mercury was initially the same in each tube, but, as the pressure was increased, it was observed that the gases were unequally compressed—the more easily liquefiable gases, such as ammonia and carbon-dioxide, being compressed more than air, whereas, at higher pressures, hydrogen was found to be slightly less compressible than air. Consequently, some of the gases, at any rate, did not strictly obey Boyle's Law.

Experiment IX.—Several glass tubes of uniform bore are sealed at one end, and are all cut to the same length. They are then filled with different dry gases—e.g. air, carbon-dioxide, ammonia, and sulphur-dioxide—and are fixed with their open ends at the same depth beneath the surface of the mercury in the reservoir of an Oersted's Piezometer (see Chapter VII., Fig. LV.). The mercury is readily brought to the same level in each of the tubes by tilting the latter, in a larger vessel of mercury, and allowing a little of the enclosed gases to escape—or, better, by enclosing the mercury reservoir and tubes in the receiver of an air-pump, and slightly exhausting, so that a little of the contained gas may escape from each tube. The mercury will then rise to the same level in each tube when the pressure in the receiver is again raised to atmospheric. The Piezometer is then filled with water, and pressure applied by means of the pump. It will be readily observed that the sulphur-dioxide and ammonia are more compressible than the carbon-dioxide, and that the latter is more compressible than the air. If the water in the Piezometer be cold, the sulphur-dioxide and ammonia may easily be liquefied at moderate pressures, and the respective pressures at which liquefaction takes place, at the temperature of the water, can be determined with sufficient accuracy by assuming that, for moderate pressures, the *air* strictly obeys Boyle's Law. For this purpose the tube containing the air should be calibrated so that the change of volume may be directly observed, and sufficient mercury poured into the reservoir to make the level of the mercury inside and outside the tubes the same before the Piezometer is filled with water. The initial volume of air, at the atmospheric pressure, is then noted. Under these circumstances it is unnecessary for the Piezometer to be fitted with a pressure gauge.

When a given mass of a gas is submitted to high pressures, the relative accuracy with which its volume can be determined decreases as the pressure increases. Twenty years after Despratz's experiments, Regnault carried out an investigation on the relation between the pressure and volume of a number of different gases at pressures ranging from the atmospheric up to about 30 atmospheres, and, by progressively increasing the quantity of gas undergoing compression, he was able to attain a uniform degree of accuracy in the measurements of the volume.

A given quantity of the dry gas was enclosed in a glass tube, connected to a long manometer tube and also to a pump, and was surrounded by a water-jacket in order to maintain a constant temperature. The pump and connecting tube were filled with mercury, and the level of the mercury was initially adjusted to be the same in the glass tube containing the gas and in the manometer. Mercury was then pumped in until the volume occupied by the gas was reduced to half the initial volume, and the pressure of the enclosed gas was obtained by adding to the Barometric pressure the pressure due to the difference in level between the mercury in the tube containing the gas and in the open manometer tube.

More of the dry gas was now pumped in under this pressure, until the original volume was restored, and the mercury pumped in until the volume was again reduced to half the initial volume, and a new reading of the pressure obtained.

By proceeding in this manner, Regnault showed that none of the gases with which he experimented strictly obeyed Boyle's Law. In general, he found that for pressures between 1 and 30 atmospheres, the product P.V. decreased as P. increased, but, in the case of hydrogen, the opposite result was obtained, P.V. increasing directly with the pressure.

In 1850, Natterer showed that, in the case of air and nitrogen, the product P.V. reached a minimum value at a certain pressure, and that, at higher pressures, P.V. increased as the pressure increased. Thus, at high pressures, these gases behaved similarly to hydrogen.

Further investigations, at very much higher pressures, were carried out by Amagat, and by Cailletet, in 1870. Amagat employed a steel manometer tube, 300 metres in length, which passed up the shaft of a mine. The lower end of the manometer tube was connected to a closed vessel containing mercury, and the mercury could be forced up the tube by means of a large screw working into this vessel. A calibrated tube, closed at its upper end, was also connected to the mercury container, and this tube was filled with dry nitrogen, and water-jacketed in order to maintain it at a constant temperature. In this manner the volume of the nitrogen at various pressures was obtained, and the nitrogen tube could subsequently be used as a pressure gauge in carrying out experiments with other gases.

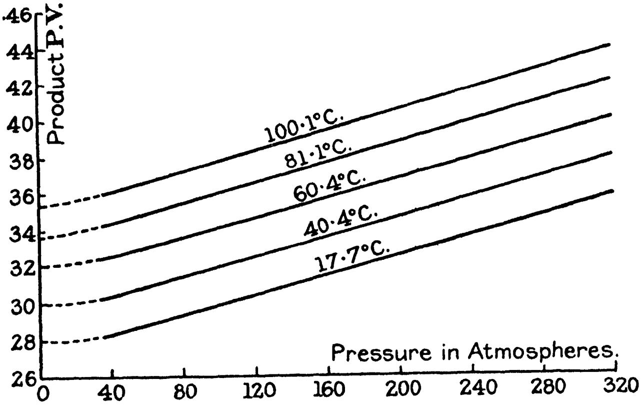

FIG. XVII.—Hydrogen.

Cailletet also worked at the bottom of a mine, using a manometer tube 250 metres in length.

Figs. XVII., XVIII., XIX., and XX. show some of Amagat's results. In these figures the products P.V. are taken as ordinates and the pressures (in atmospheres) as abscissæ. The temperature for any particular experiment is shown by the number on the corresponding curve.

In the case of nitrogen (Fig. XVIII.) it will be seen that the pressure corresponding to the minimum value of the product P.V, diminishes with rise in temperature, whereas for ethylene (Fig. XIX.), the opposite result is observed. Carbon dioxide was found to behave in a similar manner to ethylene, and Amagat showed that, at a certain temperature, the pressure corresponding to the minimum value of P.V. was a maximum, and that, at higher temperatures, the pressure corresponding to the minimum value of P.V. diminished. This is clearly shown in Fig. XX., where the dotted curve passing through the minimum points possesses a parabolic form.

At the highest temperature shown for nitrogen—viz. 100·1° C.—the sag in the curve corresponding to the minimum value of P.V. has practically disappeared.

In the case of hydrogen (Fig. XVII.), P.V. increases with the pressure at all the temperatures shown in the figure, and we may assume that this is probably due to the fact that, at ordinary temperatures, hydrogen is much farther from its critical temperature than the other gases (*vide* § 34). It is to be anticipated that, at sufficiently low temperatures, the curves for hydrogen would resemble those for nitrogen or carbon-dioxide.

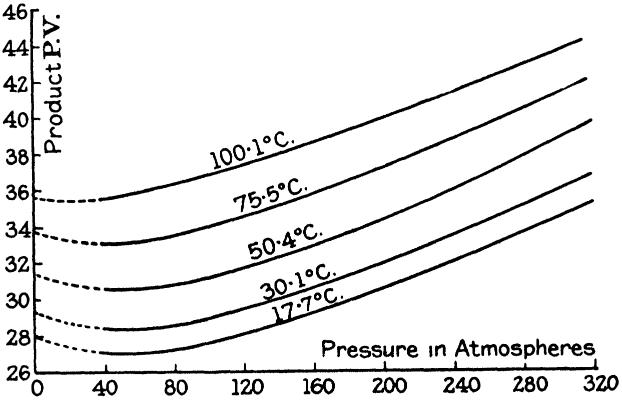

FIG. XVIII.—Nitrogen.

In a series of later experiments, Amagat employed pressures up to 3,000 atmospheres—but it is extremely probable that, at such high pressures, a considerable amount of the gas condenses upon the walls of the containing tube, and some of the gas may even be forced into the walls themselves. Consequently the results of experiments at very high pressure must be accepted with reservation.

At very low pressures, the gas which is condensed on the walls of the containing tube gradually comes off from the latter, and it is, therefore, a matter of great difficulty to determine the existence of any deviations from Boyle's Law. Such deviations, however, if they exist, are very small indeed. Another source of error at low pressures arises from the vapour pressure of the mercury over which the gas is compressed: at high pressures the effect due to the vapour pressure is negligible.

Amagat's results agree fairly well with the relation between the pressure and the volume of a given mass of gas deduced by van der Waals. This relationship will be discussed in Chapter VI.

We may now summarise the experimental evidence which has, so far, been considered, and state that—

(*a*) At sufficiently high pressures the product P.V. for all gases increases with the pressure.

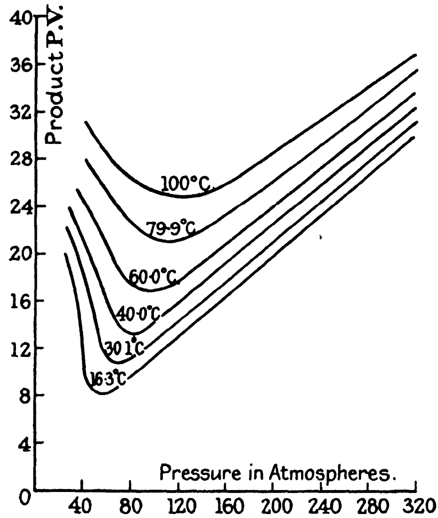

Fig. XIX.—Ethylene.

(*b*) At low pressures the product P.V., in general, decreases as the pressure increases. Probably this is true for all gases at sufficiently low temperatures.

(*c*) At a certain value of the pressure the product P.V. is, therefore, a minimum, if the temperature be sufficiently low—the sag in the curve becoming more and more fully developed as the temperature approaches the critical temperature (*vide* § 34).

(*d*) At low temperatures, the pressure corresponding to the minimum value of P.V. increases with rise in temperature, and at higher temperatures it decreases.

(*e*) As the temperature is progressively raised, the decrease in P.V., at low pressures, with rise in pressure—and hence the minimum values of P.V.—become, in all cases, less and less noticeable on the curves.

34. Andrews' Experiments.—Reference has already been made, in Experiment IX., to the liquefaction of certain gases. We shall now discuss more fully both the conditions under which such liquefaction may take place, and the relationship which exists between the liquid and gaseous states.

It will be convenient to consider, first, the classical experiments carried out by Andrews in 1863, for these experiments first supplied a definite explanation of many of the more important phenomena connected with the change of state from vapour to liquid and vice versa.

Andrews employed a tube similar to that represented in Fig. XXI. AB was a thick walled capillary tube which was fused to a tube BC of about 2·5 mms. diameter. The whole tube was accurately calibrated, after which a current of dry carbon-dioxide was passed through it for many hours, until the amount of air mixed with the carbon-dioxide issuing from the tube was found to be very small and constant.

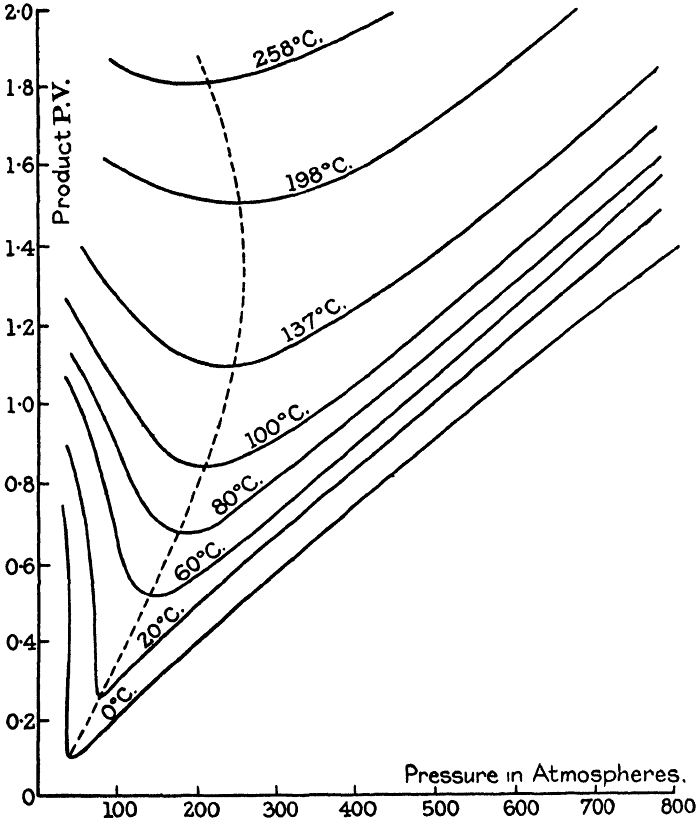

Fig. XX.—Carbon-dioxide.

This amount of air, which constituted about 0·1 per cent. to 0·2 per cent. of the whole gas, was determined, and allowed for in the subsequent experiments.

The capillary tube was then sealed off at A, and the open end D placed below the surface of some mercury. By heating the tube, and then allowing it to cool, a small stopper of mercury was drawn into the lower part, and the whole apparatus was then placed inside the receiver of an air pump and the pressure reduced, so that about one quarter of the enclosed gas escaped. On again raising the pressure in the receiver to the atmospheric pressure mercury filled the tube DC and part of CB.

The glass tube was next fixed inside a strong copper compression chamber with the capillary tube, AB, projecting outside, and—the copper chamber being filled with water—pressure was applied by means of a steel screw. The volume occupied by the carbon-dioxide was determined by observing the position of the mercury surface in the capillary tube, and the applied pressure was measured by having a similar compression apparatus containing air instead of carbon-dioxide, with a copper tube connecting the two compression chambers. The pressures thus obtained from the compression of the air in the second tube were very approximately correct, since, under these conditions, the deviation of air from Boyle's Law is only small. The change in the internal volume of the tubes under pressure may also be treated as negligible. Each of the tubes was surrounded by a

Fig. XXI.

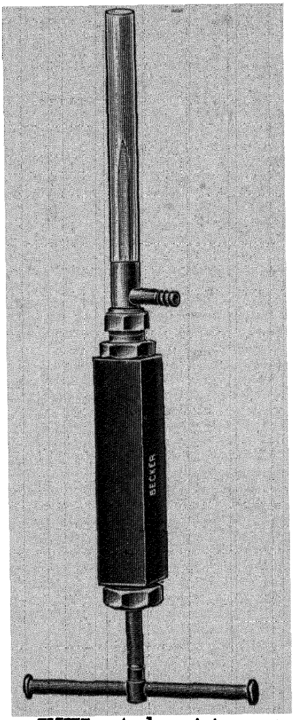

Fig. XXII.—Andrews' Apparatus (simple form).

water jacket, the temperature being kept constant throughout for the air, whereas the carbon-dioxide was maintained at any temperature desired.

Fig. XXII. illustrates a simple form of Andrews' compression apparatus. The connecting copper tube is not shown in the figure.

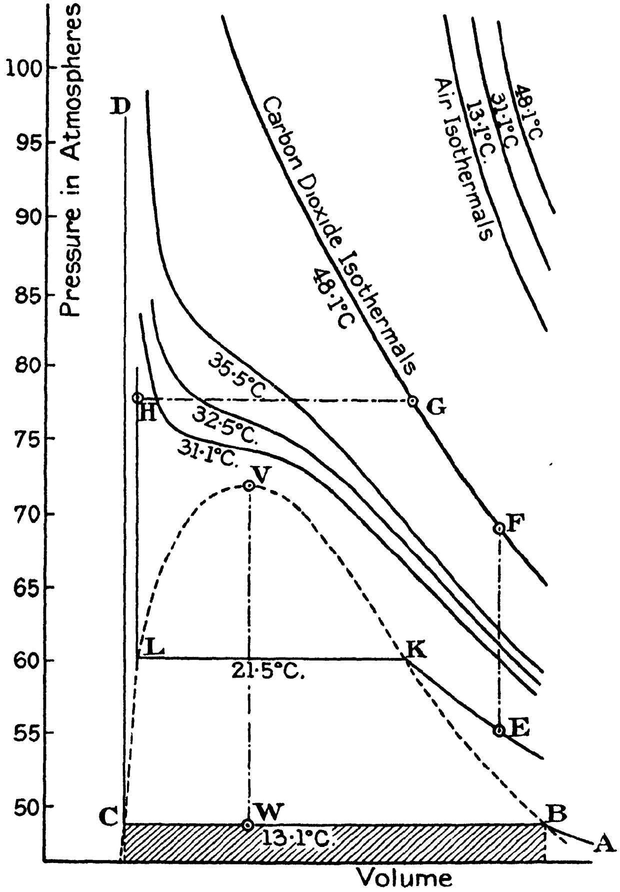

Fig. XXIII.—Carbon-dioxide Isothermals (Andrews).

The results obtained by Andrews are shown in Fig. XXIII. which gives the isothermals for carbon-dioxide. In the case of the 13·1° C. isothermal it was found that, at low pressures, the carbon-dioxide—although somewhat more compressible than a perfect gas—approximately obeyed Boyle's Law, as shown by the curve AB. When the pressure reached 48·89 atmospheres it was observed that liquefaction commenced, and the pressure now remained constant while the volume was diminished, until all the carbon-dioxide had assumed the liquid state. This is indicated by the horizontal line BC in the diagram, the ordinate of which is, of course, the saturation vapour pressure at 13·1° C. Any further reduction in the volume of the liquid carbon-dioxide required a very considerable increase in the pressure, and the remainder of the isothermal, CD, approximated to a straight line, slightly inclined towards the axis of pressure.

The work which must be expended in order to completely convert the saturated vapour into liquid, at 13·1° C., is represented by the shaded area in Fig. XXIII. In Andrews' actual results it was noticed that, owing to the small quantity of air which was present, the pressure increased slightly during the condensation of the carbon-dioxide, so that the line BC was not exactly straight and parallel to the axis of volume, and, also, the corners at B and C were slightly rounded. The 21·5° C. isothermal exhibited similar characteristics, but here liquefaction did not commence until the pressure had risen to approximately 61 atmospheres.

In the case of the 31·1° C. isothermal, however, no discontinuity corresponding to the coexistence of the gaseous and liquid states was observed, and the carbon-dioxide remained homogeneous throughout the compression, the diminished slope at one part of the curve being the only indication of what, at lower temperatures, represented a change of state. The higher isothermals resembled, in general, the 31·1° C. isothermal, but the diminution in the slope at one part of the curve became less and less conspicuous as the temperature was raised, and practically disappeared at 48·1° C., the isothermal corresponding to the latter temperature approximating to that of a perfect gas.

It was found by numerous trials that the highest temperature at which the carbon-dioxide could, by pressure, be visibly reduced to the liquid state was 30·92° C., and this temperature is therefore termed the *critical temperature* for carbon-dioxide, and the isothermal corresponding to this temperature the *critical isothermal.*

The behaviour of many other substances has been similarly studied by Andrews and by other investigators, and the same general results obtained in all cases.

The dotted curve in Fig. XXIII., which passes through the extremities of the horizontal portions of the isothermals, includes within its area all the conditions of coexistence at a given temperature of the gaseous and liquid states. This curve is called the *border-curve,* and it was suggested by Andrews that the term *vapour* should be applied to the condition of a substance below the critical isothermal and to the right of the border-curve, and the term *liquid* to the substance when below the critical isothermal and to the left of the border-curve, and that the term *gas* should only be given to a substance when above the critical isothermal.

In the case of a vapour, the decrease in volume with increase in pressure is greater than in accordance with Boyle's Law, i.e. P.V. diminishes as P. increases, whereas for a liquid the reverse is true, and P.V. increases as P. increases.

For isothermals above the critical temperature it is found that for the right-hand portion of each curve P.V. diminishes as P. increases, and, having reached a minimum value, P.V. then increases as P. is further increased. The point where P.V. has its minimum value in a gas may thus be regarded as indicating what at temperatures below the critical would correspond to a change of state, and the initial decrease, and subsequent increase, in the value of the product P.V., with increase in P., may be taken as a survival of the vaporous and liquid states. The investigations of Regnault, Natterer, and Amagat, which have been previously described, thus acquire a fuller significance.

The vertex of the border-curve, V, is termed the *critical point.* For carbon-dioxide it corresponds to a critical temperature of 30·92° C., and a pressure, called the *critical pressure,* of about 73 atmospheres. The *critical volume* is sometimes defined as the ratio of the volume of a given mass of the gas at the critical temperature and critical pressure to the volume of the same mass of the gas at 0° C. and 76 cms., and sometimes as the volume of unit mass of the gas at the critical temperature and pressure. Adopting the former definition, the critical volume for carbon-dioxide is, approximately, 0·0066, and, adopting the latter definition, it is approximately 3·36 c.cs.

The critical isothermal just touches the border-curve at the critical point, and since at that point the isothermal becomes horizontal it is to be anticipated that in the neighbourhood of the critical point very small changes in pressure will correspond to considerable changes in the volume, and, consequently, in the density of a gas. Andrews, in fact, observed that at temperatures slightly above the critical temperature and for pressures near the critical pressure any change in the pressure gave rise to flickering movements throughout the tube, somewhat similar to those observed when liquids of different densities are mixed together. These flickering movements are due to relatively great local changes in the density of the gas. It should be noted, in this connection, that the weight of the gas will exercise a considerable influence when near the critical point, since the lower layers of gas will be under a higher pressure, and will have, in consequence, a considerably higher mean density than the upper layers in the tube.

Andrews further observed that a substance could be transformed from the vaporous to the liquid state, or vice versa, without visible condensation or vaporisation taking place. The manner in which such a transformation may be effected will be readily understood by a study of Fig. XXIII.

Let us start with the carbon-dioxide in Andrews' compression apparatus at a temperature of 21·5° C., and at 55 atmospheres pressure. Its condition will then be represented by the point E, and it will be in the state of vapour. If the temperature be raised to 48·1° C., while the volume remains unchanged, the pressure will rise to approximately 68 atmospheres, and the carbon-dioxide will now be in the gaseous condition represented by the point F—no discontinuity in the properties of the carbon-dioxide being observed when crossing the critical isothermal and changing from the state of vapour to that of gas.

Next compress the gas isothermally to any pressure greater than the critical pressure, so that it reaches a point such as G on the 48·1° C. isothermal.[1]

Now cool the gas to its initial temperature of 21·5° C., keeping the pressure constant by reducing the volume by means of the steel compression screw. The carbon-dioxide will now have reached the point H, and will, consequently, be in the liquid state, but no discontinuity will have been observed when crossing the critical isothermal and changing from gas to liquid.

The carbon-dioxide is clearly a vapour at E, for if it be compressed isothermally condensation will commence at K, and it is equally clearly a liquid at H, for on reducing the pressure at constant temperature ebullition will commence at L, with the appearance of a definite liquid meniscus. Above the critical temperature the carbon-dioxide is in the gaseous state. Yet the contents of the compression tube have remained perfectly homogeneous during the transformation from E to H.

Andrews was thus led to the conclusion that the vaporous and liquid states of matter are "only distant stages of a long series of continuous physical changes."

35. Cagniard de la Tour's Experiment.—It is apparent from Fig. XXIII. that, as the temperature is raised, the horizontal portions of the isothermals grow shorter and shorter, and, consequently, the volume occupied by the saturated vapour approaches more nearly to the volume of the liquid when just completely condensed. At the critical point the horizontal portion vanishes, and the volumes of vapour and liquid coincide. Thus the densities of the vapour and liquid become equal at the critical point. The approach of the vapour and liquid states until they coincide at the critical point was first observed, in 1822, by Cagniard de la Tour. He employed a sealed tube of the form shown in Fig. XXIV. The end A contained air, which served to indicate the pressure, and the end B contained a suitable quantity of alcohol and its vapour, the intervening space being filled with mercury. On raising the temperature of

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[1] If the gas be compressed isothermally until the volume corresponding to G is less than the volume of the carbon-dioxide when completely liquefied at 21·5° C.—i.e. is less than the volume corresponding to L—it may next be cooled *at constant volume* to its initial temperature.

B ebullition did not occur, but the alcohol evaporated silently and its vapour pressure increased, compressing the air in A. Cagniard de la Tour observed that, as the temperature was progressively raised, the meniscus between the alcohol and vapour grew flatter, indicating a diminution in the surface tension of the liquid, and that, finally, at about 243° C., the meniscus completely lost its curvature—grew indistinct—and disappeared. The space above the mercury at the end B was now apparently filled with a perfectly homogeneous substance. Other liquids were also investigated, and were found to behave in a similar manner.

This apparently sudden vaporisation at a certain temperature receives a clear explanation from Andrews' researches. For, on again referring to Fig. XXIII., it will be seen that if, for example, we start with the carbon-dioxide in the condition represented by the point W, where it consists partly of liquid and partly of saturated vapour, and then heat it at constant volume, it will pass along the line WV, and, on reaching the critical point, both the liquid and vapour phases will pass directly into the gaseous state.[1]

If the heating be uniform, the vapour pressure exerted upon the surface of the liquid at each point along the line WV will be the saturation pressure at the corresponding temperature, and, therefore, ebullition will not occur.

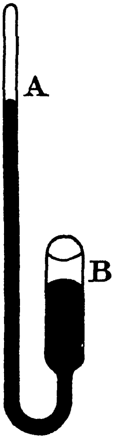

FIG. XXIV.—Cagniard de la Tour's Apparatus.

36. Phenomena at the Critical Point.—*Experiment X.*—Many of the phenomena exhibited by fluids in the neighbourhood of the critical point may be readily observed by means of the simple apparatus illustrated in Fig. XXV. A short and thick walled glass tube, of 3 or 4 mms. internal diameter, containing a liquid and its saturated vapour, is supported inside a large test-tube by means of a wire framework. The relative volumes of liquid and vapour inside the tube must initially be adjusted within fairly narrow limits for the reasons explained below. The test-tube is nearly filled with a liquid that boils at a temperature higher than the critical temperature of the liquid inside the sealed tube, and is gradually heated.[2]

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[1] In Cagniard de la Tour's experiments the volume occupied by the liquid and vapour in B (Fig. XXIV.) increased slightly with rise in temperature, owing to the compression of the air in A (Fig. XXIV.), and, consequently, the point W (Fig. XXIII.), corresponding to the initial condition of the liquid and vapour, should be taken slightly nearer C.

[2] The sealed tube may, conveniently, contain carbon-dioxide, sulphur-dioxide, or ether. For the first-named the test-tube can be filled with water, and, in the other two cases, with glycerine or paraffin-wax.

If, now, the liquid inside the sealed tube occupy initially a relatively large volume compared with that of the saturated vapour, it will be observed that, on raising the temperature, the increase in volume of the liquid due to expansion will exceed the diminution due to evaporation, so that the liquid will soon completely fill the tube, and, if the temperature be further raised, the pressure will increase so much that the tube will probably burst. If, on the other hand, the volume of the liquid be initially small the reverse result will be obtained, the whole of the liquid vapourising before the critical temperature is reached. These changes may be conveniently followed out with the aid of Fig. XXIII. However, if the quantity of liquid inside the sealed tube be neither too large nor too small, the liquid meniscus will remain visible until the critical temperature is attained, and it will be observed that, on approaching the critical temperature, the curvature of the liquid surface decreases, until, at the critical point, the meniscus becomes quite flat and fades away, being replaced by a broader band of mist which vanishes completely at a slightly higher temperature. The tube is now apparently filled with a perfectly homogeneous substance. On allowing the tube to cool the mist reappears, and then a very thick cloud, from which the meniscus suddenly takes form.

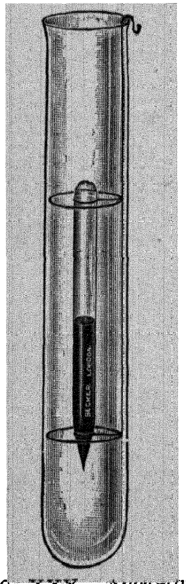

FIG. XXV.—Apparatus for demonstrating critical phenomena.

The appearance of flickering striæ throughout the tube is also very noticeable when the tube has nearly cooled to the critical temperature. The phenomenon of critical opalescence at and near the critical point, which has been investigated by Travers and Usher, may further be observed. If the meniscus disappear near the bottom of the tube, it will be seen that, at a temperature slightly lower than the critical, the liquid below the meniscus becomes opalescent, having a brown colouration by transmitted light, and a white by neglected light. When the meniscus vanishes the opalescence gradually diffuses throughout the tube. If, however, the meniscus disappear near the top of the tube, the opalescence appears above the meniscus in the vapour phase. When the meniscus remains approximately stationary near the middle of the tube, the fluid phase becomes uniformly opalescent throughout, at a temperature slightly below the critical, but in this case the opalescence is much less marked. In all cases the opalescence vanishes at a temperature slightly above the critical.

It should be noted that it is only at the level where the meniscus vanishes that the density within the tube is the true critical density.

Higher up in the tube the density is slightly lower, whereas lower down it is greater. This, as has already been pointed out, is due to the weight of the fluid within the tube. Thus if the meniscus finally vanish near the top of the tube the average density of the fluid will exceed the critical density, and, conversely, if the meniscus vanish near the bottom of the tube the average density will be less than the critical. It is owing to this that the relative volumes of the liquid and vapour initially contained inside the tube can vary within narrow limits, and the critical phenomena still be obtained, for, at the critical temperature, the fluid inside the tube does not merely represent the condition of one point on the critical isothermal, but corresponds to a certain length of this isothermal, and if this length include the critical point the critical phenomena can be observed.

Some uncertainty still exists, however, as to the actual state of a fluid when at, or slightly above, its critical temperature. It has been urged by MM. Cailletet and Colardeau, for example, that the liquid state persists above the critical temperature, and the following experiment would appear to be confirmatory of this point of view.

A very small quantity of iodine was sublimed inside the upper end of a compression-tube, and carbon-dioxide was then compressed in this tube, as in Andrews' experiments, the mercury being protected from the action of the iodine by means of a layer of sulphuric acid. Now, liquid carbon-dioxide will dissolve iodine, forming a violet-coloured solution, but the vapour of carbon-dioxide exerts no such solvent action. Consequently, when the carbon-dioxide was compressed, and partially liquefied, the liquid carbon-dioxide, on reaching the level of the iodine, became coloured violet, the vapour remaining colourless. On now raising the tube to the critical temperature, the meniscus was observed to vanish in the usual manner, but the colouration remained in the portion of the tube which had previously contained the liquid carbon-dioxide, and did not spread to the upper part of the tube. Further, the absorption spectrum of iodine when in solution is unlike its absorption spectrum when in the state of vapour, but spectroscopic examination of the tube revealed no change on passing through the critical point. Consequently the iodine must be regarded as still in solution, and hence it would appear that the liquid state can exist even above the critical temperature. This supports the view suggested previously by Ramsay in 1880, and by M. Jamin in 1883, that at the critical temperature the surface tension of the liquid becomes zero, and, therefore, the meniscus vanishes, but that the liquid state still persists above the critical point. It was inferred by them that the various phenomena observed at the critical point could be accounted for on the assumption of the equality of the liquid and vapour densities at that point, but the fact that the meniscus vanishes implies only that the molecular attraction is equal in the liquid and vapour states, and it does not necessarily follow that the densities of these states are identical. Conversely, if the equality of the liquid and vapour densities at the critical point be postulated, it does not follow, of necessity, that the molecular attraction is also equal and that the meniscus will disappear. MM. Cailletet and Colardeau concluded that the vapour and liquid densities were not necessarily equal at the critical point, but that the vanishing of the meniscus merely implied the equality of molecular attraction, the vapour and liquid then becoming mutually soluble in all proportions. The experiment with iodine, previously described, was regarded as evidence that liquid carbon-dioxide can exist in invisible solution in its own gas at temperatures above the critical, and can only become visible as a liquid phase when cooled below that temperature.

37. **The Mutual Solubility of Liquids.**—The mutual solubility, or miscibility, of liquids supplies an analogy. If we start with any pure liquid and add to it a second liquid with which it is only partially miscible at the ordinary temperature, the second liquid will dissolve in the first and form a homogeneous solution until the concentration reaches some definite value. Beyond this value the second liquid ceases to dissolve, and any further addition now causes the formation of another liquid phase consisting of a solution of the first liquid in the second, the two phases being separated by a distinct meniscus. If the temperature be raised, the second liquid phase will disappear, if the solubility increase with rise in temperature, and a further addition of the second liquid must be made before two liquid phases reappear. If the pressure be kept constant, the concentration of the components in each of the liquid phases will, at any particular temperature, be constant for a given pair of liquids. These two corresponding solutions, at any temperature, are known as *conjugate solutions*. On changing the temperature, the composition of the two solutions will change, and thus two solubility curves may be obtained showing the respective solubilities of the first liquid in the second, and of the second liquid in the first. Now, when one liquid dissolves in another at any particular temperature heat may be evolved or absorbed, and, therefore, in accordance with Le Chatelier's theorem (*vide* Appendix B), the solubility may decrease or increase with rise of temperature.

M. Duclaux, in 1876, and Alexéeff, in 1886, found that although certain pairs of liquids were only partially miscible at the ordinary temperature, yet, on raising the temperature, the mutual solubility increased until, at a certain temperature, they became miscible in all proportions. The temperature corresponding to such infinite miscibility is termed the *critical solution temperature.*

In such cases the concentration-temperature curve possesses the form shown in Fig. XXVI., which illustrates the case of phenol and water. It will be seen from this figure that, starting at the ordinary temperature, the solubility of phenol in water, and of water in phenol, increases with rise in temperature, until, at about 68·4° C., the two solubility curves meet, and, consequently, above this temperature phenol and water are miscible in all proportions. The critical solution temperature is thus 68·4° C.—and the corresponding *critical concentration* is 36·1 per cent. of phenol.

It was further observed by Rothmund that, in several cases, the mutual solubility increased on lowering the temperature, and that at a *lower* critical solution temperature infinite miscibility was attained. Fig. XXVII. illustrates the concentration-temperature curve for triethylamine and water.

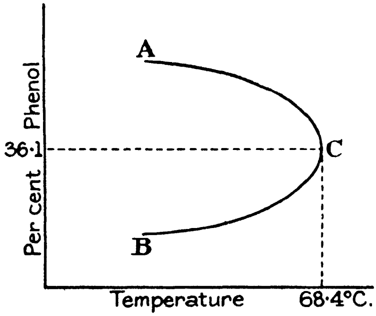

FIG. XXVI.

Finally, it was shown by Hudson for nicotine and water, and by Flaschner and McEwen for 2-methylpiperidine and water, that both an upper and a lower critical solution temperature can be experimentally realised. In the case of nicotine and water the upper and lower critical solution temperatures were 210° C. and 61° C., respectively; for 2-methylpiperidine and water the corresponding temperatures were found to be 227° C. and 79·3° C.

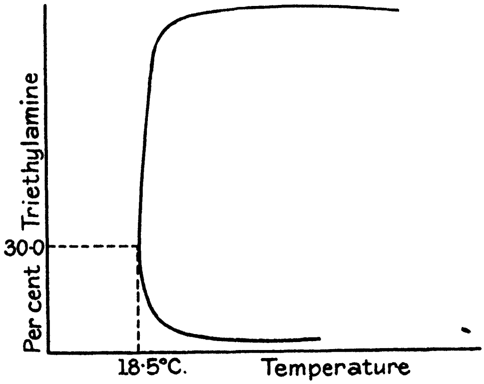

FIG. XXVII.

Consequently for these two pairs of liquids the complete solubility relations are represented by closed curves of an ellipsoidal form, and, in all probability, this is the general form of the concentration-temperature curve for all pairs of liquids.

The concentration-temperature curve for 2-methylpiperidine and water is shown in Fig. XXVIII.

If two liquids, which at the ordinary temperature do not mix in all proportions, be shaken up together, they will in general separate on standing into two distinct layers. On raising, or lowering, the temperature, one of the layers will usually disappear, and a condition corresponding to a point on the solubility curve for one of the liquids will be attained. If, however, the two liquids be taken in the proportion corresponding to the upper critical concentration, and the temperature be gradually raised, it will be observed that the meniscus separating the liquids becomes flatter, and finally disappears at the critical solution temperature, a homogeneous mixture being obtained. On again cooling to the neighbourhood of the critical solution temperature flickering movements may be observed, and, on reaching the critical solution temperature, separation into two layers occurs. The same phenomena occur when a mixture corresponding to the lower critical concentration is cooled below the lower critical solution temperature. A marked critical opalescence may often be noticed. In the case of 2-methylpiperidine and water this opalescence was very strong in the vicinity of the lower critical solution point, but was not observed at the upper point.

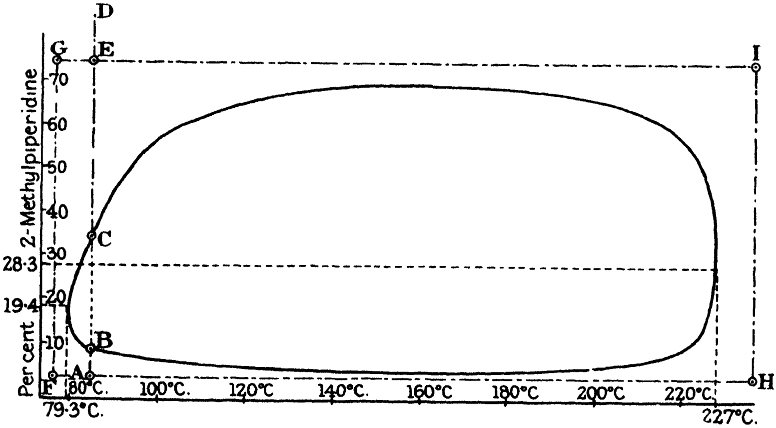

Fig. XXVIII.—Temperature.

Experiment XI.—The concentration-temperature curve for 2-methylpiperidine and water may be determined in the following manner. In order to obtain the lower half of the curve, definite quantities of the base and water are introduced by means of a capillary pipette into a narrow tube, which is blown out at one end into a small bulb, and drawn out at the other end into a capillary (Fig. XXIX.). The mixture having been weighed, the capillary is sealed, and the temperature determined at which separation into two layers takes place. The capillary is then broken off at the end, and, after the addition of a further quantity of water, the tube is again sealed and used for another determination. The determination of the upper half of the curve may next be carried out in small tubes of hard glass of about 5 mms. external, and 3 mms. internal diameter (Fig. XXX.). These tubes are drawn out into thick capillaries at one end, and should only be used for one determination, although, even at 230° C., the glass is only very slightly attacked by the base. The 2-methylpiperidine for this experiment may conveniently be prepared by the reduction of α-picoline with sodium and absolute alcohol.

A similar investigation may be carried out with phenol and water, using tubes of the form shown in Fig. XXIX, but in this case, only the upper half of the curve can be experimentally realised.

It thus becomes evident that two liquids which possess different densities may mix completely at a given temperature, if taken in suitable proportions, and that above or below the respective upper or lower critical solution temperatures they will mix completely if taken in any proportions. Again, two liquids which possess the same density may not be completely miscible, as is illustrated in Plateau's experiments (*vide* Cap. VIII.).

Consequently, as stated before, the mutual solubility of two fluids does not necessarily imply equality of density, nor does equality of density necessarily determine miscibility, and therefore, as pointed out by MM. Cailletet and Colardeau, it must not be *assumed* that a liquid and its pure vapour become *of necessity* identical in all respects at the critical point, the critical phenomena merely indicating that the liquid and vapour have become mutually soluble in all proportions.

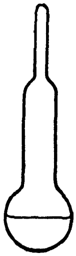

FIG. XXIX.

FIG. XXX.

Measurements of the density of a liquid and of its saturated vapour show that the density of the former decreases and the density of the latter increases as the temperature is raised, until approximate equality is attained in the neighbourhood of the critical point. It is a matter of some difficulty to make accurate determinations of the densities near the critical point, on account of the considerable changes in volume produced by relatively small variations in the pressure, but the results of experiments by a number of different investigators indicate that, at the critical point, the liquid and vapour densities accurately coincide.

The Law of Cailletet and Mathias.—If the densities of the liquid and saturated vapour be plotted as abscissæ, and the temperatures as ordinates, a curve of the form shown in Fig. XXXI. is obtained. This curve represents the case of normal pentane.

Cailletet and Mathias pointed out that if the means of the densities of the liquid and saturated vapour be plotted against the corresponding temperatures the result is a straight line. This is shown as AB in the figure. The Law of Cailletet and Mathias has been found to hold in most cases with fair accuracy. The point A in the figure is the critical point for normal pentane.

Referring again to Fig. XXVIII., if we start with a 3 per cent. solution of 2-methylpiperidine in water, at 85° C., its condition will be represented by the point A. On adding more of the 2-methylpiperidine, it will dissolve, and the concentration of the solution will change along the line AB. At B the solution is saturated, and any further addition will cause the formation of a second liquid phase consisting of a solution of water in the 2-methylpiperidine, and having a composition corresponding to the point C. If more and more of the 2-methylpiperidine be added, the *composition* of the two liquid phases will remain unchanged, but the *amount* of the second phase will increase, and the *amount* of the first phase will decrease, until the first phase disappears. The concentration of the remaining phase now corresponds to the point C, and any further addition of 2-methylpiperidine will merely cause the concentration of the solution to change along the line CD. It is possible, however, on reaching the point B, to dissolve still more 2-methylpiperidine in the water, and so to experimentally realise portions of the dotted line BC. The solution is then supersaturated, but an abrupt separation into two layers of the composition corresponding to B and C takes place if the supersaturation be increased to any considerable extent. Similarly, portions of the dotted line BC in the neighbourhood of C correspond to a supersaturated solution of water in 2-methylpiperidine. In the determina-

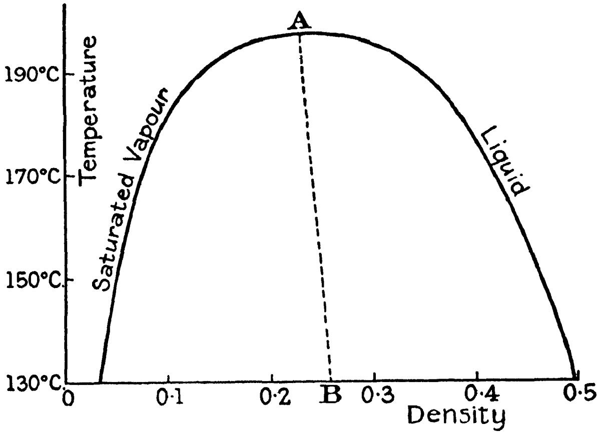

FIG. XXXI.—Normal Pentane.

tion of the concentration-temperature curve for 2-methylpiperidine and water supersaturation was actually obtained at a few temperatures.

A minimum value for the solubility of 2-methylpiperidine in water occurs at about 90° C., and a minimum value for the solubility of water in 2-methylpiperidine at about 160° C.

It will be seen that, starting from the condition A we can pass to a condition such as E without any appearance of two distinct liquid phases, by following a path of transformation such as AFGE or AHIE. For such a transformation the temperature is first lowered, or raised, beyond the critical solution temperature, and then, after the addition of the necessary amount of 2-methylpiperidine, the original temperature is restored.

38. General Conclusions.—Reviewing the experimental evidence which has been considered, we may conclude that, at the critical point, both the molecular attraction and the density become equal throughout the liquid and vapour phases, and that, consequently, the two phases possess the same state of molecular aggregation and are identical in every respect. The experiment with iodine and carbon-dioxide which has been described may appear to be opposed to this view, but in reality it merely shows that the carbon-dioxide which *as liquid* possessed the power of dissolving iodine still *retains* the power of *holding it in solution* at a temperature above the critical. We may, indeed, regard the solution of iodine in the gaseous carbon-dioxide as "super-saturated," and may assume that, if the iodine were separated out, the carbon-dioxide would no longer have the power of *dissolving it again.* Further, it must be pointed out that although, in the case of two liquids of different density, infinite miscibility occurs above or below the respective critical solution temperatures, yet, *in order to realise the actual critical solution points,* it is necessary to have two liquid phases present, and the concentrations, and consequently the densities, of these phases *become identical* when each of the respective critical solution points is reached.

Thus at the critical point of a pure fluid we have the vapour, liquid, and gaseous states coinciding, and this coincidence must be regarded not as an equilibrium of three different phases, as in the case, for example, of ice, water, and vapour at the *triple point,* but as an actual identity of the three states.

We have seen that no discontinuity occurs in passing across the critical isothermal at pressures lower than the critical pressure—i.e. in the passage from vapour to gas, or vice versa—and, also, that no discontinuity occurs at higher pressures in the passage from gas to liquid, or from liquid to gas. At the critical point the three states coincide, and a fluid may, therefore, pass from any one of the states to either of the others without any discontinuity in its properties.

It should indeed be noted that the only essential difference between a gas and a liquid is the possession by the latter of a definite surface due to surface tension. In accordance with Laplace's theory of capillarity (*vide* § 113) we may assume that the attractive force between two molecules in a liquid becomes insensible when the distance between the molecules exceeds a certain value. Thus a molecule of a liquid situated at the surface of separation between the liquid and its vapour is acted upon mainly by forces from the liquid side of the surface, there being few, if any, molecules on the other side within the range of molecular action. This lack of symmetry gives rise to the phenomenon of surface tension. Within the liquid the molecular attractive forces are symmetrically distributed, and are manifested in the phenomenon of cohesion. At the critical point the molecular attraction becomes equal throughout the liquid and vapour phases, and there being no longer any lack of symmetry the surface of separation disappears.

The close analogy between the concentration-temperature curve for liquids and the border curve for a liquid and its saturated vapour should also be borne in mind. On reaching a point such as B in Fig. XXIII. separation of the liquid phase commences and the pressure and density of the vapour phase remain constant while the latter diminishes in amount until finally the vapour phase disappears, leaving the pure liquid at C. Similarly, in Fig. XXVIII., on reaching the point B, separation of the phase corresponding to C commences and the *concentrations* of the phases B and C remain constant during further addition of 2-methylpiperidine until, finally, only the phase C is left.

We shall see later that the curves AB and DC in Fig. XXIII. may be prolonged some distance inside the border curve without condensation or vaporisation taking place, corresponding to the respective conditions of supercooling and superheating. The continuation of the lines AB and EC inside the concentration-temperature curve in Fig. XXVIII. has, similarly, been shown to correspond to supersaturation.

It might be suggested, from analogy, that the border curve for a liquid and its saturated vapour should also form a *closed curve,* and that, consequently, there should exist a *lower* critical point at which the vapour and liquid states again coincide. This would require the liquid density to decrease and the density of the saturated vapour to increase at low temperatures. It is significant that, in the case of water, the specific volume increases progressively when cooled below 4° C. At present, however, there is not sufficient evidence to justify the assumption of a lower critical point, and, in any case, it is doubtful if it could be experimentally realised.

39. J. Thomson's Hypothesis..—In 1871, Professor James Thomson published an account of an extension of Andrews' theory of the essential continuity of the liquid and vapour states. Thomson suggested that "although there be a practical breach of continuity in crossing the line of boiling-points from liquid to gas or from gas to liquid, there may exist, in the nature of things, a theoretical continuity across this breach having some real and true significance."

Referring to Fig. XXIII., Thomson pointed out that condensation of the saturated vapour or ebullition of the liquid need not *necessarily* commence at points such as B and C—but that, under suitable conditions, the vapour and liquid states may persist inside the area enclosed by the "border-curve" without the occurrence of a partial change of state. Thus, in a dust-free and unionised space a vapour may be cooled below, or compressed above, its normal condensing point without condensation occurring (*vide* Expt. LXXIX.). Consequently the curves such as AB and A′B′ (Fig. XXXII.) may be prolonged along BE and B′E′—these latter portions representing a condition of supersaturation of the vapour.

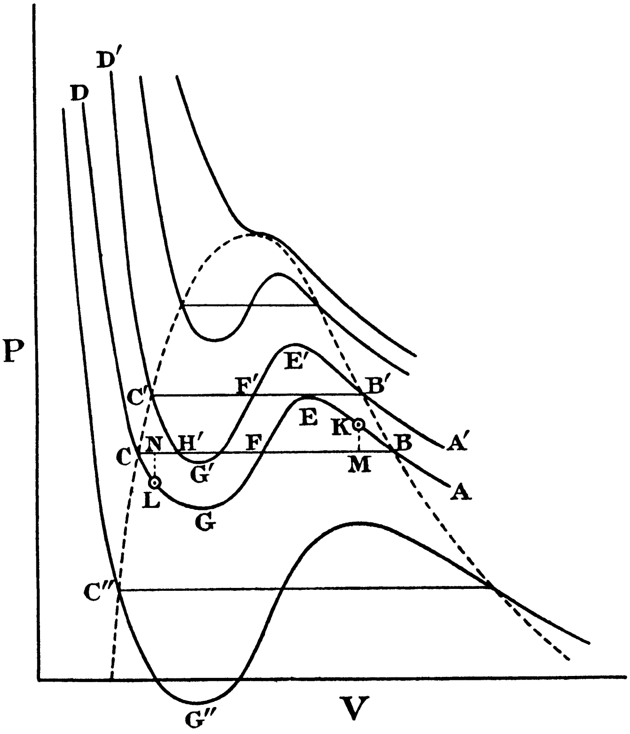

FIG. XXXII.

Similarly, a liquid may be heated considerably above its boiling-point without ebullition taking place. For example, water in a very clean glass vessel may be heated, at the atmospheric pressure, to 106° C. without boiling occurring. Dufour even succeeded in heating drops of water suspended in a mixture of linseed oil and oil of cloves having the same density as the water to a temperature as high as 178° C., the pressure being the atmospheric. If ABCD represent the 100° C. isothermal for water, the pressure corresponding to the horizontal portion BC being atmospheric, then, on heating water at atmospheric pressure, and reaching the condition corresponding to the point C, ebullition should normally commence. The water in Dufour's experiment was heated at constant pressure and therefore expanded along the line CB. On reaching a point such as H′ the temperature of the water was 178° C., but boiling had not begun. H′, consequently, must lie on the water portion of the 178° C. isothermal, and if A′B′C′D′ be this isothermal it must be possible to continue D′C′ downwards to meet BC in H′. Thus the curves such as DC and D′C′ may be prolonged downwards along CG and C′G′—and these portions correspond to the superheating of a liquid.

These latter portions may even extend below the line of zero pressure, as in the curve C″G″, in which case the liquid is under a negative pressure or tension. The sticking of the mercury at the top of a clean barometer-tube illustrates this condition, and other examples are referred to in Chapter VII. (§ 63).

In view, therefore, of the above phenomena of the supersaturation of a vapour, and the superheating of a liquid, and also from the assumption that all natural changes are *essentially continuous*, Thomson suggested that the discontinuous portions of the isothermals such as BC (Fig. XXXII.) should be replaced by continuous curves of the form BEFGC. The general form of the isothermals as the critical isothermal is approached from a higher temperature also suggest, by analogy, that at temperatures below the critical the curves might be of this nature.

For portions of the continuous curves such as GE the pressure and volume increase simultaneously, and it is doubtful if such an unstable condition is capable of experimental realisation. If it were possible to take a substance through the transformation represented by the curve ABEFGCD, it would pass from the state of vapour to that of liquid without any separation into two distinct phases taking place during any part of the change. In general, on reaching the condition corresponding to a point such as K or L, in Fig. XXXII., sudden partial condensation, or vaporisation, occurs, and, if the temperature be kept constant, the system changes to a condition represented by a point such as M or N, on the horizontal line BC, where both the liquid and vapour phases exist simultaneously in contact with each other.

The phenomenon of bumping in superheated liquids illustrates the change from the continuous portion C′G′ of one isothermal to the horizontal portion CB of a lower isothermal, the sudden evolution of vapour producing a marked fall in the temperature.

We shall see in Chapter VI. that an extension of the Kinetic Theory of Gases, developed by van der Waals, lead to equations for the isothermals of a fluid which, when plotted graphically, agree in general form with the continuous curves suggested by Thomson, provided the temperature be less than a certain value. Above this critical value the curves obtained by van der Waals are in fair agreement with those found experimentally by Andrews for carbon-dioxide when above its critical temperature.[1]

40. The Liquefaction of Gases.—A brief historical account of the methods by which all the known gases have been liquefied will now be given.

The earliest attempt at the liquefaction of gases appears to have been made by Priestley in the latter part of the eighteenth century, but the first substance, regarded under ordinary conditions as a true gas, that was liquefied was chlorine. This gas was obtained in the liquid state by Northmore in the year 1806, and subsequently, he liquefied hydrogen-chloride and sulphur-dioxide.

Faraday, in March, 1823, also obtained liquid chlorine, by heating chlorine octo-hydrate in one limb of a bent glass tube, the other limb being immersed in ice, or in a freezing mixture. The chlorine liberated by heating the octo-hydrate was thus liquefied by its own pressure in the cold limb of the tube. In a similar manner, by heating substances which respectively yielded sulphur-dioxide, cyanogen, and ammonia, Faraday succeeded in liquefying these gases, and, later, by compressing the gas with a small compression pump, and, cooling with a freezing mixture, he liquefied several other gases, such as hydrogen-chloride, carbon-dioxide, sulphuretted hydrogen, and nitrous oxide.

Bussy, in 1824, published accounts of investigations in which he used low temperatures, but did not employ high pressures. He liquefied sulphur-dioxide, and observed the important fact that when the liquid sulphur-dioxide was made to evaporate rapidly, by blowing air through or over it, the temperature fell considerably lower. Employing the low temperature obtained by the evaporation of liquid sulphur-dioxide, Bussy liquefied ammonia and chlorine.

In 1834 Thilorier liquefied carbon-dioxide in large quantities. The gas was generated inside a strong copper cylinder, by the action of sulphuric acid upon sodium bicarbonate, and by placing the interior of the generating vessel in communication with the interior of another vessel, kept at a lower temperature, the carbon-dioxide condensed in the latter.

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[1] No equation, of course, can be obtained to represent a discontinuous curve such as ABCD.

It will be seen from Fig. XXIII. that if the temperature of the second vessel be 15° C. condensation will occur at a pressure of about 50 atmospheres. Thilorier also obtained carbon-dioxide in the solid state by allowing the liquid to escape through a narrow jet into a box of poorly conducting material, when the cooling produced by the volatilisation of part of the liquid solidified the remainder. He observed that a very powerful refrigerant was obtained by mixing the solid carbon-dioxide with ether, and this refrigerating agent is often called "Thilorier's Mixture."

In 1845 Faraday published an account of experiments which were undertaken with a view to liquefying the so-called "permanent gases," such as oxygen, nitrogen, carbon-monoxide, and hydrogen. He employed higher pressures than in his earlier experiments, and obtained much lower temperatures by using "Thilorier's Mixture," but although he was able to liquefy phosphine, ethylene, etc., and also to solidify several other gases, such as ammonia, sulphur-dioxide, nitrous oxide, hydrogen bromide, and cyanogen, he found that the "permanent gases" resisted all attempts at liquefaction.

In the same year Natterer, also, was unsuccessful in an attempt to liquefy the "permanent gases," although he employed pressures exceeding 3000 atmospheres, and used solid carbon-dioxide and ether as a refrigerant.

We have seen, previously, how Cagniard de la Tour first observed that, above a certain temperature, the liquid and vapour states coincide, and it should be noted that Faraday first made the very important suggestion that, in the case of the "permanent gases," this limiting or critical temperature is far lower than the ordinary atmospheric temperature, and that, consequently, these gases cannot be liquefied at ordinary temperatures merely by increasing the pressure to which they are subjected. It was, however, largely due to the celebrated researches of Andrews that the existence of such a critical temperature, above which a gas could not be liquefied by pressure, came to be clearly recognised, and it then became evident that the liquefaction of the "permanent gases" was to be achieved only by attaining sufficiently low temperatures, and not by employing very high pressures.

In 1877, M. Cailletet and M. Pictet succeeded, independently, in liquefying oxygen. Cailletet compressed the oxygen inside a capillary tube to about 400 atmospheres, and cooled the compressed gas by means of liquid sulphur-dioxide which was allowed to evaporate freely. On releasing the pressure and allowing the gas to suddenly expand a further cooling occurred, due to the work done by the gas during the expansion, and partial liquefaction was obtained, the oxygen appearing as a mist inside the tube. Cailletet also succeeded in liquefying carbon-monoxide, nitrogen, and air.

Pictet generated oxygen by heating potassium chlorate in a steel retort, connected with a closed steel tube, the latter being surrounded by a copper vessel. Liquid carbon-dioxide was pumped into the copper vessel, where it was made to evaporate rapidly by maintaining a low pressure. The carbon-dioxide consequently solidified, and a temperature of about – 140° C. was thus produced. The carbon-dioxide gas which was pumped off from the copper vessel was cooled and condensed, with the aid of liquid sulphur-dioxide, and then pumped back again. The same carbon-dioxide was thus used continuously as a refrigerating agent, and, similarly, the sulphur-dioxide used for cooling the carbon-dioxide was itself condensed under pressure and used over again. After several hours working, when the pressure of the enclosed oxygen exceeded 300 atmospheres, a stop-cock was opened and some of the oxygen issued as a liquid jet.[1] The expansion of the remaining compressed gas produced a further cooling, owing to the work done by the gas behind in pushing out the gas in front, and more of the oxygen was liquefied and issued from the nozzle in the liquid state.

Cailletet and Pictet also experimented with hydrogen, but the evidence of liquefaction in the case of this gas was not conclusive.

Further researches on the liquefaction of gases were carried out by the Polish chemists Wroblewski and Olzewski in 1883. Using liquid ethylene, boiling under reduced pressure, as a refrigerant, they were able to liquefy oxygen at a pressure of only about 20 atmospheres. The following year they succeeded in liquefying hydrogen. Compressed hydrogen was cooled with liquid oxygen, boiling under reduced pressure, and was then allowed to suddenly expand. A further cooling was thus obtained and a very small quantity of liquid hydrogen was produced. Carbon-monoxide and nitrogen were also liquefied, and by rapidly evaporating the liquids, under diminished pressure, they were solidified.

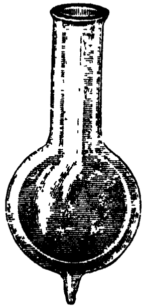

Fig. XXXIII.

Wroblewski and Olzewski determined the boiling-points and critical constants of various liquefied gases, and by employing liquid ethylene as a refrigerant, in a method similar to that used by Pictet, they succeeded in producing liquid air in quantity.

Dewar, in 1886, devised an improved form of the same apparatus for the liquefaction of air on a large scale, and, in 1893, he solidified air. The introduction, by Dewar, of "vacuum-jacketed" vessels greatly facilitated the manipulation of these liquefied gases. Fig. XXXIII. illustrates such a vessel. If a very small quantity of mercury be present in the vacuous space its vapour will be condensed on the walls of the inner vessel in the form of a mirror, and this will help further to diminish the rate at which heat is gained by radiation.

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[1] It should be noted that the critical temperature of oxygen is – 118° C., and its critical pressure 50 atmospheres. Thus the *initial liquefaction* in Pictet's experiment was produced in essentially the same manner as in the method employed by Faraday.

Kamerlingh Onnes also employed the Pictet double cycle method, using methyl chloride and ethylene in place of sulphur-dioxide and carbon-dioxide as refrigerating agents, and he carried out a number of important investigations on the variation of various physical "constants" with change of temperature.

Reference has already been made, in Chapter I., to the researches of Joule and Thomson on the passage of a gas through a porous plug, and it was stated that on the mere expansion of a gas some work is done against internal molecular cohesive forces.

It therefore follows that for any gas which strictly obeys Boyle's Law a cooling effect will be produced on free expansion owing to the conversion of a part of the kinetic energy possessed by the molecules into potential energy in the performance of this internal work.[1]

If, however, a gas does *not* obey Boyle's Law it cannot be predicted *a priori* whether, on free expansion, a cooling or a heating effect will result, or whether the temperature will remain unchanged. For if the product P.V. increase with decrease in the pressure, P, there will be a cooling effect on free expansion due to the increase in P.V., and if P.V. decrease with decrease in pressure a heating effect will be produced (*vide* Appendix A). The total cooling or heating effect observed when such a gas expands without doing external work will, consequently, be the algebraic sum of the cooling due to the work done against molecular cohesion, and the cooling or heating effect due to the variation in P.V. with the pressure. Joule and Thomson found that, in general, a cooling effect occurred on expansion, but that, in the case of hydrogen, a heating effect was obtained. They also found that the cooling effect diminished with rise in temperature, and this agrees with the observed fact that, as the temperature is raised, the decrease in P.V. with rise in pressure becomes less marked (*vide* § 33). It has further been found that at a certain temperature the cooling effect disappears, being replaced at higher temperatures by a heating effect. The temperature at which this transition occurs is called *the temperature of inversion of the Joule-Thomson effect.*

The "Regenerative" method for the liquefaction of gases, which was introduced about the year 1895, will now be readily understood. This method is based upon the Joule-Thomson effect, and was first utilised for the production of liquid air, without the aid of any refrigerant, by Hampson in England, and Linde in Germany. The gas to be liquefied is compressed by means of a suitable gas compressor to about 200 atmospheres, and the heat generated by this compression is absorbed both by enclosing the compression cylinder in a tank

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[1] "Free expansion" must be carefully distinguished from the case where a gas in expanding performs *external* work, and, consequently, grows colder unless heat be communicated to it from an external source.

through which water circulates and by passing the compressed gas through a copper coil contained in the same tank.[1]

The compressed gas now flows on at approximately the temperature of the room, and, after passing through a water-separator and a high pressure purifier, is delivered to the liquefier. The liquefier consists usually of two or four coils which are wound in numerous turns around a vertical spindle, and which unite at their lower ends in a vertical expansion valve. The compressed gas travels down these regenerator coils, and is allowed to escape at the expansion valve which can be opened or closed at will by means of a spindle and a hand wheel. The gas on escaping through the valve expands to approximately the atmospheric pressure, and flows back over the coils, finally passing from the outlet of the liquefier back into the gas-holder, and thence to the compressor to be recompressed. The expansion at the valve causes a considerable cooling of the escaping gas, and the latter, in flowing back over the coils, lowers their temperature, so that the next portions of the gas are cooled before reaching the valve, and, consequently, on expansion, fall to a still lower temperature. The regenerator coils being enclosed in a cylinder of badly conducting material, this progressive cooling effect continues until, finally, part of the gas begins to liquefy and collect in a receiver beneath the expansion valve. The liquefied gas can then be run off into a Dewar's vacuum vessel.

Now the expansion of the gas at the valve may be regarded as approximately free expansion, for the compressor is working continuously and supplies almost all the energy needed for the work of pressing back the atmosphere. Consequently the cooling effect produced is similar to that observed in the Joule-Thomson experiment on the passage of a gas through a porous plug, and mainly arises from the work done during expansion against internal molecular cohesive forces. It has been seen that the magnitude of these cohesive forces in a gas at the ordinary density is only small—but when the gas is subjected to the combined influence of high pressure and low temperature a large proportion of its molecules are brought close together, and, in consequence, its cohesion is greatly increased. Thus, in the "regenerative" method, the magnitude of the cohesive forces called into play increases progressively as the temperature falls, with a corresponding increase in the cooling effect produced by the expansion of the compressed gas. It might, therefore, be anticipated that the heating effect observed by Joule and Thomson during the free expansion of hydrogen would be replaced, at a sufficiently low temperature, by a cooling effect due to the increased cohesion. A study of Amagat's results further shows that the effect of lowering the

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[1] The gas is usually compressed in two stages, each compression cylinder being fitted with a copper coil. Both the cylinders and coils are water-cooled, to absorb the heat generated by the compression,

temperature is to increase the cooling effect, or diminish the heating effect, due to the variation in P.V. with the pressure.

Dewar, in 1900, showed that hydrogen is, in fact, cooled by free expansion when initially at a sufficiently low temperature, and he was thus able to employ the "regenerative" method for the production of liquid hydrogen in quantity.

Hence the behaviour of hydrogen cannot be regarded as in any way exceptional, and the heating effect observed by Joule and Thomson is merely due to the fact that, in the case of hydrogen, the "*temperature of inversion*" is much lower than the ordinary atmospheric temperature. For air (expanding from about 100 atmospheres to the atmospheric pressure), the temperature of inversion of the Joule-Thomson effect is nearly 100° C., whereas for hydrogen (under the same conditions), the temperature of inversion was found by Olzewski to be about—80° C.

The boiling-point of liquid hydrogen, under atmospheric pressure, was found to be approximately 20·5° A., and by boiling the liquid under reduced pressure Dewar succeeded in obtaining solid hydrogen. The melting-point of hydrogen was found to be about 14·5° A.

Finally, in 1908, helium was liquefied by Kamerlingh Onnes, and by Dewar—its boiling-point being only 4·3° A. By the evaporation of liquid helium under very reduced pressure Kamerlingh Onnes has, recently, reached a temperature of 0·9° A.—the lowest temperature yet attained—but even at this low temperature the helium exhibited no sign of solidification.

Most gases when condensed form colourless liquids, but liquid chlorine and nitrogen tetroxide are yellow, liquid oxygen is blue, and liquid ozone a deep indigo blue. Liquid air possesses a slight greenish-blue colour. In spite of the very low boiling-points of such liquids as hydrogen, oxygen, air, etc., they can be poured into the hand, if the latter be dry, and allowed to evaporate for a short time without any extreme sensation of cold. This is due to the liquid assuming the spheroidal state. The density of liquid hydrogen, at the boiling-point, is only about 0·06, and when poured on the hand the impact is scarcely perceptible. The density of liquid oxygen, at its boiling-point, is approximately 1·13, or nearly nineteen times as great. If india-rubber be cooled in liquid air it becomes hard and brittle. Lead when similarly treated becomes fairly elastic. Many bodies, such as cotton-wool, leather, etc., if placed in liquid air, and then exposed for a short time to a bright light, are found to be highly phosphorescent when examined in the dark. Cotton-wool which has been dipped in liquid air burns rapidly, if ignited while still wet, and a glowing taper or wooden splint will also burn energetically if immersed in liquid air—ice and solid carbon-dioxide being formed during the combustion.

Liquid air is now frequently employed in scientific work as a refrigerant, and it is also used commercially for the preparation of oxygen. Liquid oxygen boils at 90·5° A., and liquid nitrogen at 77·5° A. Consequently, by liquefying air and allowing it to partially evaporate the nitrogen vaporises much more readily than the oxygen, and after a time the remaining liquid consists of nearly pure oxygen. The gas coming off is then compressed into steel cylinders. It contains approximately 3 per cent. of argon, the boiling-point of the latter being 87° A., which is nearly the same as the boiling-point of oxygen. Liquid hydrogen is occasionally used as a refrigerant when very low temperatures are required. If a piece of metal be cooled in liquid hydrogen and then hung up in the air it will be observed that it rapidly becomes covered with a white layer of solid air. The latter soon melts and drips off the metal. By employing these liquefied gases as refrigerating agents, Dewar and Fleming have shown that at low temperatures the electrical resistance of pure metals decreases to a considerable extent. Iron, and copper, at 50° A. were found to become nearly perfect conductors.

It has also been found that many seeds and micro-organisms are uninjured by prolonged cooling with liquid hydrogen.

41. Experimental Methods for the Liquefaction of Gases.—The following experiments illustrate the various methods by which the liquefaction of gases may be effected.

Experiment XII.—A moderately wide glass tube is taken, and a narrow tube is fused to one end. The narrow tube is then bent at right angles. A plug of loosely packed asbestos having been pushed up to the joint, a quantity of freshly heated charcoal is introduced into the wide tube, and the latter is drawn off to a narrow neck. A stream of dry sulphur-dioxide is then passed through for about half an hour, after which both ends of the tube are sealed[1] (Fig. XXXIV.). On placing the narrow tube in a freezing mixture and gently heating the wide tube, the sulphur-dioxide is driven off from the charcoal and condenses as a colourless liquid at the narrow end. When the tube is again allowed to assume the temperature of the room the liquid sulphur-dioxide boils off into vapour and is reabsorbed by the charcoal; the experiment may thus be repeated as often as required. The plug of asbestos is introduced in order to prevent any fragments of charcoal from being accidentally shaken into the narrow tube.

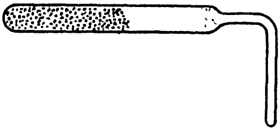

FIG. XXXIV.

Dry silver chloride may be introduced into a similar tube and, after passing a stream of dry ammonia, the tube is sealed as before. On gently heating, the ammoniacal silver chloride melts and gives up

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[1] The charcoal may conveniently be heated in the tube itself,—and allowed to become cold while the sulphur-dioxide is passing,—the tube being then sealed off.

its ammonia, the latter liquefying at the cold end of the tube. It is desirable to mix the silver chloride with a little charcoal to prevent the melted chloride from running together. In this way a larger surface is maintained for the subsequent reabsorption of the ammonia.

Experiment XIII.—Fig. XXXV. illustrates a simple apparatus for the liquefaction of a gas requiring a pressure of only a few atmospheres at the ordinary temperature. Sulphur-dioxide may conveniently be employed for this experiment. A little mercury is introduced into the apparatus until it just covers the elbow at C, and the dry sulphur-dioxide is then admitted at the open end of the tube E, and allowed to bubble through the mercury and escape through the wide tube G until all the air is expelled from the latter. The tube G is now sealed off at BB. Mercury is then poured into the tube D, and the valve A is inserted and air pumped in until the mercury is forced to the top of the tube E. In this way the sulphur-dioxide in the tube E is driven out, and on releasing the pressure, by removing the valve A, air enters the tube E. This tube is now sealed off at F, and the tube D is nearly filled with mercury, and the valve replaced. On pumping in air at A the sulphur-dioxide in the tube G is compressed and soon appears as a liquid in the narrow part of the tube. On releasing the pressure the sulphur-dioxide boils off into gas. Ammonia may similarly be readily liquefied in this manner at the ordinary temperature. By observing the initial volume of the enclosed air after the tube E is sealed off, and by applying Boyle's Law to the change of volume, the approximate pressure required to produce liquefaction may be obtained. A correction should, of course, be made for the difference of level of the mercury in the tubes containing the gas and the air. The upper part of the tube containing the gas may also be water-jacketed, and the respective pressures necessary to produce liquefaction at various temperatures may thus be observed.

Experiment XIV.—The liquefaction of ammonia and sulphur-dioxide by means of an Oersted's Piezometer was described in Experiment IX. For gases which are less easily condensed Cailletet's apparatus may conveniently be employed. It consists of an hydraulic pump which communicates with a steel compression chamber by means of a copper tube of small internal diameter. The gas to be liquefied is contained in a glass tube to which a gun-metal collar is cemented, and, after pouring mercury into the compression chamber, the glass tube is lowered into position and firmly secured by means of a nut. On working the pump, water is forced into the upper part of the compression chamber, and the mercury is, in consequence, driven up into the glass tube, thereby compressing the gas. The experimental tube and compression chamber are shown in Fig. XXXVI. The projecting portion of the glass tube is surrounded by a jacket in order to cool the gas, and also by an outer guard jacket. By means of this apparatus pressures up to 1000 atmospheres may be obtained and many gases readily liquefied. If a gas with a critical temperature slightly lower than the atmospheric be compressed without the use of a refrigerant no liquefaction will result,—but on suddenly releasing the pressure to a moderate extent the gas will be cooled by its expansion and will be liquefied. Ethylene may conveniently be used for this experiment, its critical temperature being 10° C. A similar result may be obtained with a gas such as carbon-dioxide if the jacket be

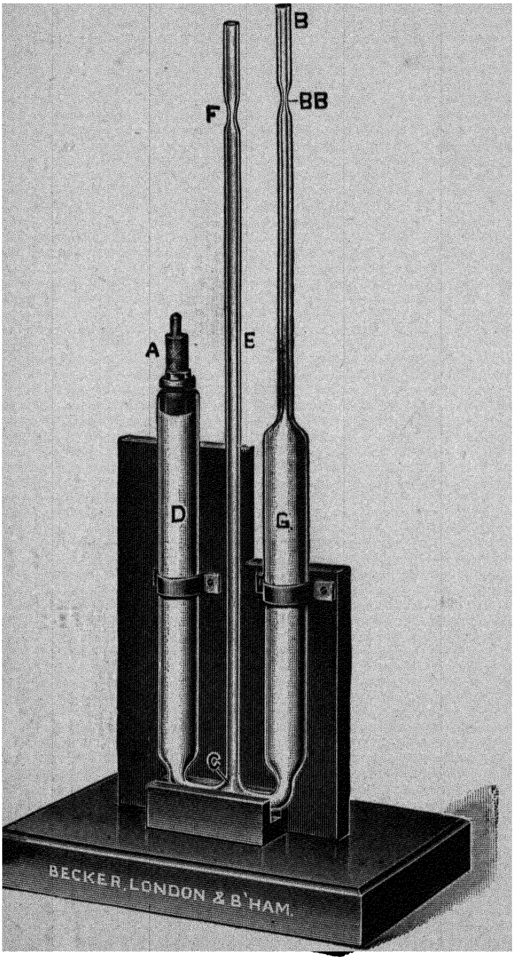


FIG. XXXV.

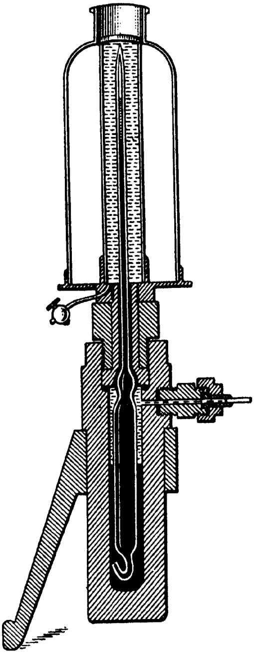


FIG. XXXVI.—Cailletet's experimental tube and compression chamber.

first filled with water at a temperature a few degrees above the critical temperature of the gas. The critical temperature of the carbon-dioxide may also be readily shown by compressing it until partially liquefied, and then raising the temperature of the water in the jacket until the meniscus within the tube disappears.

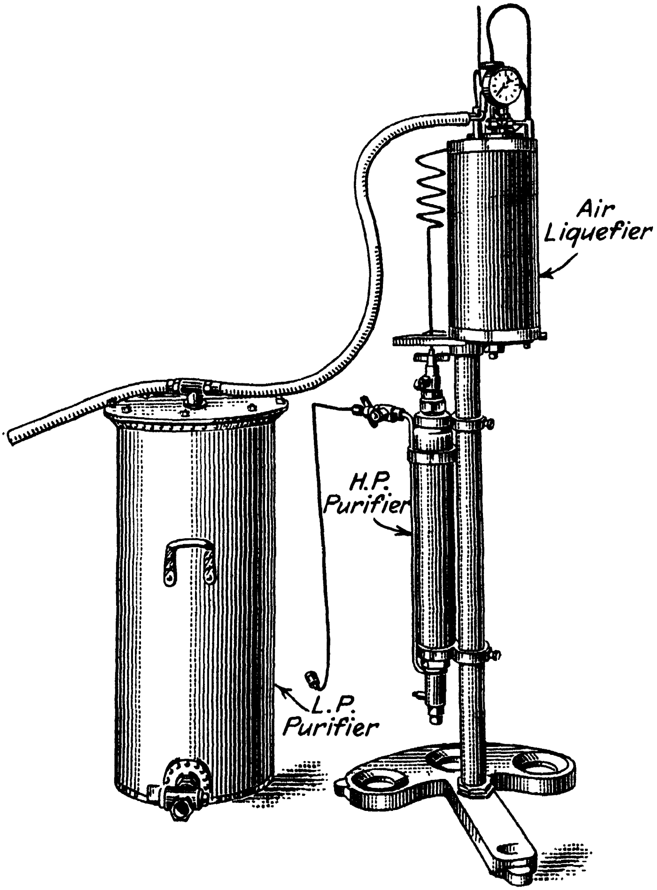
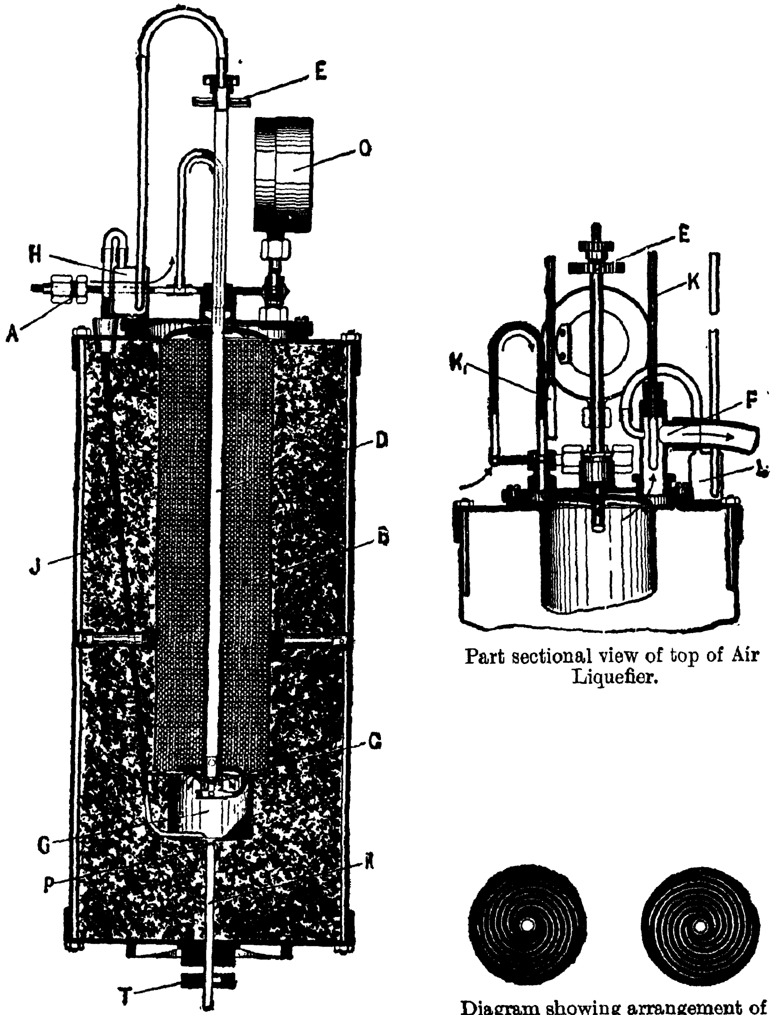


Fig. XXXVII.—Air Liquefier (Hampson).

Experiment XV.—Liquid air in quantity may readily be produced by means of the Hampson liquefier shown in Fig. XXXVII., and, in section, in Fig. XXXVIII.

In the installation at His Exalted Highness the Nizam's College, Hyderabad, the air is compressed to 200 atmospheres by means of a

Whitehead torpedo-compressor driven by an 8 horse-power electric motor. The air is first drawn into the compressor through the low pressure purifier, which contains moist slaked lime, by means of which carbon-dioxide is absorbed. After compression, the air passes through a water separator, not shown in the figure, and thence to the high



Part sectional view of top of Air Liquefier.

Full length sectional view of Air Liquefier.

Diagram showing arrangement of Regenerator Coils.

Fig. XXXVIII.

pressure purifier which contains solid caustic potash. The caustic potash removes water vapour and any remaining carbon-dioxide, and the pure and dry air passes on through the connection, A, and the regenerator coils, B, and escapes at the expansion valve, C, the latter being regulated by means of the hollow spindle, D, and the hand wheel, E. After flowing over the regenerator coils the air passes from the outlet, F, back to the inlet of the low pressure purifier, and thence to the compressor to be recompressed. An additional opening at the bottom of the low pressure purifier allows extra air to be drawn in as required. A gauge, L, containing glycerine indicates the pressure at the outlet, and this pressure should be regulated so as to correspond to about 8 inches of glycerine.

After the liquefier has been working for about a quarter of an hour liquid air commences to collect in the receiver G. By turning the hand wheel, T, the discharge valve, P, .may be opened, and the liquid air then flows out through the hollow spindle, R, into a vacuum vessel placed ready to receive it. The gauge, H, contains coloured water, and communicates with the receiver, G, by means of the hollow spindle, D, and the pipe, J. When the liquid air collects in the receiver it compresses the air in the pipe, J, and displaces the coloured water in the gauge: the latter thus indicates the depth of the liquid air in the receiver. The thermometer, K, registers the temperature of the air leaving the liquefier, and a second thermometer may be placed inside the socket, K_1, to register the temperature of the compressed air when it enters the regenerator coils. The pressure of the compressed air on entering the coils is indicated by means of the pressure gauge, O.

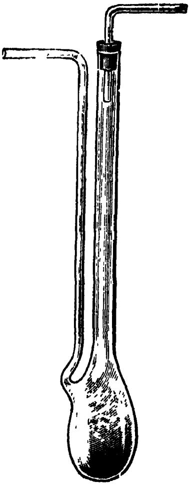


FIG. XXXIX.

Using the liquid air thus produced as a refrigerant, a large number of gases may be liquefied and solidified at the ordinary atmospheric pressure. A glass condensing flask of the form shown in Fig. XXXIX. may be conveniently employed for this purpose. The flask is immersed in liquid air contained in a cylindrical vacuum vessel, and the gas is passed in through the small tube in order to obtain the maximum cooling effect. If it be desired to preserve a specimen of the liquefied gas a straight tube of thick glass, closed at one end, may be substituted for the condensing flask—the gas being admitted by means of a narrow tube passing down to the bottom. The open end of the thick glass tube should be previously constricted, so that it can be sealed off with a small blowpipe flame after a sufficient quantity of the gas has been condensed. In this manner ammonia, chlorine, hydrogen chloride, hydrogen bromide, hydrogen iodide, sulphuretted hydrogen, nitrous oxide, sulphur-dioxide, and many other gases may be readily liquefied and also solidified.

CHAPTER V.

THE THERMAL EXPANSION, DIFFUSION, AND SOLUBILITY OF GASES.

42. The Thermal Expansion of Gases.—The expansion of gases when heated at constant pressure was first investigated by Charles (1787), Priestley (1790), Dalton (1801), and Gay-Lussac (1802), and it was found that different gases possessed approximately equal coefficients of thermal expansion. This experimental result is commonly referred to as the Law of Charles. A much fuller investigation was subsequently carried out by Regnault, who studied both the expansion of gases at constant pressure, and the increase of pressure at constant volume. Regnault found that for the so-called "permanent gases" the coefficients of expansion at constant pressure were approximately equal, and of the mean value 0·003665, and that the coefficients of increase of pressure at constant volume for such gases were approximately the same as their coefficients of expansion at constant pressure.

The coefficient of expansion of a gas at constant pressure is defined as the increase in volume of unit volume at 0° C. per degree rise in temperature, when the pressure is constant. Similarly, the coefficient of increase of pressure at constant volume is defined as the ratio of the increase in pressure to the initial pressure when a given quantity of a gas is heated from 0° C. to 1° C., its volume remaining unchanged.

A detailed description of the apparatus used by Regnault in his researches will not be given, but two experiments will be described which illustrate the methods employed in investigating the thermal expansion of gases.

Experiment XVI. Determination of the Coefficient of Expansion of a Gas at Constant Pressure.—Fig. XL. illustrates a convenient apparatus for determining the coefficient of expansion of a gas at constant pressure. A "U" tube, of the form shown in the figure, is connected to a wide glass tube by means of rubber pressure tubing. The stop-cock on one limb of the "U" tube being open, mercury is poured into the wide glass tube until it just rises in each limb of the "U" tube, and the apparatus is carefully levelled so as to bring the mercury to the same graduation mark in each limb. A tube containing phosphorus pentoxide or other suitable desiccating agent is then connected to the limb of the "U" tube which carries the stop-cock, and the pure and dry gas is passed in and allowed to bubble through the mercury and escape at the open limb. When all the air is completely displaced the supply of gas is stopped, the stop-cock closed, and the drying tube removed. The "U" tube is now surrounded with clean melting ice and water, and the wide tube is raised so as to drive out the gas in the open limb, after which it is somewhat lowered. When the enclosed gas has cooled to approximately 0° C., the stop-cock is slowly opened. The gas is thus partially expelled and the mercury is brought fairly close to the graduation mark between the two bulbs. The apparatus is now allowed to stand for some time until the gas is accurately at 0° C., when the stop-cock is opened again, the mercury carefully levelled to the graduation mark, and the stop-cock once more closed.

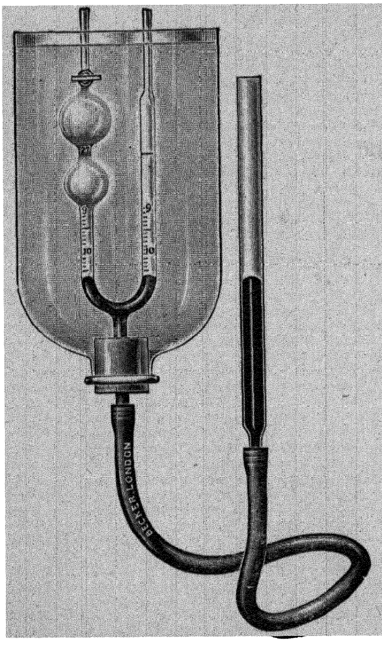


Fig. XL.—Apparatus for determining the coefficient of expansion of a gas at constant pressure.

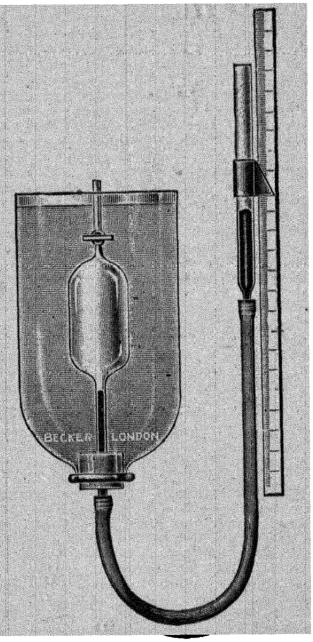


Fig. XLI.—Apparatus for determining the coefficient of increase of pressure of a gas at constant volume.

The "U" tube is next surrounded with boiling water, and the latter is kept at the boiling-point by passing in a rapid current of steam.[1]

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[1] The stop-cock should be lubricated with burnt black rubber, as ordinary lubricants will not stand the temperature of boiling water.

The wide tube is then lowered until the mercury again stands at the same level in each limb, so that the enclosed gas is at the atmospheric pressure. Since the two limbs of the "U" tube are graduated in corresponding lengths, the mercury will be level when it has again been brought to similar graduation marks in each limb. In the particular apparatus shown in the figure the upper bulb has a volume of 27 c.cs. and the lower bulb a volume of 9 c.cs.

Now, if V_0 and V_t be the respective volumes of a given mass of gas at 0° C. and t° C., when the pressure is constant, and if a be the coefficient of expansion at constant pressure, we have—

$$a = \frac{V_t - V_0}{V_0 \cdot t}.$$

$$\therefore\ V_t = V_0(1 + at).$$

Since a is nearly constant for different gases, and approximately equal to 0·003665, it follows that the 27 c.cs. of gas at 0° C. will occupy a volume of about 36·9 c.cs. at 100° C. Thus, after heating the gas to the temperature of the boiling water, and adjusting its pressure to the atmospheric pressure, the mercury will stand at a convenient level in the graduated limbs of the "U" tube and the new volume occupied by the gas can be readily observed. The limb containing the gas is accurately graduated in c.cs., but the open limb is merely graduated so that corresponding divisions in both limbs are at the same level. In this way the enclosed gas may more readily be brought to the atmospheric pressure. The temperature, t, of the boiling water may be ascertained by means of a thermometer, or by calculation from the observed barometric pressure, and the coefficient of expansion of the gas at constant pressure may then be readily calculated by substituting in the equation $a = \frac{V_t - V_0}{V_0 \cdot t}$ the values obtained for V_0, V_t, and t.

The barometer should be read when both V_0 and V_t are measured, in order to guard against any error arising from variations in the atmospheric pressure during the course of the experiment, and a correction should be applied for the expansion of the glass vessel. For this purpose the coefficient of cubical expansion of glass may, with sufficient accuracy, be taken as 0·000025.

Experiment XVII.—Determination of the Coefficient of Increase of Pressure of a Gas at Constant Volume.—The experimental details of this determination are similar, in many respects, to those already described in the preceding experiment. The pure and dry gas is enclosed in a cylindrical glass bulb which is fitted at one end with a stop-cock, and connected at the other end to an open tube by means of rubber pressure tubing (Fig. XLI.). The open tube contains mercury, and the quantity of gas is so adjusted that when the latter is at 0° C., and at atmospheric pressure, the mercury just reaches a mark on the glass tube below the cylindrical bulb. The corresponding level of the mercury in the open tube having been noted, the latter is raised in order to increase the pressure, and the gas is then heated to the boiling-point of water. If the precaution of raising the pressure before heating the gas be omitted, some of the gas may expand into the connecting tube and be lost. When the gas has attained a steady temperature, the mercury is again brought to the same mark below the bulb, and the new level of the mercury in the open tube is observed. The increase in pressure over the pressure at 0° C. produced by a known rise in temperature is thus obtained, and the coefficient of increase of pressure at constant volume is calculated from the equation

$$\beta = \frac{P_t - P_0}{P_0 . t},$$

where β is the coefficient of pressure-increase, and P_0 the atmospheric pressure.

A correction should be applied to allow for the diminished density of the mercury in the tube below the cylindrical bulb when raised to the temperature $t°$ C. This may most readily be done by finally opening the stop-cock and lowering the open tube until the mercury again stands at the same mark below the bulb, the temperature $t°$ C. of the bath being meanwhile kept unchanged. The level of the mercury in the open tube is now observed, and this level must be taken as corresponding to atmospheric pressure in obtaining the increase in pressure produced by heating the gas.

A correction should also be applied for the expansion of the glass vessel. Let V_0 be the volume of the vessel at 0° C., and γ the coefficient of cubical expansion of glass.

Then $$V_t = V_0 . (1 + \gamma . t).$$

Applying Boyle's Law to the enclosed gas we have—

$$P_t . V_t . = P_t' . V_0.$$
$$\therefore P_t . V_0 . (1 + \gamma . t) = P_t' . V_0.$$
$$\therefore P_t' = P_t . (1 + \gamma . t).$$

P_t' should then be substituted for P_t in calculating β.

The thermal expansion of gases furnishes a scale for the measurement of temperature. When a gas is employed as a thermometric substance, it is more usual to measure equal changes of temperature by equal changes in the pressure of the gas at constant volume than to adopt the alternative method and measure equal changes of temperature by equal changes in the volume of the gas under constant pressure.

In Jolly's constant volume air thermometer, to which reference was made in Experiment VIII., the dry and carefully purified air is contained in a bulb which is attached to an open tube by means of pressure tubing. These latter tubes contain mercury, and by suitably adjusting the height of the open tube, the surface of the mercury can be brought to a fixed mark on the bent tube which is joined to the bulb. To obtain greater accuracy the bent tube should be of capillary bore, for, when the bulb is immersed in a bath at a temperature which differs from the atmospheric, the temperature of the air contained in this tube will be different at different points, and an accurate correction cannot be readily applied. The capillary tube should be fused to a wider tube of the same internal diameter as the open tube, and the mark to which the mercury is brought should be engraved on the wider tube near the point where it joins the capillary. In this way any error due to unequal capillary action may be eliminated. The thermometer is graduated in accordance with the Centigrade scale, the fixed points corresponding respectively to the temperature of melting ice (0° C.), and the temperature of the vapour of water boiling under a pressure of 76 cms. of mercury (100° C.). If then the bulb is immersed in a bath at any temperature t° C., and the corresponding pressure is found to be P_t, we have—

$$P_t = P_0 . (1 + \beta . t).$$

Whence
$$t = \frac{P_t - P_0}{P_0 . \beta}.$$

Substituting the value obtained by Regnault for β, this becomes

$$t = \frac{1}{\cdot 003665} \cdot \left(\frac{P_t - P_0}{P_0}\right).$$

A correction should be applied, as in Experiment XVII., for the expansion of the bulb.

When the temperature of the bulb is raised, the pressure of the enclosed air increases, and the mass of air contained in the cooler capillary tube will be increased, while the mass of air in the bulb will be correspondingly diminished. This necessitates a further correction which becomes increasingly important at high temperatures.

The relatively large thermal expansion of the "permanent" gases for a given rise in temperature renders them particularly suitable for thermometric purposes, for small changes in temperature may be readily observed, and variations in the volume of the containing vessel produce much less effect.

The close agreement throughout the scale of temperature observed for different "permanent" gases and the large range of temperature over which they can be employed furnish additional reasons for their use in thermometry.

Regnault's researches have shown that the coefficients of thermal expansion do, however, vary to a small extent for different gases.

Thus for hydrogen, air, and carbon-dioxide, at 0° C., Regnault found that 273·1, 272·4, and 269·6 volumes, respectively, expanded 100 volumes when raised to 100° C., the pressure being maintained constant. The coefficient of expansion at constant pressure, α, was moreover found to differ slightly from the coefficient of increase of pressure at constant volume, β.

Thus for air at 0° C., and 76 cms. of mercury, Regnault found—

$$\alpha = \cdot 003671,$$
$$\beta = \cdot 003665.$$

For hydrogen at 0° C., and 100 cms. of mercury, Chappius found—

$$\alpha = \cdot 003660,$$
$$\beta = \cdot 003663.$$

Further, the work of Regnault, Amagat, Chappius, and others has shown that, for any particular gas, α and β vary under different temperatures and pressures—the variation with respect to temperature being relative to any gas selected as a standard, which latter gas, when employed in a constant volume thermometer, furnishes the standard scale of temperature. In the case of the standard gas, under standard conditions as to pressure, it is evident that β will be constant at all temperatures, since the temperature is itself determined by equal increments in the pressure. The scale of temperature which has been adopted as a standard by the *Bureau International* is that of the constant volume hydrogen thermometer, the hydrogen being under a pressure of 1000 mms. of mercury at 0° C. The usual fixed points, corresponding respectively to the temperature of melting ice (0° C.), and the temperature of the vapour of water boiling under a pressure of 76 cms. of mercury (100° C.), are employed.

The bulb of the constant volume hydrogen thermometer at the *Bureau International* consists of an iridio-platinum cylinder of about 1000 c.cs. capacity.

Somewhat above 500° C. iridio-platinum becomes permeable with respect to hydrogen, and a constant volume thermometer filled with nitrogen is therefore employed at high temperatures.

43. Callendar's Compensating Constant-Pressure Air Thermometer.—Fig. XLII. illustrates a simple and accurate form of constant-pressure air thermometer devised by Callendar. A and B are two bulbs connected to one another through the pressure gauge, C, which contains sulphuric acid. The bulb A is directly connected to the measuring burette, D, which is accurately graduated, and is filled with mercury. The bulb B is joined to a capillary tube similar to that connecting A and D, and these capillary tubes are placed close together. In this manner an automatic correction is made for the error arising from the variation in the temperature of the air in the connecting tube. The apparatus is initially exhausted through a two-way stop-cock, E, the stop-cocks F and H being closed. Pure dry air is then admitted through E, and the level of the mercury in D is adjusted so that the volume of air enclosed on each side of the pressure gauge is the same. The stop-cock E is now turned so as to place A and B in direct communication, and the sulphuric acid consequently remains at the same level in each limb of the gauge, C, on opening the stop-cock, F.

The whole instrument is next placed in melting ice, and when a steady temperature has been attained the stop-cock E is closed. Since equal volumes of air have been enclosed at the same temperature and pressure, it follows that the mass of dry air on each side of the pressure gauge is the same. If now the bulb A be placed in a bath at a higher temperature, while B and D are still kept in melting ice, the pressure of the air in A will increase, and mercury must be run out from D to again restore the level of the sulphuric acid in C.[1]

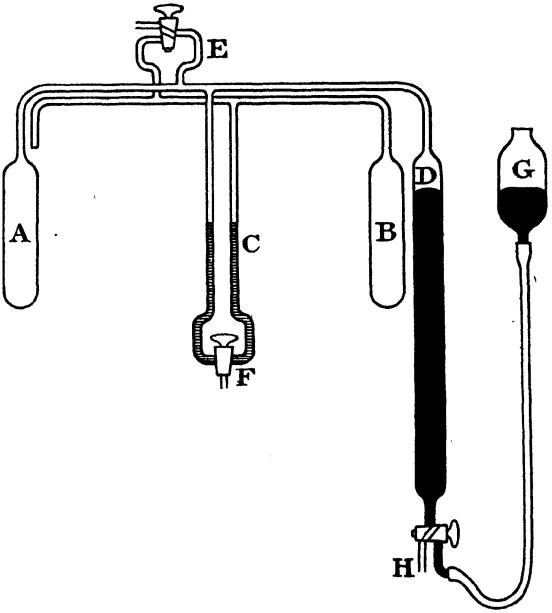

FIG. XLII.—Callendar's Compensating Constant-Pressure Air Thermometer.

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[1] The mercury may be run out of D either by lowering the reservoir G, or by means of the tube at H. In the latter case the volume of air which has passed into D can be obtained from the weight of the mercury run off, and the *total* volume of the air in D is then obtained by adding to this quantity the original volume of the air in D when at 0° C.

The volume of mercury run out gives the volume of air which has passed from A into D, and the pressure of the air is practically the same as the initial pressure, since it is equal to that of the air in B, which is constant, except for the very small increase due to the rise in temperature of the air in the capillary tube.

Consider, first, the air enclosed in the bulb A, the burette D, and the connecting capillary tube.

Let V_A = volume of the air in A when at the temperature of melting ice, and let θ_0 represent this temperature on the scale of the air thermometer.

Let V_A' = volume of the air in A at θ_t on the air scale.

Also let v_a = volume of the air in the capillary tube connecting A and D when at θ_0.

When the bulb A is at θ_t, the temperature of the air in the capillary tube will be different at different points. Let the mean of the reciprocals of these temperatures be $\frac{1}{\theta'}$, and v_a' the volume of the air in the capillary tube under the new conditions.

Further, let V_D = the initial volume of the air in D at θ_0, and V_D' = the final volume of the air in D at θ_0.

Similarly, for the air enclosed in the bulb B and its capillary tube, let V_B = volume of the air in B at θ_0, v_b = volume of the air in the capillary tube at θ_0, and v_b' = volume of the air in the capillary tube while θ_t is being measured.

When A is at θ_t the mean of the reciprocals of the temperatures at different points of this tube may also be taken as $\frac{1}{\theta'}$, since the two capillary tubes are exactly similar, and are placed close together, so that they follow the same course. Further, for each system, let the initial pressure of the air = P, the subsequent pressure when measuring θ_t = P′, and the mass of air = m.

Since the change in pressure, P′ − P, is very small we may apply Boyle's Law with sufficient exactness.

If, then, ρ be the density of the air at a temperature θ_0 and a pressure P, we have—

Initial mass of air in A, at θ_0 and P, $= \rho \, . \, V_A$.
,, ,, ,, ,, capillary tube, at θ_0 and P, $= \rho \, . \, v_a$.
,, ,, ,, ,, D, at θ_0 and P, $= \rho \, . \, V_D$.
Final ,, ,, ,, A, at θ_t and P′, $= \frac{\rho \, . \, V'_A \, . \, P' \, . \, \theta_0}{P \, . \, \theta_t}$.

Final mass of air in capillary tube, when the mean of the reciprocals of the temperatures at different points is $\frac{1}{\theta'}$ and the pressure is P′, $= \frac{\rho \, . \, v'_a \, . \, P' \, . \, \theta_0}{P \, . \, \theta'}$.

Final mass of air in D, at θ_0 and P', $= \frac{\rho \,.\, V'_D \,.\, P'}{P}$.

$$\therefore \rho \,.\, (V_A + v_a + V_D) = \frac{\rho \,.\, \theta_0 \,.\, P'}{P} \,.\, \left(\frac{V'_A}{\theta_t} + \frac{v'_a}{\theta'} + \frac{V'_D}{\theta_0}\right) = m.$$

Similarly, for the other system, we have—

Initial mass of air in B, at θ_0 and P, $= \rho \,.\, V_B$.

,, ,, ,, ,, capillary tube, at θ_0 and P, $= \rho \,.\, v_b$

Final ,, ,, ,, B, at θ_0 and P', $= \frac{\rho \,.\, V_B \,.\, P'}{P}$.

,, ,, ,, ,, capillary type, when the mean of the reciprocals of the temperatures at different points is $\frac{1}{\theta'}$ and the pressure is P', $= \frac{\rho \,.\, v'_b \,.\, P' \,.\, \theta_0}{P \,.\, \theta'}$.

$$\therefore \rho \,.\, (V_B + v_b) = \frac{\rho \,.\, \theta_0 \,.\, P'}{P} \,.\, \left(\frac{V_B}{\theta_0} + \frac{v'_b}{\theta'}\right) = m.$$

Whence
$$\frac{V'_A}{\theta_t} + \frac{v'_a}{\theta'} + \frac{V'_D}{\theta_0} = \frac{V_B}{\theta_0} + \frac{v'_b}{\theta'}.$$

Since the capillary tubes are made of equal capacity we have $v_a = v_b$, and since they are exactly similar and acquire the same temperatures at corresponding points we have $v'_a = v'_b$.

$$\therefore \frac{V'_A}{\theta_t} + \frac{V'_D}{\theta_0} = \frac{V_B}{\theta_0}.$$

$$\therefore \theta_t = \frac{\theta_0 \,.\, V'_A}{V_B - V'_D}.$$

Any effect due to the capillary tubes thus disappears, and the only correction which need be applied is for the expansion of the bulb A. Let γ be the coefficient of cubical expansion of the material of the bulb. Then since the internal volume is V_A at θ_0, we have—

$$V'_A = V_A \,.\, \{1 + \gamma \,.\, (\theta_t - \theta_0)\},$$

and substituting in the previous equation, we have—

$$\theta_t = \frac{\theta_0 \,.\, (V_A - V_A \,.\, \gamma \,.\, \theta_0)}{V_B - V'_D - V_A \,.\, \gamma \,.\, \theta_0}.$$

When Callendar's constant-pressure thermometer is employed for the measurement of temperatures not differing greatly from the normal atmospheric temperature, the bulbs A and B may, conveniently, be made of equal volume. In this case the measuring burette will be completely filled with mercury when the whole instrument is initially at θ_0, and, on raising A to θ_t, the volume of mercury run out of the burette will at once give V'_D. For the measurement of low temperatures the bulb A should be considerably smaller than B, otherwise it will be impossible to make the pressure in the two systems equal.

44. Diffusion.—One of the characteristic properties of gases is their mutual miscibility in all proportions. Thus, if two different gases, which are not uniformly mixed together, be kept in a confined space, each gas will flow from the regions where its density is higher to those where its density is lower until, finally, each gas will be uniformly diffused throughout the whole space.

Experiment XVIII.—Three tall glass cylinders of the same size are filled, respectively, with hydrogen, air, and carbon-dioxide, and are closed with glass plates. Three thin glass bulbs each containing a few drops of bromine are then taken, and, after removing the glass plates, a bulb is dropped, as nearly as possible simultaneously, into each of the three cylinders, the glass plates being immediately replaced. The bulbs are broken by the fall, and a layer of bromine vapour is rapidly formed at the bottom of each cylinder. After standing for a short time it will be observed that the bromine vapour has diffused much farther in the cylinder containing hydrogen than in the one containing air, and that the diffusion is least in the case of the carbon-dioxide. Finally, however, after standing for a sufficient length of time, the bromine vapour will be uniformly diffused throughout each of the cylinders.

The law relating to the conduction of heat, which was enunciated by Fourier, supplies an analogy to the law governing gaseous diffusion, and it will therefore be convenient to refer first to the phenomenon of thermal conductivity.

If a plate of any material be taken, of 1 cm. thickness, and if its two faces be kept, respectively, at constant temperatures t°. C., and $(t - 1)^\circ$. C., then the thermal conductivity of the material of which the plate is made is defined as the quantity of heat which, in one second, flows through each unit of area of the plate. Further, if the thickness of the plate be x cms., and the respective temperatures of the two faces be t and t', it is found by experiment that, when a steady state is attained, the flow of heat per second, per unit area, is proportional to $\frac{t - t'}{x}$, provided the value of this latter quantity be sufficiently small.

The quantity $\frac{t - t'}{x}$, which represents the fall of temperature per centimetre, is termed the "temperature gradient." If, then, the area of the plate be A sq. cms., the total quantity of heat, Q, which passes in S seconds is given by the equation—

$$Q = K . A . \frac{t - t'}{x} . S,$$

where K is a constant for the given material, and is defined as the thermal conductivity.

More generally, the flow of heat through any surface is given by the equation—

$$Q = K . A . - \frac{d\theta}{dx} . S,$$

where $-\frac{d\theta}{dx}$ is the temperature gradient *at* the surface. It should be noted, however, that K is not *rigidly* constant, but is, in fact, a function of the temperature, so that Q is proportional to $- f(\theta) . \frac{d\theta}{dx}$.

If a steady state has not been attained we must consider an infinitely short time interval during which the temperature gradient is sensibly constant. In this case we must replace S by dS in the previous equation.

It was shown by Fick, in 1855, that a similar relationship holds for the phenomenon of diffusion, both in the case of liquids and gases, the concentration, or density of the fluid corresponding to temperature in the thermal formula. Thus, let two gases which, initially, are not uniformly mixed together be enclosed in a cylindrical vessel, and let the density of each gas throughout any horizontal section of negligible thickness be uniform. Then if ρ be the density of one of the gases at a height x, measured from any fixed horizontal reference plane, and if ρ decrease with increase in x, the mass, M, of the gas which flows across the horizontal plane at height x is given by the equation—

$$M = \eta . A . - \frac{d\rho}{dx} . S,$$

where η is defined as the interdiffusity of the two gases.

As in the case of thermal conductivity, this equation will, in general, become more nearly exact the shorter the time interval, S, for the density gradient, $-\frac{d\rho}{dx}$, will usually vary with S.

If the value of the density gradient be not too great, we may assume that it is uniform, and write $M = \eta . A . - \left(\frac{\rho' - \rho}{x' - x}\right) . S$, where ρ and ρ' are the respective densities at heights x and x' from the horizontal reference plane.

Both the conduction of heat and the interdiffusion of miscible fluids find a simple explanation from the standpoint of the kinetic theory of matter. For if two adjoining layers of any material be at different temperatures, the average kinetic energy of the molecules in the layer at the higher temperature is greater than the average kinetic energy of the molecules in the cooler layer. Consequently, when collisions take place at the plane of separation, the molecules in the cooler layer will, on the average, gain energy, and the molecules in the warmer layer will experience a corresponding loss. Heat energy is thus transferred from the hotter to the cooler portions of the material, and, if undisturbed by external influences, a uniform temperature will ultimately be acquired.

Again, in the case of miscible fluids, if the number of molecules per unit volume of one fluid in any layer exceed the number of molecules per unit volume of the same fluid in an adjoining layer, then, since the molecules are in constant motion, more molecules of the given fluid will pass in unit time across the plane of separation from the side of greater to that of less concentration than in the reverse direction. Thus a flow of the fluid will take place from regions of greater to those of less concentration, and, in the absence of disturbing influences, will continue until the fluid mixture has become perfectly homogeneous. This homogeneity, once acquired, will not be affected by the molecular motion.

Further, in the case of a gaseous mixture, if the pressure be diminished the length of the mean free path of the molecules will be increased, and, consequently, diffusion will take place more rapidly. A rise in temperature will also increase the rate of diffusion, since the average velocity of the molecules is thereby increased.

These conclusions are in agreement with the experimental results obtained by Loschmidt, Von Obermayer, Waitz, and other investigators, who have measured η for different pairs of gases.

Loschmidt determined the value of η by enclosing the two gases in a vertical glass tube 975 mms. in length and 26 mms. in diameter, which was divided in the centre by means of a thin steel plate, the heavier gas being in the lower half of the glass tube. The steel plate was furnished with a hole of the same size as the internal bore of the tube, and by carefully moving the plate the two gases were brought into contact. After a given time the steel plate was again interposed, and the quantity of the heavier gas which had diffused into the upper half of the tube was determined by analysis. η could then be calculated by applying equations deduced by Stefan from the kinetic theory.

Waitz determined η for carbon-dioxide and air by enclosing the gases in a tube and allowing the carbon-dioxide to diffuse upwards into the air, the progress of the diffusion being observed by measuring the refractive indices of various horizontal layers at definite times. The proportion of air and carbon-dioxide in any layer was then calculated from its refractive index. It was found by Waitz that η varied to a small extent with variation in the proportion between the two gases.

The rate at which a liquid evaporates is, in general, dependent upon the rate at which its vapour diffuses into the surrounding atmosphere, and the diffusivity of the vapour into the air can be ascertained by measuring the rate of evaporation.

Thus, if some of the liquid be placed at the bottom of a tube of uniform cross-section, and vapour-free air be blown steadily across the mouth of the tube, the density gradient of the vapour will, after a certain time, become uniform, provided the tube be not too short. The value of the density gradient in this steady uniform state is $\frac{\rho}{x}$, where ρ is the density of the vapour at a pressure equal to the saturation vapour pressure of the liquid at the temperature of the room, and x the distance between the surface of the liquid and the mouth of the tube.

Hence the mass of vapour which escapes from the tube in any time, S, is given by the equation $M = \eta . A . \frac{\rho}{x} . S$, and this mass is, of course, identical with the mass of liquid which evaporates in the same time.

Thus, by measuring the various quantities in the above equation, η can be readily ascertained.

An error arises in this method due to the increase in the value of x produced by the evaporation of the liquid at the bottom of the tube. If, however, the tube be of moderate length the variation in the value of x during any short time may be treated as negligible.

It was first shown experimentally by Stefan that the rate of evaporation of a liquid contained in a long tube varied inversely as the distance between the surface of the liquid and the mouth of the tube, and both he and Winkelmann have employed the method which has been described to determine the value of η for the vapours of a number of liquids diffusing into air and other gases.

A more general equation, applicable to both the conduction of heat and the diffusion of a fluid will now be deduced.

Consider a thin rod of any material of good thermal conductivity, and of uniform cross-section, A (Fig. XLIII). Let the rod be heated at one end, and let us confine our attention to a small element of the rod of length dx bounded by two parallel planes a and b at right angles to the axis of the rod. The curve of temperature along the rod at any time may be determined experimentally by means of thermo-electric junctions and is of the form XY.

Now, in the infinitely short time, ds, the heat entering the element at a is given by the equation—

$Q_a = -K . A . \frac{dT}{dx} . ds$, where $-\frac{dT}{dx}$ is the temperature gradient at the surface a.

The temperature gradient is less at b than at a, as is shown in the figure by the diminished slope of the tangent to the curve XY.

If we assume that K is constant, the heat flowing out from the element through b during the time interval ds is given by the equation—[1]

$$Q_b = -K \cdot A \cdot \left\{ \frac{dT}{dx} + \frac{d}{dx}\left(\frac{dT}{dx}\right) \cdot dx \right\} \cdot ds.$$

Therefore, taking the algebraic sum, we have for the total heat *entering* the elementary piece in the time interval ds—

$$Q_a - Q_b = -K \cdot A \cdot \frac{dT}{dx} \cdot ds + K \cdot A \left\{ \frac{dT}{dx} + \frac{d}{dx}\left(\frac{dT}{dx}\right) \cdot dx \right\} \cdot ds.$$

But the rod is also cooling and giving out heat to surrounding bodies, for both the temperature and the temperature gradient at b are always less than the corresponding quantities at a.

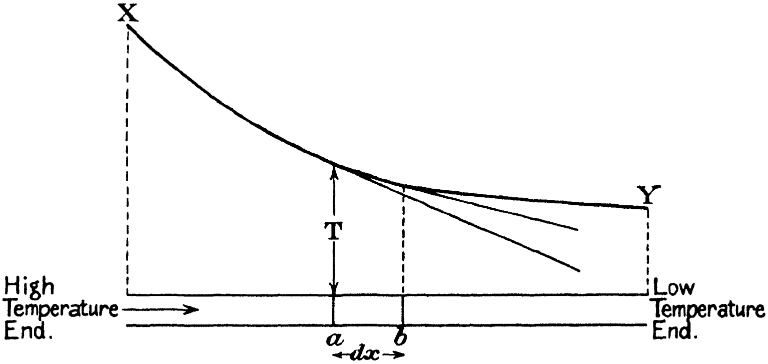

FIG. XLIII.

The quantity of heat given out depends upon the emissivity, E, the area from which radiation is taking place, the time interval, and the temperature difference between the radiating body and the surroundings.[2]

If p = the circumference of the rod, the area of the element is $p \cdot dx$. Let α = the temperature of the surroundings, so that the temperature difference, θ, is equal to $T - \alpha$.

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[1] It has been tacitly assumed that the cross-section, A, remains constant, whereas, in reality, the rod expands more towards the high temperature end. For moderate ranges of temperature, however, the effect due to this expansion may be neglected.

[2] The assumption that the rate of loss of heat to the surroundings is proportional to the temperature difference between the element and the surroundings is in accordance with Newton's Law of Cooling. This law is only true however when the difference in temperature between the radiating body and the surroundings is small.

Thus, the total heat entry for the element is—

$$-\mathrm{K}\,.\,\mathrm{A}\,.\,\frac{d\mathrm{T}}{dx}\,.\,ds+\mathrm{K}\,.\,\mathrm{A}\,.\left\{\frac{d\mathrm{T}}{dx}+\frac{d}{dx}\left(\frac{d\mathrm{T}}{dx}\right).\,dx\right\}.\,ds-\mathrm{E}\,.\,pdx\,.\,(\mathrm{T}-a)\,.\,ds.$$

When a steady state has been attained, the sum of these three terms is zero, and the temperature of the element remains unchanged. If, however, the sum be *not* zero, the temperature of the element must be changing, and, consequently, we have—

$$-\mathrm{K}\,.\,\mathrm{A}\,.\,\frac{d\mathrm{T}}{dx}\,.\,ds+\mathrm{K}\,.\,\mathrm{A}\,.\left\{\frac{d\mathrm{T}}{dx}+\frac{d}{dx}\left(\frac{d\mathrm{T}}{dx}\right).\,dx\right\}.\,ds=\mathrm{E}\,.\,pdx\,.\,(\mathrm{T}-a)\,.\,ds$$

$$=\rho\,.\,\mathrm{A}dx\,.\,\mathrm{C}\,.\,d\mathrm{T},$$

where ρ is the density and C the specific heat of the material of the rod, Adx the volume of the elementary piece, and dT its change in temperature.

We have assumed that the temperature is the same at all points of the same cross-section. Now this assumption is not rigidly true, for heat is flowing from the centre of the rod out through the surface, and, consequently, the temperature must be somewhat higher in the centre. It can be shown, however, that in the case of a very thin rod possessing good thermal conductivity the temperature is sensibly uniform over any cross-section at right angles to the axis of the rod, and that the error involved in our assumption is quite negligible.

Simplifying the last equation we have—

$$\mathrm{K}\,.\,\mathrm{A}\,.\,\frac{d^2\mathrm{T}}{dx^2}-\mathrm{E}\,.\,p\,.\,(\mathrm{T}-a)=\rho\,.\,\mathrm{A}\,.\,\mathrm{C}\,.\,\frac{d\mathrm{T}}{ds}.$$

If the temperature of the surroundings, a, be constant, then, since $\theta = \mathrm{T} - a$, we have—

$$\frac{d^2\theta}{dx^2}-\frac{\mathrm{E}\,.\,p\,.\,\theta}{\mathrm{K}\,.\,\mathrm{A}}=\frac{\rho\,.\,\mathrm{C}}{\mathrm{K}}\,.\,\frac{d\theta}{ds},$$

$$=\frac{1}{\mathrm{D}}\,.\,\frac{d\theta}{ds},$$

where $\mathrm{D}=\dfrac{\mathrm{K}}{\rho\,.\,\mathrm{C}}$.

D is defined as the thermal diffusivity of the material of the rod, and may be regarded as the conductivity with respect to *temperature*, whereas K is the conductivity with respect to *heat*. When a state of equilibrium is attained, the temperature of the element remains constant, and, therefore—

$$\frac{d^2\theta}{dx^2}=\frac{\mathrm{E}\,.\,p\,.\,\theta}{\mathrm{K}\,.\,\mathrm{A}},$$

the term containing D vanishing from the equation.

If, on the other hand, there be no lateral loss of heat, the term containing E vanishes, and we have—

$$\frac{d^2\theta}{dx^2} = \frac{1}{D} \cdot \frac{d\theta}{ds},$$

Or—

$$\frac{d\theta}{ds} = D \cdot \frac{d^2\theta}{dx^2}.$$

Now, the change in temperature at any cross-section of the rod can, of course, occur in an infinite number of ways, depending upon the way in which the temperature at, for example, the heated end of the rod is made to vary. The last differential equation, however, shows how the rate of change of temperature at any cross-section depends upon the *rate* of rate of change of temperature at another section at a distance dx from the first.

An exactly similar relation holds for the diffusion of a fluid. If, for example, we again consider the case of two gases enclosed in a vessel, with layers of equal density horizontal, then, if the gases be not uniformly mixed together, we have—

$$\frac{d\rho}{ds} = \eta \cdot \frac{d^2\rho}{dx^2},$$

where ρ is the density of one of the gases at any horizontal plane, and η the interdiffusity of the gases. In such a case, of course, no lateral diffusion can occur.[1]

45. The Passage of Gases through Porous Septa; Effusion.—The term *diffusion* should strictly be applied only to the mixing of gases across a free surface of separation.

We pass now to a consideration of the phenomena exhibited during the passage of gases through porous septa. In the case of a *thin* septum in which the holes or apertures are *not too fine*, the passage of the gas is termed *effusion*. During effusion the gas flows as a whole through the aperture, and, in the case of a gaseous mixture, no separation into the constituents is produced. The effusion of gases was first studied by Leslie, in 1804, and subsequently by Schmidt, Graham, and other investigators. It was found that, at a constant temperature, the velocity of effusion of a gas into a vacuum was directly proportional to the square root of the pressure of the gas, and inversely proportional to the square root of the gaseous density,

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[1] It is evident, since the density, ρ, is the mass of gas in unit volume, that the quantity D in this case is identical with η. For the difference between the mass of gas flowing in across any horizontal plane, a, and the mass flowing on through a horizontal plane, b, at a distance dx from a, is equal to $A \,.\, dx \,.\, d\rho$, where A is the uniform cross-section of the vessel.

and, therefore, for two different gases at the same temperature and pressure the rates of effusion were inversely proportional to the square roots of their respective densities.[1]

This result was utilised by Bunsen in 1857 ("Gasometrische Methoden") for the experimental determination of the densities both of pure gases and of gaseous mixtures. A certain volume, V, of the gas under examination was allowed to escape through a fine hole in a thin platinum plate, and the time taken, t_1, was observed. This was then compared with the time, t_2, required for an equal volume of a gas of known density to escape through the hole, under the same conditions of temperature and pressure.

Then, since the rates of effusion are inversely proportional to the square roots of the respective gaseous densities, ρ_1 and ρ_2, we have—

$$\frac{\frac{V}{t_1}}{\frac{V}{t_2}} = \sqrt{\frac{\rho_2}{\rho_1}},$$

Or—

$$\frac{t_2}{t_1} = \sqrt{\frac{\rho_2}{\rho_1}}.$$

Since ρ_2 is known ρ_1 can readily be calculated.

More recently Donnan has carried out a very accurate investigation on the rate of effusion of gases, using a hole of about $\frac{1}{50}$ mm. in diameter, pierced in a disc of platinum foil of about $\frac{1}{25}$ mm. thickness, as the effusion aperture. The gas at a pressure of approximately 70 cms. was allowed to escape through this aperture into a vacuum—until the back-pressure had risen to about 6 cms.—the time being measured by means of a stop watch. The time of escape for a second gas, under identical conditions as to the limits of pressure, temperature, etc., was then determined, and the gaseous densities compared as explained above.

The phenomenon of effusion finds a ready explanation from the standpoint of the kinetic theory. For the number of molecules, N, which flow through an aperture in unit time will be very approximately proportional to the area, A, of the aperture, to the number of molecules, n, per unit volume, and to their average velocity, Ω.

$$\therefore N = K . A . n . \Omega, \text{ where K is a constant.}$$

We have assumed that all the molecules coming up to the aperture pass through, and that none collide with molecules on the opposite

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[1] It should be noted that the rate of effusion refers to the *volume* of the gas, measured at a fixed pressure, which passes through the septum in unit time, and *not* to the *mass* of the gas. The mass which passes in unit time is sometimes termed the rate of efflux, and varies *directly* as the square root of the gaseous density.

side of the aperture and rebound again. This assumption will be justified if the effusion take place into a vacuum, and will be very approximately true if the pressure on one side of the aperture be much lower than that on the other.

Thus the mass of the gas, M, which escapes in unit time is given by the equation—

$$M = m \,.\, N = K \,.\, A \,.\, n \,.\, \Omega \,.\, m, \text{ where } m \text{ is the mass of a molecule.}$$

$$\therefore M = K \,.\, A \,.\, \rho \,.\, \Omega.$$

Since $\bar{C} = \sqrt{\frac{3P}{\rho}}$, and since Ω is proportional to $\bar{C}$, we have—[1]

$$M = K' \,.\, A \,.\, \rho \,.\, \sqrt{\frac{3P}{\rho}} = K' \,.\, A \,.\, \sqrt{3 \,.\, P \,.\, \rho}, \text{ where } K' \text{ is a constant.}$$

Hence for two different gases at the same temperature and pressure—

$$\frac{M_1}{M_2} = \frac{K' \,.\, A \,.\, \sqrt{3 \,.\, P \,.\, \rho_1}}{K' \,.\, A \,.\, \sqrt{3 \,.\, P \,.\, \rho_2}} = \sqrt{\frac{\rho_1}{\rho_2}}.$$

$\therefore \frac{V_1}{V_2} = \sqrt{\frac{\rho_2}{\rho_1}}$, where V_1 and V_2 are the respective volumes of the two gases which pass through the aperture in unit time.

Thus the rates of effusion are inversely proportional to the square roots of the respective gaseous densities, and this is the relationship experimentally ascertained.

46. Transpiration.—In the case of a thick septum in which the apertures are *not too fine*, the passage of the gas is termed *transpiration*. No change in the composition of a gaseous mixture is produced by transpiration, and the passage of the gas is conditioned by the ordinary laws of viscosity which are applicable to the flow of gases through long tubes.

The first systematic investigation on the transpiration of gases was carried out by Graham, and the results of his experiments were published in 1846 and 1849.

Graham's method was to allow the gas to flow through a capillary tube into the exhausted receiver of an air-pump, and to observe the time required to produce a given rise in pressure. Experiments were carried out with different gases, and with tubes of various lengths and internal diameters, and the rates of transpiration were also determined under different conditions of temperature and pressure.

When the tube is *exceedingly* short, as in the case of a thin septum, we have seen that the gas flows through the aperture into a vacuum by *effusion*, and Graham found that as long as the diameter of such an aperture was sufficiently large in comparison with the thickness of the septum the effect of viscosity was negligible. When, however, the

[1] $\Omega = \cdot 921 \,.\, \bar{C}$. *Vide* § 18.

length of the tube, or the thickness of the septum, is large compared with the diameter of the aperture, the rate of flow is determined by the viscosity of the gas, and it is to this mode of flow that the term transpiration is applied. A tube of any diameter may be employed for experiments on transpiration, provided it be of sufficient length, i.e. provided the ratio of the length to the diameter be large.

Meyer showed, in 1866, that the results of Graham's experiments on transpiration furnished a proof that the viscosity of gases is independent of the pressure, but increases with the temperature, and he calculated, from Graham's data, the coefficients of viscosity for a number of different gases.

Maxwell had, indeed, in 1860, deduced from the Kinetic Theory of Gases the theoretical law that *the coefficient of viscosity of a gas is independent of its density*, and an elementary proof of this law will now be given.

47. Molecular Mean Free Path.—The kinetic theory, as developed in Chapters II. and III., leads to a number of important conclusions relative to the velocity and energy possessed by molecules in motion. It will now be necessary to examine more closely the nature of this molecular motion, and, in particular, to calculate the average distance traversed by a molecule of a gas between successive collisions with neighbouring molecules.

Clausius, in 1858, first showed how the molecular mean free path might be theoretically deduced, and the following calculation is based upon his method of analysis.

Consider a cubic centimetre of a gas containing N molecules, and let a single molecule enter this cube. As a first approximation we shall imagine the N molecules to be at rest, and then proceed to calculate the probable length of path traversed by the entering molecule before a collision occurs.

Since the density of the gas is assumed to be uniform, we may imagine the cubic centimetre divided up into N small cubes, each of which *on the average* will contain one molecule. Let the edge of one of these small cubes be λ, its volume being λ^3.

Then $$N . \lambda^3 = 1.$$

The length λ was called by Clausius the mean distance between neighbouring molecules.

If ρ be the density of the gas, and m the mass of a molecule, we have—

$$\rho = N . m.$$

$$\therefore \rho = \frac{m}{\lambda^3}.$$

Now, we are ignorant as to the exact nature of a molecular collision, and as to the range at which the molecules affect each others motion.

If we regard a collision as an actual *contact* of two equal symmetrical spherical molecules, then it is clear that the distance between their centres of mass at the moment of impact is the molecular diameter. For molecules which are not spherical we may, in accordance with the calculus of probabilities, take this distance as the *mean* molecular diameter. But since actual *contact* need not necessarily occur during molecular collision, we must, in general, assume that the centre of mass of each molecule is surrounded by a region within which the centre of mass of another molecule cannot enter. This region may, in the absence of any evidence to the contrary, be regarded as spherical, and was named by Clausius the *molecular sphere of action.*

Thus the shortest distance between the centres of mass of two molecules during a " collision " is s, where s is the radius of the sphere of molecular action.[1]

If a collision be, indeed, an actual *molecular* contact, it is clear that for equal symmetrical spherical molecules we have $s = 2r$, whero r is the molecular radius. In this case, therefore, the volume of the molecular sphere of action is eight times the volume of the molecule itself.

If, however, contact does not occur during a collision, the sphere of action will obviously have a still larger volume. Consider, then, the single molecule which has entered the cube, and let it travel a distance equal to the mean distance between neighbouring molecules, i.e. λ.

The molecule is surrounded by a sphere of action of radius s, and of central section $\pi \, . \, s^2$, and, consequently, when the molecule moves a distance λ the anterior hemispherical surface of this sphere of action traverses a volume equal to $\lambda \, . \, \pi \, . \, s^2$. But since, on the average, a volume of λ^3 will only contain one molecule, the probability of the smaller volume $\lambda\pi s^2$ containing a molecule will be in the ratio of $\lambda\pi s^2$ to λ^3.

Hence the probability of the single molecule colliding while it traverses the distance λ is given by the ratio $\frac{\lambda\pi s^2}{\lambda^3}$, i.e. by $\frac{\pi s^2}{\lambda^2}$; and the probability of a collision *not* taking place is given by the ratio $\frac{\lambda^3 - \lambda\pi s^2}{\lambda^3}$, i.e. by $\frac{\lambda^2 - \pi s^2}{\lambda^2}$.

Consider next the case of M molecules entering normally at one face of the cubic centimetre and all moving with the same speed. Divide the cube up into layers, each of thickness λ, parallel to the face at which the M molecules enter.

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[1] We may, alternatively, regard *each* molecule as surrounded by a sphere of action of radius $\frac{s}{2}$, a collision occurring whenever two such spheres of action meet.

Then, in the first layer, $\frac{M \,.\, \pi \,.\, s^2}{\lambda^2}$ molecules will probably undergo collision, while $M \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right)$ molecules will probably pass on.

Similarly, in the second layer, $M \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right) \,.\, \frac{\pi s^2}{\lambda^2}$ molecules will probably undergo collision, while $M \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right)^2$ molecules will probably pass on.

In the n^{th} layer, $M \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right)^{n-1} \,.\, \frac{\pi s^2}{\lambda^2}$ molecules will probably undergo collision, while $M \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right)^n$ molecules will probably pass on.

We need not, of course, limit ourselves to the consideration of a single cubic centimetre, but can apply exactly the same argument to the case of M molecules moving forward simultaneously, with the same velocity, normally to any surface in an extended field containing N stationary molecules per cubic centimetre.

Now, the molecules which collide in the n^{th} layer have clearly traversed paths varying in length between $(n - 1)\lambda$ and $n\lambda$. But since we shall show that the mean free path of a molecule in a gas is very great in comparison with λ, except when the gas is under extremely high pressure, we may, without appreciable error, take the path traversed by a molecule which collides in the n^{th} layer as the maximum value, $n\lambda$, up to the end of the layer, provided the gaseous density be low. If, then, we reckon the paths traversed by the molecules which undergo collision in *each* layer in the same manner, we can readily calculate the sum of the paths for the M molecules, and, on dividing this sum by M, we shall obtain the probable mean molecular free path.

Since $\frac{M \,.\, \pi \,.\, s^2}{\lambda^2}$ molecules probably collide in the first layer, the sum of their paths is $\frac{M \,.\, \pi \,.\, s^2}{\lambda^2} \times \lambda = \frac{M \,.\, \pi \,.\, s^2}{\lambda}$.

Similarly, $M \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right) \,.\, \frac{\pi s^2}{\lambda^2}$ molecules probably collide in the second layer, and the sum of their paths is

$$M \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right) \,.\, \frac{\pi s^2}{\lambda^2} \times 2\lambda = 2M \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right) \,.\, \frac{\pi s^2}{\lambda}.$$

In general, $M \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right)^{n-1} \,.\, \frac{\pi s^2}{\lambda^2}$ molecules probably collide in the n^{th} layer, and the sum of their paths is

$$M \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right)^{n-1} \,.\, \frac{\pi s^2}{\lambda^2} \times n\lambda = n \,.\, M \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right)^{n-1} \,.\, \frac{\pi s^2}{\lambda}.$$

Therefore, the total sum of *all* the paths described by the M molecules is given by—

$$\sum n \,.\, \mathrm{M} \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right)^{n-1} . \frac{\pi s^2}{\lambda},$$

for all integral values of n between 1 and ∞.

Hence the probable mean molecular free path, L, is given by the equation—

$$\mathrm{L} = \sum n \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right)^{n-1} . \frac{\pi s^2}{\lambda} = \frac{\pi s^2}{\lambda} . \sum n \,.\, \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right)^{n-1}.$$

But $\sum n \,.\, \phi^{n-1}$, for all integral values of n between 1 and ∞, is given by—

$$\sum n \,.\, \phi^{n-1} = 1 + 2\phi + 3\phi^2 + \ldots = (1 - \phi)^{-2}.$$

$$\therefore \mathrm{L} = \frac{\pi s^2}{\lambda} . \left\{1 - \left(\frac{\lambda^2 - \pi s^2}{\lambda^2}\right)\right\}^{-2} = \frac{\pi s^2}{\lambda} . \left\{\frac{\pi s^2}{\lambda^2}\right\}^{-2} = \frac{\lambda^3}{\pi s^2}.$$

L, it should be noted, is the mean free path for a molecule moving amongst other molecules *at rest.*

Since a gas at its ordinary density exhibits an almost complete absence of cohesion, we must regard the mean distance, λ, between neighbouring molecules as *very considerably* greater than the radius, s, of the sphere of molecular action. For otherwise, at any given instant, a relatively large proportion of the molecules would be close together and would be exerting cohesive forces.

Hence, in the equation $\frac{\mathrm{L}}{\lambda} = \frac{\lambda^2}{\pi s^2}$, λ^2 must be very much greater than πs^2, and, consequently, L must be proportionally greater than λ.

Thus our previous method of reckoning the free path traversed by a molecule as extending up to the *end* of the layer in which a collision occurred, and which, in effect, added a fraction of λ to the value of L, has not affected to any marked extent the accuracy of our result.

Since L is much greater than λ, it follows that a molecule must pass by many other molecules between successive collisions.

Now, in an actual gas *all* the molecules are in motion, and, therefore, a correction must be applied to the value found for the mean free path of a molecule moving amongst other molecules at rest in order to allow for the general distribution of the molecular velocities.

The effect of the general molecular motion is to increase the probability of collision, and, consequently, to shorten the molecular mean free path.

On the assumption that the molecules all possess *equal* velocities, and move in every direction, Clausius calculated the value $\frac{3}{4} . \frac{\lambda^3}{\pi s^2}$

for the mean free path, and Maxwell obtained the more accurate equation, $L = \frac{\lambda^3}{\pi s^2 . \sqrt{2}}$, by assigning to the molecules different velocities in accordance with the law of the distribution of velocities deduced by him from the calculus of probabilities.

48. Viscosity of Gases.—In order to maintain relative motion between the different parts of any fluid it is necessary to apply an external force, and when this force is removed the relative motion soon disappears. If, for example, we stir a fluid, the relative motion thus produced vanishes soon after the stirring is stopped. Similarly, the waves on a stormy sea subside when the wind abates.

The fact that a fluid offers resistance to the relative motion of its parts is otherwise expressed by saying that the fluid possesses internal friction, or *viscosity*.

Viscosity, then, is brought into action whenever two portions of a fluid medium move with different velocities, and the magnitude of the viscous resistance is dependent only upon the *relative* motion of the two portions, i.e. upon the difference between their respective velocities.

We shall assume that when a fluid flows over a solid surface there is *no slip* between the solid and the layer of fluid in actual contact with it. This assumption is in accordance with experimental evidence,[1] except in the case of a gas at *very* low pressure, when the layers of gas in contact with any solid surface can no longer be regarded as fixed relatively to the latter. Under these circumstances side-slip does, in fact, occur at the surface when the solid moves relatively to the gas.

We shall assume, further, in accordance with an hypothesis due to Newton, that the viscosity is directly proportional to the difference in velocity of neighbouring layers.

It is evident, however, that the magnitude of the viscous resistance must also be conditioned by the chemical nature of the fluid medium, and, consequently, in deducing our equation for the force necessary to maintain relative motion between two layers of the medium we must introduce a numerical factor which is called the coefficient of viscosity of the fluid, and is denoted by the symbol κ.

Consider, then, a horizontal layer of fluid, AB, moving with a steady velocity, V, relatively to a parallel layer of the fluid, CD, at a distance x from it (Fig. XLIV.). For simplicity, we may regard the layer CD as stationary. Then it is clear that the velocity of any intermediate layer is a linear function of its distance from CD. For consider a layer such as EF, at a distance x' from CD, and moving with a velocity V′. In the steady state of motion of the fluid which

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[1] In the case of *liquids*, at any rate, no appreciable slip appears to exist. The relatively slow rate at which the banks and bottom of a river wear away may thus be explained.

we are investigating, the velocity V′ is constant, and, consequently, the viscous forces acting on the upper surface of EF and dragging it forward must be equal and opposite to those acting on its lower surface and dragging it backward. But, in accordance with Newton's hypothesis, the viscosity is directly proportional to the difference in velocity of neighbouring layers, and, therefore, the velocity of the layer EF must be the arithmetic mean of the velocities of the layers immediately above and immediately below it. The same argument applies to any other layer we may select for investigation. Hence we can write $V = cx$, and $V' = cx'$, where c is a constant.

Since $c = \frac{V}{x}$, it is, of course, the "velocity gradient."

Let the tangential force on an area, A, of the layer AB required to maintain its relative velocity, V, be F. On an area, A, of the layer CD the same force must act, but in the opposite direction.

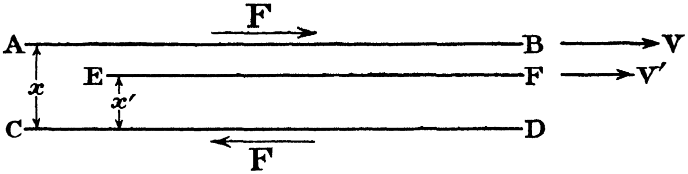

FIG. XLIV.

Then—

$$F = \kappa . A . \frac{V}{x},$$

or $$\kappa = \frac{F . x}{A . V},$$ where κ is the coefficient of viscosity.

It is found, by experiment, that κ is constant for a given fluid, under standard conditions as to temperature and pressure. Hence Newton's hypothesis that the viscosity is proportional to the relative velocity is shown to be justified.

From the equation $F = \kappa . A . \frac{V}{x}$ it is clear that $F = \kappa$ if A, V, and x be each equal to unity. We may, therefore, give the following formal definition:—

The viscosity of a fluid is measured by the tangential force per unit area of either of two horizontal planes, at unit distance apart, required to maintain a relative velocity of unity between them, the intervening space being filled with the viscous fluid.

We shall now investigate the phenomenon of gaseous viscosity from the standpoint of the kinetic theory, and deduce those theoretical laws of viscous resistance which are applicable to gaseous media.

In accordance with the kinetic theory, we may regard the viscosity of a gas as originating in the transfer of translatory motion from one layer to another, in consequence of molecular motion, and the subsequent transformation of the regular translatory motion thus carried over into irregular heat motion, owing to molecular interaction. This transformation of the homogeneous motion of translation into the heterogeneous motion of heat will, in time, cause all *relative* translatory motion to be lost, unless such relative motion be maintained by the application of external force.

Since, then, the viscous resistance of a gas is dependent upon molecular motion, and since, in accordance with the kinetic theory, such molecular motion is very rapid and increases with the temperature, we may conclude that all gases will probably exhibit fairly considerable viscosity and that, in all probability, gaseous viscosity will increase with rise in temperature. Both of these conclusions are found to be in agreement with experimental results.

Consider, then, a gas flowing over and parallel to a horizontal solid surface, and, when a steady state of flow has been attained, let the velocity, which is zero in contact with the surface, be equal to $c.x.$ for a layer of the gas at a distance x from that surface.

Then, as previously, $V = c.x.$

If the value of the "velocity-gradient," c, be small, no appreciable error will arise in calculating the number of molecules which pass in unit time from any layer of the gas into an adjoining layer, if we treat the relative translatory velocity as negligible in comparison with the very much greater molecular velocity (*vide* § 18).

Now, in accordance with a method of calculation due to Joule, we may imagine that the irregular heat-motion of the molecules can be divided up into three components, so that only *one-third* of the molecules in any space occupied by the gas need be considered as moving in a direction perpendicular to any given plane. Half of this number—i.e. one-sixth of the molecules—will move in one sense, and the other half in the reverse sense.

If, then, we assume, as an approximation, that all the molecules possess the same velocity, $\bar{C}$—i.e. the velocity of mean square[1]—it is clear that, in unit time, only those molecules which are present in a right prism of length measured by the velocity $\bar{C}$ and of unit cross-section, and which are moving perpendicularly in a given sense to one end of the prism, will cross, in that sense, the unit plane bounding the end of the prism.

Since the volume of the right prism is numerically equal to $\bar{C}$, it contains $N . \bar{C}$ molecules, if, as previously, we take N to represent the number of molecules in unit volume.

Consequently, in the case of the gas flowing over the horizontal solid surface, we may conclude that the number of gaseous molecules

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[1] If all the molecules have the *same* velocity it follows that this velocity is the same as their velocity of mean square.

which, in unit time, pass in either direction across unit area of a horizontal plane at any height x above the solid surface is given by $\frac{1}{6} . \mathrm{N} . \bar{\mathrm{C}}$.

Now, although this method of calculation gives, approximately, the *number* of molecules passing in either direction, it is nevertheless certain that, on account of molecular collisions, the *actual molecules* which cross the unit area in unit time will not have come from distances commensurate with $\bar{\mathrm{C}}$.

We may indeed assume that, *on the average*, the molecules which in unit time cross a horizontal plane at a height x have come from planes situated, respectively, at heights $x + \mathrm{L}$ and $x - \mathrm{L}$, where L is the molecular mean free path.

The average translatory velocity, V_1, of the molecules in the plane at a height $x + \mathrm{L}$ is given by the equation $\mathrm{V}_1 = c(x + \mathrm{L})$, and, similarly, for the plane at a height $x - \mathrm{L}$ we have $\mathrm{V}_2 = c(x - \mathrm{L})$.

Hence, if m be the mass of a molecule, the total momentum carried downwards across unit area of the plane at a height x, in unit time, is $\frac{1}{6} . \mathrm{N} . \bar{\mathrm{C}} . m . \mathrm{V}_1$, i.e. $\frac{1}{6} . \mathrm{N} . \bar{\mathrm{C}} . m . c(x + \mathrm{L})$, and the total momentum carried upwards across the unit area is, similarly, $\frac{1}{6} . \mathrm{N} . \bar{\mathrm{C}} . m . \mathrm{V}_2$, i.e. $\frac{1}{6} . \mathrm{N} . \bar{\mathrm{C}} . m . c(x - \mathrm{L})$.

Thus the gas above the plane loses in unit time the momentum $\frac{1}{6} . \mathrm{N} . \bar{\mathrm{C}} . m . c(x + \mathrm{L}) - \frac{1}{6} . \mathrm{N} . \bar{\mathrm{C}} . m . c(x - \mathrm{L}) = \frac{1}{3} . \mathrm{N} . \bar{\mathrm{C}} . m . c . \mathrm{L}$, while the gas below the plane gains this amount.

But this transfer of momentum in unit time measures the tangential force, F, per unit area of the plane.

$$\therefore \mathrm{F} = \tfrac{1}{3} . \mathrm{N} . \bar{\mathrm{C}} . m . c . \mathrm{L}.$$

We have also seen that the tangential force per unit area is given by—

$$\begin{aligned} \mathrm{F} &= \kappa . \frac{\mathrm{V}}{x}, \\ &= \kappa . c, \end{aligned}$$

where κ is the coefficient of viscosity.

Therefore $\kappa = \frac{1}{3} . \mathrm{N} . \bar{\mathrm{C}} . m . \mathrm{L}$.

Since the density, ρ, of the gas is equal to $\mathrm{N} . m$, we have—

$$\kappa = \tfrac{1}{3} . \rho . \bar{\mathrm{C}} . \mathrm{L}.$$

In the above calculation we assigned the same value of the velocity, $\bar{\mathrm{C}}$, and the same value of the free path, L, to *all* the molecules. But, in reality, these quantities will vary amongst the gaseous molecules, and a more exact investigation, in accordance with the calculus of probabilities, gives the relation—

$$\kappa = 0{\cdot}30967 . \rho . \Omega . \mathrm{L},$$

where Ω is the arithmetical mean of the molecular speeds calculated from Maxwell's law of the distribution of velocities, and is equal to 0·921 $\bar{C}$ (§ 18), and where L has the value $\frac{\lambda^3}{\pi s^2 . \sqrt{2}}$, (§ 47).

If, however, we employ the equation $\kappa = \frac{1}{3} . N . \bar{C} . m . L$, we must replace L by $\frac{3}{4} . \frac{\lambda^3}{\pi s^2}$—the value obtained by Clausius on the assumption of equal molecular velocity.

$$\therefore \kappa = \frac{1}{4} . \frac{N . \bar{C} . m . \lambda^3}{\pi s^2} .$$

Since $N . \lambda^3 = 1$, we have—

$$\kappa = \frac{1}{4} . \frac{m . \bar{C} .}{\pi s^2} .$$

Now, the right-hand side of the last equation contains no term which is dependent upon the pressure, and, consequently, we must conclude that *the coefficient of viscosity of a gas is independent of its density*. This important theoretical conclusion was first reached by Maxwell, and is known as Maxwell's Law.

If we examine the right-hand side of the equation $\kappa = \frac{1}{3} . \rho . \bar{C} . L$, we find that only ρ and L are variable with the pressure, and it is clear that, to a first approximation, L will vary inversely as ρ. Thus Maxwell's Law is capable of a simple explanation. For as we have already seen, the viscosity of a gas is merely conditioned by the transfer of momentum in unit time, and this transfer depends upon the number of molecules per unit volume, their average velocity, and their mean free path. Since the average molecular velocity is independent of the pressure, and since the molecular free path varies *inversely* as the number of molecules per unit volume, which latter varies *directly* as the pressure, it follows that the viscosity of a gas will be independent of variations in its pressure.

We have seen that $\bar{C} \propto \sqrt{\theta}$, where θ is the absolute temperature of the gas, whereas it is probable that the value of L does not change greatly with change in temperature, except in so far as it varies inversely as ρ if thermal *expansion* occur.

Consequently we may anticipate that gaseous viscosity, unlike liquid viscosity, will *increase* with rise of temperature.

The theoretical laws of gaseous viscosity were deduced by Maxwell, in 1860, from the Kinetic Theory of Gases, and their subsequent experimental confirmation must be regarded as constituting an important proof of the general correctness of the kinetic theory.

Two important methods have been employed for the experimental determination of the viscosity of gases. Maxwell and Meyer used the Oscillating Disc method which was originally devised by Coulomb for measuring the viscosity of liquids. In Maxwell's apparatus three circular discs were rigidly fixed to a common axis, the latter being suspended at one end by means of a fibre so that the whole system could be set in torsional vibration. In order to increase the frictional resistance exerted by the surrounding gas, Maxwell introduced four fixed discs above, below, and between the oscillating discs, at equal distances from the latter and as close to them as possible. The viscosity of the surrounding gas could then be calculated from the logarithmic decrement of the amplitude of oscillation.

Meyer used a similar form of apparatus but without the four fixed discs. The results obtained showed that Maxwell's theoretical law, that the coefficient of viscosity of a gas is independent of its density, held at any rate for pressures from about 76 cms. to 1 cm. of mercury. At greater rarefaction, as was shown by Kundt and Warburg, a correction must be applied for the slipping of the gas on the surface of the discs. It is moreover evident that the method fails if the exhaustion be carried so far that the distance between the discs approximates to the molecular mean free path, for then any further diminution in the pressure will only reduce the density without increasing the free path of the molecules between the discs. Crookes, in 1881, employed an oscillating vane of mica, and, by means of formulæ developed by Stokes, he showed that Maxwell's Law held good down to exceedingly small pressures. At still greater rarefaction a sudden fall in the value of the coefficient of viscosity was, however, observed.

At very high pressures Maxwell's Law is not in strict agreement with the results of experiment—nor would such agreement be expected. For, when the gaseous density is very great, the curved paths traversed by the molecules while casually within the sphere of action of other molecules will bear a sensible ratio to their mean free path, and this is contrary to the theoretical assumptions as to the nature of molecular interaction on which Maxwell's Law was based. It is, indeed, clear from the equation $\kappa = \frac{1}{3} . \rho . \bar{C} . L$, that the coefficient of viscosity can only remain constant as long as L varies inversely as ρ. Such variation, however, becomes impossible when the gas is so far compressed that the magnitude of the mean free path approximates to molecular dimensions.

The coefficient of viscosity of a gas may also be measured by means of Poiseuille's transpiration method. This method will be considered more fully in Chapter VII. (§ 70).

It was previously stated that Meyer utilised the results of Graham's experiments on transpiration to prove the validity of Maxwell's theoretical conclusions. Starting with the assumption that the coefficient of viscosity of a gas was independent of its pressure, Meyer developed a theoretical law for the rate of flow of a gas through a long tube, similar to Poiseuille's law for the flow of liquids.

Thus, if a volume, Q_1, of the gas enters the transpiration tube at a pressure p_1, and a volume, Q_2, flows out at a pressure p_2, we have, in accordance with Meyer's theory—

$$p_1Q_1 = p_2Q_2 = \frac{(p_1^2 - p_2^2) . \pi . a^4 . t}{16 . l . \kappa},$$

where a is the radius, and l the length of the tube, t the time in seconds, and κ the coefficient of viscosity of the gas.

Whence $$\kappa = \frac{(p_1^2 - p_2^2) . \pi . a^4 . t}{16 . l . p_2 . Q_2}.$$

The numerical values of the coefficients of viscosity for several cases were thus calculated from Graham's experimental results, and the constancy of the values so obtained for the respective gases proved the legitimacy of the assumption on which Meyer's Law was based. Graham's results further showed that κ increased with rise of temperature, as might be anticipated from the kinetic theory, but since subsequent investigations by other observers have shown that the coefficient of viscosity increases more rapidly than the square root of the absolute temperature we must conclude that the free path, L, also increases somewhat with rise of temperature.

49. Numerical Values.—We shall now proceed to calculate the numerical values of the mean free path and the "collision frequency" for several gases.

Since $\kappa = 0{\cdot}30967 . \rho . \Omega . L$, we can at once obtain the value of L when κ is known.

For oxygen at 0° C., for example, κ has been found by Obermayer to have the value $1{\cdot}87 \times 10^{-4}$ gms./cm. sec.

If then we take the density, ρ, of oxygen, at 0° C. and 76 cms., as $1{\cdot}43 \times 10^{-3}$ gms./cm.^{3}, and the mean molecular velocity, Ω, of oxygen, at 0° C., as $4{\cdot}25 \times 10^4$ cms./sec. (§ 18), we obtain, on substituting these values—

$$\text{Mean free path, } L = 0{\cdot}00000994 \text{ cm., i.e. } 9{\cdot}94 \times 10^{-6} \text{ cm.}$$

The number of collisions per second, or the "collision frequency," will equal $\frac{\Omega}{L}$, and, therefore, for oxygen at 0° C. and 76 cms. we have—

$$\text{Collision frequency, } \frac{\Omega}{L} = \frac{4{\cdot}25 \times 10^4}{9{\cdot}94 \times 10^{-6}} = 4{\cdot}28 \times 10^9 \text{ per second.}$$

If we had employed the simpler formula, $K = \frac{1}{3} . \rho . \bar{C} . L$, we should have obtained the values—

$$L = 8{\cdot}5 \times 10^{-6} \text{ cm.};$$

$$\frac{\bar{C}}{L} = 5{\cdot}4 \times 10^9 \text{ per second,}$$

which are of the same order of magnitude as those previously calculated.

The following table gives, in C.G.S. units, the values for several other gases at 0° C. and 76 cms. Air, for the purpose of calculation, is regarded as a simple gas :—

	Coefficient of Viscosity, K.	Density, ρ.	Mean Molecular Velocity, Ω.	Mean Free Path, L.	Collision Frequency, $\frac{\Omega}{L}$.
Hydrogen	$0·86 \times 10^{-4}$	$0·0899 \times 10^{-3}$	$16·94 \times 10^{4}$	$18·2 \times 10^{-6}$	$9·3 \times 10^{9}$
Nitrogen .	$1·66 \times 10^{-4}$	$1·251 \times 10^{-3}$	$4·54 \times 10^{4}$	$9·4 \times 10^{-6}$	$4·8 \times 10^{9}$
Air . .	$1·71 \times 10^{-4}$	$1·293 \times 10^{-3}$	$4·47 \times 10^{4}$	$9·6 \times 10^{-6}$	$4·6 \times 10^{9}$

A molecule of air is thus seen to collide with other molecules between four and five thousand million times per second, while between consecutive collisions it only travels about one hundred-thousandth of a centimetre.

The small value which has been found for the mean free path furnishes a clear explanation of the slowness with which gaseous diffusion proceeds. For though the molecules of a gas such as ammonia possess, at 0° C., a mean velocity of nearly sixty thousand centimetres per second, yet, since at 0° C. and 76 cms. the mean free path is only about seven-millionths of a centimetre, a molecule will collide with other molecules more than eight thousand million times per second. If, then, ammonia be diffusing through the air, we may take the mean free path for the heterogeneous molecules as lying, approximately, between seven-millionths and ten-millionths of a centimetre, with a collision frequency of approximately five to eight thousand million per second. Thus a molecule of ammonia will not, in one second, reach a point 60,000 cms. from its starting-point, but, owing to the enormous number of molecular collisions, will traverse a very irregular path hither and thither, and, consequently, the gas will diffuse only slowly.

Since in a gas at the ordinary density the molecular mean free path, L, must be very much greater than the mean distance, λ, between neighbouring molecules (§ 47), it follows that the dimensions of a gaseous molecule must be exceedingly small, and that the number of molecules, N, in a cubic centimetre must be exceedingly great.

For $$L > \lambda;$$

but $$N \, . \, \lambda^3 = 1.$$

$$\therefore N \, . \, L^3 > 1.$$

$$\therefore N > \frac{1}{L^3}.$$

For air, at 0° C. and 76 cms., $L = 9{\cdot}6 \times 10^{-6}$; whence $L^3 = 8{\cdot}8 \times 10^{-16}$.

$$\therefore N > 1{\cdot}1 \times 10^{15}.$$

It is possible to calculate the *approximate* value of N from other physical properties of gases, and the value obtained is—

$$N = 6{\cdot}1 \times 10^{19}.$$

Thus a cubic centimetre of air, at 0° C. and 76 cms., contains some sixty trillion molecules, and, in accordance with Avogadro's Law, the same number of molecules must be present in an equal volume of other gases at "normal temperature and pressure."

Since $N \cdot \lambda^3 = 1$,

$\lambda = 2{\cdot}6 \times 10^{-7}$ cm., for any gas at 0° C. and 76 cms.

Further, since for air $L = 9{\cdot}6 \times 10^{-6}$ cm., and $\lambda = 2{\cdot}6 \times 10^{-7}$ cm., we have—

$$\frac{L}{\lambda} = \frac{9{\cdot}6 \times 10^{-6}}{2{\cdot}6 \times 10^{-7}} = 37, \text{ approximately.}$$

Hence, for air at 0° C. and 76 cms., the molecular mean free path is about forty times greater than the mean distance between adjacent molecules.

If we divide the mass of a cubic centimetre of any gas by N we obtain the mass, m, of the gaseous molecule.

Thus, for oxygen—

$$m = \frac{\rho}{N} = \frac{1{\cdot}43 \times 10^{-3}}{6{\cdot}1 \times 10^{19}} = 2{\cdot}3 \times 10^{-23} \text{ gm.}$$

For hydrogen—

$$m = \frac{0{\cdot}0899 \times 10^{-3}}{6{\cdot}1 \times 10^{19}} = 0{\cdot}15 \times 10^{-23} \text{ gm.}$$

The molecule of hydrogen consequently weighs only about one and a half quadrillionths of a gramme.[1]

50. "Transfusion."—There is still another method by which a gas may pass through a porous septum. When the apertures in the septum are *exceedingly fine*, such as those which occur in plates of

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[1] Direct evidence as to the approximate size of molecules has been obtained by various investigators. Thus Faraday prepared gold leaves of approximately 5×10^{-7} cm. thickness; from which it followed that the diameter of an atom of gold could not exceed this value. Measurements of thickness of very thin liquid films also lead to values of the same order for molecular magnitudes (*vide* §§ 108, 109). Reference must also be made to the investigations of Perrin, and Einstein, on "Brownian Movement" by means of which the approximate number of molecules in one-gram molecule of a gas was found to be 70×10^{22}, i.e. approximately $3{\cdot}1 \times 10^{19}$ molecules per c.c. at N.T.P.

biscuit-ware, or compressed graphite, the passage of the gas is commonly termed diffusion, but since, as we have already seen, this term is applied to the mixing of gases across a free surface, it is desirable to employ another appellation, and we shall therefore distinguish the passage of the gas in this case by the title of *transfusion.*

During transfusion a gaseous mixture undergoes a partial separation into its constituents, the lighter constituent passing more readily through the porous septum.

Graham found that, at a constant temperature, the rate of transfusion[1] of a gas was directly proportional to the difference of the pressures of the gas on the two sides of the septum, and inversely proportional to the square root of the molecular mass of the gas, and, therefore, for two different gases at the same temperature, and with the same difference of pressure, the rates of transfusion were inversely proportional to the square roots of their respective molecular masses.

We have already seen, in Chapter II., that the kinetic theory is in agreement with these experimental results.

Experiment XIX.—Fig. XLV. illustrates a simple form of apparatus for measuring the rate of transfusion of a gas. The vessel, A, and the space above the mercury in the barometer tube, B, are exhausted by means of an air pump, and the gas, at a definite pressure, is then admitted to A. The gas passes through the porous septum, C, which is cemented to the top of the barometer tube, and the rate of transfusion is measured by the rate of fall of the mercury in B. Several gases, such as oxygen, hydrogen, and carbon-dioxide, may be admitted in turn to the vessel A, and the respective rates of transfusion compared. The rate of transfusion of the hydrogen, for example, will be found to be approximately four times that of the oxygen, since the molecular masses of these gases are very nearly in the ratio of 1 to 16.

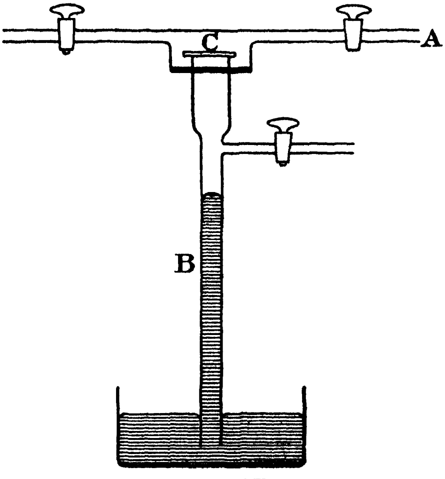

FIG. XLV.

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[1] The rate of transfusion refers, of course, to the *volume* of the gas, measured at a fixed pressure, which passes through the septum in unit time.

Experiment XX.—The difference in the rates of transfusion of different gases may be readily demonstrated by fitting a long glass tube to a porous pot by means of a cork. The tube is then fixed vertically, with its open end dipping beneath the surface of some coloured water in a beaker. On bringing a cylinder containing hydrogen over the porous pot, the hydrogen transfuses in through the walls faster than the enclosed air transfuses out, and the rise in pressure thus produced causes a rapid escape of gas through the water. On removing the cylinder, the hydrogen inside the porous pot will escape by transfusion faster than air can transfuse in, and the coloured water will rise rapidly in the glass tube. Before the cylinder was placed over the porous pot the air, of course, transfused in and out at equal rates and, consequently, the pressure inside the pot remained constant.

The porous pot may next be surrounded with carbon-dioxide when the water will be observed to rise in the tube. For this latter experiment it is desirable to bend the glass tube twice at right angles so that the cylinder containing the carbon-dioxide may be brought underneath the porous pot. On removing the cylinder the pressure inside the porous pot gradually rises again to the atmospheric.

Atmolysis.—A partial separation of a mixture of gases of different densities may be effected by allowing transfusion to take place through a porous septum, the separation being more complete the greater the difference in the densities of the constituents of the gaseous mixture.

This method was originally employed by Graham, who termed it "Atmolysis"—ἀτμός (vapour); λύω (I loosen). The mixed gases were allowed to flow through a long porous tube, such as can be made from the stems of clay tobacco pipes, and the gas which passed through the walls of the tube was pumped off and collected. In order that this might be effected, the porous tube was fixed inside a wider glass tube by means of two corks, and a glass tube which was connected to an air-pump was inserted through one of the corks so that the space between the porous tube and the wider glass tube could be exhausted.

The gas which passed through the porous walls was thus enriched in the less dense constituents of the gaseous mixture, while a corresponding increase in the proportion of the heavier constituents was produced in the gas which flowed on through the tube.

Experiment XXI.—Pass a slow current of a mixture of hydrogen and oxygen, obtained by the electrolysis of water, through a long porous tube, and collect the issuing gas over water at the pneumatic trough. On testing the gas so collected with a flame it will be found to be no longer explosive, but on introducing a glowing splint of wood the latter will be rekindled. A large proportion of the hydrogen must, consequently, have escaped through the walls of the porous tube by transfusion. It should be noted in this experiment that the difference of the pressures on the two sides of the porous tube differs considerably for the hydrogen and the oxygen. Since the electrolytic gas contains, approximately, two volumes of hydrogen to one volume of oxygen, and since it is, approximately, at atmospheric pressure, we may take the partial pressures of the two gases on entering the porous tube as, respectively, two-thirds and one-third of an atmosphere. The partial pressures of the hydrogen and oxygen outside the tube may be taken as zero and one-fifth of an atmosphere, respectively. Thus the difference of the pressures of the oxygen on the two sides of the tube is, approximately, two-fifteenths, and of the hydrogen two-thirds of an atmosphere. Consequently, in accordance with Graham's Law, the hydrogen will transfuse some twenty times faster than the oxygen. This relative rate of transfusion will, of course, decrease as the gases flow along the tube, owing to the increase in the proportion of oxygen.

Experiment XXII.—Place a little ammonium chloride in a hard glass bulb-tube, and fix a porous tube inside the latter by means of two corks. Fit one of the corks with an exit tube. On heating the bulb-tube, the ammonium chloride dissociates largely into ammonia and hydrogen chloride, and the ammonia, being the lighter gas transfuses more readily into the porous tube. On blowing a gentle stream of air through the porous tube the excess of ammonia in the issuing gas will turn a strip of red litmus paper blue, whereas the excess of hydrogen chloride in the vapour of ammonium chloride which escapes from the exit tube will redden blue litmus.

51. Passage of Gases through Solids and Liquids.—A number of cases are known of the passage of gases through solid bodies. Many gases, for example, will pass through thin india-rubber, notably carbon-dioxide and hydrogen. Thus a rubber balloon filled with carbon-dioxide will rapidly collapse. Palladium and platinum, at high temperatures, are readily permeable by hydrogen, but not by other gases. Hydrogen also passes readily through red-hot iron, and, at the same temperature, iron is fairly permeable by carbon-monoxide.

It would appear in these cases that a certain amount of the gas is absorbed by the layers of the solid with which it is in contact, the amount which can be so absorbed increasing with the gaseous pressure. As the surface layers become saturated, the gas is absorbed by the adjacent layers, and so on through the solid. If, then, the pressure of the particular gas on the second surface of the solid be less than its pressure on the first surface, the layers at the second surface will be unable to retain all the gas which passes through, and, consequently, some of the gas will escape.

The passage of gases through liquids may be explained in a similar manner. For, as will be seen later, the mass of gas which will dissolve in a given quantity of a liquid also increases with the gaseous pressure. If, then, for example, a soap-bubble be blown with a gas such as carbon-dioxide which is moderately soluble in water, more carbon-dioxide will go into solution at the inner surface than can be retained by the layers at the outer surface where the pressure of the carbon-dioxide is very low, and, consequently, the soap-bubble will rapidly shrink. It is also found, as would indeed be anticipated, that those gases which are most soluble in a given liquid pass through it most readily. In some cases it is probable that the "absorption" is due to the formation of unstable chemical compounds which decompose on the side where the gaseous pressure is low. Thus the passage of carbon-monoxide through iron at a high temperature is probably due to the formation of iron carbonyls, and it is possible that hydrogen forms an unstable compound with palladium, although, in this latter case, the product is, in part at least, a solid solution.

52. Dalton's Law of Partial Pressures.—The permeability of palladium at moderately high temperatures by hydrogen is of particular interest in that it furnishes a method of experimentally measuring the partial pressure exerted by a gas, in the presence of another, exactly analogous to that employed for the measurement of the osmotic pressure exerted by a substance in solution (*vide* Cap. VII.).

If a palladium tube, or a platinum tube to which a palladium cap has been sealed, be filled with a gas, such as nitrogen, at a fairly high temperature—(say 300° C. or 400° C.)—and at atmospheric pressure, and if it be then surrounded with hydrogen, the latter being also at atmospheric pressure, it is found that the pressure inside the tube soon rises to two atmospheres. For the hydrogen passes in until its pressure both inside and outside is the same, but the nitrogen cannot pass through the walls of the tube and, consequently, continues to exert its original pressure of one atmosphere. If the nitrogen had been initially under a pressure of, say, two atmospheres, the final pressure inside the tube would have been three atmospheres, i.e. the sum of the pressures due to the two gases. We can obtain a similar result in a somewhat different manner. If we take a glass vessel containing, say, nitrogen, at atmospheric temperature and pressure, and pump in an equal volume of hydrogen, the pressure of the enclosed gases will rise to two atmospheres. The same volume of any other gas may now be pumped in, and, provided the gases do not interact chemically, the pressure will be found to be three atmospheres. In general, it is found that *each constituent of a gaseous mixture exerts pressure on the walls of a containing vessel proportionally to its relative amount,* i.e. *each constituent exerts the same pressure as if it alone occupied the whole vessel, and the total pressure is the sum of the partial pressures due to each gas.*

This law was first enunciated by Dalton, in 1802, and is known as Dalton's Law of Partial Pressures.

It can be readily shown that Dalton's Law follows as a necessary consequence of the Kinetic Theory of Gases.

For, as was seen in § 21, if K_V be the kinetic energy—(and, therefore, the total intrinsic energy)—per unit volume of a perfect gas, we have the relation—

$$K_V = \frac{3P}{2}, \text{ where P is the gaseous pressure.}$$

Now in a gaseous mixture, as in the case of a simple gas, the pressure is merely the total force exerted by all the molecules on unit area, i.e. the total momentum given up to unit area in unit time. If, then, K'_V, K''_V, etc., be the respective values of the kinetic energy per unit volume for the molecules of each constituent of the gaseous mixture, we obtain, as previously for a simple gas—

$$P_m = \tfrac{2}{3}(K'_V + K''_V + \ldots),$$

where P_m is the pressure exerted by the gaseous mixture.

But if each constituent occupied the whole volume of the mixture alone, the respective pressures exerted would be—

$$P' = \tfrac{2}{3}K'_V,\ P'' = \tfrac{2}{3}K''_V,\ \ldots$$
$$\therefore\ P_m = P' + P'' + \ldots,$$

i.e. the pressure exerted by the gaseous mixture is equal to the sum of the pressures each constituent would exert if it alone occupied the whole volume, and this is Dalton's Law of Partial Pressures.

Dalton's Law will only hold rigidly when the constituents of a gaseous mixture exert no chemical action on one another, and when neither attractive nor repulsive forces arise between their molecules. For if, on mixing the constituents, intermolecular forces are brought into play, a variation in potential energy will also arise, with a consequent change in kinetic energy and in pressure. Since, in any real gas, intermolecular forces are present to a greater or less extent, Dalton's Law is only approximately true.

53. Solutions of Gases in Liquids.—In accordance with the kinetic theory we may regard the phenomenon of solution as due to the penetration of the particles of one substance into the spaces between the particles of another. There is, thus, no essential difference between solubility and miscibility. When, for example, a gas is brought into contact with a liquid, some of the gaseous molecules which impinge upon the surface of the liquid will be absorbed, and as these molecules move about in all directions in the liquid some of them will escape back through the surface into the gas. The number of gaseous molecules which, in unit time, escape from the liquid will increase as the concentration of the dissolved gas increases, and ultimately, if the temperature and pressure be constant, a state of dynamic equilibrium will be attained, when as many molecules of gas are absorbed as escape in unit time. The solution is then "saturated" with the gas. If, now, the pressure of the gas be doubled, the molecular concentration of the gas will also be doubled, and, consequently, twice as many molecules will be absorbed by the liquid in unit time. The concentration of the dissolved gas will therefore increase, and equilibrium will be attained when the rate of escape of gaseous molecules from the liquid has also doubled, i.e. when the solution has acquired a concentration twice as great as when saturated under the original pressure. This conclusion is in agreement with the relationship between the solubility of a gas and its pressure discovered experimentally by Henry, in 1803, and generally known as Henry's Law. We may state Henry's Law, formerly, as follows :—

"At a given temperature, and with a given solvent, the concentration of the dissolved gas is proportional to the gas pressure." [1]

Thus, at a given temperature, the ratio of the concentrations of the gas in the solution, and in the gas phase in contact with the latter, remains constant under all pressures. This ratio is usually termed the "*coefficient of solubility*" of the gas in the particular solvent. Since, therefore, the mass of gas dissolved by a solvent, at a given temperature, is proportional to the pressure to which the gas is subjected, and since, in accordance with Boyle's Law, the density of a gas varies directly as its pressure, we may state Henry's Law in the alternative form :—

"At a given temperature, a given liquid dissolves the same volume of a gas at all pressures."

Henry's Law holds well for sparingly soluble gases, but fails when the gases dissolve readily in the solvent. If, for example, we take water as a solvent, the solubilities of gases like oxygen, nitrogen, and hydrogen, under moderate pressures, are in close agreement with the law, but there is an appreciable deviation with carbon dioxide, which is more soluble in water, and the law is not even approximately obeyed by such easily soluble gases as ammonia and hydrogen chloride. In the case of, say, carbon dioxide the deviation may be ascribed to the partial formation of carbonic acid, according to the equation $H_2O + CO_2 \rightleftarrows H_2CO_3$, for Henry's Law is applicable only to that portion of the carbon-dioxide which is present, *as such*, in physical solution, and it applies neither to the molecules of carbonic acid, nor to the very few ions which are formed by electrolytic dissociation.

The great solubility of gases like ammonia is probably due to the partial chemical combination of the gas and the solvent, and also, to the presence of considerable attractive forces between the molecules of the solvent and the gas. Great solubility may also arise from cohesive forces brought into play between the molecules of the dissolved gas. In the presence of such disturbing factors, Henry's Law,

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[1] Henry's Law is a particular case of the more general Distribution Law of Nernst which states the conditions necessary for equilibrium in heterogeneous systems as deduced from the standpoint of the kinetic theory.

as deduced from the kinetic theory, would not be expected to apply, for, in obtaining the theoretical law, we tacitly assumed that the gaseous molecules where chemically and physically independent of each other, and of the solvent.

When the molecular state of the gas in the gas phase is different from that in the solution, i.e. when either polymerisation or dissociation occurs on dissolving the gas, Henry's Law also requires modification.

Thus direct proportionality between the gas pressure and the concentration of the dissolved gas can only be postulated in the case of dilute solutions, and when the dissolved gas undergoes neither polymerisation nor dissociation.[1]

The solubility of different gases in water, and the effect of pressure upon the solubility, may readily be demonstrated by means of the following experiments.

Experiment XXIII.—A round-bottomed glass flask is fitted with an india-rubber stopper carrying a narrow glass tube, the latter nearly reaching to the bottom of the flask. The stopper is removed and the flask filled with either ammonia or hydrogen chloride by displacement of the contained air. The stopper is then reinserted, and the flask supported neck downwards, so that the end of the glass tube which projects beyond the caoutchouc stopper may dip beneath the surface of some water in a trough. The water slowly rises in the tube until the first few drops enter the flask, when their absorption of the gas produces a partial vacuum and the water is forced up the tube in the form of a fountain until the flask is filled. The initial rise of the water in the tube may be accelerated by cooling the flask with a few drops of ether.

Experiment XXIV.—In the case of a less soluble gas, such as sulphuretted hydrogen, a stoppered cylinder may be filled with the gas, a little water introduced, the stopper inserted, and the cylinder well shaken. On opening the cylinder under water, a further quantity of water will enter, and the shaking may then be repeated. By proceeding in this manner complete solution of the gas can be effected.

Experiment XXV.—The effect of pressure upon the solubility of a gas may be demonstrated by connecting two barometer tubes, of uniform bore, to a mercury reservoir by means of a "T" piece and pressure tubing. One of the barometer tubes is filled with ammonia, and the other with air, and a few cubic centimetres of a saturated aqueous solution of ammonia are introduced above the mercury in the former

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[1] It should be noted that the union of *simple gas molecules* with the *solvent* will *not* affect the applicability of this statement, for the concentration of *hydrated* gas molecules will also be proportional to the gas pressure.

tube. The volumes of the air and ammonia are initially adjusted to be the same, when the pressure is approximately atmospheric, but on raising the mercury reservoir until the volume of the air is reduced to one-half it will be observed that the ammonia occupies *less* than half its original volume owing to its increased solubility at the higher pressure. Care must be taken not to raise the pressure much above two atmospheres, since, otherwise, the greater compressibility of the ammonia will appreciably influence the result (cf. Expt. IX.). If the second barometer tube be also filled with ammonia instead of with air, any variation due to differences in the *compressibility* of the gases in the two tubes will be eliminated.

The solubility of different gases in various solvents may be determined, quantitatively, by means of the Bunsen's absorptiometer shown in Fig. XLVI.

Measured volumes of the gas and the solvent are introduced into the inner graduated tube, and the latter is screwed down upon an india-rubber pad by means of the screw attachment shown separately in the side figure. The graduated tube is then lowered into the outer cylinder, which contains a quantity of mercury at the bottom, and, after filling the cylinder with water, the cap at the top is fastened, and the whole apparatus thoroughly shaken. The inner tube is slightly unscrewed from time to time—in order that mercury may enter and take the place of the dissolved gas—the screw being subsequently tightened before the shaking is repeated. When no more gas is absorbed, the residual volume of gas is measured, and its temperature observed by means of the thermometer attached to the upper part of

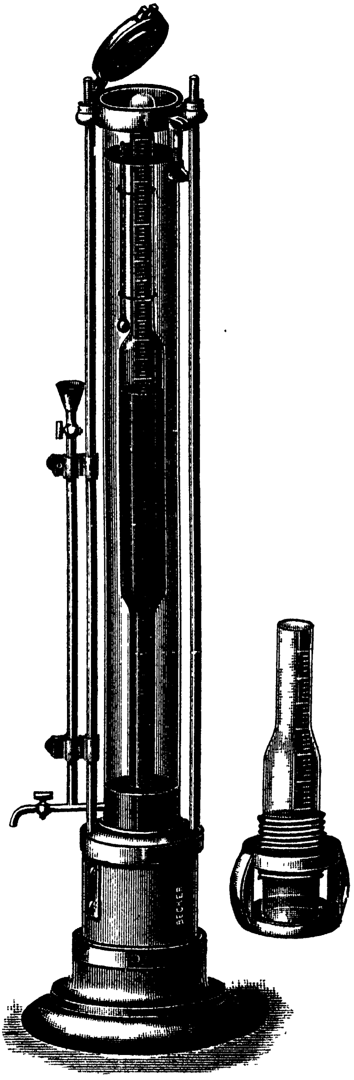

FIG. XLVI.—Bunsen's Absorptiometer.

the graduated tube. The pressure of the gas is obtained by deducting from the barometric reading the height of the mercury in the absorption tube above the mercury in the outer cylinder, a correction being, of course, applied for the pressure due to the water column in the cylinder and the column of the solvent in the inner tube. By varying the temperature of the water in the outer cylinder, the solubility at different temperatures may be ascertained.

Bunsen introduced the term "coefficient of absorption" to denote the volume of a gas, measured at 0° C. and 76 cms., which is absorbed by 1 c.c. of a solvent at the same temperature and pressure. The "coefficient of absorption" is thus, numerically, equal to the "coefficient of solubility" at 0° C.

A distinction must be drawn between the volume of gas absorbed by 1 c.c. of a liquid when the *total pressure* at the surface of the liquid is 76 cms., and the volume absorbed when the pressure of the *gas itself* at the liquid surface is 76 cms., *independent of the vapour pressure of the solution.* According to Winckler the "*coefficient of absorption*," A, is defined as the number of cubic centimetres of a gas, measured at 0° C. and 76 cms., which are absorbed by 1 c.c. of a solvent at 0° C., the gas itself being at a uniform pressure of 76 cms. when in equilibrium with the saturated solution. The number of cubic centimetres of a gas, measured at 0° C. and 76 cms., which are absorbed by 1 c.c. of a solvent at 0° C., the pressure of the gas *plus* the vapour pressure of the solution being 76 cms. when a state of equilibrium has been attained, is defined by Winckler as the "solubility," S.

Thus, in accordance with Henry's Law—

$$S = A \,.\left(\frac{76 - \sigma}{76}\right),$$

where σ is the vapour pressure of the solution, and, for dilute solutions, is approximately the same as the vapour pressure of the pure solvent at 0° C.

Experiment XXVI.—The coefficient of solubility of a gas may be determined more readily by means of the apparatus shown in Fig. XLVII. This apparatus is a simplified form of the absorptiometer used by Heidenhain and Meyer (1863). The gas is introduced into the graduated tube, A, through the three-way stop-cock, *a*, by first raising and then lowering the levelling tube, B. The flexible metal tube, of capillary bore, which connects the tube, A, to the absorption pipette, C, is also filled with the gas by passing the latter in at *a* and out at *b*. The stop-cocks are then closed, and the volume of the gas in A is read, after levelling the mercury in A and B. The absorption pipette, C, of known volume is next filled with the gas-free solvent by applying suction at the three-way stop-cock, *b*, and drawing the liquid up through the stop-cock, *c*. The stop-cocks *a* and *b* are then turned so that A and C are placed in communication through the flexible metal tube, and by raising the tube B, and opening the stop-cock, *c*, a definite volume of the liquid is run out from the pipette, C, into a measuring vessel, while, at the same time, gas enters the pipette from the tube A. The gas and the liquid are then thoroughly shaken together until the latter is saturated, the mercury in A and B being adjusted to the same level when A and C are in communication. The stop-cock, *c*, is then opened under mercury, after lowering the tube B, and the mercury is allowed to enter the pipette until the latter is again filled with liquid, the gas passing back into A. The volume of gas in A is now read, and the diminution gives the volume absorbed by a known volume of the liquid. Both the measuring tube, A, and the pipette, C, should be immersed in a water-bath—(not shown in the figure)—so that they may be maintained at any required temperature.

It must be noted that just as the liquid becomes saturated with the gas, so does the gas itself become saturated with the vapour of the liquid, and, consequently, when a state of equilibrium is attained, and when the mercury is at the same level in A and B, the partial pressure of the gas in contact with the liquid is equal to the barometric pressure *minus* the vapour pressure of the solution at the temperature of the experiment. For sparingly soluble gases the vapour pressure of the solution may, without appreciable error, be taken as equal to the vapour pressure of the pure solvent at the same temperature.

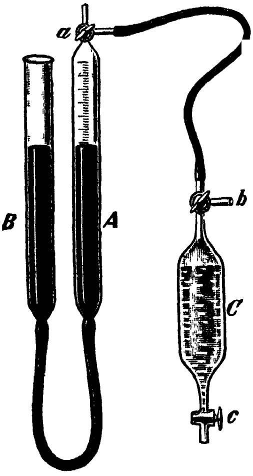

FIG. XLVII.—Heidenhain and Meyer's Absorptiometer.

Since only that portion of the gas which is driven over into the pipette, C, becomes saturated with the vapour of the liquid, an error arises in calculating the diminution in volume, owing to the uncertainty which exists as to the partial pressure of the gas when its volume is finally read in the tube, A. This source of error may most readily be eliminated by introducing a small quantity of the liquid above the mercury in the measuring tube, A, and allowing both the liquid and the gas to become saturated, at the temperature of the experiment, before reading the initial volume of the gas in A. The determination of the solubility may then be carried out as described above.

54. The Solubility of Mixed Gases.—In the case of a gaseous mixture in contact with a solvent, dynamic equilibrium will be attained when, for *each* constituent, as many molecules of gas are absorbed by the solvent as escape from it in unit time. Consequently, the amount of each constituent dissolved will depend upon its solubility, and upon its partial pressure. The statement that "*The amount of each constituent of a gaseous mixture which is dissolved by a solvent is proportional to the partial pressure of the constituent*" is known as Dalton's Law (1807)—this law follows at once from Dalton's Law of Partial Pressures (§ 52), and from Henry's Law (§ 53).

For example, the composition of air by volume may be taken as, approximately, nitrogen, 78 per cent., oxygen, 21 per cent., and argon, 1 per cent., and, if the atmospheric pressure be equal to 76 cms. of mercury, the partial pressure of the nitrogen will be $\frac{78}{100} \times 76$ cms.; of the oxygen $\frac{21}{100} \times 76$ cms.; and of the argon $\frac{1}{100} \times 76$ cms.

Now, 1 c.c. of water at, say, 15° C. will dissolve the following volumes, measured at 0° C. and 76 cms., of nitrogen, oxygen, and argon, respectively, each gas being at a uniform pressure of 76 cms., when in equilibrium with the solution :—

Nitrogen = 0·018 c.c.
Oxygen = 0·034 c.c.
Argon = 0·040 c.c.

The solvent action of water upon the atmosphere can, consequently, be calculated, and we obtain :—

$\frac{78}{100} \times 0{\cdot}018 = 0{\cdot}0140$ c.c. nitrogen,
$\frac{21}{100} \times 0{\cdot}034 = 0{\cdot}0071$ c.c. oxygen,
$\frac{1}{100} \times 0{\cdot}040 = 0{\cdot}0004$ c.c. argon,

for the respective volumes of nitrogen, oxygen, and argon, which will be dissolved, at 15° C., by 1 c c. of water.[1]

Thus, 100 c.cs. of water at 15° C. will dissolve 2·15 c.cs. of air, when the atmospheric pressure is 76 cms., and if the dissolved air be expelled, either by boiling the solution or by placing it in a vacuum, the composition of the gaseous mixture so obtained will be—

Nitrogen = 65·1 per cent.
Oxygen = 33·0 per cent.
Argon = 1·9 per cent.[2]

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[1] Air contains about 0·03 per cent. of its volume of carbon-dioxide, and 1 c.c. of water at 15° C. dissolves 1·019 c.cs. of carbon-dioxide, measured at 0° C. and 76 cms., the pressure of the gas being 76 cms. Hence, approximately, 0·0003 c.c. of carbon-dioxide will be dissolved from the atmosphere, at 15° C., by 1 c.c. of water. If it were not for the very low partial pressure of the carbon-dioxide a large proportion of this gas would be removed from the atmosphere by a heavy fall of rain, since, at 15° C., its solubility is nearly thirty times that of oxygen.

[2] Whereas 2·15 c.c. of ordinary air contain, approximately, 0·43 c.c. of oxygen, 2·15 c.c. of *dissolved* air contain 0·71 c.c. of oxygen. It is this dissolved oxygen which is breathed by fish.

It must be noted that when a gaseous mixture is shaken up with a solvent the amount of each constituent which dissolves is determined by the partial pressure of the constituent *after* the solvent has become saturated, and *not* by its partial pressure *before* solution. In the preceding example we assumed that the water was freely exposed to the atmosphere, and that, consequently, the composition of the latter could be treated as constant. If, however, water be shaken with air *in a confined space*, the relative partial pressures of the gaseous constituents will be slightly different after the water has become saturated, owing to the unequal solubilities of the nitrogen, oxygen, and argon, and, in consequence, the relative amounts of the more soluble gaseous constituents which pass into solution will be slightly reduced.

Experiment XXVII.—It can be readily shown that air is enriched in oxygen on solution in water, by boiling a quantity of water which has been well shaken up with air, and collecting the expelled gas. A glowing splint of wood will be rekindled if introduced into this gas, thus showing that a greater proportion of oxygen is present than in air; or the oxygen in a measured volume of the gas may be determined by absorption with an aqueous solution of sodium pyrogallate, and compared with the oxygen present in an equal volume of air at the same temperature and pressure.

55. Additional Factors influencing Gaseous Solubility.—The solubility of a gas in a solvent is *diminished* by a rise in temperature.[1]

Between 25° C. and 50° C., helium is an exception to this rule, the solubility of the gas increasing to a small extent.[2]

Gas.	0° C.	10° C.	15° C.	20° C.	30° C.	40° C.	50° C.	60° C.
	c.cs.	c.cs.	c.cs.	c.cs.	c.cs.	c.cs.	c.cs.	c.cs.
Ammonia .	1300	910	802	710	595 at 28° C.	—	—	—
Argon . .	0·058	0·045	0·040	0·037	0·030	0·027	—	—
Carbon-dioxide	1·713	1·194	1·019	0·878	0·66	0·53	0·44	0·36
Helium . .	0·0150	0·0144	0·0139	0·0138	0·0138	0·0139	0·0140	—
Hydrogen .	0·0215	0·0198	0·0190	0·0184	—	—	—	—
Nitrogen .	0·0239	0·0196	0·0179	0·0164	0·0138	0·0118	0·0106	0·0100
Oxygen . .	0·049	0·038	0·034	0·031	0·026	0·023	0·021	0·019

The above table gives the number of cubic centimetres of various gases, measured at 0° C. and 76 cms., which dissolve in 1 c.c. of

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[1] It therefore follows, in accordance with Le Chatelier's Theorem (Appendix B), that when a gas dissolves the solution is accompanied by a rise in temperature.

[2] It appears probable, however, that for each gas there is a point of minimum solubility, and that, at higher temperatures, the solubility again increases.

water at the temperatures stated, the gas in each case being at a uniform pressure of 76 cms. when in equilibrium with the saturated solution.

Since the solubility of a gas in a solvent is diminished by raising the temperature, it follows that if a saturated solution be heated some of the dissolved gas must be expelled.

In the case of aqueous solutions, for example, it is found that in general, the whole of the dissolved gas can be driven off by boiling the solution (cf. Expt. XXVII.). Several aqueous solutions are, however, known which, when boiled distil at a definite concentration and at a definite temperature. Thus an aqueous solution of hydrochloric acid containing 20·2 per cent. of hydrogen chloride has a constant boiling-point of 110° C. at 76 cms. pressure, and can be distilled without change in composition. If a weaker solution of hydrochloric acid be boiled it becomes more concentrated, and if a stronger solution of hydrochloric acid be heated it becomes weaker, until in both cases an acid of 20·2 per cent. concentration is obtained. Similarly a solution of nitric acid in water of 68 per cent. concentration has a constant boiling-point of 120·5° C., at the atmospheric pressure.[1]

Such mixtures with constant boiling-points were originally supposed to be definite chemical compounds, but Roscoe and Dittmar have shown that the composition of the constant-boiling mixture is merely a function of the pressure under which the solution is boiled. Thus, under a pressure of two atmospheres, the constant-boiling mixture for an aqueous solution of hydrochloric acid contains only 19 per cent. of hydrogen chloride. It therefore follows that these mixtures with constant boiling-points are *not* chemical compounds.

Not only may dissolved gases be expelled from a solution by the action of heat, but also by placing the solution in a vacuum. This follows from Henry's Law, for since the concentration of a dissolved gas is proportional to its pressure, the concentration must be zero when the pressure is zero. Similarly a dissolved gas may be completely removed from a solution by bubbling through the latter a different gas, and a dissolved gas will also escape although less rapidly if its solution be placed in an atmosphere of another gas.

Experiment XXVIII.—Expose an aqueous solution of ammonia to the air for some time, and observe that it rapidly becomes weaker. Then pass a rapid stream of air from a foot bellows through another portion of the solution and observe that, in this case, the escape of ammonia is much accelerated.

Provided no chemical action takes place the power of solution possessed by a liquid is diminished by the addition of a soluble solid.

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[1] The distillation of liquid mixtures will be considered more fully in Chapter VII.

Experiment XXIX.—Add a quantity of sugar to a tumbler-full of "soda-water,"[1] and observe the rapid evolution of gas. Since, however, any porous substance—such as a piece of earthenware—will also promote the evolution of the gas, it is preferable to first dissolve the sugar in a little water, and then to add the syrup thus formed to the "soda-water," when a rapid escape of gas will occur.

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[1] An aqueous solution of carbon-dioxide, prepared under a pressure of about 10 atmospheres.

CHAPTER VI.

EQUATIONS OF STATE.

56. Deviations from the Simple Gas Law.—The general equation to the isothermal of a perfect gas at an absolute temperature θ was deduced in Chapter II. from the standpoint of the kinetic theory, and was shown to possess the form

$$P.V. = R.\theta.$$

The curve corresponding to such an isothermal, as was shown in Fig. XIV., is a rectangular hyperbola.

Now, it is evident from an examination of Fig. XXIII., which gives the isothermals for carbon-dioxide, that this simple gas law is not fully applicable to *actual* gases and vapours. For, although at temperatures above the critical temperature, and for vapours at low pressures, the isothermals approximate to rectangular hyperbolæ, yet, when partial or complete liquefaction has taken place, the curves no longer possess this form.

It must, however, be remembered that the simple gas law, $P.V. = R.\theta$, was deduced for a perfect gas on the assumption that both the size of the molecules and the time occupied by molecular collisions could be treated as negligible.

When, however, any real gas is subjected to the combined influence of high pressure and low temperature, its molecules will be crowded together, and, in consequence, the curved paths traversed by the molecules while casually within the sphere of action of other molecules will bear an appreciable ratio to their mean free path. Since, under these conditions, the time occupied by molecular collisions bears a sensible ratio to the time of free molecular movement, it is evident that, at any instant, an appreciable fraction of the total number of the molecules in the gas will be in collision, and this will give rise to marked cohesion. The greater the time occupied by such molecular collisions, the fewer the number of impacts per second of the gaseous molecules on the walls of the containing vessel, and, consequently, the molecules will exert a pressure on the walls less than that calculated for a perfect gas.

Thus, starting with a rarefied gas, we may anticipate that, as the pressure is increased, the product P.V. for any real gas will *decrease*, owing to increased molecular cohesion, until such time as the molecules are crowded up within distances approximating to the radius of the sphere of molecular action, when any further increase in the pressure will result in an *increase* in P.V., the volume, V, remaining approximately constant (cf. § 33).

It has been seen, in Chapter IV., that a close relationship exists between the liquid and gaseous states of matter, and, in consequence, many attempts have been made to modify the equation $P.V. = R.\theta$, so as to make it more generally applicable to *both* these states. Such modified equations are usually called "characteristic equations," or "equations of state," and, in the present chapter, four of the more important of these equations will be briefly examined. It must be noted that "equations of state" are only applicable to homogeneous systems which may be either entirely liquid or entirely gaseous. Such equations do *not* apply to systems which are heterogeneous, as in the case of a liquid in contact with its saturated vapour.

57. The Ramsay-Young Equation.—This equation is only applicable to systems *at constant volume*, and may be written $P = k.\theta - c$, where P is the pressure, k and c are constants, and θ the absolute temperature.

A more general form of the equation is—

$$P = \theta . f(V) - F(V),$$

where $f(V)$ and $F(V)$ are different functions of the volume, and are, of course, constant when V is constant.

In the case of a perfect gas, at constant volume, the simple gas equation $P.V. = R.\theta$ may be written $P = k.\theta$, where k is a constant. Thus the Ramsay-Young equation for either gaseous or liquid systems at constant volume only differs from the relation which holds for a perfect gas, under the same conditions, by the introduction of the term c. This constant, c, is the negative pressure, *for the particular constant volume under consideration*, which corresponds to the absolute zero of temperature, for, when $\theta = 0$, $P = -c$.

If the volume of the system be varied, the numerical values of the constants k and c must also be changed, the actual values of the constants, in each case, being determined by experiment. Ramsay and Young tested their equation for a number of different substances, and found that for ether, $\{(C_2H_5)_2O\}$, and for methyl alcohol, $\{CH_3OH\}$, ethyl alcohol, $\{C_2H_5OH\}$, and propyl alcohol, $\{C_3H_7OH\}$, the relation agreed, approximately, with the experimental results, the best agreement being observed in the case of ether, $\{(C_2H_5)_2O\}$. Water, however, exhibited marked variations in its behaviour. Amagat showed that the equation applied to carbon-dioxide, $\{CO_2\}$, and to ethylene, $\{C_2H_4\}$, in the gaseous state, but less accurately when they were liquefied.

Fig. XLVIII. shows some of the results obtained by Ramsay and Young in the case of ether, $\{(C_2H_5)_2O\}$. The curves, which represent the variation of P with θ, at constant volume, are called *isochores*, and it will be seen that for ether they are practically straight lines, both in the gaseous and liquid states. This is in agreement with the Ramsay-Young equation, according to which the pressure is a linear function of the absolute temperature, the volume being constant.

The dotted line, AB, in the figure is the vapour pressure curve for ether. θ_c is the critical temperature for ether, and P_c the corresponding critical pressure. At B the vapour pressure curve becomes vertical. To the right of the vertical line, CD, the system is gaseous; to the left of ABC it is liquid. The area ABD corresponds to vapour.

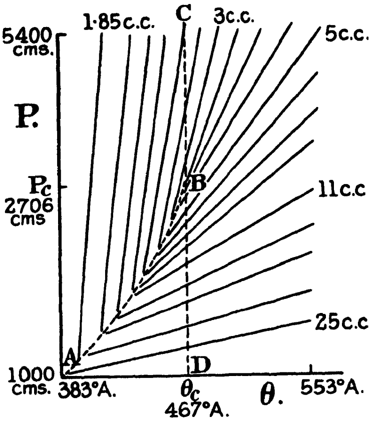

FIG. XLVIII.—Isochores for Ether.

If the equation $P = k.\theta - c$ be differentiated with respect to θ, we obtain the result—

$$\frac{\partial P}{\partial \theta} = k,$$

the differentiation being partial since the volume is constant.

Now, $\frac{\partial P}{\partial \theta}$ is the tangent, at any given temperature, to the particular isochore under consideration, and may be obtained graphically.[1]

The value of k having thus been found, the value of c may be obtained by substituting for k in the equation $P = k.\theta - c$ for any two values of P and θ corresponding to the given isochore.

Other values of P, corresponding to different values of θ, may then be calculated for the same isochore, and compared with the values obtained by experiment. The same method may also be applied to other isochores, in order to test the general validity of the Ramsay-Young equation in the case of the particular substance under examination.

In the case of ether, for example, Ramsay and Young calculated the pressures, for a number of different isochores, which corresponded to a temperature just above the critical temperature. The following results were obtained :—

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[1] If the pressure, at constant volume, be a linear function of the absolute temperature, the value of $\frac{\partial P}{\partial \theta}$ for a given isochore will, of course, be the same at *all* temperatures.

Temperature 470° A.		
Volume of 1 gm. of Ether.	Pressure Observed in mms. of Mercury.	Pressure Calculated in mms. of Mercury.
33·17 c.cs.	10,108	10,055
38·07 ,,	8,972	8,965
47·84 ,,	7,312	7,320
67·33 ,,	5,356	5,340
86·75 ,,	4,219	4,220
96·44 ,,	3,820	3,820

In the case of isopentane, Young obtained the following values for k, at different temperatures, for a number of isochores :—

Volume = 4·0 c.cs.		Volume = 50 c.cs.		Volume = 3000 c.cs.	
Temperature.	$k = \frac{\partial P}{\partial \theta}$.	Temperature.	$k = \frac{\partial P}{\partial \theta}$.	Temperature.	$k = \frac{\partial P}{\partial \theta}$.
460·8° A. (critical)	405	373° A.	21·5	303° A	31
463° A.	418	383° A·	21·0	313° A.	31
468° A.	428	393° A.	21·0	323° A.	29
473° A.	434	403° A.	20·5	333° A.	27
478° A.	430	413° A.	19·5	343° A.	28
483° A.	443	433° A.	20·0	353° A.	31
493° A.	439	453° A.	18·5	363° A.	32
513° A.	446	473° A.	19·25	373° A.	29

It will be seen that, for each isochore, the values of $\frac{\partial P}{\partial \theta}$ are, approximately, constant.

58. The van der Waals' Equation.—It was pointed out, at the beginning of the present chapter, that the simple gas law $P.V. = R.\theta.$ is only applicable to a *perfect gas*—for which both the size of the molecules and the magnitude of the internal molecular cohesive forces may be treated as negligible.

In 1873, van der Waals published a dissertation in which he developed the simple equation obtained from the kinetic theory so as to allow, in the case of actual gaseous or liquid systems, for both the molecular attraction and the finite size of the molecules.

The cohesive forces which arise from molecular attraction are very small in a gas at the ordinary density, but become considerable when the gas is subjected to the combined influence of high pressure and low temperature, and are exceedingly great in the case of liquid systems.

Now, the molecules in the interior of a fluid will, on the average, be attracted equally in all directions by neighbouring molecules, but those at the *surface* will only be attracted inwards by the molecules of fluid behind them. In consequence, the molecules which arrive at the surface layer will be retarded by the molecular attraction, and, at the moment of impact with the walls of any containing vessel, will possess a velocity less than the average velocity of the molecules in the interior of the fluid. Thus the pressure exerted by the molecules on the boundary walls is lessened owing to the existence of internal molecular cohesion, and, if the *actual* pressure exerted by a fluid be P, the pressure which a perfect gas would exert under the same conditions may be written $(P + p)$, where p is the diminution in pressure which arises from molecular attraction.

Since p is due to the mutual actions of attracting and attracted molecules, it is proportional to the number of *each*, and, therefore, is proportional to the *square* of the density. For, if we consider a thin layer of unit area at the surface of the fluid, it is clear that both the number of molecules in the layer, and also the number of adjacent molecules within the range of molecular action, are proportional to the density, and, consequently, the force of molecular attraction must vary as the square of the density.

Hence it follows that p is *inversely* proportional to the square of the *volume* occupied by the fluid, and we may write $p = \frac{a}{V^2}$, where a is *assumed* to be a constant, for a given fluid, at all temperatures—an assumption which van der Waals found to be approximately in agreement with the results of the experiment.[1]

Therefore the value of the pressure in the gas equation now becomes—

$$\left(P + \frac{a}{V^2}\right),$$

where P is the actual pressure exerted by the fluid on the walls of the containing vessel; i.e. the actual pressure *observed*.

This modified expression involves the assumption that the molecular attraction varies inversely as the *fourth* power of the mean distance between neighbouring molecules.

For the force of attraction across any unit area in the interior of a fluid is dependent upon the number of molecules distributed over the area and upon the mean distance of molecular separation. If, then, as in § 47, we take λ to represent the mean distance between neighbouring molecules, the number of molecules distributed over unit area will vary inversely as λ^2. Now the force of molecular attraction also

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[1] The value of a is actually found to diminish with rise in temperature.

varies as some unknown function of the mean distance of molecular separation—say, as λ^x. Hence the force of attraction exerted normally across the unit area varies as $\frac{\lambda^x}{\lambda^2}$; i.e. as $\frac{1}{\lambda^{2-x}}$.

If V. be the volume of unit mass of the fluid, it is clear that V. varies as λ^3.

Therefore, the force of attraction varies as $\frac{1}{(V)^{\frac{2-x}{3}}}$.

In accordance with van der Waals' equation, however, the force due to molecular attraction may be written $\frac{a}{V^2}$, where a is a constant.

Whence it follows that $x = -4$.

Thus, as previously stated, van der Waal's equation involves the assumption that the force of molecular attraction varies inversely as the fourth power of the mean distance of molecular separation.

It will be seen that the effect of molecular cohesion will be to diminish the volume *more rapidly* than the pressure increases, and, in consequence, the product P.V. will *decrease* with rise in pressure.

In deducing the simple gas law it was further assumed that the space actually occupied by the molecules might be treated as negligible in comparison with the space in which they were contained. Now, although such an assumption is, approximately, justifiable in the case of a gas at very low pressures, it ceases to be admissible when the gaseous density is great, for the molecular volume will then bear a sensible ratio to the whole volume, V.

Since, therefore, the free space in which the molecules move about is less than the observed volume, V, the frequency of molecular collision, and, consequently, the magnitude of the pressure exerted, will be greater than were calculated for a perfect gas. The pressure exerted will, also, *increase at a greater rate than the volume, V, diminishes*, for a given diminution in the observed volume, V, will correspond to a *greater proportional diminution* in the free space in which the molecules move, since the compressibility of the actual molecules themselves may be assumed to be very small. The product P.V. will, on this account, *increase* with rise in pressure. This mode of variation of P.V. with change in pressure is the reverse of that occasioned by molecular cohesion, and an examination of the experimental evidence, as summarised in § 33, shows that at low temperatures and low pressures the influence of cohesion predominates, whereas at sufficiently high pressures the influence of the finite size of the molecules on the variation of the product P.V. is the decisive factor.[1]

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[1] The influence of the finite size of the molecules on the variation of the product P.V. is also the decisive factor at *high temperatures*, owing to the diminution in the value of the molecular cohesion with rise in temperature.

Now, since we have seen that the free space in which the molecules move is less than the observed volume, V, we may write $(V - b)$ instead of V in the simple gas equation, where b denotes the amount by which the observed volume must be diminished in order to allow for the finite size of the molecules. It would appear, at first sight, that b must be equal to the sum of the molecular spheres of action, *taking the radius of the molecular sphere of action as* $\frac{s}{2}$ (cf. footnote to § 47), but a moment's consideration will show that this would only be correct if the gas were at absolute zero, and the molecules *at rest*. For, as the molecules move about, they will obstruct one another to a greater extent than if some were at rest, and, in consequence, b must be taken as some multiple of the sum of the molecular spheres of action. Now, in calculating the probability of molecular collision, in § 47, it was seen that the anterior hemispherical surface of the sphere of action of a molecule traversed a volume equal to $\lambda \, . \, \pi \, . \, s^2$ when the molecule advanced through a distance λ—(the radius of the sphere of action being taken as s, and not as $\frac{s}{2}\Big)$. The volume similarly traversed when the molecule advances through a distance equal to the mean free path, L, will be $L \, . \, \pi \, . \, s^2$. But it must be noted that the *space occupied by the sphere of action of the molecule* while it advances a distance L is *greater than* $L \, . \, \pi \, . \, s^2$, since the cylindrical space traversed has *hemispherical ends*, and no allowance was made for this in our previous calculation. Thus the probability of molecular collision will be increased, and the mean molecular free path correspondingly reduced.

In the case of direct molecular collisions the free path will be shortened by the radius of the sphere of action, s, but, when the molecules collide obliquely, a smaller diminution in the free path will result. It can be shown that, on the average, the diminution in the free path is equal to $\frac{\sqrt{2}}{3} \, . \, s$, and, in consequence, we must now write

$$L = \frac{\lambda^3}{\pi \, . \, s^2 \, . \, \sqrt{2}} - \frac{\sqrt{2}}{3} \, . \, s \text{ (cf. § 47).}$$

Since, therefore, $L = \frac{\lambda^3 - \frac{2}{3} \, . \, \pi \, . \, s^3}{\pi \, . \, s^2 \, . \, \sqrt{2}}$, the correction for the finite size of the molecules diminishes, in effect, the volume, λ^3, of the small cube occupied by a single molecule by a volume $\frac{2}{3} \, . \, \pi \, . \, s^3$; i.e. by $4 \, . \, \frac{1}{6}\pi \, . \, s^3$.

If, then, we regard *each molecule as surrounded by a sphere of action of radius* $\frac{s}{2}$ (cf. footnote to § 47), the volume of each such molecular sphere will be $\frac{4}{3} \, . \, \pi \, . \, \frac{s^3}{8}$, i.e. $\frac{1}{6} \, . \, \pi \, . \, s^3$, and, therefore, the volume λ^3 is diminished by *four times the actual volume occupied by the molecular sphere.*

Consequently, for a volume V, containing n molecules, we have $V = n . \lambda^3$, and this volume must be diminished by $4 . \frac{1}{6} . \pi . s^3 . n$. in order to allow for the finite size of the molecules.

Thus the value of b in van der Waals' expression for the volume is given by the relation $b = 4 . \frac{1}{6} . \pi . s^3 . n$; i.e. it is equal to four times the actual volume occupied by all the molecular spheres in the volume V, and this was the conclusion reached by van der Waals. If it be assumed that the molecules actually come into *contact* at a collision, b is equal to four times the actual volume of the *molecules themselves.*

It was assumed by van der Waals that b was constant at all temperatures, and this agrees, approximately, with the results of experiment.[1]

If, then, we substitute the terms $\left(P + \frac{a}{V^2}\right)$, and $(V - b)$ in the simple gas equation $P.V. = R . \theta$, we obtain the relation—

$$\left(P + \frac{a}{V^2}\right)(V - b) = R . \theta,$$

where a, b, and R may be considered as constants.

This relationship was deduced by van der Waals, in 1873, by means of a more rigid mathematical analysis.

The equation of van der Waals is a cubic equation in V, and may be written—

$$V^3 - \left(\frac{P . b + R . \theta}{P}\right) . V^2 + \frac{a}{P} . V - \frac{a . b}{P} = 0.$$

There are three roots to the equation, of which either all three are real, or one is real and two are imaginary. These roots are the values of V which correspond to any given temperature and pressure. If the isothermals corresponding to the equation be plotted, we obtain the curves shown in Fig. XLIX., and these curves possess the same general form as those suggested by J. Thomson (Fig. XXXII.), for the isothermals of a fluid for which the change from vapour to liquid may be assumed *continuous*, so that the fluid system remains homogeneous throughout the transformation. For isothermals below a certain temperature there are either three real values of V, or else one value is real and two are imaginary, according to the value assigned to the pressure P. Thus, in Fig. XLIX., for the θ_1 isothermal, and for pressures between P_1 and P_2, there are three real and different roots, as represented by points such as A, B, and C,

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[1] Since the molecules themselves cannot be regarded as absolutely incompressible, it would appear probable that b becomes *smaller* at high pressures.

corresponding to the pressure P_3. For the same isothermal, and for either the pressure P_1 or P_2, there are still three real roots, two of which, however, have the same value. Thus for the pressure P_1, for example, two roots correspond to the point D, and one root to E. For pressures either less than P_1, or greater than P_2, only one of the roots is real, the other two being imaginary (cf. the points K and L in the figure). In the case of the higher isothermal θ'_1, the three real roots, such as A′, B′, and C′, are closer together.

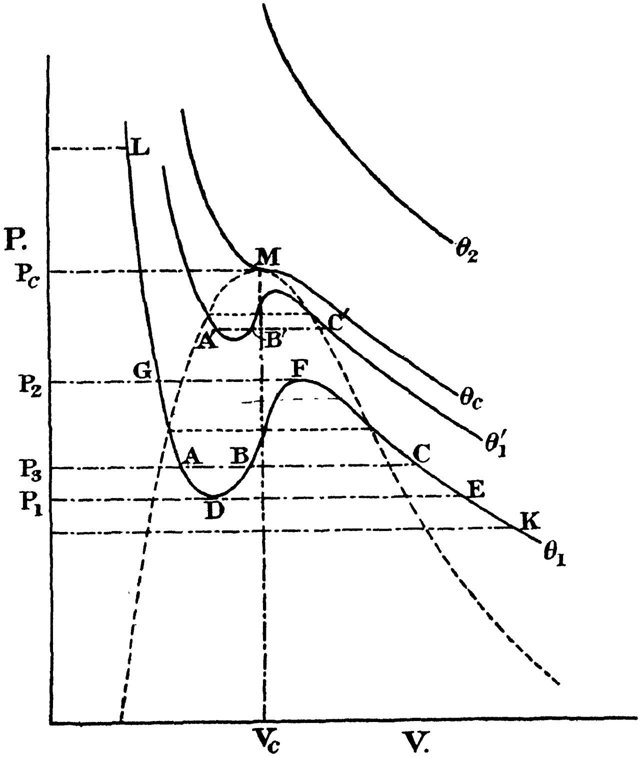

FIG. XLIX.—Van der Waals' Isothermals.

For a particular isothermal, θ_c, which corresponds to the critical isothermal in Fig. XXXII., the three real roots coincide at a particular pressure, P_c. This is shown by the critical point, M, at which the three real values of V become identical and equal to V_c.

For isothermals above this temperature *only one real root* can be found for any given pressure, as is clear from an inspection of the θ_2 isothermal in Fig. XLIX.

Since the three real roots of the equation coincide at the critical point, M, the values of P_c, V_c, and θ_c can readily be calculated in terms of the constants a, b, and R.

For a cubic equation in V, with three real roots, may be written—

$$(V - V_c)^3 = 0, \text{ where } V_c \text{ is the value of each of the equal roots.}$$
$$\therefore V^3 - 3V_c . V^2 + 3V_c^2 . V - V_c^3 = 0.$$

Now, van der Waals' equation at the critical point may also be written—

$$V^3 - \left(\frac{P_c . b + R . \theta_c}{P_c}\right) . V^2 + \frac{a}{P_c} . V - \frac{a . b}{P_c} = 0.$$

Equating the coefficients of equal powers of V in the two equations, we have—

$$3V_c = \frac{P_c . b + R . \theta_c}{P_c}, \quad 3V_c^2 = \frac{a}{P_c}, \text{ and } V_c^3 = \frac{a . b}{P_c}.$$

Whence—

$$\text{Critical volume, } V_c = 3b\,;$$
$$\text{Critical pressure, } P_c = \frac{a}{27 . b^2}\,;$$
$$\text{Critical temperature, } \theta_c = \frac{8 . a}{27 . R . b}.$$

The values of a, b, and R in van der Waals' general equation can be obtained by substituting corresponding values of P and V for the homogeneous fluid, as experimentally ascertained at various temperatures, and the values of the critical constants can then be calculated. Thus, employing the data obtained by Regnault for the compression of carbon-dioxide, and taking pressures in atmospheres, and the volume of the gas, at 0° C. and 1 atmosphere, as the unit volume, we have—

$$a = 0{\cdot}00874,$$
$$b = 0{\cdot}0023,$$
$$R = 0{\cdot}003687.$$

Therefore—

$$V_c = 0{\cdot}00699, \ P_c = 61 \text{ atmospheres, and } \theta_c = 305{\cdot}4° \text{ A.}$$

The experimental values obtained for carbon-dioxide are:—

$V_c = 0{\cdot}0066$, $P_c = 73$ atmospheres, and $\theta_c = 303{\cdot}92°$ A., the agreement in the case of the critical temperature being particularly noticeable.

Conversely, if the critical constants be known for any fluid, the values of a, b, and R can be calculated.

Van der Waals' equation may be written in the form—

$$P = -\frac{a}{V^2} + \frac{R.\theta}{V - b}.$$

If, for any isothermal, P be differentiated with respect to V, we obtain the result—

$$\frac{\partial P}{\partial V} = \frac{2.a}{V^3} - \frac{R.\theta}{(V - b)^2},$$

the differentiation being partial since the temperature is constant.

Now, $\frac{\partial P}{\partial V}$ is the tangent, at any given volume, to the particular isothermal under consideration. If, then, we substitute the values of the critical constants, we obtain—

$$\frac{\partial P_c}{\partial V_c} = \frac{2.a}{V_c^3} - \frac{R.\theta_c}{(V_c - b)^2} = \frac{2.a}{27.b^3} - \frac{8.a.R}{27.R.b.4b^2} = 0.$$

Therefore, at the critical point the slope of the critical isothermal is zero, i.e. the tangent to the isothermal is *horizontal*.

Since
$$\frac{\partial^2 P}{\partial V^2} = -\frac{6.a}{V^4} + \frac{2.R.\theta}{(V - b)^3},$$

we have, at the critical point of inflexion—

$$\frac{\partial^2 P_c}{\partial V_c^2} = -\frac{6.a}{V_c^4} + \frac{2.R.\theta_c}{(V_c - b)^3} = -\frac{6.a}{81.b^4} + \frac{16.a.R}{27.R.b.8.b^3} = 0.$$

At points such as D and F (Fig. XLIX.), which are, respectively, minimum and maximum points, we have in each case—

$$\frac{\partial P}{\partial V} = 0; \text{ but, at D, } \frac{\partial^2 P}{\partial V^2} > 0, \text{ and, at F, } \frac{\partial^2 P}{\partial V^2} < 0.$$

For isothermals not far above the critical isothermal a point of inflexion occurs, but neither $\frac{\partial P}{\partial V}$, nor $\frac{\partial^2 P}{\partial V^2}$, is equal to zero. At sufficiently high temperatures the point of inflexion disappears.

For very large values of the volume V, we may write $\frac{\partial P}{\partial V} = -\frac{R.\theta}{V^2}$, neglecting the term in which V^3 occurs in the denominator, and taking V − *b* as approximately equal to V. Thus, for very large values of V, the slope of the isothermal is always negative (i.e. downwards) and of very small value, and, consequently, the isothermal itself approximates to a straight line, slightly inclined towards the axis of volume.

If, on the other hand, V approximates to the value *b*, the slope of the isothermal approaches the value $-\infty$; i.e. the isothermal approximates to a perpendicular line.

Thus the volume b represents the theoretical limit of compression, and, in accordance with van der Waals' equation, this limiting volume is equal to $\frac{V_c}{3}$. If it be assumed that at the absolute zero of temperature, θ_0, the density of a *saturated* vapour is zero, and if the further assumption be made that the law of Cailletet and Mathias (§ 37) holds down to absolute zero, then, by extrapolating the Cailletet and Mathias mean density line to θ_0 and doubling the mean density we obtain the density of the *liquid* at that temperature. This has been done for a number of different substances, and the limiting volume of the liquid, at θ_0, has been found to be approximately $\frac{V_c}{4}$. It may be doubted, however, if the assumptions made in deducing the limiting volume from the law of Cailletet and Mathias are really justifiable (cf. § 38).

We may write $F(V) = \frac{a}{V^2}$, and $f(V) = \frac{R}{V - b}$, when van der Waals' equation assumes the form—

$$P = -F(V) + \theta . f(V),$$

which we have seen is the general form of the Ramsay-Young equation. Thus the isochores corresponding to van der Waals' equation will also be straight lines.

In the case of a perfect gas $P.V. = R.\theta$, and, consequently, $\frac{R.\theta}{P.V.} = 1$. If, however, we calculate the value of the same ratio, at the critical point, for any fluid obeying van der Waals' equation, we obtain the result—

$$\frac{R.\theta_c}{P_c.V_c} = \frac{8}{3} = 2{\cdot}67.$$

Now, the ratio $\frac{R.\theta_c}{P_c.V_c}$ has been experimentally ascertained for many different substances, and has been found to possess the approximately constant value 3·7 in the case of "normal" fluids, i.e. fluids which have the same molecular complexity both in the liquid and gaseous states.[1]

For fluids which undergo molecular dissociation in passing from the liquid to the gaseous phase the value of the ratio is found to be higher than 3·7. Thus van der Waals' equation, although agreeing more nearly than the simple gas law with the results of experiment, must nevertheless be regarded as merely a first approximation to an accurate Equation of State.

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[1] It is, of course, assumed in van der Waals' equation that neither molecular association nor dissociation occurs.

It was seen, in § 33, that the pressure P, at which the product P.V. for an actual gas was a minimum varied with the temperature, increasing—in the case of a gas at a sufficiently low initial temperature—with rise in the temperature up to a maximum value, and then decreasing again. This was shown by the dotted parabolic curve in Fig. XX., and is illustrated more clearly in Fig. L. which represents the lower part of the isothermal curves in Fig. XX. on an extended scale.

If the upper portion of the dotted parabolic curve be extrapolated, the point at which it cuts the P.V. axis will represent the minimum value of P.V. on the particular isothermal for which this minimum value corresponds to zero pressure. For higher temperatures the minimum value of P.V. would correspond to a negative value of the pressure, and, therefore, would not be realisable in practice, as was seen to be the case, for example, with hydrogen at ordinary temperatures (cf. Fig. XVII.). Now, for a fluid which obeys van der Waals' equation, we can calculate the temperature at which the minimum value of P.V. corresponds to zero pressure in the following manner :—

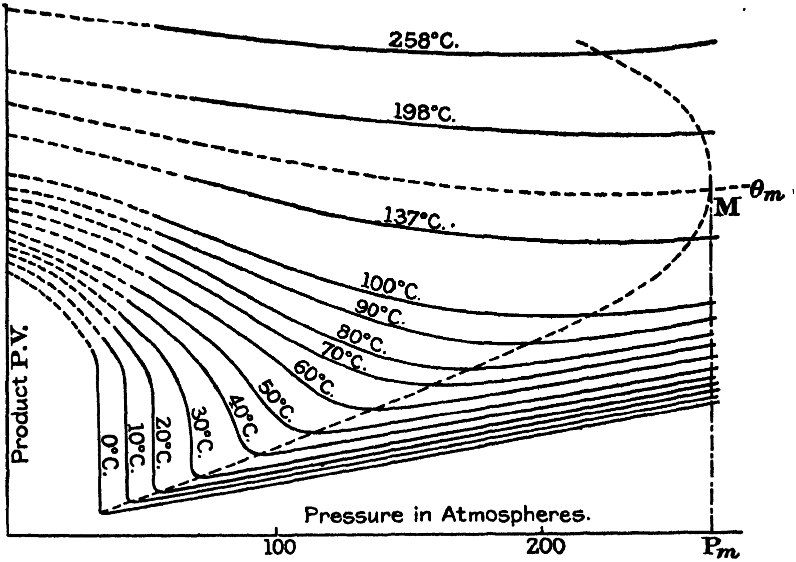

Fig. L.—Carbon-dioxide.

Since
$$P = -\frac{a}{V^2} + \frac{R.\theta}{V - b},$$
$$\therefore P.V. = -\frac{a}{V} + \frac{R.\theta.V}{V - b}.$$
$$\therefore \frac{\partial(P.V.)}{\partial P} = \left\{\frac{a}{V^2} - \frac{R.b.\theta}{(V - b)^2}\right\}.\frac{\partial V}{\partial P}.$$

Now, for all minima on the isothermal curves, in Fig. L., $\frac{\partial(P.V.)}{\partial P} = 0$, and since in the above equation the term $\frac{\partial V}{\partial P}$ is not equal to zero, it follows that, at any minimum point—

$$\frac{a}{V^2} = \frac{R.b.\theta}{(V-b)^2}; \text{ i.e. } \frac{(V-b)^2}{V^2} = \frac{R.b.\theta}{a}.$$

Let θ_1 be the temperature at which the minimum value of P.V. corresponds to *zero* pressure. Then at the minimum point, $\frac{R.b.\theta_1}{a} = 1$—since $V = \infty$ when $P = 0$—and, therefore, $\theta_1 = \frac{a}{R.b}$.

The critical temperature, θ_c, however, has been shown to be given by the relation $\theta_c = \frac{8.a}{27.R.b}$.

Whence—

$$\theta_1 = \frac{27}{8}.\theta_c; \text{ i.e. } \theta_1 = 3{\cdot}375\theta_c.$$

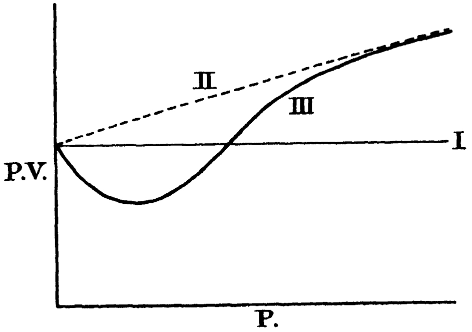

FIG. LI.

In the case of carbon-dioxide, for example, Amagat's data show that θ_1 is approximately 636° C.; i.e. 909° A.; but since θ_c for carbon-dioxide is 30·92° C., or 303·92° A., it follows that $\theta_1 = 2{\cdot}99.\theta_c$, and approximately the same relationship has been obtained in the case of other gases. The proportion given by van der Waals' equation is, consequently, somewhat too high.

Fig. LI. shows the general form of the curves representing the isothermal variation of the product P.V. with P, both for a perfect gas and for one obeying van der Waals' equation. For a perfect gas $P.V. = R.\theta$, and consequently the product P.V. remains constant when the temperature is constant, as is shown by the horizonta line I.

For a "van der Waals' fluid," we have the relation—

$$\left(P + \frac{a}{V^2}\right)(V - b) = R . \theta ;\ \text{i.e.}\ P.V. = R . \theta . + P . b . - \frac{a(V - b)}{V^2}.$$

The dotted line II, in the figure, corresponds to the equation $P.V. = R . \theta + P . b$, and the curve III to the complete relation

$$P.V. = R . \theta . + P . b . - a\frac{(V - b)}{V^2}.$$

When $P = 0$, $V = \infty$, and, in each equation, $P.V. = R . \theta$.

When $P = \infty$, $V = b$, and II and III again meet.

For intermediate values of P. and V., the curve III will lie *below* II, and *may* come below I. At high temperatures the volume corresponding to any given pressure will be greater than at low temperatures, and, therefore, if the temperature be sufficiently high, the term $a\frac{(V - b)}{V^2}$ will be less than $P . b.$; i.e. the curve III will exhibit no minimum value of the product P.V. If the temperature be low, however, $a\frac{(V - b)}{V^2}$ may be greater than $P . b.$, in which case the curve III will have a minimum value for P.V.

In Fig. L., the point M lies on the particular isothermal, θ_m, for which the pressure corresponding to the minimum value of P.V. has its *maximum* value. It is, therefore, of interest to ascertain what values of the temperature, θ_m, the pressure, P_m, and the volume, V_m, correspond to this point.

For *any* point on an isothermal, θ, we have the relation—

$$P = -\frac{a}{V^2} + \frac{R . \theta}{V - b}.$$

Further, for the *minimum* point on the same isothermal we have the relation—

$$\frac{(V - b)^2}{V^2} = \frac{R . b . \theta}{a}.$$

Substituting in the first equation the value of $R\theta$ determined by the second equation, we obtain the result—

$$P = -\frac{a}{V^2} + \frac{a}{b} . \frac{(V - b)}{V^2},$$
$$= \frac{a}{b} . \frac{(V - 2b)}{V^2}.$$

An examination of Fig. LII., which represents the isothermal variation of P.V. with P. in the case of air, as well as of Fig. L. for carbon-dioxide, indicates that V_m must be approximately equal to $3 . b$: i.e. equal to V_c.

For, if $$V_m = 3 . b . = V_c,$$

then, $$P_m = \frac{a}{9 . b^2} = 3 . P_c; \text{ and } \theta_m = \frac{4}{9} . \frac{a}{R . b} = \frac{3}{2} . \theta_c.$$

Thus, for carbon-dioxide, P_c is, approximately, 73 atmospheres,

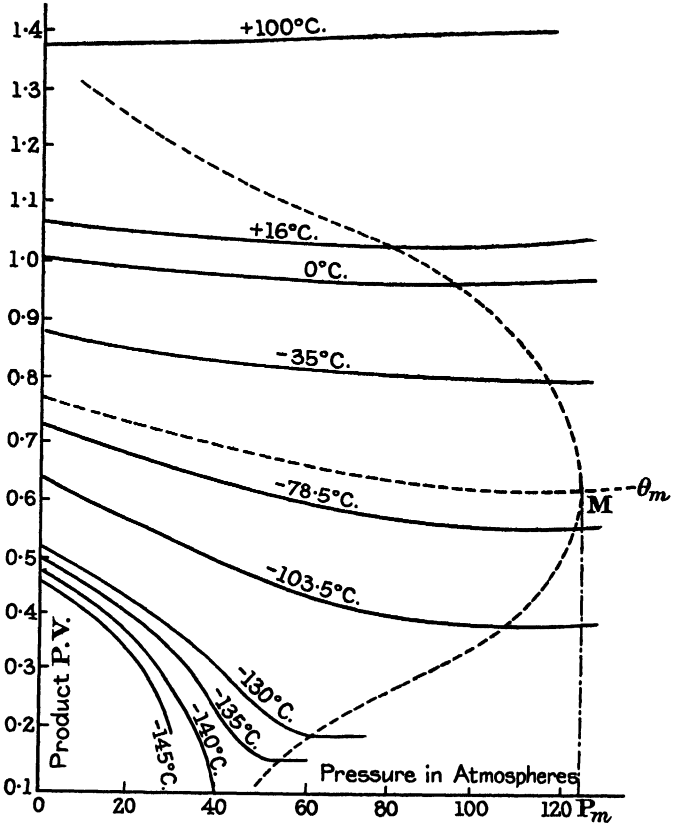

FIG. LII.—Air.

and θ_c, approximately, 304° A.; and, for air, we may take P_c as 39 atmospheres, and θ_c as 133° A.

If, then, we take P_m as $3 . P_c$, and θ_m as $\frac{3}{2} . \theta_c$, we obtain for carbon-dioxide, the values—

$P_m = 219$ atmospheres, and $\theta_m = 456°$ A. (i.e. 183° C.)—and, similarly, for air—

$P_m = 117$ atmospheres, and $\theta_m = 199·5°$ A. (i.e. − 73·5° C.).

These values will be seen to agree fairly well with the experimental results as shown in the figures.[1]

The preceding relationships, as far as the writer is aware, have not been previously observed.

59. Corresponding States.—If any two fluids, either in the gaseous or in the liquid states, be taken at temperatures which are the same fraction of their respective critical temperatures, then the two fluids are said to be at "corresponding temperatures"; and a similar definition applies to the terms "corresponding pressures" and "corresponding volumes."

Now, for any homogeneous fluid, we may express P, V, and θ in van der Waals' equation as fractions of the respective critical constants of the fluid, and write—

$$\left(\alpha \,.\, P_c + \frac{a}{(\beta \,.\, V_c)^2}\right)(\beta \,.\, V_c - b) = R \,.\, \gamma \,.\, \theta_c,$$

where $P = \alpha \,.\, P_c$, $V = \beta \,.\, V_c$, and $\theta = \gamma \,.\, \theta_c$.

Substituting for a, b, and R, in terms of the critical constants, we obtain the result—

$$\left(\alpha \,.\, P_c + \frac{3 \,.\, P_c \,.\, V_c^2}{\beta^2 \,.\, V_c^2}\right)\left(\beta \,.\, V_c - \frac{V_c}{3}\right) = \frac{8 \,.\, P_c \,.\, V_c \,.\, \gamma \,.\, \theta_c}{3 \,.\, \theta_c}.$$

Whence

$$\left(\alpha + \frac{3}{\beta^2}\right)(3 \,.\, \beta - 1) = 8 \,.\, \gamma.$$

This last equation is independent of any constants whose numerical values are conditioned by the particular substance under consideration, and is known as the "Reduced Equation of State."

This reduced equation can, of course, be applied *directly* to any fluid obeying van der Waals' general equation of state, and it follows that if any such fluids, either in the gaseous or in the liquid states, be taken under "corresponding" conditions with respect to any two of the variables P, V, and θ, then they will also be under "corresponding" conditions with respect to the third variable, i.e. the fluids will be in "corresponding states."

The principle of corresponding states has been investigated for a number of different fluids, and has been found to be in fair agreement with the results of actual experiment.

60. The Clausius Equation.—Clausius, in 1880, suggested the equation

$$\left(P + \frac{a}{\theta \,.\, (V + c)^2}\right)(V - b) = R \,.\, \theta,$$

---

[1] Ethylene exhibits a similar close agreement.

where the term $\frac{a}{V^2}$ in van der Waals' equation is replaced by $\frac{a}{\theta . (V + c)^2}$, c being a constant for the given homogeneous fluid, and θ the absolute temperature.

In accordance with this equation, the force due to molecular attraction should vary inversely as the absolute temperature. Since there are now *four* constants, the Clausius equation will not be in agreement with the principle of "corresponding states," unless, indeed, it be assumed that c is the same function of b for all fluids. For the principle of "corresponding states" requires the same number of constants as there are variables, (P, V, and θ); i.e. *three* constants. It is found, moreover, that the Clausius equation does not represent the properties of different fluids with much greater exactness than the equation of van der Waals, whilst it possesses an arbitrary constant, c, which has no direct physical significance.

61. The Dieterici Equation.—Dieterici, in 1901, suggested the equation

$$P = \frac{R . \theta}{(V - b)} . \epsilon^{-\frac{A}{R . \theta . V}},$$

A being a constant characteristic of the molecular attraction and ϵ the base of natural logarithms, (2·718281828 . . .). This may be written in the alternative form—

$$\log_\epsilon P = \log_\epsilon R . \theta - \log_\epsilon (V - b) - \frac{A}{R . \theta . V},$$

if hyperbolic logarithms be taken of both sides of the equation.

The Dieterici equation is in fair agreement with the experimental results obtained in the case of actual fluids, and, in particular, it gives the value 3·695 for the ratio $\frac{R . \theta_c}{P_c . V_c}$;—a value which agrees very well with that obtained by experiment (cf. § 58).

On the other hand, the critical volume, as deduced from this equation, is given by the relation $V_c = 2b$, and the limiting volume, at infinite pressure, is equal to b; i.e. $\frac{V_c}{2}$ (cf. § 58).

Numerous other equations of state have been suggested, but they exhibit little, if any, closer agreement with the results of experiment than is shown by the equations which have already been examined.[1]

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[1] It was pointed out in Chapter V. (§ 42), that the thermal expansion of gases furnished a scale for the measurement of temperature, and that it was more usual to measure equal changes of temperature by equal changes in the pressure of a gas

at constant volume than by equal changes in the volume of the gas under constant pressure.

Now, in the case of a perfect gas, P.V. = R . θ, and $\frac{\partial P}{\partial \theta}$ = constant, if the volume be constant, and, similarly, $\frac{\partial V}{\partial \theta}$ = constant, if the pressure be constant.

In the case of any fluid obeying, for example, van der Waals' equation, we have—

$$P = -\frac{a}{V^2} + \frac{R.\theta}{V - b}.$$

$$\therefore \frac{\partial P}{\partial \theta} = \frac{R}{V - b} = \text{constant, if the volume be constant.}$$

Thus, at constant volume, the increase in the pressure is proportional to the increase in the absolute temperature—as for a perfect gas.

If, however, a "van der Waals' fluid" be employed as the thermometric substance in a *constant pressure* thermometer we have—

$$\frac{\partial V}{\partial \theta} = \frac{R}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}$$

and, therefore, the volume is *not* a linear function of the absolute temperature when the pressure is constant.

Thus, when different gases are used as thermometric substances, a knowledge of their mode of variation from the simple gas law P.V. = R . θ. becomes of considerable importance in an accurate system of thermometry.

CHAPTER VII.

LIQUIDS.

62. Fluids and Solids.—In the preceding chapters the more important consequences of the kinetic theory have been developed, in so far as they are applicable to matter in the gaseous state. We now pass to the consideration of the properties of liquids and solids from the standpoint of the kinetic theory, and it will be found that here, also, our theory is in agreement with the results of experiment, after making due allowance for the greater proximity of the molecules, and the consequent diminution in the mean free path, which characterise the liquid and solid states.

It is customary to divide matter into two classes: fluids and solids. The fluid state is defined as that in which matter yields continuously to an applied tangential or shearing stress, however small the magnitude of the latter may be, whereas, in the case of a solid body, such a tangential stress, if not too great, may be resisted permanently. Thus, let Fig. LIII. represent a vertical section through a heap of sand resting on a horizontal plane AB, and divided into two portions by a plane CD which is inclined to the horizon. Both the action and reaction between the two portions may be resolved into components which are, respectively, normal to CD, and in the plane CD, the latter constituting a shearing stress which tends to make the upper portion of the heap slide down over the lower portion. Provided this shearing stress be not too great, it can, in the case of a solid, be resisted *permanently*. In the case of a fluid, however, no such permanent resistance is offered, and a fluid heap will give way *continuously*, the rate at which it flows being conditioned by viscosity. Pitch, for example, is a fluid, and not a solid, for a block of pitch flows continuously, although very slowly. Thus a specimen of very hard pitch which was kept in the Cavendish Laboratory for many years, in a vertical funnel, gradually flowed through the latter. In another experiment, due to Lord Kelvin, lumps of lead were placed upon a plate of pitch, and gradually sank through to the bottom of the plate.

FIG. LIII.

Fluids are further divisible into gases, vapour, and liquids, the last named being distinguished by the resistance they offer to compression (cf. § 34).

In view of the close relationship which has been seen to exist between the gaseous and liquid states, we shall now proceed to a more detailed study of the properties of liquids, the properties of solids being reserved for subsequent consideration.

63. The Properties of Liquids.—The general properties of liquids find a ready explanation from the standpoint of the kinetic theory, adopting the hypothesis that matter is possessed of an atomic or molecular structure.

Thus the evaporation of a liquid is due to the gradual escape of the molecules through the liquid surface, and, since the more rapidly moving molecules escape more readily, it follows that a cooling effect will be produced by the evaporation.

If evaporation proceed in the open, the molecules will escape into the surrounding atmosphere, but if, on the other hand, it take place into a closed space, the molecules of vapour will collect, and, ultimately, a state of dynamic equilibrium will be attained when as many molecules are condensed back into the liquid as escape from it in unit time. The space above the liquid will then be saturated with the vapour, and the pressure exerted by the latter will be the saturation pressure at the particular temperature. A rise in temperature will increase the average molecular velocity, and the saturation pressure, which corresponds to the state of dynamic equilibrium, will, consequently, be increased. Similarly, from the standpoint of the kinetic theory, the inter-diffusion of miscible liquids may be explained as due to the entry of the constantly moving molecules into the interspaces separating neighbouring molecules.

Since the molecules in a liquid must, in general, be in much greater proximity than the molecules in a vapour or gas, the curved paths traversed by the molecules while casually within the sphere of action of other molecules must bear a sensible ratio to the mean free path. Consequently it is to be anticipated that, in the case of liquids, considerable internal molecular cohesive forces will be developed.

The existence of these internal cohesive forces in liquids is shown by the phenomenon of surface-tension which will be discussed more fully in the next chapter—on Capillarity.

The fact that liquids possess very considerable cohesion may also be shown directly, since a liquid can be made to support a very large tension without rupture.

Thus the sticking of the mercury at the top of a clean barometer-tube, to which reference was made in § 39, shows that the mercury can sustain a tension.

Berthelot succeeded in measuring the strain which various liquids could support without rupture by enclosing the given liquid, from which bubbles of free air or other gases had been previously removed by prolonged boiling, in a straight and thick-walled glass-tube, a small space being left containing only the vapour of the liquid. On carefully heating the tube, the liquid expanded and filled the whole space, and, on subsequently cooling, it was observed that the tube remained filled with the liquid until, ultimately, the liquid column suddenly broke with a metallic click, and the vapour reappeared. By measuring the length of the bubble of vapour, the extension of the liquid was obtained. In the case of water, for example, Berthelot obtained an extension of volume of $\frac{1}{120}$.

It is only for liquids that wet the glass that the maximum strain can be thus obtained; i.e. when the adhesion between the liquid and the glass is greater than the liquid cohesion. Reynolds measured the stress various liquids could sustain without rupture by employing a sealed glass "U" tube containing the given liquid and its vapour (Fig. LIV.). Free air, or other gases, were expelled by previously boiling the liquid, and, after sealing off the "U" tube, the latter was fixed to a board and rotated rapidly about a perpendicular axis, O. If, then, ABCD be the arc of a circle with O as centre, the liquid in EB will be in a state of tension during the rotation, the tension increasing from B to E. The maximum stress which could be sustained was then calculated from the greatest velocity of rotation which the liquid could support without rupture.

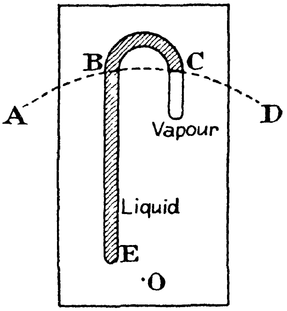

FIG. LIV.

64. Compressibility of Liquids. — The great resistance which liquids offer to compression is a further indication that their molecules are sufficiently close together to exert considerable forces upon one another. It was seen, in Fig. XXIII., that the isothermals for the liquid state approximate to straight lines which are only very slightly inclined towards the axis of pressure, and, indeed, it was thought, for a long time, that all liquids were absolutely incompressible.

An attempt was made in 1660, at Florence, to show the compressibility of water, by filling silver globes with water and then deforming the globes. Negative results were, however, obtained owing to the water being forced through the metal.

More than a hundred years later (1762), Canton succeeded in demonstrating the fact that water is compressible, but he failed to obtain an accurate value for the compressibility.[1]

Canton employed a large glass bulb joined to a fine capillary tube. The bulb and part of the tube were initially filled with mercury, and, by heating the bulb, the mercury was made to expand and completely fill the apparatus. The fine tube was then sealed, and, on cooling,

---

[1] The terms compression, compressibility, and elasticity have been previously defined in § 32.

the mercury sank in the tube—the pressure on the surface of the mercury being merely the small vapour pressure of the mercury at the particular temperature of the experiment. On breaking off the end of the capillary tube, air entered, and the mercury sank lower in the tube, the contraction under the increased internal pressure being due, in part, to the expansion of the glass bulb, and, possibly, in part to the compression of the mercury. On repeating the experiment with water, Canton observed that the apparent contraction was greater than in the case of the mercury, and, consequently, for the water, at any rate, part of the contraction was due to the actual compression of the water itself.

Experiment XXX.—The compressibility of different liquids may be readily demonstrated by means of Oersted's piezometer which is shown in Fig. LV. The glass bulb and capillary tube are filled with the liquid under examination, and the open end of the capillary tube is placed beneath the surface of the mercury in the small reservoir.[1]

The reservoir is then introduced into the piezometer, and, after filling the latter with water, pressure is applied by means of the pump; when the mercury will be observed to rise in the capillary tube.

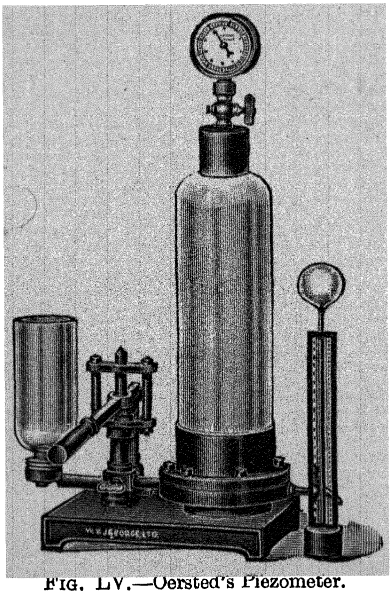

FIG. LV.—Oersted's Piezometer.

Since the pressure is applied both inside and outside the glass bulb, it might be supposed that the change in the volume of the latter could be treated as negligible, provided the walls of the bulb were sufficiently thin. This supposition, however, may be shown to be erroneous. For consider the case of a solid glass sphere inside the piezometer. On applying pressure the sphere becomes smaller, the pressure being the same throughout the sphere. If, now, we imagine the inside portion of the sphere removed, and replaced by a material of the same elasticity, there will be no change in the outside shell. Consequently, in the case of a liquid enclosed in a glass bulb, if the bulk modulus of elasticity[2] of the liquid be the same as that of the glass, the bulb would be compressed to the same extent as if a solid glass sphere had been employed.

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[1] Care must be taken to get rid of all air-bubbles.

[2] *Vide* § 120.

Thus the bulk modulus of elasticity of the bulb must be known before the real compressibility of the liquid can be ascertained.

Let Fig. LVI. represent the glass bulb and capillary tube, the liquid initially occupying the volume V_1. Then, if the compressibility of the liquid and the glass be the same, the level of the liquid in the capillary tube will remain unchanged on compression, but, if the compressibility of the liquid be greater than that of the glass, the level of the liquid will fall on compression to, say, a volume V_2.

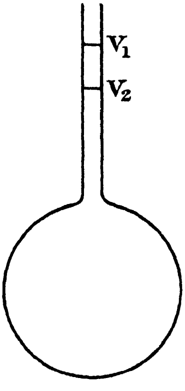

Fig. LVI.

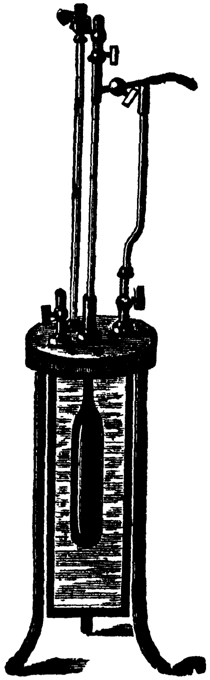

Fig. LVII.—Regnault's Piezometer.

Whence, the *apparent compression* of theliquid $= \frac{V_1 - V_2}{V_1} = m \, . \, P$, where m is the *apparent compressibility*, and P the applied pressure producing the given diminution in volume.

The *apparent bulk modulus of elasticity* of the liquid $= \frac{1}{m}$.

The real compression of the liquid is, clearly, greater than the apparent compression observed, and is given by the relation—
real compression = apparent compression
+ compression of the glass bulb.

Regnault employed the piezometer shown in Fig. LVII., the arrangement being such that the compressibility of the containing bulb, as well as the compressibility of the liquid, could be determined. The side tube was connected to a supply of compressed air, the pressure being measured by means of a manometer. The inner cylindrical bulb contained the liquid under examination, and the volume of the latter was observed in the accurately graduated stem by means of a mercury index. The whole apparatus was kept in a large vessel full of water (not shown in the figure), in order to maintain a constant temperature throughout the experiment. By turning the appropriate stop-cocks, pressure could be applied to (*a*) the outside only of the cylindrical bulb; (*b*) both the outside and the inside; (*c*) the inside only. From the apparent change in volume produced by applying pressure to the outside only of the bulb, the bulk modulus of elasticity of the latter could be obtained, and the bulk modulus of the liquid could then be deduced by observing the apparent diminution in its volume when the pressure was applied both outside and inside the bulb simultaneously. The actual calculation of the result was conditioned by the shape of the cylindrical bulb.

If the bulk modulus for any liquid be accurately known, the bulk modulus for any other liquid may be readily determined by observing the apparent compression of each liquid in the piezometer when pressure is applied equally both outside and inside. Two equations are thus obtained, from which the bulk moduli for both the bulb and the other liquid may be deduced. Either Oersted's or Regnault's piezometer may be used in this experiment.

65. Determination of the Elasticity of a Liquid from the Velocity of Propagation of Sound.—The fact that liquids transmit sound with finite velocity shows that they possess elasticity, and the velocity of propagation of sound enables the elasticity of a liquid to be readily calculated.

We have seen (§ 26) that the velocity, V, of sound in any medium is given by the equation—

$$V = \sqrt{\frac{\text{Elasticity}}{\text{Density}}}.$$

Thus, in the case of water, Martini found that the velocity of sound at 4° C. was $13{\cdot}99 \times 10^4$ cms./sec., and at 25° C. was $14{\cdot}57 \times 10^4$ cms./sec.

Therefore, at 4° C.,

the elasticity of water $= (13{\cdot}99 \times 10^4)^2 \times 1 = 1{\cdot}96 \times 10^{10}$ dynes/cm.^{2}

Similarly, at 25° C., the elasticity of water

$$= (14{\cdot}57 \times 10^4)^2 \times {\cdot}997 = 2{\cdot}12 \times 10^{10} \text{ dynes/cm.}^2$$

Whence the compressibility of water at 4° C.

$$= ({\cdot}510 \times 10^{-10}) \times (76 \times 13{\cdot}596 \times 981);\ \text{i.e. } 5{\cdot}17 \times 10^{-5},$$

when the pressure is expressed in atmospheres.

If the megabar (i.e. 10^6 dynes per square centimetre = ·987 atmosphere) be taken as the unit of pressure, the compressibility at 4° C. $= 5{\cdot}10 \times 10^{-5}$.

At 25° C. the compressibility of water

$$= (\cdot 472 + 10^{-10}) \times (76 \times 13{\cdot}596 \times 981)\text{; i.e. } 4{\cdot}79 \times 10^{-5},$$

when the pressure is measured in atmospheres; and $4{\cdot}72 \times 10^{-5}$, when the pressure is measured in megabars.

These results are in fair agreement with those obtained by the compression of water in a piezometer.

Thus Regnault found the compressibility of water for pressures from about 1 to 10 atmospheres to be $4{\cdot}8 \times 10^{-5}$, the temperature not being specified, and Grassi found $4{\cdot}99 \times 10^{-5}$ at 4° C., and $4{\cdot}56 \times 10^{-5}$ at 25° C., the pressures, in each case, being expressed in atmospheres.[1]

66. Effects of Pressure and Temperature on Compressibility.—As might be expected, the compressibility of any liquid diminishes as the pressure increases. In general, the compressibility increases with rise in the temperature, but water has a minimum compressibility at about 50° C. (Amagat.).

67. Compressibility of Aqueous Solutions.—Röntgen and Schneider investigated the compressibility of aqueous solutions, and found that their compressibility was less than that of water, and diminished as the concentration increased.

68. Viscosity of Liquids.—A definition of viscosity was given in § 48, and the coefficient of viscosity, κ, defined by means of the relation $F = \frac{\kappa . A . V}{x}$. This equation is only true for relatively small values of the "velocity-gradient," for it is only under such circumstances that the steady state of flow which was postulated can exist.

Experiment XXXI.—The viscosity of a liquid may conveniently be measured by Poiseuille's method, by observing the rate of flow of the liquid through a cylindrical capillary tube. As long as the rate of flow does not exceed a certain critical value, depending upon the viscosity of the liquid and the radius of the capillary tube, a steady state of motion parallel to the axis of the tube will be attained. Fig. LVIII. represents a simple form of apparatus for determining the coefficient of viscosity of a liquid. The liquid flows in at the tube A, and any required head can be obtained by adjusting the position of

---

[1] The compressibility of mercury at 4° C. is, approximately, $\cdot 38 \times 10^{-5}$, i.e. about $\frac{1}{13{\cdot}6}$ times that of water ($5{\cdot}17 \times 10^{-5}$), but in other cases the compressibility has not been found to vary inversely as the density of the liquid.

the tube B. CD is the capillary tube, and the quantity of liquid which flows out at D in a definite time is carefully measured.

The capillary tube must initially be tested for uniformity of bore by introducing a column of mercury a few centimetres long, and measuring the length of the column at different parts of the tube. A tube of uniform bore having been obtained, its length, l, is measured, and its mean radius found by nearly filling the tube with mercury, measuring the length of the mercury column with a vernier microscope, and then running out the mercury and weighing it. If l' be the length of the mercury column, and ρ' the density of the mercury at the temperature of the experiment, then $a = \sqrt{\frac{m'}{\pi\rho' l'}}$, where m' is the mass of the mercury, and a the radius of the capillary tube.

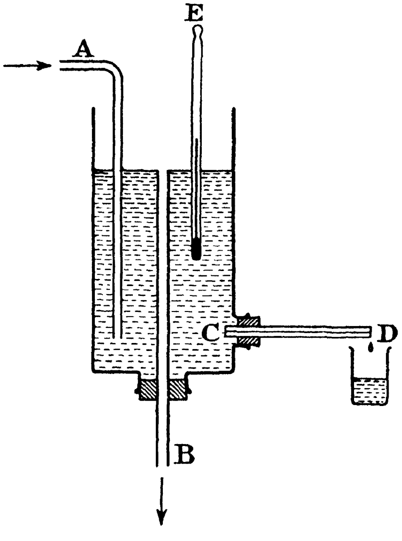

FIG. LVIII.

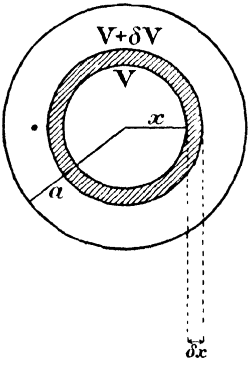

FIG. LIX.

In measuring l', a correction must be applied for the curvature of the ends of the mercury column. For a narrow tube, the curved ends of the mercury column may be regarded as hemispheres, and, consequently, if the length be measured to the extremity of the convex surface at each end, we must take $(l' - \frac{2}{3} . a)$ as the length of the equivalent *cylindrical* column. Alternatively, the internal diameter of the tube may be measured with the vernier microscope in two directions at right angles to one another so as to eliminate any small error due to irregularity of bore, and the radius, a, thus obtained. The temperature of the liquid is also noted by means of the thermometer, E.

Now, we may assume, as in § 48, that when a liquid flows over a solid surface there is no slip between the solid and the layer of liquid in actual contact with it. Thus the velocity with which the liquid flows is zero at the internal surface of the capillary tube, and increases up to a maximum value along the axis of the tube. Let Fig. LIX. represent a section of the liquid taken at right angles to the axis of the capillary tube CD, and let the velocity of the liquid parallel to the axis of the tube at a distance x from the axis be v, and at a distance $x + \delta x$ be $v + \delta v$, δv being negative when δx is positive. Then the volume, δQ, of liquid flowing across the shaded annular section of the tube in unit time is given by the equation:—

$\delta Q = v \,.\, 2\pi x \,.\, \delta x$, which becomes rigidly exact when δx is taken infinitely small; i.e. $dQ = v \,.\, 2\pi x \,.\, dx$.

Since the liquid can be regarded as practically *incompressible*, and since, in the steady state of motion, it flows parallel to the axis of the tube, the velocity, v, at a distance x from the axis, must be the same for all cross-sections along the tube; for the volume δQ, flowing in through an annular section at any part of the tube must be the same as the volume flowing out through any corresponding annular section further down the tube. Moreover, since the liquid flows parallel to the axis of the tube the pressure is sensibly the same over a given cross-section of the tube.[1]

Let p_1 be the pressure at C (Fig. LVIII.), and p_2 the pressure at D. Then the pressure difference, P, between the ends of the capillary tube is given by—

$P = (p_1 - p_2) = h \,.\, \rho \,.\, g$, where h is the head, and ρ the density of the liquid.

Consider the motion of the inner *cylinder* of liquid of radius x, and length l. When a steady state of flow has been attained there is no change in the momentum of the liquid, and, consequently, the force, F, urging the liquid cylinder forward must be equal and opposite to the viscous resistance opposing its motion. Since the area of the end of the cylinder is πx^2, and the area of its curved surface is $2\pi x \,.\, l$, we have—

$$F = P \,.\, (\pi x^2) = -\kappa \,.\, A \,.\, \frac{dv}{dx},$$

$$= -\kappa \,.\, 2\pi x \,.\, l \,.\, \frac{dv}{dx}.$$

Whence

$$dv = -\frac{P}{2 \,.\, \kappa \,.\, l} \,.\, x \,.\, dx.$$

$$\therefore\ v = -\frac{P \,.\, x^2}{4 \,.\, \kappa \,.\, l} + C.$$

---

[1] We may neglect the *very* small pressure due to the weight of the upper layers of the liquid in the horizontal capillary tube on those below.

At the internal surface of the capillary tube, $x = a$, and $v = 0$.

$$\therefore\ C = \frac{P \,.\, a^2}{4 \,.\, \kappa \,.\, l}.$$

Hence
$$v = \frac{P}{4 \,.\, \kappa \,.\, l}\,(a^2 - x^2).$$

Since $dQ = v \,.\, 2\pi x \,.\, dx$, the volume, Q, of liquid flowing across the *whole* cross-section of the tube in unit time is given by the equation—

$$\begin{aligned} Q &= \int_0^a v \,.\, 2\pi x \,.\, dx, \\ &= \frac{2 \,.\, \pi \,.\, P}{4 \,.\, \kappa \,.\, l}\int_0^a (a^2 - x^2) \,.\, x \,.\, dx, \\ &= \frac{\pi \,.\, P}{2 \,.\, \kappa \,.\, l} \,.\, \frac{a^4}{4}, \\ &= \frac{\pi \,.\, P \,.\, a^4}{8 \,.\, \kappa \,.\, l}. \end{aligned}$$

By employing this relation the coefficient of viscosity, κ, may be readily ascertained.

In the preceding investigation we have omitted to take any account of the kinetic energy possessed by the liquid issuing from the capillary tube at D. Since part of the head of liquid has been used in supplying this kinetic energy, a correction must be applied if the velocity of efflux of the liquid be large. In the case of long tubes of fine bore, however, this correction becomes negligible.

The volume, Q, of liquid which flows in unit time across a section of the tube may also be deduced in the following modified manner. Consider the liquid bounded by two coaxial cylinders of radii x, and $x + \delta x$, and by two planes at right angles to the axis of the capillary tube at a distance δl apart (Figs. LIX. and LX.).

The tangential viscous force on the curved surface of the cylinder of radius x, and length δl, is—

$$\kappa \,.\, \delta l \,.\, 2\pi x \,.\, \frac{dv}{dx}.$$

Similarly, the tangential force on the curved surface of the cylinder of radius $x + \delta x$, and length δl, is—

$$\kappa \,.\, \delta l \,.\, 2\pi \,.\left\{x \,.\, \frac{dv}{dx} + \frac{d}{dx}\left(x \,.\, \frac{dv}{dx}\right) .\, \delta x\right\}.$$

Consequently the difference in the tangential forces over the two curved surfaces is—

$$-\ \kappa \,.\, \delta l \,.\, 2\pi \,.\, \frac{d}{dx}\left(x \,.\, \frac{dv}{dx}\right) .\, \delta x.$$

If, further, the pressure gradient along the tube be $\frac{dp}{dl}$, the force due to the difference in the pressures over the two plane ends of the liquid ring is—

$$2\pi x \,.\, \delta x \,.\, \frac{dp \,.\, \delta l}{dl}.$$

When the liquid has attained a steady state of flow this force must be equal and opposite to the resultant tangential viscous force opposing the motion of the liquid ring.

Hence $$2\pi x \,.\, \delta x \,.\, \frac{dp}{dl} \,.\, \delta l = -\kappa \,.\, \delta l \,.\, 2\pi \,.\, \frac{d}{dx}\left(x \,.\, \frac{dv}{dx}\right) \,.\, \delta x.$$

i.e. $$x \,.\, \frac{dp}{dl} = -\kappa \,.\, \frac{d}{dx}\left(x \,.\, \frac{dv}{dx}\right).$$

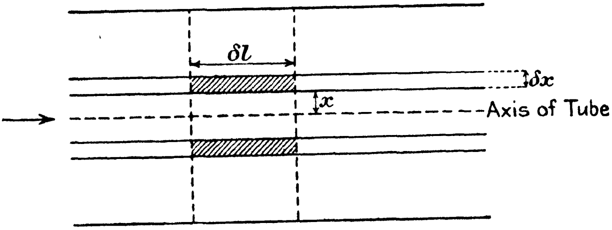

FIG. LX.

It has been shown, previously, that the pressure is sensibly the same over a given cross-section of the tube, and, also, that the velocity, v, at a distance x from the axis of the tube, must be the same for all cross-sections. Thus the pressure gradient, $\frac{dp}{dl}$, is independent of x, whereas, for any given liquid under the conditions of the experiment, the right-hand side of the last equation is dependent merely upon x. Consequently the pressure gradient, $\frac{dp}{dl}$, must be constant, and equal to $\frac{p_1 - p_2}{l}$; i.e. $\frac{P}{l}$.

Therefore, integrating the last equation, we have—

$$\frac{x^2}{2} \,.\, \frac{P}{l} + C = -\kappa \,.\, x \,.\, \frac{dv}{dx},$$ where C is a constant.

Dividing by x and again integrating, we have—

$$\frac{x^2}{4} \,.\, \frac{P}{l} + C \,.\, \log_e x + C' = -\kappa \,.\, v,$$ where C′ is another constant.

If $x = 0$, i.e. along the axis of the tube—

$$C \,.\, \log_e 0 + C' = -\kappa \,.\, v.$$

But $\log_e 0 = -\infty$, and therefore, C must be zero, for otherwise the velocity, v, would be infinite along the axis of the tube.

Again, if $x = a$ (i.e. at the internal surface of the tube where $v = 0$), we have—

$$\frac{a^2}{4} \cdot \frac{P}{l} + C' = 0.$$

$$\therefore C' = -\frac{a^2}{4} \cdot \frac{P}{l}.$$

Whence—

$$\kappa . v . = \frac{P}{4 . l} . \left(a^2 - x^2\right).$$

Thus, as previously—

$$Q = \int_0^a v . 2\pi x . dx,$$

$$= \frac{\pi . P . a^4}{8 . \kappa . l}.$$

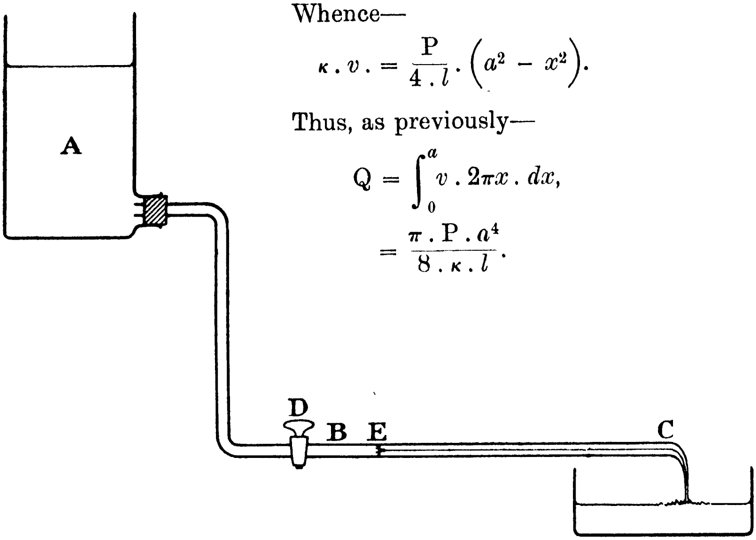

FIG. LXI.

This law for the viscous flow of liquids through capillary tubes was first obtained by Poiseuille, and is known as Poiseuille's Law. As long as the rate of flow of the liquid is less than a certain critical value, depending upon the viscosity of the liquid and the radius of the capillary tube, Poiseuille's Law is found to hold good, but it ceases to be applicable when this critical value is exceeded.

Reynolds has shown that the steady state of motion parallel to the axis of the tube, which was assumed in deducing Poiseuille's Law, only exists when the rate of flow is less than this critical value, and that, at greater values, the motion of the liquid becomes irregular.

Experiment XXXII.—Water is allowed to flow from a reservoir, A (Fig. LXI), through a long horizontal glass tube, BC, of say, 1 cm. internal diameter, the rate of flow being regulated by means of the stop-cock, D. The tube, BC, contains a very small piece of glass tube, E, inside which a fragment of magenta, or other colouring material, has been inserted. A thin piece of wire serves to hold the tube E in position inside the wider tube, BC. As long as the rate of flow is small, the coloured water from E follows a straight path parallel to the axis of the tube (Fig. LXII.), but, as the rate of flow is increased, the path becomes undulating and finally quite irregular[1] (Fig. LXIII.).

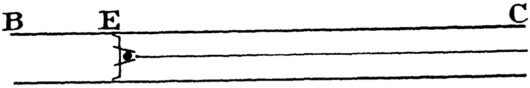

Fig. LXII.

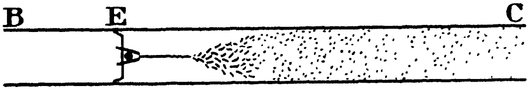

Fig. LXIII.

If the volume, Q, of liquid which flows in unit time across a section of the tube be plotted against the pressure difference, P, between the ends of the tube, we obtain at first—in accordance with Poiseuille's Law—the straight line AB (Fig. LXIV.). Beyond a certain critical velocity eddies are set up in the liquid flowing through the tube, and the relation between Q and P is now given by the curve BC.

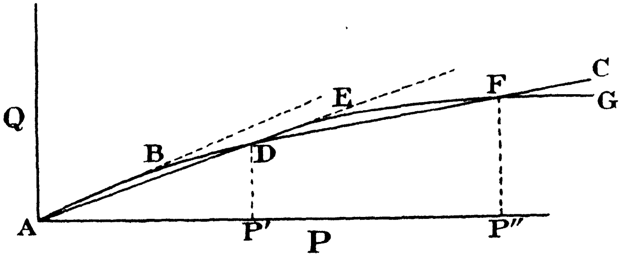

Fig. LXIV.

It is possible for a more viscous liquid, under certain conditions, to flow more rapidly than one of lower viscosity, since the eddies will be damped out more readily by the former liquid than by the latter.

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[1] According to Reynolds the steady state of flow parallel to the axis of the tube cannot exist if the mean velocity ($Q/\pi a^2$) exceeds the value $1000 . \kappa/\rho . a$, where κ is the coefficient of viscosity, ρ the density of the liquid, and a the radius of the tube, expressed in C.G.S. units.

Thus in Fig. LXIV., if ADEFG represent the relation between Q and P for a more viscous liquid, it will be seen that for pressure differences between P′ and P″ this liquid will flow the faster—the formation of eddies being prevented until a pressure difference corresponding to the point E has been attained.

69. Variation of Viscosity with Temperature.—In the case of liquids the viscosity *decreases* rapidly with rise in temperature, whereas for gases the reverse effect is observed (§ 48). It must therefore be assumed, in accordance with the kinetic theory, that the principal effect produced by a rise in temperature, in the case of liquids, is a reduction of the considerable inter-molecular cohesive forces which characterise the liquid state.

The following table gives the values of the coefficient, κ, for a few liquids at various temperatures:—

COEFFICIENT OF VISCOSITY, κ.

	0° C.	20° C.	50° C.
	C.G.S.	C.G.S.	C.G.S.
Water . . .	·0179	·0101	·0055
Mercury . . .	·0169	·0156	·0140
Ether . . .	·0029	·0023	—
Glycerine . .	46·0	8·5	—

70. The Coefficient of Viscosity of a Gas.—As pointed out at the end of § 48, Meyer developed a theoretical law for the rate of flow of a gas through a long tube which was similar to Poiseuille's law for the flow of liquids. Meyer's law of gaseous *transpiration* may now conveniently be deduced.

In considering the flow of a viscous liquid through a cylindrical capillary tube, we treated the liquid as incompressible, but an important difference arises in the case of gaseous transpiration owing to the variation in the density of the gas at different parts of the tube due to variation in the pressure. Thus, in the case of a gas, the volume, in unit time, flowing in across a given cross-section of the tube will *not* be the same as the volume flowing out across a cross-section farther down the tube, and, in consequence, the velocity, V, of the gas parallel to the axis of the tube, at a fixed distance, x, from the axis, will vary as we move along the tube.

Since, however, when a steady state of flow has been attained, equal *masses* of the gas flow across each cross-section of the tube in unit time, it follows that $\rho.V.$ must be constant at a fixed distance, x, from the axis, where ρ is the gaseous density. But the density varies directly as the pressure, p, of the gas, and, consequently, the product,

$p \,.\, V$, of the pressure and the velocity, at a distance x from the axis, must remain constant as we move along the tube.

Since, then, the velocity V, at a distance x from the axis, varies along the tube—due to variation in the pressure p—relative motion will arise between portions of the gas which are equi-distant from the axis. The viscous forces brought into play by this relative motion may, however, be treated as negligible, for, if the maximum velocity of the gas be V′, the velocity-gradient *along* the tube is of the order $\frac{V'}{l}$, and the velocity-gradient *across* the tube is of the order $\frac{V'}{a}$, and since a is very much less than l, the second gradient is correspondingly greater than the first. In consequence, the viscous forces arising from the first gradient of velocity may be neglected in comparison with those due to the second gradient.

Therefore, as in § 68, we have—

$$x \,.\, \frac{dp}{dl} = -\kappa \,.\, \frac{d}{dx}\left(x \,.\, \frac{dV}{dx}\right),$$ but, in this case, the pressure-gradient, $\frac{dp}{dl}$, is *no longer constant.*

Since the pressure, p, may be assumed constant over a given cross-section of the tube, we have, on multiplying both sides of the last equation by p—

$$x \,.\, p \,.\, \frac{dp}{dl} = -\kappa \,.\, \frac{d}{dx}\left(x \,.\, \frac{d(p \,.\, V)}{dx}\right).$$

$$\therefore \frac{x}{2} \,.\, \frac{dp^2}{dl} = -\kappa \,.\, \frac{d}{dx}\left(x \,.\, \frac{d(p \,.\, V)}{dx}\right).$$

Now, we have seen that $p \,.\, V$ is independent of l, and, consequently, the right-hand side of the last equation is independent of l.

$$\therefore \frac{dp^2}{dl} \text{ is } \textit{constant}\text{, and equal to } \frac{(p_1{}^2 - p_2{}^2)}{l}.$$

Integrating the equation $\frac{x}{2} \,.\, \frac{dp^2}{dl} = -\kappa \,.\, \frac{d}{dx}\left(x \,.\, \frac{d(p \,.\, V)}{dx}\right)$, we get—

$$\frac{x^2}{4} \,.\, \frac{dp^2}{dl} + C = -\kappa \,.\, x \,.\, \frac{d(p \,.\, V.)}{dx},$$ where C is a constant.

Dividing by x, and again integrating, we get—

$$\frac{x^2}{8} \,.\, \frac{dp^2}{dl} + C \,.\, \log_e x + C' = -\kappa \,.\, p \,.\, V,$$ where C′ is another constant.

If, then, $x = 0$ (i.e. along the axis of the tube)—

$$C \,.\, \log_e 0 + C' = -\kappa \,.\, p \,.\, V,$$ and, since the velocity is not infinite, C must equal zero.

If $x = a$, the velocity V is zero, whence—

$$\frac{a^2}{8} \cdot \frac{dp^2}{dl} + C' = 0.$$

$$\therefore C' = -\frac{a^2}{8} \cdot \frac{dp^2}{dl}.$$

Substituting the values found for C and C′, we obtain the equation—

$$\kappa . p . V = \frac{1}{8} \cdot \frac{dp^2}{dl} \cdot (a^2 - x^2),$$

$$= \frac{1}{8} \cdot \frac{(p_1^2 - p_2^2)(a^2 - x^2)}{l}.$$

Whence, if Q_1 be the volume of the gas *entering* the tube, in unit time, at pressure p_1, and Q_2 be the volume of the gas *leaving* the tube, in unit time, at pressure p_2, we have—

$$p_1 \cdot Q_1 = p_2 \cdot Q_2 = \int_0^a 2\pi x . dx . V . p,$$

$$= \int_0^a \frac{2\pi x . dx . (p_1^2 - p_2^2)(a^2 - x^2)}{8 . \kappa . l},$$

$$= \frac{2\pi(p_1^2 - p_2^2)}{8 . \kappa . l} . \int_0^a x . dx(a^2 - x^2),$$

$$= \frac{2\pi(p_1^2 - p_2^2)}{8 . \kappa . l} \cdot \frac{a^4}{4},$$

$$= \frac{\pi(p_1^2 - p_2^2) . a^4}{16 . \kappa . l}.$$

This was the theoretical law deduced by Meyer for the transpiration of a gas (§ 48).

71. Couette and Mallock's Method of Determining Viscosity.—The viscosity of a liquid may also be determined by a method employed by Couette and Mallock, in which a couple is applied to a cylinder to prevent it moving while an outer coaxial cylinder is rotated with uniform velocity, the intervening space being filled with the viscous liquid. The apparatus is shown diagrammatically in Fig. LXV.

Consider a cylinder in the liquid of length h and radius x (Figs. LXV. and LXVI.), the radii of the inner and outer solid cylinders being, respectively, a and b (Fig. LXVI.).

The tangential viscous force on the curved surface of the liquid cylinder is—

$$\kappa . h . 2\pi x . \frac{dV}{dx},$$

and the moment T of this force about the central axis O is given by—

$$T = \kappa \,.\, h \,.\, 2\pi x^2 \,.\, \frac{dV}{dx}.$$

Now, provided the rate of rotation of the outer cylinder be less than a certain critical value, the liquid acquires a steady state of motion and travels in concentric circles around the axis of rotation O, the angular velocity with which the liquid moves increasing from zero at the surface of the inner cylinder to a maximum at the surface of the outer cylinder.

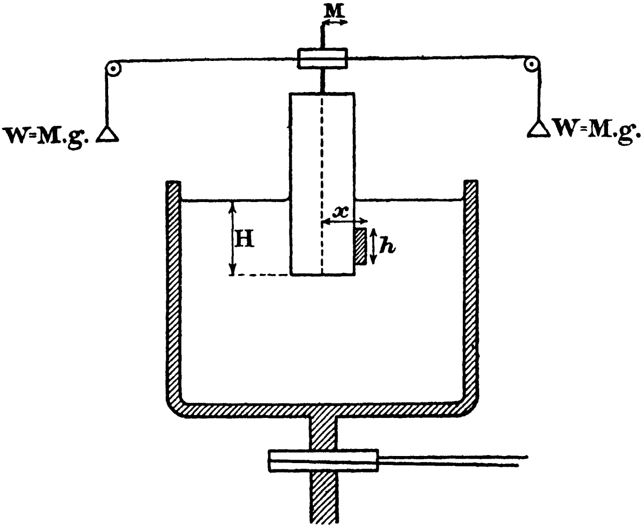

FIG. LXV.

Let A and B (Fig. LXVI.) be points on a radius of the cylinders, at distances x, and $x + \delta x$, respectively, from the axis O. In unit time A will move to C, but B will move to D, where AC = V, and BD = V + δV.

Let OC produced cut BD at E.

If δx be sufficiently small, the difference between AC and BE becomes negligible.

Therefore, the velocity gradient at A is given by—

$$\frac{\delta V}{\delta x} = \frac{ED}{\delta x}.$$

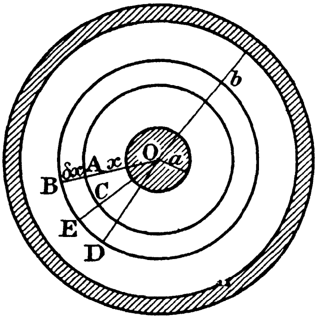

FIG. LXVI.

Let the angular velocity be ω at A, and $\omega + \delta\omega$ at B.

Then
$$\omega = \frac{V}{x} = \frac{AC}{x},$$
$$= \frac{BE}{x + \delta x},$$

since OC produced cuts BD at E.

But
$$\omega + \delta\omega = \frac{V + \delta V}{x + \delta x} = \frac{BD}{x + \delta x} = \frac{BE}{x + \delta x} + \frac{ED}{x + \delta x} = \omega + \frac{ED}{x + \delta x}.$$
$$\therefore \delta\omega = \frac{ED}{x + \delta x}.$$

The velocity gradient at A may therefore be written—
$$\frac{\delta V}{\delta x} = \frac{(x + \delta x) \,.\, \delta\omega}{\delta x}.$$

When δx is infinitely small this becomes—
$$\frac{dV}{dx} = \frac{x \,.\, d\omega}{dx}.$$

Substituting in the equation $T = \kappa \,.\, h \,.\, 2\pi x^2 \,.\, \frac{dV}{dx}$, we get—
$$T = \kappa \,.\, h \,.\, 2\pi x^3 \,.\, \frac{d\omega}{dx}.$$

Now, if we consider the liquid bounded by any two coaxial cylinders of radii x and y, respectively, and by two planes at right angles to the axis O at a distance h apart, then, when the liquid has acquired the steady state of motion previously postulated, it is clear that the moment about the axis O of the tangential viscous force on each of the curved surfaces of the liquid annulus must be equal, but oppositely directed.

Hence the moment T about the axis O of the tangential viscous force is *constant* throughout the liquid, and is equal to the moment of the couple acting on a length, h, of the outer cylinder (where $x = b$), and equal and opposite to the moment of the couple acting on a length, h, of the inner cylinder (where $x = a$).

Therefore, integrating the equation $\kappa \,.\, h \,.\, 2\pi x^3 \,.\, \frac{d\omega}{dx} = T$, we get—
$$2\pi \,.\, \kappa \,.\, h \,.\, \omega \,. = -\frac{T}{2x^2} + C,$$ where C is a constant.

At the surface of the inner cylinder $x = a$, and $\omega = 0$, and the last equation becomes—

$$0 = -\frac{T}{2a^2} + C.$$

$$\therefore C = \frac{T}{2a^2}.$$

At the surface of the outer cylinder $x = b$, and $\omega = \bar{\omega}$, where $\bar{\omega}$ is the angular velocity with which the outer cylinder is rotated.

Whence $$2\pi . \kappa . h . \bar{\omega} . = \frac{T}{2}\left(\frac{1}{a^2} - \frac{1}{b^2}\right).$$

$$\therefore \kappa = \frac{T}{4\pi h\bar{\omega}}\left(\frac{b^2 - a^2}{a^2b^2}\right).$$

If the radius of the pulley wheel attached to the inner cylinder be r (Fig. LXV.), then the total couple, T, applied to the cylinder to prevent its rotation is given by—

$$\begin{aligned} T &= 2W . r, \\ &= 2M . g . r, \end{aligned}$$

and this couple corresponds to the whole length, H, of the inner cylinder immersed in the liquid.

It is difficult to allow for the motion of the liquid in the region at the lower end of the inner cylinder, but this end effect may be eliminated by varying the depth to which the inside cylinder is immersed in the liquid and so obtaining an expression corresponding to the *difference* in the depth, h.

Thus if the angular velocity of rotation, $\bar{\omega}$, of the outer cylinder be kept constant, the weights, W, must be increased when the inner cylinder is immersed deeper in the liquid, in order to prevent the inner cylinder rotating, and the additional applied couple will correspond to the increased viscous drag due to the extra length of the cylinder immersed. This method has also been employed for the determination of gaseous viscosity.

72. Measurements of Viscosity by other Methods.—The oscillating disc method for the determination of viscosity has already been referred to in § 48, and may be used for both gases and liquids. This method is particularly suitable for comparative measurements of the viscosities of different fluids, and also for the determination of variations in viscosity due to changes in temperature and pressure. The viscosity of a fluid may also be measured by a method developed by Stokes in which the logarithmic decrement of the amplitude of oscillation of a pendulum immersed in the given fluid is observed;[1] and measurements of the logarithmic decrement of a sphere vibrating about a diameter, when immersed in a fluid, have, similarly, been employed for the determination of the coefficient, κ.

73. Viscous Resistance offered to the Motion of a Solid through a Fluid.—Since, when a solid body moves through a fluid there is no slip between the solid and the layer of fluid in actual contact with it, relative motion of the fluid will be produced, and, in consequence, viscous forces will be brought into play tending to stop the motion of the solid. In the case of a spherical solid moving with a *small* uniform velocity, V, through a fluid, the viscous resistance was shown by Stokes, in 1849, to be equal to $6\pi . \kappa . a . \mathrm{V}$, where κ is the coefficient of viscosity of the fluid, and a the radius of the sphere.

If, then, a sphere be allowed to fall through a viscous medium, its velocity will increase until a maximum terminal velocity, V', is attained at which the weight of the sphere is exactly equalled by the viscous resistance exerted by the medium.

Let ρ be the density of the sphere and ρ' the density of the fluid medium. Then, since the weight of the sphere is virtually decreased by the weight of an equal volume of the fluid, its effective weight is $\frac{4}{3}\pi a^3 . (\rho - \rho') . g$, and we have—

$$\tfrac{4}{3}\pi a^3 . (\rho - \rho') . g = 6\pi . \kappa . a\mathrm{V}'.$$

Whence $$\mathrm{V}' = \tfrac{2}{9} . \frac{a^2 . (\rho - \rho') . g}{\kappa}.$$

This relation will only be applicable for *small* values of the terminal velocity, for if V' exceed a certain critical value eddies are set up in the surrounding fluid, and the viscous resistance is no longer given by the expression $6\pi . \kappa . a . \mathrm{V}$.

Thus, in general, the preceding relation will only hold good for very small spheres, or for spheres of density only slightly greater than that of the surrounding medium. The same theory applies to the case of spherical liquid drops falling through a fluid medium, provided that the volume of the drops does not change. due to evaporation or condensation, and that the spherical shape is not sensibly affected by the viscous resistance of the medium. The size of very small drops of water, for example, may be determined from the rate at which they fall through saturated air. J. J. Thomson utilised this fact in counting the number of ions produced in air under the influence, say, of Röntgen rays. For, as will be seen in the next chapter, vapour will condense at the ordinary dew-point on these electrical nuclei, in dust-free air; the mist globules formed being, in general, of uniform size, and, consequently, falling through the air at the same

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[1] Boyle, in 1660, found that the oscillations of a pendulum in air decreased at the same rate, irrespectively of the pressure of the air, thus anticipating Maxwell's law that the coefficient of viscosity of a gas is independent of its density.

rate. The rate of fall may readily be ascertained by watching the fairly definite upper surface of the mist as the latter settles, and, from a knowledge of the rate of fall, the size, and hence the number, of water globules may be ascertained—since the total quantity of vapour condensed may be calculated from the measured amount of expansion which was employed in Thomson's experiment to produce condensation. The number of water globules thus found corresponds with the number of condensation-centres or ions present in the air.

Since—in accordance with the relation $V' = \frac{2}{9} \cdot \frac{a^2 \cdot (\rho - \rho') \cdot g}{K}$ deduced by Stokes—the terminal velocity varies directly as the square of the radius of the moving sphere, it follows that, *cæteris paribus*, large bodies will fall more quickly than small ones through a viscous medium. The slow rate at which a fine powder settles, when suspended in water, in comparison with the rate of fall of coarser granules, and the difference in the rates at which, respectively, clouds of very fine mist, small raindrops, and large raindrops fall, are familiar examples of this fact.

If, for example, the radius, a, of a mist globule be 0·001 mm., then, since for air, at 15° C., $K = 1{\cdot}8 \times 10^{-4}$, we have—

$$V' = {\cdot}01 \text{ cm./sec.}$$[1]

Experiment XXXIII.—Finely pulverise a small quantity of sand, and shake a little of the powder and some of the original sand with water. Observe how much more rapidly the coarser sand granules settle, when the shaking is stopped, than the fine powder.

If ρ be less than ρ' in the equation for the terminal velocity, V' will, of course, be negative. The following simple experiment furnishes an interesting example of a negative value for V':—

Experiment XXXIV.—Pour out a tumbler-full of "soda-water," and observe that the smaller the bubbles of gas the slower the rate at which they float up to the surface of the liquid.

74. Liquid Diffusion.—We have seen in § 44 that the interdiffusion of miscible liquids finds a ready explanation from the standpoint of the kinetic theory of matter, and that, as was shown by Fick, the law of such liquid diffusion is exactly analogous to Fourier's Law of thermal conductivity.

The slowness of liquid diffusion, as compared with that of gases, is,

[1] The value taken for K is for *dry* air. If, however, the air be dry, vaporisation will proceed, the rate of fall of the globules becoming slower as they grow smaller, until, ultimately, the mist disappears. If the air be saturated with water vapour, the value of K will be slightly less than for dry air, and V′ will be correspondingly increased.

further, a necessary consequence of the diminished mean free path which is characteristic of both the liquid and solid states.

Experiment XXXV.—Place a strong aqueous solution of a coloured substance, such as copper sulphate, or potassium dichromate,[1] at the bottom of a tall cylinder, and carefully fill the latter with water, taking care to disturb the solution as little as possible.

At first a fairly definite plane of separation will be observed between the coloured solution and the water, but interdiffusion will slowly proceed until the liquid mixture becomes perfectly homogeneous. The rate of diffusion will be seen to be very much slower, however, than in the case of gaseous diffusion (cf. Experiment XVIII.). Thus if a cylinder 30 cms. long were employed in the experiment, and were half filled with a strong solution of copper sulphate, and then carefully filled up with water, the liquids would not become uniformly mixed until, approximately, one year had elapsed.

The earliest experiments of importance on liquid diffusion were carried out by Graham in 1850 and the following year. In these experiments a wide-mouthed bottle was filled with a solution of a given substance, and was placed in a larger vessel which was then filled with water above the level of the open mouth of the bottle. After several days, the amount of the dissolved substance which had diffused out into the larger vessel was determined.

The following results were obtained, in this manner, by Graham :—

(*a*) Rise of temperature produces an increase in the rate of diffusion.

(*b*) Solutions of different concentration of the same substance diffuse at rates proportional to the concentrations.

(*c*) Solutions of equal concentration of different substances diffuse at different rates.

(*d*) The proportion of two substances in a mixture is, in general, altered by diffusion.

(*e*) Substances may be divided into two main classes, viz. crystalloids and colloids. The former can, in general, be obtained in crystalline form, and diffuse much more rapidly than the latter, which are amorphous. Amongst the crystalloids, acids in general diffuse more rapidly than salts.

In 1855, Fick showed that the law of fluid diffusion was similar to the law of the conduction of heat. Thus, referring to § 44, we may define the interdiffusity of two miscible liquids as follows :—

Let the two liquids which, initially, are not uniformly mixed together be enclosed in a cylindrical vessel, and let the concentration of each liquid throughout any horizontal section of negligible thickness be uniform. Then if c be the concentration (i.e. the quantity in gms.

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[1] Note that the copper sulphate, and potassium dichromate, become themselves *liquids* when dissolved in water.

per c.c. of solution) of one of the liquids at a height x, measured from any fixed horizontal reference plane, and if c decrease with increase in x, the mass, M, of the liquid which flows across the horizontal plane at height x is given by the equation—

$$M = \eta . A . - \frac{dc}{dx} . S,$$

where η is the interdiffusity of the two liquids, A the area of the plane, and S the time interval.

This equation will, in general, become more nearly exact the shorter the time interval, S; for the concentration gradient, $= \frac{dc}{dx}$, will usually vary with S.

Various experimental methods have been employed for determining the value of the coefficient, η, in the case of liquids, and thus verifying the accuracy of Fick's Law.

Since the withdrawal of any portion of the solution will set up disturbing currents, it is necessary to determine the concentration of different layers by measuring some physical property of the undisturbed solution. Thus the concentration of sugar solutions, for example, may be determined by measuring the rotation of the plane of polarisation of light. Other optical methods have also been employed for determining concentration—such as the measurement of the refractive indices of various horizontal layers at definite times—and, in certain cases, the concentration has been ascertained by means of similar colorimetric observations.

In a method due to Lord Kelvin a number of small glass beads of different densities were employed. A cylindrical vessel was half filled with a solution of a given substance, and then carefully filled up with water. The small glass beads were immersed in the fluid, and initially floated at the surface of separation of the solution and the water, but, as diffusion proceeded, the beads floated up or down. From the positions of the various beads at any instant the densities, and hence the concentrations, of the corresponding horizontal fluid layers could be ascertained. Owing to bubbles of air, and, possibly, crystals of salt forming on the beads, and so altering their density, the method is not susceptible of very great accuracy.

One of the most exact methods of measuring the progress of liquid diffusion was devised by Weber in 1879. Two plates of amalgamated zinc were placed horizontally in respective aqueous solutions of zinc sulphate of different concentrations contained in a cylindrical vessel, the more concentrated solution occupying the lower half of the vessel. The electromotive force between the two zinc plates depended upon the difference in the concentration of the two solutions in contact with the plates. Consequently, the progress of diffusion could be followed by observing the electromotive force at definite times—the manner in which the electromotive force depended upon the concentration of the solutions having been determined in a preliminary experiment. As the diffusion proceeded the difference in concentration, and, consequently, the electromotive force, became smaller, until, ultimately, a homogeneous solution was obtained, and the electromotive force vanished.

The law of Fick has been found to be in very close agreement with the experimental results obtained by numerous investigators. Just as it was seen, however, that the thermal conductivity, K, was not rigidly constant but was, in fact, a function of the temperature—and just as the interdiffusity, η, of two gases was found to vary slightly with a variation in the proportion between the two gases—so, in the case of liquids, η depends to a small extent upon the concentration of the solution.

As in the case of gases, the rate of diffusion of liquids increases with rise in temperature. Provided a uniform temperature be maintained throughout a homogeneous solution, the phenomenon of diffusion enables the solution to be preserved indefinitely without any change in its homogeneity. This property is obviously of very great importance in volumetric chemical analysis.

75. The Solvent Action of Liquids.—The phenomenon of solubility, or miscibility, to which reference has already been made in § 37, must now be investigated in somewhat greater detail from the standpoint of the kinetic theory.

It is well known that both the solubility of different substances in the same solvent, as well as the solubility of the same substance in different solvents, may vary very considerably. Thus sulphur is scarcely soluble in water to an appreciable extent, whereas sugar will readily dissolve;—silver fluoride is extremely soluble in water, while the other halides of silver are only very sparingly soluble. Again, although sulphur is almost insoluble in water, yet it dissolves easily in carbon-disulphide. Consequently, the ability to dissolve depends upon a *mutual affinity* between the solvent and the solute, and is not conditioned by the properties of either of them *alone*.

The term *solvent* is usually applied to the substance which constitutes the larger part of the solution, while the substance which is dissolved in the solvent is called the *solute*. It should be noted, however, that, theoretically, there is no distinction between solvent and solute.[1]

At a given temperature two substances may be infinitely miscible (cf. § 37), or there may be a limit to their mutual solubility. Thus

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[1] The phenomenon of solution must be regarded as purely a physical change for the constituents of a solution may be separated by changing their respective physical states (e.g. by boiling off one of the constituents), and, further, the composition of a saturated solution, unlike that of a chemical compound, does *not* correspond to integral multiples of the atomic weights of the constituent elements. The composition of a saturated solution also varies with change in the temperature.

at, say, 20° C., water and alcohol are miscible in all proportions, but, at the same temperature, a saturated solution of water in ether contains only 1·2 gms. per 100 gms. of the ethereal solution, and a saturated solution of ether in water contains 6·5 gms. per 100 gms. of the aqueous solution. Again, at 20° C., 1·33 gms. of lithium carbonate, 34·0 gms. of potassium chloride, and 204·0 gms. of cane sugar, respectively, will dissolve in 100 gms. of water to form saturated solutions. A saturated solution may be defined as that solution which, at the particular temperature, is in equilibrium when in contact with an excess of the solute.[1]

Now, if a liquid be placed in a closed space, we have seen (§ 63) that evaporation proceeds, due to the escape of molecules through the liquid surface, until, ultimately, a state of dynamic equilibrium is attained when as many molecules are condensed back into the liquid as escape from it in unit time. The pressure exerted by the vapour when this equilibrium state has been reached is the saturation pressure at the particular temperature.

Similarly, in the case of a solid body, there is a maximum vapour-pressure at each particular temperature, but this pressure is, in general, exceedingly small. A number of solids, however, evaporate to an appreciable extent even at the ordinary temperature. Thus the vaporisation of camphor or naphthalene may be readily detected by their respective odours.

As in the case of liquids we must suppose that the maximum vapour-pressure for a solid corresponds to a state of dynamic equilibrium in which as many molecules land back upon the surface of the solid, in unit time, as escape from it into the space in which it is enclosed.

Now, although a solid will vaporise into air, or into a vacuum, under ordinary conditions, to an extremely small extent, yet the molecules of the solid will disseminate themselves much more freely throughout a space occupied by a suitable solvent. Thus, for example, the vapour pressure exerted by cane sugar at the ordinary temperature is practically negligible, but if a moderate quantity of sugar be placed at the bottom of a vessel full of water it will dissolve, and gradually diffuse upwards until the solution becomes perfectly homogeneous. The upward diffusion of the heavier sugar molecules through the lighter water shows that they are in motion, just as the upward diffusion of a heavier gas into a lighter one is due to the motion of the gaseous molecules.

We have seen, however, that, in accordance with the kinetic theory, the pressure exerted by a gas upon the walls of a containing vessel is due to the impacts of the gaseous molecules occasioned by their very rapid motion, and, similarly, it can be shown that the

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[1] Since, under suitable conditions, *supersaturated* solutions can be obtained it is incorrect to define a saturated solution as one in which the solvent contains all of the solute it can take up at the given temperature.

motion of the molecules of the dissolved sugar gives rise to an analogous pressure, which is termed "*diffusion pressure*," or "*osmotic pressure*." This pressure, as will be seen later, can be experimentally measured, and it is found, in the case of *dilute* solutions, that *the osmotic pressure is proportional to the concentration.*

It must be noted that, in the solid state, the molecules of sugar are relatively close together, whereas in a *dilute* solution, at any rate, they are very much farther apart, their cohesion having been overcome by the action of the solvent. We may, therefore, regard the sugar in a dilute solution as being in a quasi-gaseous state, and this conception will be found very useful in elucidating a number of important experimental results.[1]

76. The Process of Solution.—In order to obtain a definite mental picture of the dynamical actions involved during the process of solution let us consider the case of, say, the dissolving of potassium chloride in water at a temperature of 20° C. As stated above, 34·0 gms. of potassium chloride will dissolve in 100 gms. of water, at 20° C., to form a saturated solution. Suppose we take about 50 gms. of solid potassium chloride, and add 100 gms. of water. In the solid potassium chloride the molecules are close together, and very few of them would escape by vaporisation if the solid were surrounded with air, but when the potassium chloride is placed in contact with water the molecular cohesion is overcome at the surface, by the action of the water, and the molecules escape into the liquid. These free molecules gradually diffuse away, and other molecules take their place. The rate of solution, if the liquid be not stirred, is conditioned by this *rate of diffusion*, just as the rate at which a liquid evaporates is dependent upon the rate of diffusion of its vapour into the surrounding atmosphere (*vide* § 44). We have seen that the tendency to dissolve —i.e. the tendency of the molecules of the solid potassium chloride to escape from the cohesive action of other potassium chloride molecules—is not merely dependent upon the nature of the solute itself, but also depends upon the nature of the solvent.[2]

Thus in the case of a solute dissolved in a solvent it is incorrect to speak of the tendency of the molecules of the solute to dissolve off the solid surface as a *solution pressure*, and it is equally incorrect to

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[1] See, however, § 85.

[2] It is only in the case of a liquid, or a solid, vaporising into a vacuum, or into a space filled with an indifferent gas, that we can regard the saturation, or maximum vapour pressure, at a given temperature, as a measure of the *independent* tendency of the molecules to escape. Thus, for example, if an excess of ether be placed in a closed space, a definite saturation pressure will be attained—corresponding to a definite concentration of the ether molecules in the vapour phase —and this saturation pressure will be the same whether the ether evaporate into a vacuum or into a space filled with an indifferent gas. If, however, the ether be placed in contact with, say, water, quite a different concentration of the ether molecules in the space occupied by the solvent (water), will result.

regard the whole action as due to the tendency of the solvent to absorb the solute and to speak of the solvent as possessing a *solution tension.* Since the tendency to dissolve is due to the mutual affinity of the solute and solvent we shall call this tendency the *solution stress*[1] between them.

Now, as the dissolved molecules of the potassium chloride move about in the liquid in all directions, some of them will land back upon the solid surface of the undissolved potassium chloride and again cohere, and, as the concentration of the dissolved molecules increases, the more frequently will molecules get caught back by the undissolved solute.

Ultimately, just as in the case of a liquid in contact with its saturated vapour, a state of dynamic equilibrium will be attained when the solution in contact with the solute has acquired such a concentration that as many molecules land back upon the solid surface and cohere, in unit time, as escape from the surface of the solid and pass into solution; and this state of equilibrium will moreover be *permanent* when, through the process of diffusion, the *whole* of the solution has acquired a corresponding concentration.

It is clear that this state of dynamic equilibrium will be reached when the *osmotic pressure* of the dissolved substance becomes equal to the *solution stress:* the solution will then be *saturated,* and any excess of the solute will remain undissolved. Thus, in the case under particular examination, the osmotic pressure of the dissolved potassium chloride increases as the concentration of the solution increases, until, when 34·0 gms. have dissolved, the osmotic pressure of the dissolved potassium chloride equals the solution stress between the potassium chloride and the water, and no further increase in the concentration of the solution can then occur.

77. Osmosis.—Before proceeding to a consideration of the experimental methods employed in determining the osmotic pressure of a dissolved substance, it will be necessary to investigate very briefly the phenomena exhibited during the passage of liquids through porous septa. The interdiffusion of two miscible liquids which are initially separated by a porous membrane is termed *osmosis* (ὠσμός, a push). The Abbé Nollet, in 1748, recorded that a bladder filled with alcohol and immersed in water swelled out and nearly burst, owing to the water entering more rapidly than the alcohol escaped, and that if the bladder were filled with water and immersed in alcohol, the water, similarly, escaped more rapidly and the bladder shrank.

Experiment XXXVI.—Attach a piece of bladder very securely to the head of a short thistle-funnel, and fill the latter with, say, alcohol, or a concentrated solution of cane sugar. Join the thistle-funnel to a

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[1] The dimensions of a stress are those of a force divided by an area, and are, therefore, the same as for a pressure (*vide* Cap. XI.).

capillary tube by means of a small rubber stopper, and immerse the funnel in distilled water. After standing for some time it will be observed that the liquid has risen in the capillary tube, due to the water entering more rapidly than the alcohol, or sugar, can escape.

It must be noted, in this experiment, that the membrane is *not* "semi-permeable," for appreciable quantities of alcohol, or sugar, pass out through the membrane into the water.

A little more than a century after Abbé Nollet's observations, Graham (as was stated in § 74) divided substances into two main classes, viz. crystalloids and colloids, the former diffusing much more rapidly, when dissolved, than the latter.[1]

The colloids (κόλλα, glue) include such substances as albumen, starches, and gums, and possess the property of forming jellies when mixed with a small quantity of water. Crystalloids will diffuse through many of these colloidal jellies nearly as rapidly as through water, whereas the jellies are impervious, or nearly so, to colloids. When crystalloids are dissolved in water the freezing-point of the solution is found to be lower, and the boiling-point higher, than in the case of the pure solvent. Colloids, however, when similarly dissolved, are found to produce very little effect, and, in many cases, it would appear that the colloid does not form a true solution at all, but merely remains suspended throughout the solvent in a very fine state of division.

The difference in the permeability of colloidal jellies or membranes by crystalloids and colloids was utilised by Graham for the separation of these two classes of substances.

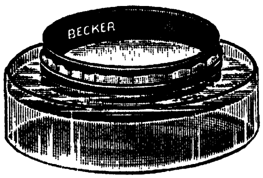

Fig. LXVII.—Dialyser.

The process is called *dialysis* (δια, through; λέω, I loosen). The solution containing the crystalloids and colloids is poured into a tray, the bottom of which is closed with a colloidal membrane of, for example, parchment paper[2] or bladder.

The tray is then placed in another vessel containing distilled water (Fig. LXVII.).

The crystalloids pass through the membrane much more rapidly than the colloids, and, if the water in the outer vessel be renewed frequently, practically all the crystalloids can be removed, while most of the colloids remain behind in the tray.

Experiment XXXVII.—Pour a solution of sodium silicate into concentrated hydrochloric acid, keeping the latter in considerable

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[1] Since many substances possess both crystalloid and colloidal forms it is more accurate to refer to the crystalline and colloidal states than to "crystalloids" and "colloids."

[2] Parchment paper is made by treating filter paper with a mixture of two volumes of sulphuric acid and one volume of water. The paper is then freed from acid and dried.

excess. Silicic acid is formed and remains in colloidal suspension. On dialysing the mixture hydrochloric acid and sodium chloride are removed, and a dilute solution of silicic acid is obtained.

The dialysis may be effected very readily by keeping a continuous current of water flowing through the outer vessel.

Experiment XXXVIII.—Add a little potassium iodide solution to an emulsion of starch, and pour the mixture into a dialyser which is placed in a vessel containing distilled water. After a short time remove the dialyser, and add a little chlorine water to the solution in the outer vessel. Iodine will be liberated, and the solution will turn brown, but no blue colouration will be produced, showing that the starch has not passed through the dialyser. If, now, a few drops of starch emulsion be added to the solution, a deep blue colour will appear, due to the adsorption of the iodine by the starch which is in colloidal suspension in the emulsion.

78. Osmotic Pressure.—We have seen (§ 75) that when some sugar, for example, is placed in water, the sugar dissolves, and the heavier molecules of sugar diffuse upwards into the lighter water, while the molecules of water also diffuse amongst the molecules of sugar. As the molecules of dissolved sugar move hither and thither in the solution, their motion gives rise to a pressure which is termed *osmotic pressure*. Since, however, the molecules of water are also in motion, they must exert a similar kind of pressure (*vide* § 85).

Now, it is possible to measure the partial pressure exerted by a solute in a similar manner to that employed for experimentally measuring the partial pressure of one gas in the presence of another (*vide* § 52). For this purpose a "semi-permeable" diaphragm which is permeable by the *solvent*, but not by the *solute*, must be employed. Animal membranes cannot be used since they are not absolutely semi-permeable (cf. Experiment XXXVI.). Artificial semi-permeable membranes were first prepared by Traube, and these were utilised by Pfeffer in his investigations on osmotic pressure. Pfeffer obtained the best results by using a film of copper ferrocyanide, which he precipitated inside the walls of a porous pot by filling the pot with a very

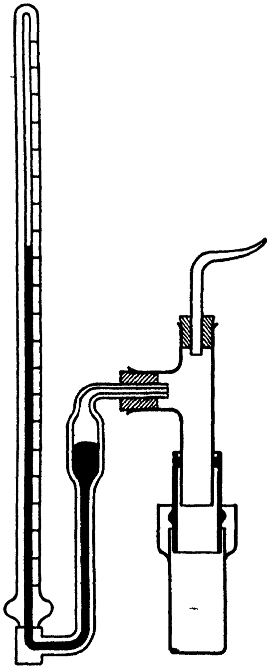
FIG. LXVIII.—Pfeffer's Apparatus.

dilute aqueous solution of copper sulphate, and immersing it in a weak aqueous solution of potassium ferrocyanide. The solutions diffused into the walls, and, on meeting, formed a continuous film of the gelatinous precipitate of copper ferrocyanide; the porous pot supplying the necessary support to enable the film to withstand a fairly considerable pressure.

The pot was next carefully washed out, and, after being attached to a manometer, was completely filled with a dilute aqueous solution of, say, sugar, and then sealed.

The whole apparatus was next immersed in distilled water which was maintained at a constant temperature. Since a copper ferrocyanide film is easily permeable by water, but not by dissolved sugar, the water gradually entered the porous pot, and the pressure inside increased until a state of equilibrium was attained when as many molecules of water passed in through the semi-permeable membrane as passed out in the same time. The excess of pressure inside the porous pot was, consequently, the osmotic pressure exerted by the dissolved sugar, and this could be ascertained by means of the manometer.[1]

Pfeffer's apparatus is illustrated in Fig. LXVIII. The porous pot is filled through the smaller bent tube, and the latter is then sealed before the blow-pipe. The whole apparatus, including the manometer, is then immersed in water.

In the case of cane sugar solutions, for example, at approximately the same temperature (14° C.), Pfeffer obtained the following results :—

C, Concentration.	P, Osmotic Pressure in cms. of Mercury.	$\frac{P}{C}$.
1 per cent.	53·5 cms.	53·5
2 ,, ,,	101·6 ,,	50·8
4 ,, ,,	208·2 ,,	52·1
6 ,, ,,	307·5 ,,	51·3

Thus, for these dilute solutions, the osmotic pressure, P, is directly proportional to the concentration, C.

Pfeffer also investigated the effect of variations in the temperature on the osmotic pressure.

For a 1 per cent. solution of cane sugar the following results were obtained :—

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[1] By artificially increasing the pressure inside the pot, part of the solvent may be forced out and the concentration of the solution increased. Similarly, the flow of water through the semi-permeable membrane into the pot can be prevented by the application of a definite pressure; viz. the osmotic pressure of the solution.

Temperature.	Osmotic Pressure, P.
6·8° C.	50·5 cms.
13·2° C.	52·1 ,,
22·0° C.	54·8 ,,
36·0° C.	56·7 ,,

The osmotic pressure in this case, therefore, increases with rise in temperature.

The relationship which exists between the osmotic pressure of a dissolved substance, in a dilute solution, and the pressure exerted by a gas was pointed out, in 1887, by van't Hoff.

Thus the osmotic pressure of a dilute solution varies directly as its concentration, and, similarly, in accordance with Boyle's Law, the density (i.e. *concentration*) of a gas varies directly as its pressure.

Again, the osmotic pressure of a dilute solution increases with rise in temperature, and, as far as Pfeffer's results go, the coefficient of increase of pressure is found to be approximately 0·00367, i.e. the osmotic pressure varies directly as the absolute temperature (cf. Charles' Law).

The applicability of Avogadro's Law to the osmotic pressure of dilute solutions furnishes further corroborative evidence of the analogy between osmotic and gaseous pressures, for it is found that solutions of "*non-electrolytes*" (*vide ut infra*) which have equal osmotic pressures have the same number of gramme-molecules in equal volumes, i.e. possess concentrations proportional to the molecular weights of the respective solutes. It is found, moreover, that the osmotic pressure of a dilute solution of a "non-electrolyte" is the *same* as the pressure that would be exerted by the solute if the latter were capable of existing in the state of gas and occupying the volume of the solution at the same temperature.

Thus Pfeffer's 1 per cent. solution of cane sugar contained 1 gm. of sugar dissolved in 100 gms. of water, and, therefore, 1 gm. of sugar was present in approximately 100·6 c.cs. of the aqueous solution at 6·8° C., i.e. 222·5 gms. of sugar were present in 22,380 c.cs. of solution.

The molecular weight of cane sugar is 342, and, if the sugar could exist as gas, 342 gms. in 22,380 c.cs., at 0° C., should exert a pressure of 76 cms. of mercury, and, consequently, 222·5 gms. of sugar, in the same volume, and at 6·8° C., should exert a pressure of $\frac{76 \times 222{\cdot}5 \times 279{\cdot}8}{342 \times 273}$ cms., or 50·7 cms.

The actual osmotic pressure observed (50·5 cms.) is in fairly close agreement with this result.

Van't Hoff pointed out, however, that very many substances in solution exerted a *greater* osmotic pressure than would be anticipated if the laws of gas-pressure applied directly to the osmotic pressure of dilute solutions.

For such substances the general gas equation $P.V. = R . \theta$, which contains the combined laws of Boyle and Charles (*vide* § 17), and which applies to the osmotic pressure of dilute solutions of substances like cane sugar, must be modified, and written—

$$P.V. = i . R . \theta,$$

where i is a factor greater than unity.

Arrhenius subsequently showed how the greater osmotic pressure exerted by such solutions could be readily explained by means of the theory of "electrolytic dissociation," just as deviations from Avogadro's Law, in the case of gases, were explained by the assumption of molecular dissociation. Those solutes (viz. acids, bases, and salts) which give a greater osmotic pressure than that corresponding to the equation $P.V. = R . \theta$ are called "electrolytes," whilst substances like cane sugar are termed "non-electrolytes."

79. Measurement of the Relative Osmotic Pressures of Solutions.— The direct experimental determination of the absolute osmotic pressures of solutions is a matter of some difficulty. Several simple methods, however, have been devised for measuring *relative* osmotic pressures. De Vries employed the cells from certain plants, notably from *Tradescautia discolor*, *Begonia manicata*, and *Curcuma rubricaulis*. The cell-walls of the leaves are lined with a thin semi-permeable membrane, which contains the coloured contents of the cell. When such a cell is placed in a solution possessing a greater osmotic pressure than its own contents, water will pass out from the cell into the solution, through the semi-permeable membrane, and the membrane will, consequently, shrink away from the walls. Thus, by commencing with a solution of greater osmotic pressure than the cell contents, and gradually diluting it, a concentration can be obtained at which the membrane will just maintain its shape without any shrinkage.

The osmotic pressure of the solution will then be equal to that of the contents of the cell. The contraction of the protoplasmal envelope is, of course, observed under the microscope. In this manner solutions of a number of different substances can be prepared, all possessing the same osmotic pressure—viz. the osmotic pressure of the cell contents.

Solutions having the same osmotic pressure are termed "*isotonic*." By analysing such isotonic solutions De Vries found that, in the case of non-electrolytes, their concentrations were proportional to the molecular weights of the respective solutes. This method has been used in certain cases for the determination of molecular weights.

Semi-permeable membranes also occur in certain animal cells—such as red blood corpuscles—and the latter may, consequently, be employed in the preparation of isotonic solutions. If a small quantity of an aqueous solution of potassium nitrate be added to some blood, the red corpuscles settle down to the bottom of the containing vessel. The corpuscles can then be washed and transferred to a microscope slide. If the corpuscles be surrounded by a solution possessing a greater osmotic pressure than their own contents, they shrink, and their walls become concave, whereas, if the contents of the corpuscles possess an osmotic pressure greater than the solution, the corpuscles swell, and their walls become convex. The concentration of the solution can therefore be varied till the corpuscles neither shrink nor swell; the solution and the contents of the corpuscles are then isotonic.

An optical method for the preparation of isotonic solutions was devised by Tammann in 1888. A drop of an aqueous solution of potassium ferrocyanide, at the end of a fine pipette, is immersed in an aqueous solution of copper sulphate. The drop immediately becomes covered with a film of copper ferrocyanide. If the potassium ferrocyanide solution possess a greater osmotic pressure than the solution of copper sulphate, water will pass in through the semi-permeable film of copper ferrocyanide, and the drop will expand. At the same time the solution of copper sulphate around the drop will become more concentrated and will therefore sink, owing to its increased density. The downward motion of the liquid may be observed with a refractometer, descending striæ being visible in the liquid on account of the different refractivities arising from differences in density.

If the osmotic pressure of the potassium ferrocyanide solution be less than that of the copper sulphate solution, water will pass out from the drop, and the latter will contract. In this case the solution of copper sulphate around the drop will become more dilute, and the striæ will be seen to ascend. By varying the concentration of either the potassium ferrocyanide or the copper sulphate until striæ are no longer visible, isotonic solutions may be obtained.

80. Relation between Lowering of Freezing-Point and Osmotic Pressure.—Van't Hoff, in 1887, showed that the osmotic pressure exerted by a solute could be calculated from the lowering of the freezing-point of the solvent produced by the solute, and also from the rise in the boiling-point of the solvent, due to the same cause.

A proof of the relation between the lowering of the freezing-point and the osmotic pressure will now be given. Let an aqueous solution of the given solute at its absolute freezing-point $\theta - \delta\theta$, be separated by a semi-permeable membrane from the pure solvent (water), at its absolute freezing-point, θ. Let a small volume, v, of the water pass through the semi-permeable membrane into the solution. The work gained is $P \cdot v$, where P is the osmotic pressure of the solution. Now let this quantity of water that has passed through be frozen out from the solution, and let the pure ice be placed back again in the water and melted. The heat which must be actually supplied, at the temperature θ, to melt the ice is $\lambda \cdot v \cdot \sigma$, where λ is the latent heat and σ the density, of water.[1]

The whole system is now in its original condition, and, since the preceding cycle of operations is reversible, it follows in accordance with the Second Law of Thermodynamics that—

$$\text{Efficiency of the cycle} = \frac{\text{Work obtained}}{\text{Heat taken in at high temperature}}$$

$$= \frac{\text{Difference in temperatures of source and sink}}{\text{Absolute temperature of the source}}.$$

In the above cycle of operations, the water at the temperature θ corresponds to the source, and the solution at the temperature $\theta - \delta\theta$ to the sink.

$$\therefore \frac{P \cdot v}{\lambda \cdot v \cdot \sigma} = \frac{\delta\theta}{\theta};$$

i.e.

$$\frac{P}{\lambda \cdot \sigma} = \frac{\delta\theta}{\theta}.$$

Since, for water at 0° C., $\lambda = 79{\cdot}77 \times 4{\cdot}19 \times 10^7$, $\sigma = 0{\cdot}99987$, and $\theta = 273{\cdot}1°$ A., we have—

$$P = 1{\cdot}22 \times 10^7 \times \delta\theta.$$

The lowering of freezing-point, $\delta\theta$, is thus proportional to the osmotic pressure, P. It is evident, also, that solutions in the same solvent, having the same freezing-point, must be isotonic. Since dilute isotonic solutions of " non-electrolytes " have the same number of gramme-molecules in equal volumes, it follows that equal numbers of molecules of different solutes, in the same volume, produce equal depression in the freezing-point of a given solvent.

This result was obtained experimentally by Raoult, in 1883, and it was pointed out by him how the lowering of the freezing-point could be utilised for the determination of the molecular weight of the solute.

The lowering of freezing-point produced by, say, the hundredth part of the molecular weight of a non-electrolyte taken in grammes,

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[1] The lowering of the freezing-point, $\delta\theta$, is very small, provided the solution be sufficiently dilute, and the heat required to warm the ice from $\theta - \delta\theta$ to θ is, therefore, negligible in comparison with that needed to melt it. The heat given out by the water in cooling from θ to $\theta - \delta\theta$, on passing through the membrane, may also be neglected.

and contained in 100 c.cs. of a solution, may be readily calculated. For, as seen in § 78, the osmotic pressure will be the same as if the solute were present in the state of gas, at the same temperature, and occupying the same volume.

In the case, therefore, of an aqueous solution, at 0° C., we have—

$$\begin{aligned} 1{\cdot}22 \times 10^7 \times \delta\theta &= \text{P}, \\ &= \frac{76 \times 13{\cdot}596 \times 981 \times 22380}{100 \times 100}, \\ &= 2{\cdot}27 \times 10^6. \end{aligned}$$

Whence—

$$\delta\theta = 0{\cdot}186^\circ.$$

This agrees very closely with the experimental value ($\delta\theta = 0{\cdot}185^\circ$), found by Raoult, and equally good agreement was obtained with other solvents.[1]

The "cryoscopic" (or freezing-point) constant of any solvent is defined as the depression of the freezing-point produced when the molecular weight in grammes of any non-dissociating (and non-associating) solute is dissolved in 100 gms. of the solvent—supposing that the laws for dilute solutions held at such a concentration. Thus, for water, the cryoscopic constant, C, has approximately the value 18·6. If, then, w gms. of a solute, of molecular weight M, be dissolved in W gms. of a solvent, and produce a depression, $\delta\theta$, of the freezing-point we have—

$$\delta\theta = \frac{\text{C} \, . \, w \, . \, 100}{\text{M} \, . \, \text{W}},$$

where C is the cryoscopic constant for the given solvent.

The relationship $\text{M} = \dfrac{100 \, . \, \text{C} \, . \, w}{\delta\theta \, . \, \text{W}}$ is commonly used in the determination of molecular weights.

81. Relation between Rise in Boiling-Point and Osmotic Pressure.—The relation between the rise in the boiling-point and the osmotic pressure may be demonstrated in a similar manner to that employed in calculating the lowering of the freezing-point.

Thus, let an aqueous solution of a solute be separated by a semi-permeable membrane, from the pure solvent (water), and let the temperatures of the solvent and solution be such that their respective vapour pressures are the same. The vapour pressure may, conveniently, be taken as equal to the atmospheric pressure, and the absolute temperatures of the solvent and the solution will then be their normal boiling-points. Let a small volume, v, of the water pass through the semi-permeable membrane into the solution. The

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[1] In the preceding calculation, P is, strictly, the osmotic pressure of the solution at $\theta - \delta\theta$, but this differs inappreciably from its osmotic pressure at θ.

work gained is $P . v$, where P is the osmotic pressure of the solution. Let this quantity of water that has passed through be evaporated from the solution, and let the vapour pass back and condense again in the water. No mechanical work will be expended in this second operation, since the vapour pressures of the solvent and solution are the same. The whole system is now in its original condition, and the cycle of operations performed is reversible. If, then, θ be the absolute temperature of the solvent (water), and $\theta + \delta\theta$ that of the solution, we have, in accordance with the second law of thermodynamics—

$$\frac{\text{Work obtained}}{\text{Difference in temperatures of source and sink}}$$
$$= \frac{\text{Heat taken in at high temperature}}{\text{Absolute temperature of the source}}$$
$$= \frac{\text{Heat removed at low temperature}}{\text{Absolute temperature of the sink}}.$$

The heat removed at the low temperature θ, in order to condense the vapour, is $\lambda . v . \sigma$ where λ is the latent heat of steam, and σ the density of the water.[1]

In this cycle of operations, the solution at the temperature $\theta + \delta\theta$ corresponds to the source, and the water at the temperature θ to the sink.

$$\therefore \frac{P . v}{\delta\theta} = \frac{\lambda . v . \sigma}{\theta},$$

$$\text{i.e. } \frac{P}{\lambda . \sigma} = \frac{\delta\theta}{\theta}.$$

For water at 100° C. the latent heat of vaporisation,[2] $\lambda = 539 \times 4{\cdot}19 \times 10^7$, $\sigma = 0{\cdot}9584$, and $\theta = 373{\cdot}1°$ A.

$$\therefore P = 5{\cdot}8 \times 10^7 \times \delta\theta.$$

Similar relations therefore hold *mutatis mutandis* for the boiling-points of solutions as for their freezing-points (*vide* § 80). The rise in boiling-point is proportional to the osmotic pressure, and solutions in the same solvent having the same boiling-point are isotonic.

Similarly, solutions in a given solvent containing equal numbers of molecules of different non-electrolytes in the same volume must have the same boiling-point.

The rise in the boiling-point of a solvent produced by a dissolved non-volatile substance was utilised by Beckmann in 1891, for the determination of the molecular weight of the solute.

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[1] For dilute solutions, $\delta\theta$ is very small, and the heat given out by the vapour in cooling from $\theta + \delta\theta$ to θ may therefore be neglected in comparison with that evolved during condensation. The heat required to raise the temperature of the water from θ to $\theta + \delta\theta$, on passing through the membrane, is also negligible.

[2] Carlton-Sutton's value (1917).

We can calculate the rise in boiling-point due to the hundredth part of the molecular weight of a non-electrolyte taken in grammes, and contained in 100 c.cs. of a solution in a similar manner to that employed in calculating the lowering of the freezing-point.

Thus, for an aqueous solution at 100° C., we have—[1]

$$
\begin{aligned}
5{\cdot}8 \times 10^7 \times \delta\theta &= P, \\
&= \frac{76 \times 13{\cdot}596 \times 981 \times 22380 \times 373{\cdot}1}{100 \times 100 \times 273{\cdot}1}, \\
&= 3 \times 10^6.
\end{aligned}
$$

Whence $\delta\theta = 0{\cdot}0517°.$

The "boiling-point constant" refers to the rise in boiling-point produced when the molecular weight in grammes of any non-dissociating (and non-associating) solute is dissolved in 100 gms. of the solvent, supposing that the laws for dilute solutions applied to such a concentration. As in the freezing-point method, the molecular weight of a solute may be determined by employing the relationship

$$M = \frac{100 \, . \, C \, . \, w}{\delta\theta \, . \, W},$$

where $\delta\theta$ is the rise in boiling-point observed, and C the boiling-point constant for the given solvent.

The experimental results obtained with dilute *aqueous* solutions give an approximate value of 5·2° for the boiling-point constant, which agrees very closely with the value deduced, thermodynamically, by van't Hoff. Equally good agreement has been found with other solvents.

The freezing-point and boiling-point constants may be readily calculated from the simplified expression—

$$K = \frac{0{\cdot}02 \, . \, \theta^2}{\lambda},$$

where K is the molecular lowering of freezing-point, or molecular rise in boiling-point, corresponding to the molecular weight in grammes of the solute in 100 gms. of the solvent; θ is the absolute temperature of the freezing-point, or boiling-point, of the solvent; λ is the latent heat of fusion, or the latent heat of vaporisation, per gramme of the solvent.

For, as seen previously—

$$P = \frac{\lambda \, . \, \sigma \, . \, \delta\theta}{\theta},$$

and if V be the volume of the solution containing the molecular weight

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[1] In the following calculation P is the osmotic pressure of the solution at $\theta + \delta\theta$, which differs inappreciably from its osmotic pressure at θ.

in grammes of the solute, we have, in accordance with the general gas equation P.V. = R . θ—

$$\frac{R \, . \, \theta}{V} = \frac{\lambda \, . \, \sigma \, . \, \delta\theta}{\theta}.$$

Since R = 2 calories, approximately, this equation may be written—

$$\delta\theta = \frac{2 \, . \, \theta^2}{V \, . \, \sigma \, . \, \lambda}.$$

But, in the case of a dilute solution, V differs inappreciably from the volume of the *solvent*, and, therefore—

$$V \, . \, \sigma = 100 \text{ gms.},$$

whence

$$\delta\theta = \frac{0{\cdot}02 \, . \, \theta^2}{\lambda}.$$

It must be remembered, however, that the preceding relationships, which were deduced by van't Hoff, are strictly true only for infinitely dilute solutions. In the case of moderately concentrated solutions they are wholly inapplicable.

82. The Vapour Pressure of Solutions.—Since the boiling-point of a solution is higher than that of the pure solvent, it follows that the vapour pressure of a solvent is lowered by the presence of a non-volatile solute. In 1848, von Babo found that the relative lowering of the vapour pressure, in the case of dilute solutions, was independent of the temperature. The relative lowering of the vapour pressure is defined as the ratio of the lowering of the vapour pressure produced by the solute, at the given temperature, to the vapour pressure of the pure solvent, at the same temperature. Thus if f be the vapour pressure of the solvent, and f' that of the solution, von Babo found that $\frac{f - f'}{f}$ was independent of the temperature.

Wüllner, in 1858, observed that the lowering of the vapour pressure of water by non-volatile, dissolved substances was proportional to the amount of the solute present.

These generalisations, as applied to dilute solutions, were confirmed by the work of Raoult, who further investigated the lowering of vapour pressure produced by equimolecular quantities of different solutes in the same solvent. The " molecular lowering," K, which was found by Raoult to be constant for a given solvent, is given by the equation—

$$K = \frac{f - f'}{f} \, . \, \frac{M}{x},$$

where f and f' are the respective vapour pressures of the solvent and the solution, M the molecular weight of the solute, and x the mass in grammes of the solute dissolved in 100 gms. of the solvent.[1]

If n represent the number of gramme-molecules of the solute in 100 gms. of the solvent, we have—

$$n = \frac{x}{\mathrm{M}}.$$

$$\therefore \mathrm{K} = \frac{f - f'}{f \,.\, n}.$$

It was also found by Raoult that the quotient of the "molecular lowering" of vapour pressure K by the molecular weight M′ of the solvent was constant.

Since $$\mathrm{K} = \frac{f - f'}{f \,.\, n},$$

$$\frac{\mathrm{K}}{\mathrm{M}'} = \frac{f - f'}{f \,.\, n \,.\, \mathrm{M}'}.$$

Now n represents the number of gramme-molecules of the solute in 100 gms. of the solvent, and, therefore, $n\mathrm{M}'$ represents the number of gramme-molecules of the solute in 100 *gramme-molecules* of the solvent. If, then, $n\mathrm{M}' = 1$, $\frac{\mathrm{K}}{\mathrm{M}'} = \frac{f - f'}{f}$.

Thus the quotient, $\frac{\mathrm{K}}{\mathrm{M}'}$, of the "molecular lowering" of vapour pressure by the molecular weight of the solvent represents the relative lowering of vapour pressure produced by one gramme molecule of the non-volatile solute in 100 gramme-molecules of the solvent, and this quotient was found by Raoult to have the approximately constant value 0·0105.

This law was stated formally by Raoult as follows:—

"One molecule of a non-saline,[2] non-volatile substance, dissolved in 100 molecules of any volatile liquid, lowers the vapour pressure of this liquid by a nearly constant fraction of its value—approximately 0·0105."

Since $0{\cdot}0105 = \frac{\mathrm{K}}{\mathrm{M}'} = \frac{f - f'}{f \,.\, n \,.\, \mathrm{M}'}$, we have—

$$\frac{f - f'}{f} = 0{\cdot}0105 \,.\, n \,.\, \mathrm{M}'.$$

---

[1] It must be noted that K is only constant for dilute solutions of non-volatile non-electrolytes in a given solvent.

Several of the *solutes* employed by Raoult (such as turpentine and benzaldehyde) possess appreciable vapour pressures even at ordinary temperatures. Raoult, however, used a solvent (*ether*), which, at the ordinary temperature, has a high vapour pressure, and, consequently, the relatively low vapour pressure of the solute could be neglected.

[2] A "non-saline" substance = a "non-electrolyte."

If, then, 100 gms. of the solvent represent N *gramme-molecules*, we have—

$$\frac{100}{\mathrm{N}} = \mathrm{M}'.$$

Whence $$\frac{f - f'}{f} = \frac{0{\cdot}0105 \,.\, n \,.\, 100}{\mathrm{N}},$$

$$= \text{(approximately) } \frac{n}{\mathrm{N}}.$$

But n represents the number of gramme-molecules of the solute in 100 gms. of the solvent, i.e. in N gramme-molecules of the solvent. Consequently, in a very dilute solution of a non-volatile non-electrolyte, containing n gramme-molecules of the solute in N gramme-molecules of the solvent, the relative lowering of the vapour pressure, $\frac{f - f'}{f}$, is equal to $\frac{n}{\mathrm{N}}$.

Raoult pointed out that the lowering of the vapour pressure of solvents, produced by dissolved substances, could be utilised for the determination of molecular weights, but this method was quickly replaced by the more convenient and more accurate boiling-point method devised by Beckmann, to which reference has already been made.

83. Relation between Lowering of Vapour Pressure and Osmotic Pressure.—The relationship between the lowering of the vapour pressure of a solvent, due to the presence of a non-volatile solute, and the osmotic pressure exerted by the solute, may be readily demonstrated. Consider an aqueous solution of a solute, separated by means of a semi-permeable membrane from the pure solvent (water), the temperatures of the solvent and of the solution being the same. Let the pressure of the vapour above the water be p, and above the solution $p - \delta p$. Let a small volume, v, of water be driven through the semi-permeable membrane *from* the solution into the water. To effect this a quantity of work, $\mathrm{P} \,.\, v$, must be expended, where P is the osmotic pressure of the solution. Now let this quantity of water that has been driven through evaporate, and let the vapour pass back into the space above the solution and then condense. If V be the volume of vapour formed from the volume v of water, the work gained in this second operation is $\delta p \,.\, \mathrm{V}$. The system is now in its original condition, and the cycle of operations performed is reversible. Since the whole transformation is carried out isothermally, it follows, in accordance with the Second Law of Thermodynamics, that there is no gain or loss of mechanical work.

$$\therefore \mathrm{P} \,.\, v = \delta p \,.\, \mathrm{V}.$$

$$\therefore \frac{\delta p}{\mathrm{P}} = \frac{v}{\mathrm{V}} = \frac{\sigma}{\rho},$$

where σ is the density of the vapour, and ρ the density of the water.

The same result, as was shown by Arrhenius, can be obtained by examining the problem from the standpoint of the kinetic theory.

Thus, consider a tube partly filled with a solution, A (Fig. LXIX.), and closed at the bottom with a semi-permeable membrane. Let the lower end of the tube dip into the pure solvent, B.

If, initially, the length of the column of solution be not too great, the solvent will pass through the semi-permeable membrane into the tube, until the solution has reached a height, h, at which the hydrostatic pressure is just equal to the osmotic pressure of the solution in its final state of dilution.[1]

If the whole apparatus be enclosed in a space which has become saturated with the vapour of the solvent, a state of equilibrium will then be attained. For simplicity we shall assume that the enclosure has been exhausted of air.

Let σ be the average density of the vapour throughout the height h. The hydrostatic pressure due to the column of vapour of height h is consequently $h \,.\, \sigma \,.\, g$, and this must be equal to the difference between the saturation vapour pressure of the pure solvent, at the level C, and the saturation vapour pressure of the solution, at the level D.[2]

If, then, the saturation vapour pressure of the solvent be p, and of the solution be $p - \delta p$, we have—

$$\delta p = h \,.\, \sigma \,.\, g.$$

Let ρ be the average density of the solution throughout the height h. The density of the solution is practically uniform, and in the case of dilute solutions may be taken as differing inappreciably from the density of the pure solvent.

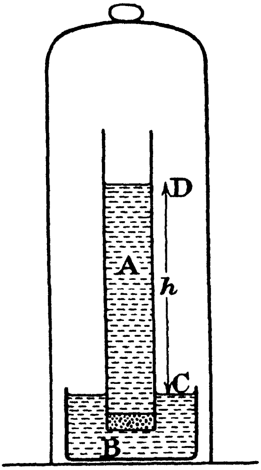

Fig. LXIX.

Thus, the hydrostatic pressure due to the column of solution of height h is $h \,.\, \rho \,.\, g$, and this must equal the osmotic pressure, P.

Hence
$$P = h \,.\, \rho \,.\, g.$$
$$\therefore \frac{\delta p}{P} = \frac{\sigma}{\rho},$$

which was the relation previously obtained.

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[1] It is assumed, of course, that the dimensions of the tube are such that capillary effects can be neglected.

[2] It is clear that if the vapour pressure of the solution at D were not equal to the vapour pressure of the solvent *at this level*, equilibrium could not exist. For vaporisation, or condensation, would occur at D, and a flow of liquid through the semi-permeable membrane would result.

Again, let V_1 be the volume of 1 gramme-molecule of the vapour (of average density σ) at a pressure p. Applying the general gas equation, we have—

$$p \,.\, V_1 = R \,.\, \theta.$$

Let M_1 be the gramme-molecular weight of the solvent.

Then
$$\sigma = \frac{M_1}{V_1}.$$
$$\therefore \sigma = \frac{M_1 \,.\, p}{R \,.\, \theta}.$$

Further, let the solution contain n gramme-molecules of the solute in N gramme-molecules of the solvent, i.e. in $N \,.\, M_1$ gms. of the solvent.

Therefore 1 gramme-molecule of the solute is contained in $\frac{N \,.\, M_1}{n}$ gms. of the solvent.

Now, if the solution be very dilute, we may take ρ to be the density of both the solution and the solvent.

Let $\frac{N \,.\, M_1}{n}$ gms. of the solvent (or solution) have a volume V_2.

Then
$$\rho = \frac{N \,.\, M_1}{n \,.\, V_2}; \text{ i.e. } V_2 = \frac{N \,.\, M_1}{n \,.\, \rho}.$$

Applying the general gas equation to the osmotic pressure of the solute in the dilute solution, we have—

$$P \,.\, V_2 = R \,.\, \theta.$$

Substituting for P and V_2, we have—

$$\frac{h \,.\, \rho \,.\, g \,.\, N \,.\, M_1}{n \,.\, \rho} = R \,.\, \theta.$$

Whence
$$h = \frac{R \,.\, \theta \,.\, n}{N \,.\, M_1 \,.\, g}$$

If the values $\sigma = \frac{M_1 \,.\, p}{R \,.\, \theta}$, and $h = \frac{R \,.\, \theta \,.\, n}{N \,.\, M_1 \,.\, g}$, be substituted in the equation $\delta p = h \,.\, \sigma \,.\, g$, we get—

$$\delta p = \frac{R \,.\, \theta \,.\, n}{N \,.\, M_1 \,.\, g} \times \frac{M_1 \,.\, p}{R \,.\, \theta} \times g,$$
$$= \frac{n \,.\, p}{N}.$$
$$\therefore \frac{\delta p}{p} = \frac{n}{N}.$$

This is the relation which was obtained experimentally by Raoult for the relative lowering of the vapour pressure, and to which reference was made in § 82. If in the equation $\frac{f - f'}{f} = \frac{n}{N}$ (§ 82) δp be substituted for $f - f'$, and p for f, the two equations become identical in form.

84. The Vapour Pressure of Liquid Mixtures.—In our investigation into the relationship between the rise in boiling-point (or the lowering of vapour pressure) and osmotic pressure, it was assumed, either tacitly or explicitly, that the solute could be treated as non-volatile. When the solute is appreciably volatile, it is evident that our general argument will no longer apply. If, for example, one liquid be dissolved in another, both constituents of the solution will, in general, possess sensible vapour pressures, and we must now briefly consider what will be the magnitude of the resultant vapour pressure exhibited by such liquid mixtures.

We may divide these liquid mixtures into three classes.

Class I.—When the mutual solubility of the liquids is very small, that is, when the liquids are practically immiscible, the vapour pressure of the mixture is approximately the sum of the separate vapour pressures of the constituents. Since, however, each liquid is soluble to a small extent in the other, and, consequently, as will be seen later, lowers the vapour pressure of the other liquid by a small amount, the vapour pressure of the mixture is always slightly *less* than the sum of the vapour pressures exerted by the separate liquids at the same temperature. As the vapour pressure of such a liquid mixture is higher than that of either of the separate constituents, the boiling-point will be lower than that of either constituent. On boiling the mixture, a distillate will be obtained containing each of the constituents, in the same proportion, in general, as their relative vapour pressures.

These conclusions have been confirmed by the experimental work of Regnault.

Class II.—When the liquids are partially miscible it is found that each liquid lowers the vapour pressure of the other, and, consequently, the vapour pressure of the mixture is less than the sum of the vapour pressures exerted by the separate constituents. If the liquids are not very soluble in one another, the boiling-point of the mixture will be lower than that of either constituent. This is approximately the same case as previously considered in Class I. If, on the other hand, the mutual solubility of the liquids be great, each liquid will lower the vapour pressure of the other to a considerable extent, and although the boiling-point of the mixture is still generally lower than that of either constituent, yet it may be the same as (or even higher than that of the more volatile liquid present.

On boiling a mixture of liquids which are only partially miscible, a distillate will be obtained containing each of the constituents, and both the boiling-point of the mixture and the composition of the distillate will remain constant as long as two layers of liquid are present, since each solution exerts its own vapour pressure. The solution with the higher vapour pressure will, of course, vaporise the more rapidly of the two. When one of the layers has completely vaporised, the boiling-point of the mixture, and the composition of the distillate, will gradually change, until, in general, the liquid which is present in larger quantity in the remaining layer finally distils in a state of purity. The solution with the higher vapour pressure will not necessarily disappear first, if it be present in relatively large amount.

The work of Konowalow on the vapour pressures of mixtures of different alcohols, etc., with water has supplied valuable data relative to mixtures of this—(and the next)—class.

Class III.—When the liquids are miscible in all proportions the vapour pressure of the mixture is less than the sum of the vapour pressures exerted by the separate constituents. The boiling-point of such a mixture may be higher than that of the higher boiling constituent, or lower than that of the lower boiling constituent or it may lie between the two.

Three special cases arise when mixtures of this class are distilled. It may happen that, when the liquids are mixed in certain proportions, the vapour pressure of the particular mixture is higher than that of either constituent, and also higher than that of any other mixture of the two liquids. In this case the mixture cannot be separated into its constituents by fractional distillation, for, on repeated distillation, a distillate will be obtained approximating more and more closely to the mixture which possesses the highest vapour pressure, and, therefore, the lowest boiling-point.

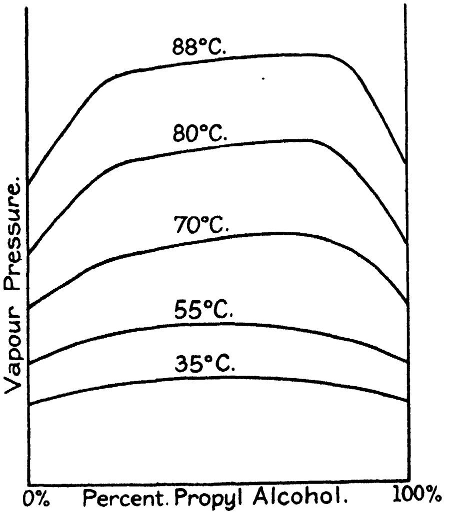

Fig. LXX.

In Fig. LXX. the vapour pressures of different solutions of propyl alcohol and water are plotted, isothermally, against the corresponding alcoholic concentrations expressed as percentages. It will be observed that each of the curves shows a maximum value for the vapour pressure, corresponding, at each temperature, to a particular proportion between the two constituents.

The second case occurs when the vapour pressure of any mixture always lies between those of the constituents, the boiling-point possessing, similarly, an intermediate value. In this case the mixture can be separated more or less completely by fractional distillation; the more volatile constituent being obtained in a nearly pure state in the first portions of the distillate, while the less volatile constituent distils last. Fig. LXXI., which gives the vapour pressure curves for mixtures of methyl alcohol and water, at several temperatures, is illustrative of this second case.

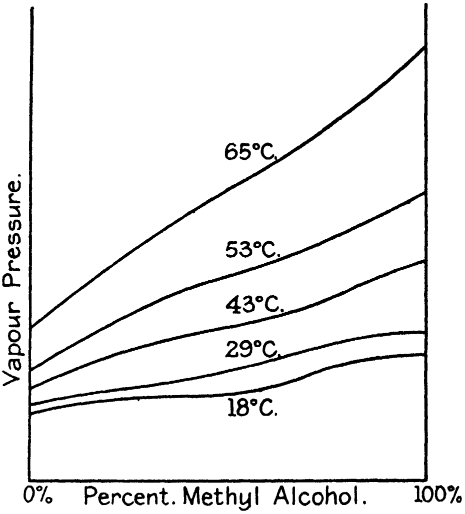

FIG. LXXI.

Similar curves for mixtures of ethyl alcohol and water are shown in Fig. LXXII. Although these curves approximate to the second case, it will be observed that they exhibit a maximum value of the vapour pressure corresponding at, say, 80° C. to a concentration of about 98·4 per cent. alcohol. Thus, strictly speaking, they resemble the curves shown in Fig. LXX.—and repeated distillation of a dilute aqueous solution of ethyl alcohol will not yield a distillate containing more than 98·4 per cent. alcohol, since, at this concentration, the vapour pressure of the mixture is a maximum.

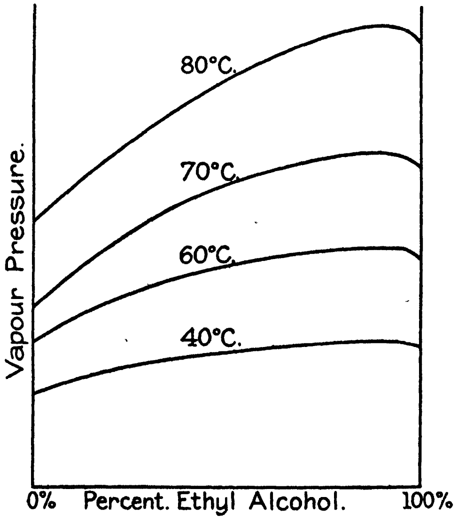

FIG. LXXII.—Ethyl Alcohol and Water.

Lastly it may happen

that, when the liquids are mixed in certain proportions, the vapour pressure of the mixture is lower than that of either constituent, and also lower than that of any other mixture of the two liquids. In this case, as in the first, the mixture cannot be separated into its constituents by fractional distillation; for repeated distillation will yield a *residue* approximating more and more closely to the mixture which possesses the lowest vapour pressure, and, therefore, the highest boiling-point. This last case is illustrated in Fig. LXXIII. which gives the vapour pressure curves for mixtures of formic acid and water.

Summarising the results obtained in these three cases we may state that mixtures whose vapour pressure curves exhibit maxima or minima cannot be separated by fractional distillation, whereas such separation is possible when maxima or minima are absent.

Liquid mixtures with constant boiling-points were originally regarded as definite chemical compounds, but that this conception is erroneous is shown by the fact that the composition of such constant-boiling mixtures varies with the pressure under which distillation is effected (*vide* § 55).

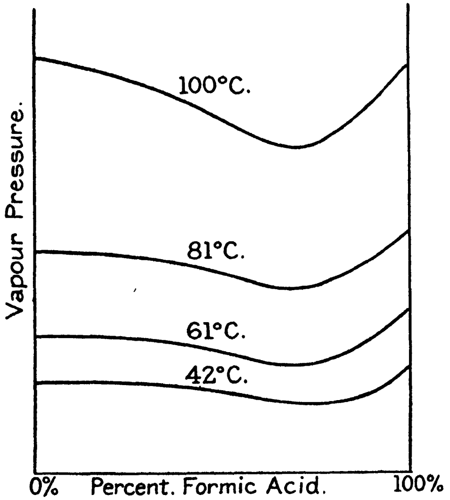

Fig. LXXIII.

85. The Dynamical State of Molecules in Solution.—We must conclude this chapter with a word of caution.

It has been seen that many of the laws which apply to dilute solutions are identical with those which are applicable to gases, and it might therefore be concluded that the dynamical condition of the molecules of a solute is similar to that of the molecules of a gas.

When, however, it is recollected that the molecules of a gas, at the ordinary density, are relatively very far apart, and that, in consequence, the time during which the molecules are within the sphere of action of other molecules is very small compared with the time during which they are moving freely about, it will be realised that such a conclusion must be entirely incorrect.

For the molecules of a solute are *not* scattered throughout an otherwise empty space, *but are disseminated amongst the molecules of* *the solvent*, and, consequently, intermolecular forces are brought into play which cannot be neglected. Indeed, as was pointed out in § 76, the tendency of the solute to dissolve is due to the mutual affinity which exists between the solute and the solvent. The conception of the quasi-gaseous state of a dissolved substance (§ 75) is undoubtedly convenient, but the analogy between the behaviour of the molecules of a gas and the molecules of a solute in a dilute solution must not lead us to regard such phenomena as osmotic pressure and gaseous pressure as identical in nature. We have seen that the pressure exerted by a gas can be explained as arising from the bombardment of its molecules on the walls of a containing vessel, but we are ignorant of the true cause of osmotic pressure. Even at moderate concentrations the gas laws cease to be applicable to substances in solution, and the "gas-analogy" hypothesis, consequently, fails. Many alternative hypothesis have been proposed to account for the phenomenon of osmotic pressure, but, so far, no satisfactory theory has been attained.

CHAPTER VIII.

CAPILLARITY.

86. The Surface-Tension of Liquids.—The existence of internal molecular cohesive forces in liquids gives rise to the phenomenon of surface-tension. Before, however, discussing the nature of these internal forces, it will be convenient to consider, in some detail, the experimental evidence upon which our knowledge of the surface-tension of liquids is based.

Many well-known phenomena show that the surface of a liquid behaves as if it were a thin stretched elastic membrane. This behaviour of a liquid surface may be readily demonstrated by means of the following simple experiments.

Experiment XXXIX.—Fasten a small piece of cotton to the middle of a thin silver plate by means of a minute fragment of sealing wax. Carefully lower the silver plate upon the surface of some water in a basin, and then gently drop the cotton upon the plate. It will be observed that the silver plate remains floating upon the water, and that the latter is depressed to a lower level beneath the plate than that of the remainder of the liquid surface, the depression being readily seen at the edge of the plate (Fig. LXXIV.). By gently tapping the silver plate with a straw, it may be made to bob up and down like a cork. If, however, the plate be pushed through the liquid surface it sinks to the bottom. A thick plate of silver will, of course, break through the surface, and sink, under its own weight.

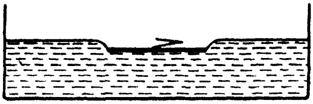

FIG. LXXIV.

As an alternative experiment a dry steel needle may be floated upon water by placing the needle very gently on the surface. It should be noted that the densities of silver and steel are, respectively, 10·5 gms./c.c. and 7·8 gms./c.c.

The surface of the water thus behaves like a very thin elastic membrane, and can support a moderate pressure without rupture. It is for this reason that a water-beetle, for example, can run across a pond, for each leg merely produces a small dimple, the pressure being insufficient to break through the surface.

Experiment XL.—Take an ordinary camel's hair brush and observe that the hairs are separate from one another. On immersing the brush in water the wet hairs still remain separate, but they cling together when the brush is taken out of the water, owing to the contraction of the liquid *surface.*

Experiment XLI.—Allow water to drip very slowly from a vertical glass tube of about 0·5 cm. internal diameter. The drops form gradually at the end of the tube and increase in size until the tension in the liquid surface can no longer support the weight. It will be observed that the drops always attain the same size before breaking away from the tube. Larger drops may be obtained by diminishing the effect of gravity by allowing the drops to form in a liquid of nearly the same density (Fig. LXXV.). Thus drops of carbon disulphide may be formed in an aqueous solution of zinc sulphate of slightly lower density, and the shape of the drops, as they increase in size, more readily observed. The carbon disulphide should be coloured by the addition of a small quantity of iodine, and the zinc sulphate solution should be contained in a flat-sided vessel, with faces of uniform thickness, to avoid apparent distortion in the shape of the drops. It will be seen that a narrow neck forms just before the drop breaks away, and that this neck is drawn out by the falling drop into a small cylinder which gathers itself into the little subsidiary droplet which falls just after the main drop. In the same manner drops of olive oil may be formed in a mixture of ethyl alcohol and water. If the glass tube be bent round (Fig. LXXV*a*.), a lighter liquid may be discharged into a heavier one, and ascending drops and droplets obtained.

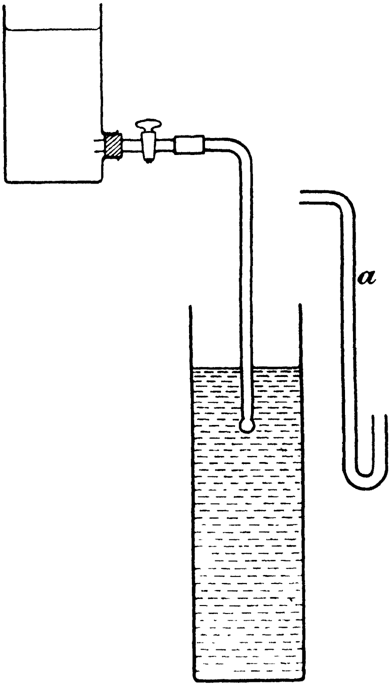

FIG. LXXV.

If, now, a very thin sheet of india-rubber be stretched over a large wooden ring, and water poured in, the rubber gradually stretches under the increasing weight, and it will be observed that, initially, the shape is almost identical with that assumed by a liquid drop. When a sufficient quantity of water has been added a neck forms, but this neck does not readily draw out and break as in the case of a liquid, for the tension in the india-rubber *increases* with the amount of stretching, whereas, in a liquid film, the tension is practically *independent* of the stretching, until the thickness of the film is reduced to about 5×10^{-6} cms., after which the tension rapidly diminishes (see Experiment XLV., and also § 108).

Experiment XLII.—Blow a small bulb at the end of a short piece of glass tube, and a larger bulb nearer the middle of the tube. Close the open end of the tube with a cork through which is inserted a thin wire, about 10 cms. in length, soldered to a plane wire frame (Fig. LXXVI.). A sufficient quantity of mercury must be poured into the small bulb to just prevent the wire frame pushing upwards through the surface of some water in a cylinder when the apparatus is completely immersed, after which the cork is securely fixed, and coated with a thin layer of shellac.

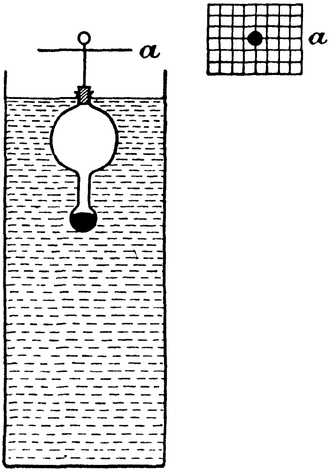

FIG. LXXVI.

When the apparatus is immersed in water, the liquid surface behaves like a very thin elastic membrane, and supports the upward pressure of the wire frame, so that the apparatus floats with the frame just submerged. If, however, a corner of the wire frame be raised out of the water, the frame jumps up, and the apparatus floats with the frame in the air (Fig. LXXVI.). A moderate weight must now be placed upon the frame in order to sink it again to the surface of the water. This experiment is analogous to Experiment XXXIX. in which the surface of the water supported a *downward* pressure.

The motion of the index in an ordinary alcohol minimum thermometer shows that the surface of the alcohol can, similarly, sustain a small pressure without rupture.

Experiment XLIII.—Pour some water from a beaker down a long glass rod into a narrow-necked bottle. The surface of the water on the wet rod forms, in effect, a tube, the tension in the surface preventing the water from escaping.

Experiment XLIV.—Take a plane wire ring with a thin silk thread tied loosely across it. Dip the ring into some soap solution, and then remove it, so as to obtain a soap film stretched over the ring. It will be observed that the silk thread can move about freely in the film, but that if the latter be broken on one side of the thread, by touching the film with a hot wire, the thread is pulled out into an arc of a circle, the remaining portion of the soap-film assuming the least possible area (Fig. LXXVII*a*.). Several shorter pieces of thread may, similarly, be tied loosely around the wire ring, the portions of the film between the threads and the wire being subsequently broken (Fig. LXXVII*b*.). Again, a loop of silk thread may be moistened with the soap-solution and carefully placed on the soap-film on the wire ring. On breaking the film inside the loop with a hot wire, the thread is pulled out into a circle (Fig. LXXVII*c*.), the area of the circle being greater than that of any other plane figure with the same perimeter, and, consequently, the area of the remaining soap-film being a minimum. If a piece of wire be now passed through the loop, the latter may be moved about in the film without losing its circular form, such movement, of course, causing no change in the area of the surrounding soap-film.

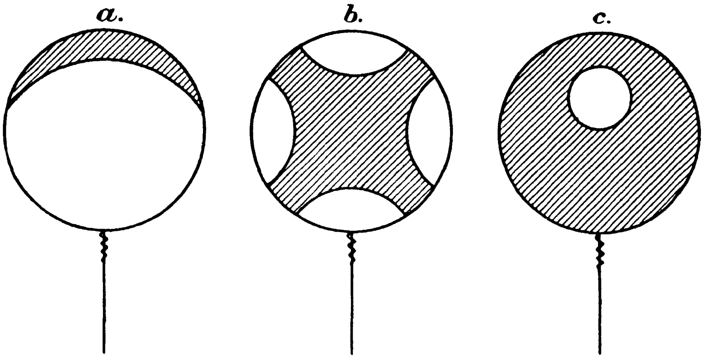

FIG. LXXVII.

Experiment XLV.—Take a plane wire ring, such as that used in the preceding experiment, and dip it into some soap-solution. Remove the ring and hold it in a vertical position, so that the adhering soap-film may drain. The upper portion of the film will thus become thinner than the lower, and will soon show the colours exhibited by very thin films. Yet in spite of the unequal thickness of the film, the tension must be the same throughout, since the film is in equilibrium. The tension in the upper portion of the film must, actually, be very slightly greater than that lower down, in order to support the weight of the film, but this difference in tension is so small that it may be treated as sensibly negligible. In the case of a stretched elastic membrane, such as india-rubber, it must be noted that the tension *increases* with the amount of stretching, and, *cæteris paribus*, equilibrium would not be attained if one portion were stretched thinner than an adjoining portion.

Experiment XLVI.—Bend a copper wire so as to form three sides of a rectangle, ABCD, and rest a thin straight wire, EF, across AB and CD, parallel to BC (Fig. LXXVIII.). Attach a piece of thread, KLM, to the movable wire EF, and, while holding the thread at L, dip the wire frame into soap-solution, and then remove it, thus obtaining a soap-film stretched over GBCH. In order to maintain this soap-film in equilibrium, when the wire frame is held in a horizontal plane, a certain pull must be applied to the thread at L, and if this pull be relaxed the film will contract, and the movable wire EF will slide along AB and CD until it reaches BC.

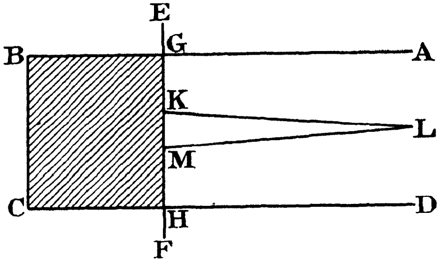

Fig. LXXVIII.

87. Definition of Surface Tension.—In the preceding experiment, the movable wire EF (Fig. LXXVIII.) will be in equilibrium when the force, F, which is applied at right angles to its length is equal to the tension exerted by both faces of the liquid film. It should be noted that the tension exerted by the liquid must be at right angles to EF, since a fluid cannot permanently support an applied tangential or shearing stress, however small the magnitude of the latter. If, then, T be the tension per unit length due to the liquid film, we have—

$$F = 2 . GH . T.$$

T is defined as the *surface tension* of the liquid.

88. Surface Energy.—It can readily be shown that the potential energy possessed by a liquid, as a result of surface tension, is equal to the product of the surface tension and the area of the liquid surface. Thus, if the movable wire EF (Fig. LXXVIII.) be pulled out through a distance x, the work done is $F . x$, and this must equal the increase in potential energy of the liquid film. Since the corresponding increase in the area of the film is $2 . x . GH$., the increase in potential energy per unit increase of area is $\frac{F . x}{2 . x . GH}$.

But $F . x = 2 . x . GH . T$.

Whence the increase in potential energy per unit increase of area is $\frac{2 . x . GH . T}{2 . x . GH}$; i.e. T.

Similarly, if the movable wire slide back along AB and CD until it reaches BC, the work done *by* surface tension, and, therefore, the decrease in potential energy of the film, is $2 . BE . GH . T$; i.e. T × (area of film).

89. The Shape of Bubbles and Liquid Drops.—Since a mechanical system is in stable equilibrium when its potential energy is a minimum, it follows that a drop of liquid, when enacted upon by external forces, must be a perfect sphere, the spherical form possessing the smallest surface for a given volume.

Thus, as was shown by Plateau, if a quantity of oil be placed in a mixture of alcohol and water of the same density, the potential energy due to gravity will be unaffected by variations in the shape of the oil, and, consequently, the oil will assume a spherical shape, the area of the surface, and the potential energy due to surface tension, being then a minimum.

Experiment XLVII.—Introduce some olive oil into a mixture of alcohol and water of the same density, contained in a flat-sided glass vessel, and observe the spherical shape assumed by the oil. The density of the lower portion of the mixture of alcohol and water may conveniently be made slightly greater, by discharging a very small quantity of water at the bottom by means of a pipette, and the density of the upper portion may be reduced, by the addition of a little more alcohol. The oil will then float in the middle of the mixture. If the contents of the vessel be agitated, the oil may be broken up into a number of globules, all of which will be perfect spheres.

By introducing a disc attached to an axle the oil may be made to adhere to the disc, if the latter be previously smeared with oil, and, on rotating the axle and disc, the sphere of oil will also rotate. On increasing the speed of rotation, the sphere of oil becomes flattened at its poles, and, with a further increase in the speed, a ring of oil breaks off, which contracts again on to the inner sphere if the speed be reduced, but which breaks up into a number of separate spheres if the speed of rotation be sufficiently increased.

Instead of employing olive oil and a mixture of alcohol and water it is more convenient to form spheres of orthotoluidine in water. At a temperature of 24° C. orthotoluidine and water possess the same density; orthotoluidine being less dense than water at higher temperatures, and denser than water at lower temperatures. If, then, a globule of orthotoluidine be placed in a flat-sided glass vessel containing cold water, it will rest upon the bottom of the vessel as a flattened drop, but, on gradually raising the temperature of the water, by immersing the vessel in a larger one containing hot water, the drop will change its shape; becoming perfectly spherical at 24° C. On raising the temperature still higher, the globule of orthotoluidine floats up, and becomes flattened at the surface of the water.

Experiment XLVIII.—Blow a soap-bubble and observe that it is spherical. In this case the weight of the soap-bubble is so small that the effect of gravity is practically negligible, and, in consequence, the bubble assumes the form in which the potential energy due to surface tension is a minimum.

When a drop of liquid is acted on by external forces its shape is determined by the condition that the *total* potential energy must be a minimum. Thus, in the case of a drop of liquid resting upon a horizontal solid surface which it does not wet, if the drop be sufficiently small its shape will be approximately spherical, for the potential energy due to gravity will be negligible compared with that arising from surface tension. In the case of a large drop, however, the potential energy due to gravity has the predominant influence, and, consequently, the drop forms a flat pool, so that its centre of gravity may be low.

Experiment XLIX.—Scatter some mercury on a glass plate and observe that the small drops are practically spherical, whereas when a larger quantity of mercury is poured out it collects into a flattened circular pool (Fig. LXXIX.). Drops of water may, similarly, be formed upon a glass plate, if the latter be covered with a thin layer of grease to prevent adhesion between the water and the glass. It will be shown, subsequently, that the depth of all large drops of a given liquid is the *same*, and that by measuring this depth the surface tension of the liquid can be ascertained.

FIG. LXXIX.

When a liquid falls freely, in a vacuum, the effect of gravity on its shape will be eliminated and it will, therefore, assume a spherical form. Approximately the same form is taken up by a rain-drop falling through the air, since the viscosity of the latter medium is small.

When molten lead is poured in a fine stream from the top of a shot tower, the stream breaks up into small drops which, similarly, acquire a spherical shape. This process is employed in the manufacture of leaden shot.

90. The Surface Tensions of Different Liquids.—A number of simple experiments may be performed to show that different liquids possess different surface tensions.

Experiment L.—Fill a porcelain dish with water, and sprinkle the surface of the latter with powdered charcoal (Fig. LXXX. *a*). This may be done most readily by placing the charcoal in a small muslin bag, and shaking the latter over the water. Touch the surface of the water in the middle with a glass rod which has been dipped in some soap solution. The water surface immediately contracts, carrying the charcoal up to the side of the dish, while the surface of the soap solution is stretched out, its tension being less than that of pure water (Fig. LXXX. *b*).

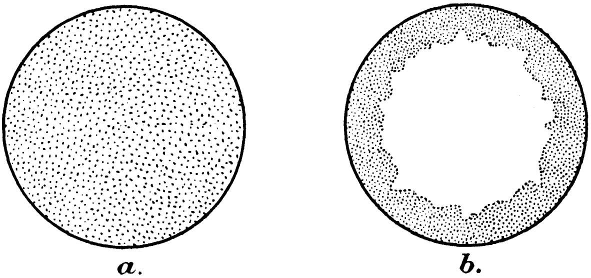

FIG. LXXX.

Experiment LI.—Pour a shallow layer of water, which may conveniently be coloured with magenta or indigo, into a flat-bottomed porcelain dish. Touch the water with a glass rod which has been dipped into alcohol, and observe that the liquid moves away from the part touched, leaving the bottom of the dish at that place dry. This action is due to the surface tension of water being greater than that of alcohol, or of a mixture of alcohol and water, the liquid being, in consequence, carried away in the direction of the greater tension.

The phenomenon of " tears in wine " is, similarly, due to the difference in surface tension between alcohol and water. If a fairly strong wine, such as port, be placed in a wine-glass, the sides of which are moistened with the wine, it will be observed that the liquid gradually rises up the sides of the glass and collects in drops, or "tears," which then trickle down again. In this case the thin layer of wine on the side of the glass loses its alcohol by evaporation more rapidly than the wine below, the latter being less exposed to the air. The surface tension of the layer on the side of the glass therefore becomes greater than that of the wine below, since the surface tension of water is greater than that of alcohol. In consequence, more wine is pulled up the sides and drops gradually form, which, when they become sufficiently heavy, break away and trickle down again.[1]

Experiment LII.—Take a wine-glass and half fill it with port, or with a mixture of about one part of alcohol and two parts of water, which may be coloured with magenta. Wet the sides of the glass with the liquid and observe the formation of the "tears."

Experiment LIII.—Take the apparatus used in Experiment XLII., and immerse it in water so that it floats with the wire frame just submerged. Pour a few drops of ether into a beaker, and then pour some of the *vapour* of the ether upon the surface of the water. The frame almost immediately jumps up out of the water, owing to the ether condensing upon the surface of the latter and diminishing the surface tension.

91. The Influence of Temperature on Surface Tension.—The surface tension of any liquid diminishes if the temperature be raised, becoming zero at the critical temperature. It follows, therefore, in accordance with Le Chatelier's theorem (Appendix B), that a liquid film when stretched adiabatically becomes cooler.

The diminution in surface tension with rise in temperature may be shown by the following simple experiment.

Experiment LIV.—Pour a shallow pool of a liquid, say water, on a horizontal thin metal plate, and sprinkle the surface of the water with powdered charcoal. On applying heat, by means of a small flame, to the centre of the lower surface of the plate, the water immediately above becomes heated, and its surface tension diminishes, as is shown by the surface of the surrounding colder water contracting, thereby carrying the charcoal away from the centre towards the edges of the pool. Instead of employing a metal plate, a shallow layer of water may be poured into a flat-bottomed porcelain dish, and sprinkled with powdered charcoal, the water being then heated at one place either by converging the rays of the sun upon its surface by means of a convex lens, or by holding a piece of hot metal close to the surface.

92. The Relation Between the Curvature of a Liquid Surface, the Surface Tension, and the Pressure.—Consider, for example, a spherical

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[1] Reference is made to this phenomenon in Proverbs xxiii. 31: "Look not thou upon the wine when it is red, when it giveth his colour in the cup, *when* it moveth itself aright."

drop of liquid. It is evident, since the curved surface of the liquid is in a state of tension, that the pressure inside the drop must be greater than the external pressure. Thus let R be the radius of the drop, P the difference between the internal and external pressures, and T the surface tension. If we imagine the drop divided into two hemispheres, and consider the equilibrium of one of them (Fig. LXXXI.), we have—

$$P \, . \, \pi R^2 = T \, . \, 2\pi R,$$

since the pressure on the plane face of the hemisphere, due to the liquid in the other hemisphere, is balanced by the surface tension acting round its circumference.

Whence $$P = \frac{2 \, . \, T}{R}.$$

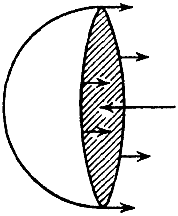

Fig. LXXXI.

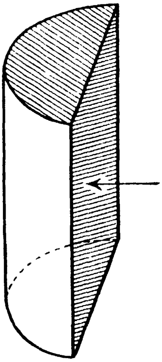

Fig. LXXXII.

Similarly, in the case of a spherical soap-bubble, which has *two* surfaces in a state of tension, we have—

$$P = \frac{4 \, . \, T}{R},$$

the radii of the inner and outer surfaces being sensibly the same.

Again, in the case of a cylinder of liquid, we may consider a portion of the liquid lying between two planes at right angles to the axis of the cylinder at a distance H apart. If we imagine this portion divided into two halves by a plane passing through the axis of the cylinder, and consider the equilibrium of one of these halves (Fig. LXXXII.), we have, on resolving perpendicularly to the dividing plane—

$$P \, . \, 2R \, . \, H = T \, . \, 2H,$$

where P is the difference between the internal and external pressures, R the radius of the cylinder, and T the surface tension.

Whence $$P = \frac{T}{R}.$$

In the case of a cylindrical soap-film, we have—

$$P = \frac{2 . T}{R}.$$

The general formula for a curved liquid surface may be deduced in the following manner :—

Consider a sufficiently small rectangular element, ABCD, of the liquid surface (Fig. LXXXIII.).

Let this element be in equilibrium under the surface tension, T, and a difference of pressure, P, between the two sides of the surface.

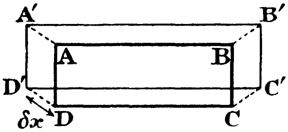

Fig. LXXXIII.

Let the element be displaced outwards through a small distance, δx, so that each point of the element moves normally to the surface, and let the new position of the element be A′B′C′D′. Then, since the forces acting on the element are in equilibrium, it follows from an elementary mechanical principle, that the algebraical sum of the work done by the forces during the displacement, δx, is zero.

Now the work done *by* the pressure during the displacement is P × area ABCD × δx, and the work done *against* surface tension is T × increase in the area of the surface;

i.e. $$T \times \{\text{area } A'B'C'D' - \text{area } ABCD\}.$$

Whence—

$$P \times \text{area } ABCD \times \delta x - T \times \{\text{area } A'B'C'D' - \text{area } ABCD\} = 0.$$

Since the element ABCD is a portion of a curved surface, it can be shown, geometrically, that the lines AB and BC, which are at right angles to one another, can be taken on the surface so that the normals to the surface at A and B intersect in O, and the normals to the surface at B and C intersect in O′, AO and BO′ being the radii of principle curvature of the surface.

When the points O and O′ both lie on the same side of the surface (Fig. LXXXIV.), we have what is termed a synclastic surface ; when, on the other hand, O and O′ lie on opposite sides of the surface (Fig. LXXXV.), we have an anticlastic surface.

In the case of a synclastic surface (Fig. LXXXIV.), we have—

$$\frac{AB}{OA} = \frac{A'B'}{OA'},$$

OAB and OA′B′ being, sensibly, similar triangles.

$$\therefore\ A'B' = AB\,.\,\frac{(R_1 + \delta x)}{R_1},$$

where R_1 is the radius of principal curvature, AO.

Similarly—

$$\frac{BC}{O'B} = \frac{B'C'}{O'B'}.$$

$$\therefore\ B'C' = BC\,.\,\frac{(R_2 + \delta x)}{R_2},$$

where R_2 is the radius of principal curvature, BO′.

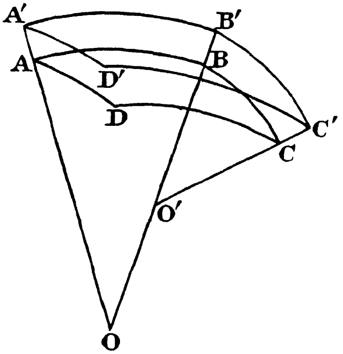

Fig. LXXXIV.

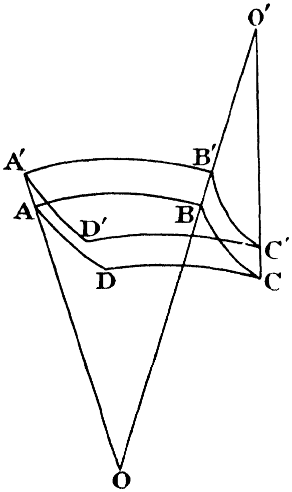

Fig. LXXXV.

Since, in the case of a sufficiently small element, ABCD and A′B′C′D′ are, sensibly, rectangles, we have—

$$\begin{aligned} \text{Area ABCD} &= AB \times BC, \\ \text{Area A'B'C'D'} &= A'B' \times B'C', \\ &= AB\,.\,\frac{(R_1 + \delta x)}{R_1} \times BC\,.\,\frac{(R_2 + \delta x)}{R_2}, \\ &= AB \times BC \times \left(\frac{R_1 + \delta x}{R_1}\right)\left(\frac{R_2 + \delta x}{R_2}\right), \\ &= \text{area ABCD} \times \frac{\{R_1\,.\,R_2 + \delta x\,(R_1 + R_2)\}}{R_1\,.\,R_2}, \end{aligned}$$

the product $\left(\frac{\delta x}{R_1}\right)\left(\frac{\delta x}{R_2}\right)$ being relatively negligible if both $\frac{\delta x}{R_1}$ and $\frac{\delta x}{R_2}$ are sufficiently small.

Whence—

$$P \times \text{area ABCD} \times \delta x - T \times \left\{\text{area ABCD} \times \frac{\{R_1 . R_2 + \delta x(R_1 + R_2)\}}{R_1 . R_2} - \text{area ABCD}\right\} = 0.$$

$$\therefore\ P . \delta x - T . \left\{\frac{\delta x(R_1 + R_2)}{R_1 . R_2}\right\} = 0.$$

$$\therefore\ P = T\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

Similarly, in the case of an anticlastic surface (Fig. LXXXV.), we have—

$$\frac{AB}{OA} = \frac{A'B'}{OA'}.$$

$$\therefore\ A'B' = AB . \frac{(R_1 + \delta x)}{R_1}.$$

Also—

$$\frac{BC}{O'B} = \frac{B'C'}{O'B'}.$$

$$\therefore\ B'C' = BC . \frac{(R_2 - \delta x)}{R_2}.$$

Whence—

$$\begin{aligned}\text{Area } A'B'C'D' &= A'B' \times B'C', \\ &= AB \times BC \times \left(\frac{R_1 + \delta x}{R_1}\right)\left(\frac{R_2 - \delta x}{R_2}\right), \\ &= \text{area ABCD} \times \frac{\{R_1 . R_2 - \delta x\,(R_1 - R_2)\}}{R_1 . R_2}.\end{aligned}$$

Consequently—

$$P \times \text{area ABCD} \times \delta x - T \times \left\{\text{area ABCD} \times \frac{\{R_1 . R_2 - \delta x(R_1 - R_2)\}}{R_1 . R_2} - \text{area ABCD}\right\} = 0.$$

$$\therefore\ P . \delta x - T\left\{\frac{\delta x(R_2 - R_1)}{R_1 . R_2}\right\} = 0.$$

$$\therefore\ P = T\left(\frac{1}{R_1} - \frac{1}{R_2}\right).$$

In general, then, we may write—

$$P = T\left(\frac{1}{R_1} + \frac{1}{R_2}\right),$$

provided the radius of curvature be taken as positive when the corresponding centre of curvature is on that side of the liquid surface where the pressure is greater, and negative when the centre of curvature is on the side where the pressure is less.

In the case of a liquid film, which has *two* surfaces in a state of tension, our general equation becomes—

$$P = 2T\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

The relationship which was previously obtained in the case of a spherical drop of liquid may be readily deduced from the general equation—

$$P = T\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

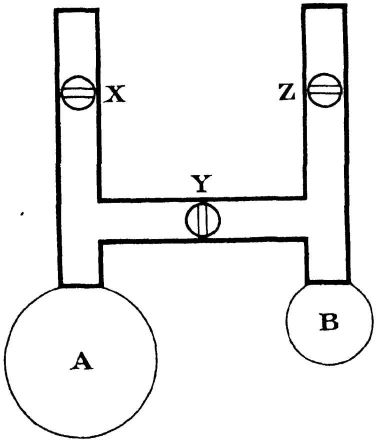

Fig. LXXXVI.

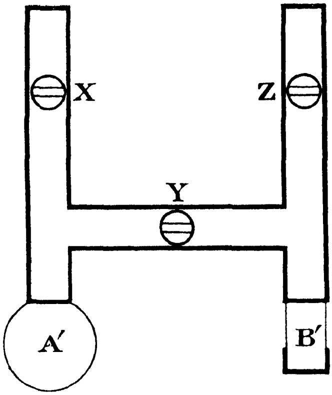

Fig. LXXXVII.

For a sphere, the two radii of curvature, R_1 and R_2, are equal, and, consequently—

$$P = \frac{2T}{R}.$$

Again, in the case of a cylinder of liquid, one radius of curvature is infinite, the other being the radius of the cylinder.

Whence $P = \frac{T}{R}$, as was previously deduced.

Experiment LV.—Blow two soap-bubbles, A and B, of unequal size at the ends of two glass tubes which are controlled by means of taps X, Y, and Z (Fig. LXXXVI.). Since, for a spherical soap-bubble

$P = \frac{4T}{R}$, the pressure inside the smaller bubble will be greater than the pressure inside the larger bubble. Thus, on opening the tap, Y, the bubble B shrinks up and blows out the larger one.

Now replace one of the soap-bubbles by a short cylindrical soap-film, and, with the tap, Y, open, blow in air until the sides of the cylinder neither bulge out nor bend in, but are perfectly straight (Fig. LXXXVII.). On measuring the sphere A′ and the cylinder B′ it will be found that the diameter of the former is exactly double that of the latter. Since the pressures inside the sphere and the cylinder are, in this case, identical, we have $P = \frac{4T}{R} = \frac{2T}{R'}$, and, therefore, $R = 2R'$, where R is the radius of the sphere and R′ the radius of the cylinder.

When there is no difference of pressure between the two sides of a liquid film, i.e. when $P = 0$, we have the relation—

$$\frac{1}{R_1} + \frac{1}{R_2} = 0.$$

Hence $$R_1 = -R_2.$$

Thus the radii of curvature in any two normal sections taken at right angles to one another are equal and on opposite sides of the liquid film, i.e. the *total curvature* of the film is everywhere zero, since, at every point, it is equally curved in opposite directions.

Experiment LVI.—Dip a rectangular wire frame into soap solution, and then remove it, so as to obtain a plane film. In this case the radii of curvature in any two normal sections at right angles to one another are both infinite, and lie on opposite sides of the film. By bending the wire frame an infinite series of surfaces can be obtained for all of which the total curvature is everywhere zero. One such surface is illustrated in Fig. LXXXVIII.

If a piece of wire be twisted into a helix, the ends being bent and fastened to a straight wire passing down the centre, and if the whole wire frame be then dipped into soap solution, and removed, a very beautiful film with a "screw-surface" will be obtained (Fig. LXXXIX.). This film similarly satisfies the relation $R_1 = -R_2$ at every point.

When a film possesses the shape of a surface of revolution, and when there is no difference of pressure between its two sides, the surface is a catenoid.[1]

Thus, consider a plane curve ABC (Fig. XC.). Let the curve revolve about an axis XY in its plane, thus describing a surface of

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[1] The catenary is the curve in which a heavy uniform string hangs when supported at each end, the surface of revolution of a catenary being a catenoid.

revolution. Let O be the centre of curvature of the plane curve at B, and let OB produced intersect XY at O′. Then it can be shown, geometrically, that O and O′ are the two principal centres of curvature of the surface of revolution at B ; OB and O′B being the corresponding radii of principal curvature, i.e. OB = R_1, and O′B = R_2. Since in the case of a liquid film with no difference of pressure between its two sides $R_1 = -R_2$, we have OB = − O′B.

Fig. LXXXVIII.

Fig. XC.

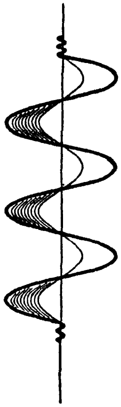

Fig. LXXXIX.

The only curve which fulfils this condition at every point is the catenary, and, consequently, the surface of the liquid film must be a catenoid.

Surfaces of this shape may be obtained experimentally by forming a soap film between two parallel rings, the planes of the latter being at right angles to the line joining their centres.

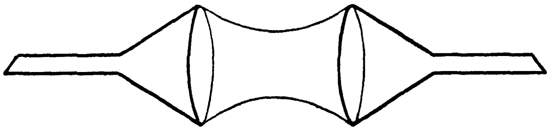

Fig. XCI.

Experiment LVII.—Take two glass funnels and form a soap film between their rims (Fig. XCI.). Since the ends of the funnels are open, the pressure is the same on both sides of the film, and the relation $R_1 = -R_2$ obtains at every point. If the funnels be held with their rims parallel, and with the planes of the latter at right angles to the line joining their centres, the surface of the soap film will be symmetrical about this line, and, consequently, will possess the form of a catenoid.

93. Stability of Cylindrical Films and Liquid Cylinders.—It can be proved that when the distance between the ends of a cylindrical film is less than half the circumference of the ends of the film the internal pressure is diminished if the film begins to develop a waist and bend in, and is increased if the film begins to bulge out, whereas when the distance between the ends of a cylindrical film is greater than half the circumference of its ends the converse is true, the internal pressure in the case of a film that bends in being greater than the internal pressure for a film that bulges out.

This, as was shown by Boys, may be readily demonstrated experimentally in the following manner :—

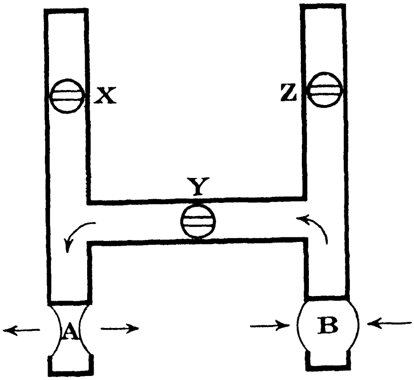

FIG. XCII.

Experiment LVIII.—Take the apparatus employed in Experiment LV. and form two cylindrical films each of length less than the semi-circumference of their ends, one film, A, bending in, and the other, B, bulging out. On opening the tap, Y, air passes from B to A and the two films become more cylindrical, thus showing that the internal pressure at B is greater than that at A (Fig. XCII.). The tubes on which the cylindrical films are formed should, of course, be of equal diameter.

Next repeat the experiment, making the length of each film greater than the semi-circumference. In this case, on opening the tap, Y, air passes in the opposite direction from A to B, so that A shrinks in and shuts itself up while B is blown out still further (Fig. XCIII.).

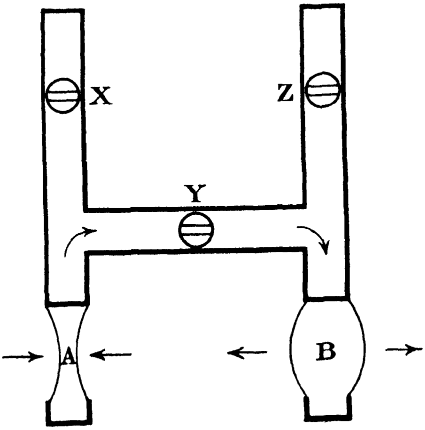

FIG. XCIII.

It is evident from the preceding experiment that a cylindrical film can only be in stable equilibrium provided its length does not exceed its circumference. For if the two films A and B, in Fig. XCIII., be imagined joined together at one end, A would blow air into B and would shut itself up until its sides met, when the film would break up into two separate bubbles. Thus, in the case of a cylindrical film of length greater than its circumference, the slightest constriction at one place leads to a relative increase in the pressure at that place, and air is blown into the wider portions of the film until the sides at the constriction close up and meet one another, the cylinder then breaking into two spherical portions. If, however, the length of a cylindrical film be less than its circumference, the formation of a waist leads to a relative diminution in the pressure at the waist, and consequently, air is blown in from the wider portion of the film, thus tending to restore the cylindrical shape.

Experiment LIX.—Form a soap film between the rims of two glass funnels of equal size, the stem of one funnel being attached to a rubber tube, and the stem of the other closed with a cork. Blow through the rubber tube until the soap film is cylindrical, and then gradually separate the funnels, continuing to blow gently so that the cylindrical form may be maintained. When the length of the cylindrical film approximates to its circumference, the film becomes difficult to control, and, if the length be further increased, a waist suddenly forms nearer one end than the other and shrinks in until the sides meet, the film then breaking into two unequal bubbles.

A liquid cylinder is, similarly, in stable equilibrium only when its length does not exceed its circumference. If a cylinder of greater length be formed it tends to break up into a series of drops. The following experiments illustrate clearly the instability of long liquid cylinders :—

Experiment LX.—Take a flat-sided glass vessel, such as was employed in Experiment XLI., containing some carbon-disulphide coloured with iodine, and nearly fill the rest of the vessel with an aqueous solution of zinc sulphate of slightly lower density than the carbon-disulphide. Dip a glass tube into the carbon-disulphide at the bottom of the vessel and let it fill. The carbon-disulphide will rise inside the glass tube to nearly the same level as the zinc sulphate solution outside. On suddenly drawing the tube out of the liquid a cylinder of carbon-disulphide will be left behind which will break up into spherical drops, small subsidiary droplets being produced from the necks which form at those places where partition occurs.

Experiment LXI.—Soften a glass tube in a gas flame and draw it out into a fine thread. On dipping a length of the glass thread into, say, water or olive oil, and then removing it, the liquid, which at first is cylindrical, gathers itself up into alternate drops and droplets along the thread.

A spider's web illustrates the same instability. When examined under a microscope the radial threads are seen to be smooth, whereas the threads which are spun round and round are covered with alternate large and small beads of sticky liquid, the larger beads being about one four-hundredth of an inch apart. In spinning the web the spider wets it with the sticky liquid which then breaks up into the drops and droplets. A wet spider's web, strung with small beads of water, furnishes another beautiful example of the instability of long liquid cylinders.

It should be noted that the instability of a long liquid cylinder may be overcome by viscosity in the case of very viscous liquids. Thus, in the preceding experiment, the semi-molten glass, on account of its high viscosity, could be drawn out into a long cylindrical thread without rupture. Similarly, any very viscous liquid—such as syrup—can be drawn into threads of considerable length.

94. Liquid Jets.—When a jet of water escapes through a circular aperture it forms, at first, a long liquid cylinder, but the latter being unstable soon develops necks and bulges, and then breaks up into separate drops. This is clearly seen if an instantaneous photograph of such a jet be taken by the light of an electric spark. The appearance of a narrow jet of water falling from a circular opening, when photographed in this manner, is illustrated in Fig. XCIV. The small subsidiary droplets are produced, as usual, from the narrow necks which are drawn out when the larger drops break away. A jet of water will, in general, break up irregularly into drops of unequal sizes and at different distances apart, owing to small accidental disturbances which are imparted to the nozzle from which the water escapes, and which impress slight necks upon the liquid cylinder. Many of the drops will bounce together and rebound, and, in consequence, the jet scatters irregularly over any surface upon which it falls. If, however, a regular series of disturbances be imparted to the nozzle, the necks will be impressed upon the issuing cylinder of water at equal distances apart, and the jet will break up into a series of equal, equidistant drops, which will follow one another in the same path.

FIG. XCIV.

Experiment LXII.—Allow a jet of water to issue from a small nozzle which is supported, at a convenient angle, on the sounding box of a tuning-fork, and let the water fall upon a sheet of paper placed on the floor. The jet will initially scatter irregularly over the paper, but on setting the tuning-fork in vibration the water will immediately gather together, and the drops will fall with a regular pattering sound.

Experiment LXIII.—Focus the light from an electric lantern so that it passes through a small hole in a fixed wooden disc and then diverges and falls upon a screen. Interpose the apparatus used in the preceding experiment between the screen and the disc so that a shadow of the jet and tuning-fork is thrown upon the screen. A second wooden disc, with a number of equidistant small holes near its circumference is then rotated rapidly, by means of an electric motor, close behind the fixed disc, so that the holes in the rotating disc may pass opposite the hole in the fixed disc, thus producing an intermittent illumination of the screen. Set the tuning-fork in vibration and adjust the speed of the motor until the number of flashes of light per second passing through the hole in the disc is equal to the frequency of vibration of the tuning-fork. The tuning-fork will then appear stationary. Next turn on the jet of water and observe the necks and bulges which are developed in the liquid cylinder, and the separate drops of water, all apparently stationary in the air. If the speed of rotation of the disc be now very slightly reduced, all the drops will appear to be moving slowly forward, and the gradual breaking away of the drops, and the formation of the subsidiary droplets, can be readily observed. Since at the moment the drops break away they are pulled out into a prolate form they will vibrate, under the influence of surface tension, becoming first spherical, and then, through inertia, oblate, the vibrations continuing until damped out by viscosity.

Experiment LXIV.—Allow drops of olive oil to form in a mixture of ethyl alcohol and water of slightly lower density, as in Experiment XLI. Gradually increase the rate of flow and observe the formation of a jet which develops necks and bulges at some distance from the end of the glass tube, and breaks up, further on, into separate drops and droplets. The vibrations of the separate drops may also be observed without difficulty. It should be noted in this experiment, and in the two preceding ones, that the length of the continuous portion of the jet is increased by increasing the rate of flow. The length of the continuous portion is also conditioned by the surface tension and viscosity of the liquid, and by the diameter of the nozzle; the greater the surface tension, and the smaller the liquid viscosity and the diameter of the nozzle, the sooner will the jet break up into drops.

95. Equilibrium of a Solid Surface and two Fluid Surfaces meeting along a Line.—Let Fig. XCV. represent a vertical, central section of a pool of mercury, ABC, resting upon a horizontal glass plate, AC. There are three surface tensions to be considered, viz. that of the surface of contact between the mercury and glass, denoted by T_{12}; that of the surface of contact between the mercury and air, denoted by

T_{23}; and that of the surface of contact between the glass and air, denoted by T_{13}. If we resolve the three surface tensions at A parallel to AC, we have, for equilibrium—

$$T_{12} - T_{13} + T_{23} . \cos \phi = 0,$$

where ϕ is the obtuse angle at which the glass and mercury meet.

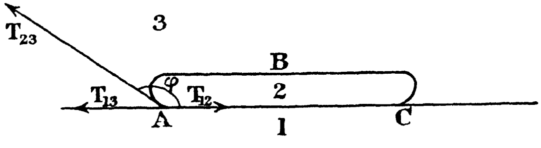

Fig. XCV.

ϕ is usually known as the *angle of contact*; for a freshly formed[1] drop of mercury on glass ϕ has the value 138° 55′.

The angle of contact between mercury and glass may be measured, experimentally, by pouring mercury into a spherical glass flask until the liquid surface, which has convex edges in the lower part of the flask, loses all its convexity and becomes a horizontal plane.

The obtuse angle, ϕ (Fig. XCVI.), between the horizontal surface of the mercury and the tangent plane to the glass globe, at the same level, gives the angle of contact.

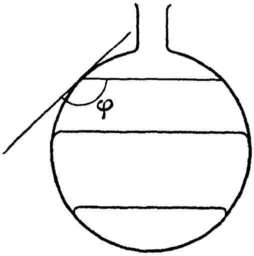

Fig. XCVI.

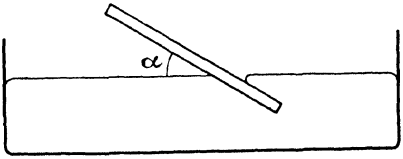

Fig. XCVII.

Experiment LXV.—Dip a clean glass plate into some mercury contained in a basin, and incline the glass plate until the surface of the mercury on one side of the plate is plain (Fig. XCVII.). Measure the angle, α, between the horizontal surface of the mercury and the glass; the supplement of this angle gives the angle of contact.

96. The Spreading of one Liquid over the Surface of Another.—No case is known where three fluid surfaces meeting along a line are in

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[1] The values of the angles of contact found for various liquids vary considerably with the freshness of the surfaces in contact.

equilibrium. Thus a drop of oil will not rest upon clean water, but will spread itself out as a film over the surface. A drop of water will, similarly, spread over the surface of clean mercury. If the surface of the mercury be contaminated with grease, a drop of water may remain floating as a globule upon the surface, but, in this case, it can be shown that the grease has spread over the surface of the water, so that there are no longer three fluid surfaces meeting at the edge of the drop. Since a mechanical system is in stable equilibrium when its potential energy is a minimum, it follows that the spreading of one liquid over the surface of another must be accompanied by a diminution in potential energy.

Thus, in Fig. XCVIII., let a flat drop of liquid, X, be floating upon the surface of another liquid, Y, and let the drop spread out to a small extent, so that the area of contact between X and Y is increased by an amount A. The area of contact between the drop, X, and the air, Z, is also increased by A, and the area of contact between Y and Z is diminished by the same amount.

The resulting diminution in the potential energy is, consequently, $T_{YZ} . A - T_{XY} . A - T_{XZ} . A$, where T_{YZ} denotes the surface tension of the surface of contact between the liquid Y and the air, T_{XY} the surface tension of the surface of contact between the two liquids, and T_{XZ} the surface tension of the surface of contact between the liquid X and the air.

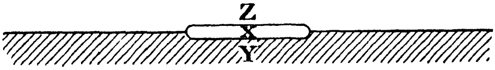

Fig. XCVIII.

In order that the drop, X, shall spread out over the surface of the liquid, Y, the expression $T_{YZ} . A - T_{XY} . A - T_{XZ} . A$ must be positive, i.e. T_{YZ} must be greater than $T_{XY} + T_{XZ}$.

If, however, *each* of the surface tensions were less than the sum of the other two, so that a triangle could be drawn with its sides proportional to T_{YZ}, T_{XY}, and T_{XZ}, the drop would contract and remain floating as a globule on the surface of the other liquid, with three fluid surfaces meeting at the edge of the drop.

As stated previously, no case is known where three fluid surfaces meeting along a line are in equilibrium, for, whatever three fluid media be selected, it is always found that one of the surface tensions is greater than the sum of the other two.

When a small quantity of, for example, olive oil is placed upon the surface of clean water the oil spreads out as a thin film covering the water, for the surface tension of the water-air surface is greater than the sum of the surface tensions for the water-oil and oil-air surfaces.

If now a further small quantity of olive oil be placed upon the surface it will remain floating as a globule, the surface tension of the water-air surface having been reduced by the covering oil film. A film of olive oil, when spread over a water surface, will remain indefinitely in equilibrium, but several cases are known where liquid films break up spontaneously into globules. This phenomenon of the breaking up of films has not, so far, been satisfactorily explained.

Experiment LXVI.—Place a drop of dimethyl aniline upon the surface of clean water. Observe that an irregular-shaped film is at first formed, but that the latter soon becomes ramified and breaks up into separate globules.

97. Interfacial Surface Tension.—The existence of the interfacial surface tension at the boundary surface of two liquids may be readily demonstrated by means of the following experiments:—

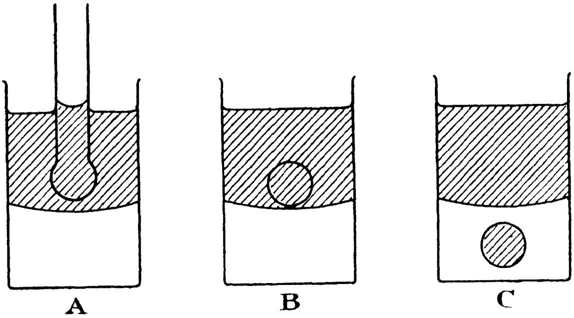

Fig. XCIX.

Experiment LXVII.—Half fill a small beaker with water, and add dimethyl aniline on top of the water until the beaker is nearly full. Next wet one end of an open glass tube with water, and push the tube down through the dimethyl aniline until the end of the tube is just below the surface of the water in the lower half of the beaker. Close the upper end of the tube with one finger and raise the tube until its lower end is well above the boundary surface of the dimethyl aniline and water. On gradually allowing air to enter the tube, by raising the finger, a globule of dimethyl aniline enclosed in a skin of water will be formed (Fig. XCIX. A), and on carefully withdrawing the tube from the upper surface of the dimethyl aniline the globule will become detached and will sink to the boundary surface between the two liquids (Fig. XCIX. B).

After resting upon the boundary surface for a few moments, the lower portion of the skin of water which surrounds the globule of dimethyl aniline merges into the water beneath, and the boundary surface between the two liquids now passes round over the top of the globule. Owing to the interfacial surface tension, the boundary surface at once flattens out to its original shape, thereby driving the globule of dimethyl aniline down into the denser water below (Fig. XCIX. c).

The globule of dimethyl aniline then rises to the boundary surface, and, after a few moments, the upper portion of the globule merges into the dimethyl aniline above, so that the boundary surface now passes round beneath the globule. The interfacial surface tension, therefore, again comes into play, assisted, now, by the action of gravity, and the boundary surface flattens once more to its original shape, the globule merging back into the liquid above.

By employing a small pipette fitted at the upper end with an india-rubber teat, and alternately drawing in small quantities of dimethyl aniline and water, it is possible, with care, to project a number of globules of water, each enclosed in a skin of dimethyl aniline, into the water at the bottom of the beaker. These will then rise to the boundary surface between the two liquids, and, after a few moments, the drops of water will be driven upwards into the lighter dimethyl aniline above.

Experiment LXVIII.—Drop some thin pieces of copper wire into the layer of dimethyl aniline floating upon water used in the preceding experiment. The pieces of wire will sink through the dimethyl aniline and remain floating at the boundary surface. If the wires be now pushed through the interface, by means of a glass rod, they will sink to the bottom of the beaker.

98. Methods of Measuring Surface Tension; The Capillary Tube Method.—A number of different methods have been experimentally employed for the measurement of surface tension. Several of the more convenient of these methods will now be described in detail.

The Capillary Tube Method.—Experiment LXIX.—Draw out a number of glass capillary tubes of 1 mm. and less internal diameter. Seal up both ends of the capillaries until required, so as to exclude dust and grease. When ready to make a measurement, fasten several of the tubes with sealing-wax to a small block of wood as nearly as possible at right angles to its lower surface, and, after cutting off the ends of the tubes, rest the block of wood on a beaker containing clean tap-water.[1]

Before reading the height of the water meniscus in each tube, the apparatus must be tilted, so that the water may rise higher in the tubes than its final position, thus ensuring the tubes being thoroughly wetted with the water. On no account must water be sucked up

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[1] Distilled water should not be employed, as it is frequently contaminated with a trace of grease.

the tubes, as doing so will almost certainly lead to contamination of the surface.

Read the height of the lowest part of the concave meniscus in each of the vertical capillary tubes by means of an accurately levelled cathetometer.

The level of the surface of the water contained in the beaker cannot be read with accuracy through the glass, and a metal rod, with pointed ends, is therefore clamped with its lower end just touching the water surface, while its upper end projects above the edge of the beaker. The height of the upper end of the rod is read after measuring the level of the water in the capillary tubes, and the length of the rod is also determined. The capillary elevation in the tubes is thus obtained.

An ink mark is next made at the height to which the water rises in each tube, and the tubes are then neatly cut across at the marked points and their diameters measured by means of a vernier microscope. The diameter of each tube should be measured in two directions at right angles to one another in order to eliminate any small error due to irregularity in the bore. It should be noted that no assumption is made that the tubes are of uniform diameter throughout their length, for the capillary elevation is merely dependent upon the diameter at the point occupied by the water meniscus. In measuring the diameter of a tube, the latter may, conveniently, be fixed in a clamp; a piece of white paper being slipped over the tube to improve the illumination.

A correction must be applied to the height in order to allow for the liquid above the lowest part of the meniscus. For small round tubes, and for liquids that wet glass, the liquid meniscus is sensibly hemispherical, so that this volume of liquid is practically equal to the difference between the volumes of a cylinder of height r and radius r and a hemisphere of radius r, where r is the radius of the capillary tube. Since this difference in volume is equal to $\frac{1}{3}\pi r^3$, the height measured to the lowest part of the meniscus must be increased by $\frac{r}{3}$.

The experimental results should be recorded in the following manner :—

$$\left.\begin{array}{ll}\text{Height of upper end of rod} & = \ldots \text{ cms.}\\ \text{Length of rod} & = \ldots \text{ cms.}\end{array}\right\}$$

Level of Liquid.		Difference of Level.	Diameter of Tube.			Corrected Height of Liquid.	Surface Tension.
Inside Tube.	Outside.		1.	2.	Mean.		
... cms.	... cms.	h cms.	... cm.	... cm.	d cm.	$\left(h+\frac{d}{6}\right)$ cms.	T. dynes/cm.

The surface tension, T, in the last column, is calculated from the relation—

$$T = \frac{d \cdot \left(h + \frac{d}{6}\right) \cdot \rho \cdot g}{4},$$

where ρ is the density of water at the temperature of the experiment, and g the acceleration of gravity.

The mean value of T is then calculated from the values obtained with the several capillary tubes. The experiment may then be repeated, using, say, alcohol, or soap solution, in place of water.[1]

The relation $$T = \frac{d \cdot \left(h + \frac{d}{6}\right) \cdot \rho \cdot g}{4}$$

employed in calculating the surface tension may be readily deduced by equating the vertical component of the surface tension with the weight of the liquid supported in the capillary tube.

If ϕ (Fig. C.) be the angle at which the liquid meets the tube, the vertical component of the surface tension is $2\pi r \cdot T \cdot \cos\phi$, since the liquid and glass meet along a circle of circumference $2\pi r$.

The weight of the liquid supported in the capillary tube[2] is

$$\pi r^2 \cdot \left(h + \frac{r}{3}\right) \cdot \rho \cdot g.$$

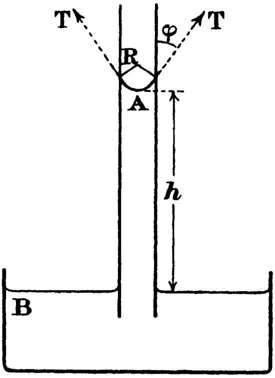

FIG. C.

Whence—

$$2\pi r \cdot T \cdot \mathrm{Cos}\,\phi = \pi r^2 \cdot \left(h + \frac{r}{3}\right) \cdot \rho \cdot g$$

(the weight of a column of air of the same height and cross-section as the liquid being treated as negligible).

Therefore—

$$T = \frac{r}{2\cos\phi} \cdot \left(h + \frac{r}{3}\right) \cdot \rho \cdot g,$$
$$= \frac{d}{4\cos\phi} \cdot \left(h + \frac{d}{6}\right) \cdot \rho \cdot g.$$

---

[1] The value of ρ must, of course, be determined for each liquid employed.

[2] It should be noted, however, that the corrected height, $h + \frac{r}{3}$, was deduced for liquids that wet the glass, and for which $\phi = 0°$. If the liquid meet the tube at a finite angle, the height measured to the lowest part of the meniscus must be increased by a smaller amount than $\frac{r}{3}$.

For liquids that wet the glass, $\phi = 0°$, and $\cos\phi = 1$.

$$\therefore T = \frac{d \cdot \left(h + \frac{d}{6}\right) \cdot \rho \cdot g.}{4}$$

If the liquid does not wet glass the value of the angle of contact must be known in order that the capillary tube method may be employed for the determination of T.

The relation for the surface tension may also be deduced in the following alternative manner: The curved liquid meniscus in a narrow capillary tube of circular cross-section is sensibly hemispherical for a liquid that wets the glass. If the liquid does not wet the glass, but meets it at an angle ϕ (Fig. C.), the curved meniscus, A, is still sensibly a portion of a hemisphere. Let R be the radius of curvature of the meniscus A. Then as shown in § 92, the difference between the pressures on the two sides of the curved meniscus must equal $\frac{2T}{R}$.

The pressure just above the meniscus A, however, is practically the same as the pressure at the plane surface of the liquid B, since the weight of the column of air, of height h, may be treated as negligible, and the pressure at B exceeds the mean pressure just below the meniscus A by an amount $\left(h + \frac{r}{3}\right) \cdot \rho \cdot g$, where ρ is the density of the liquid, $h + \frac{r}{3}$ the mean height,[1] and g the acceleration of gravity.

$$\therefore \frac{2T}{R} = \left(h + \frac{r}{3}\right) \cdot \rho \cdot g.$$

But $R \cdot \cos\phi = r$, where r is the radius of the capillary tube.

$$\begin{aligned}\therefore T &= \frac{r}{2\cos\phi} \cdot \left(h + \frac{r}{3}\right) \cdot \rho \cdot g, \\ &= \frac{d}{4\cos\phi} \cdot \left(h + \frac{d}{6}\right) \cdot \rho \cdot g,\end{aligned}$$

which is the relationship previously obtained.

Since for mercury and glass the angle ϕ is obtuse, $\cos\phi$ is negative, and, in consequence, h is negative, so that on dipping a capillary tube into mercury the surface of the mercury within the tube is depressed below the level of the plane surface outside.

99. Measurement of Surface Tension by Weighing the Pull Exerted by a Film.—*Experiment LXX.*—Draw out a glass rod into a fine capillary fibre and bend a piece of the latter, of about 12 cms. length,

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[1] See note 2 on previous page.

into a rectangular form, A (Fig. CI.). Suspend the rectangular fibre by means of fine silk thread from the end of a balance beam, and weigh the fibre when immersed in clean tap water, as shown in the figure, in the first place without the water film, B, and, secondly, with the film. The difference between the two weights gives the pull exerted by the film. It must be noted that there are *two* surfaces which are exerting tension. Measure the length, l, of the rectangular fibre.

Then, neglecting the very small weight of the film,[1] we have—

$$2 \, . \, T \, . \, l = W \, . \, g,$$

where T is the surface tension, W the difference between the two weights, and g the acceleration of gravity.

Whence— $$T = \frac{W \, . \, g}{2 \, . \, l} \text{ dynes/cm.}$$

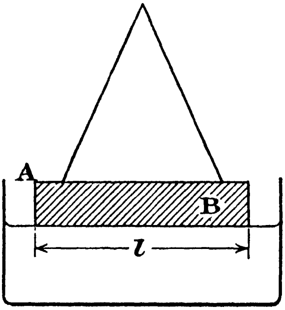

Fig. CI.

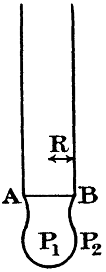

Fig. CII.

100. Measurement of Surface Tension by Determining the Weight of a Drop falling from a Tube.—*Experiment LXXI.*—Allow water to drip very slowly from a clean vertical glass tube of about 0·5 cm. internal diameter, as in Experiment XLI.[2]

Note that the drops always attain the same size before breaking away from the tube. Collect about ten of the drops in a weighed bottle, and again weigh, and calculate the weight of a single drop.

Let Fig. CII. represent the tube and drop when the latter is just about to break away and fall. Since the water wets the tube, the upward pull due to surface tension acting on the liquid below AB is $2\pi R \, . \, T$, where R is the radius of the tube, and T the surface tension

---

[1] The glass fibre should be immersed in water before weighing it without the film. The very small extra weight of the film itself may then be neglected without any appreciable error.

[2] The end of the glass tube must be cut across at right angles to its length, and should be ground perfectly smooth with fine emery powder.

of the water at the temperature of the experiment. If it be assumed that, at the moment of partition, the drop is cylindrical at the end of the tube, the pressure, P_1, inside the drop will exceed the atmospheric pressure, P_2, by an amount $\frac{T}{R}$ (§ 92), and, in consequence, there will be a downward force of $\pi R^2 . \frac{T}{R}$, i.e. πRT, acting on the liquid below AB. If, then, the liquid below AB be assumed, at the moment of partition, to be in a state of statical equilibrium under the influence of these two forces and its own weight, W, we have—

$$2 . \pi . R . T - \pi . R . T - W = 0.$$

$$\therefore T = \frac{W}{\pi . R}.$$

The above investigation is, however, by no means complete, for the partition of the drop is a *dynamical* process, and a state of statical equilibrium is not in reality attained. It has been shown by Lord Rayleigh that the expression $T = \frac{W}{3 \cdot 8 . R}$ leads to a more accurate value for the surface tension.

101. Determination of Surface Tension by the Measurement of a Drop.—*Experiment LXXII.*—Pour out some mercury upon a clean horizontal glass plate so as to form a large pool. Measure the depth, H, of this pool by means of a spherometer.

The surface tension may then be calculated from the relation—

$$T = \frac{H^2 . \rho . g}{2(1 + \cos \alpha)},$$

where ρ is the density of the mercury at the temperature of the experiment, g the acceleration of gravity, and α the supplement of the angle of contact between mercury and glass.

Instead of assuming the value of the angle of contact, the depth of the pool from its plane upper surface down to the horizontal section of greatest area may be measured by focusing a vernier microscope on one side of the edge of the pool so that the intersection of the cross-wires of the microscope coincides with the point where the edge of the pool has the maximum protuberance. A spherometer is next set with its middle leg just touching the plane upper surface of the pool, and is then carefully moved until it is sharply in focus when viewed through the microscope. On screwing up the microscope the intersection of the cross-wires may be made to coincide visually with the pointed end of the leg of the spherometer, and the difference between the two vernier readings on the microscope gives the depth of the pool between its plane upper surface and the horizontal section of maximum area. Let this depth be h. Then, employing the previous notation, the surface tension may be calculated by means of the relation—

$$T = \frac{h^2 . \rho . g}{2}.$$

The angle of contact may also be determined since, on combining the two equations, we have—

$$\cos\frac{a}{2} = \frac{H}{\sqrt{2} . h}.$$

The two equations employed for calculating the surface tension may be deduced in the following manner :—

Consider a very thin central section of the pool of mercury cut out by two parallel vertical planes *unit* distance apart, and imagine this section cut in half by a vertical plane at right angles to its length (Fig. CIII.). Provided the pool of mercury be sufficiently large, its upper surface will be sensibly plane, and the pressure just above the surface will, in consequence, be the same as the pressure just below. Thus the difference between the horizontal components of the pressure over the flat surface ABCD and the atmospheric pressure over the curved surface ABGHEFA is (since AB is unity), equal to

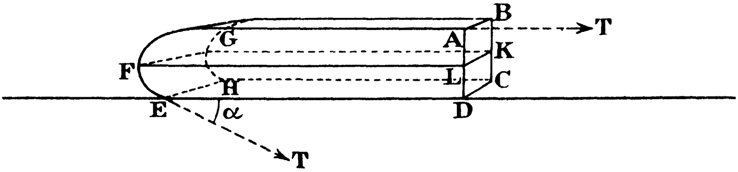

Fig. CIII.

$$\tfrac{1}{2} . AD^2 . \rho . g;^{1} \text{ i.e. to } \tfrac{1}{2} . H^2 . \rho . g.$$

Since the whole section AFEDCBGH of the pool of mercury is in equilibrium, the horizontal pressure $\frac{1}{2} . H^2 . \rho . g$ must be equal to the total horizontal component due to surface tension, and must act in the opposite direction.

Hence, equating the horizontal forces to zero, we have—

$$\tfrac{1}{2} . H^2 . \rho . g - T(1 + \cos a) = 0,$$

where a is the supplement of the angle of contact between mercury and glass.

$$\therefore T = \frac{H^2 . \rho . g}{2 . (1 + \cos a)}.$$

---

[1] The increase in the pressure of the *air* in passing from the level AB to the level CD is, of course, negligible.

Similarly, if FGKL be the horizontal plane of greatest area, it follows from the equilibrium of the section AFLKBG that—

$$\tfrac{1}{2} . AL^2 . \rho . g - T = 0.$$

$$\therefore T = \frac{h^2 . \rho . g}{2}.$$

This method of determining surface tension was originally employed by Quincke. The same method is also applicable to the case of a large bubble of air confined under a glass plate in water or other liquid.

$$\text{Since} \quad T = \frac{H^2 . \rho . g}{2 . (1 + \cos \alpha)}, \quad \text{we have } H^2 = \frac{4 . T . \cos^2 \frac{\alpha}{2}}{\rho . g}.$$

$$\therefore H = 2 . \cos \frac{\alpha}{2} \sqrt{\frac{T}{\rho . g}}.$$

It follows, therefore, that a constant depth, H, is possessed by all pools of a given liquid resting upon a plane horizontal surface, provided the pools be sufficiently large for their upper surfaces to be sensibly plane, and provided the liquid does not wet the solid surface upon which it rests. When the liquid wets the solid surface, the angle of contact, ϕ, is 0°, and its supplement, α, is 180°. In this case, therefore, H = 0, and the liquid spreads out indefinitely over the surface.

Experiment LXXIII.—Drop some water on a *quite* clean horizontal glass plate, and observe that the water spreads out into a thin film. Any other liquid which wets the glass may be employed, as, for example, ethyl alcohol, chloroform, or benzene.

102. Ripples.—A method of determining surface tension by the measurement of ripples on a liquid surface has been devised by Lord Rayleigh.

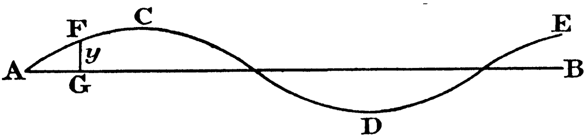

Fig. CIV.

Let AB (Fig. CIV.) represent a section of part of the surface of a liquid when at rest, while ACDE represents a harmonic wave travelling over the surface.

The velocity of propagation of a wave over the surface is conditioned both by gravity and by the surface tension of the liquid.

Consider first the case where gravity acts alone. The velocity of propagation, V, of a gravity wave on the surface of a deep liquid is equal to the velocity acquired by a body falling under the action of gravity through a height $\frac{\lambda}{4\pi}$, where λ is the wave-length.

Hence
$$V = \sqrt{\frac{2 \, . \, g \, . \, \lambda}{4 \, . \, \pi}},$$
$$= \sqrt{\frac{g \, . \, \lambda}{2 \, . \, \pi}}.$$

The vertical pressure at a point such as G on the line AB is increased through the action of gravity *alone* by an amount $y \, . \, \rho \, . \, g$, where y is the length of the vertical line FG, and ρ the density of the liquid.

Since, however, surface tension is also acting, there will be a *normal* pressure at F of $\frac{T}{R}$, where T is the surface tension of the liquid, and R the radius of curvature *at F* in the vertical plane parallel to the direction of propagation of the wave.[1]

If the amplitude of the wave be *very* small in comparison with the wave-length, the normal pressure at F will be sensibly vertical, so that the vertical pressure at the point G is increased by the total amount—

$$y \, . \, \rho \, . \, g + \frac{T}{R}.$$

It can also be shown that, when the amplitude of the wave is very small in comparison with the wave-length, the product $y \, . \, R$ is constant[2] and equal to $\frac{\lambda^2}{4\pi^2}$.

Thus the total increase in the vertical pressure at G is—

$$y \, . \, \rho \, . \, g + \frac{4\pi^2 \, . \, y \, . \, T}{\lambda^2},$$

i.e.
$$y \, . \, \rho \, . \left\{ g + \frac{4\pi^2 \, . \, T}{\lambda^2 \, . \, \rho} \right\}.$$

The action of gravity is thus effectively increased by an amount $\frac{4\pi^2 \, . \, T}{\lambda^2 \, . \, \rho}$ due to the surface tension.

---

[1] The radius of curvature in the vertical plane at right angles to the direction of propagation of the wave is infinite.

[2] The radius of curvature is thus inversely proportional to the height above AB. It should be noted that where the curve ACDE cuts the horizontal line AB the length y becomes zero, and the radius of curvature R becomes infinite.

On substituting the augmented value of g in the equation for the velocity, we have—

$$V' = \sqrt{\frac{\lambda}{2\pi}\left(g + \frac{4\pi^2 . T}{\lambda^2 . \rho}\right)},$$ where V′ is the velocity of propagation of the wave under the combined influence of gravity and surface tension.

Since V′ is equal to the square root of the sum of two terms whose product, $\frac{T . g}{\rho}$, is *constant*, it will have a *minimum* value when the two terms are equal to one another; i.e. when $g = \frac{4\pi^2 . T}{\lambda^2 . \rho}$.

In this case, $\lambda = 2\pi . \sqrt{\frac{T}{g . \rho}}$, and $V' = \sqrt{2} . \left(\frac{T . g}{\rho}\right)^{\frac{1}{4}}$.

The value of V′ will, further, be infinite both for infinitely large and infinitely small values of the wave-length. If, then, the values of V′ be plotted as ordinates against the corresponding values of λ as abscissæ, a curve will be obtained of the general form shown in Fig. CV. Waves of shorter length than λ_A—the wave-length corresponding to the minimum velocity V'_A—are termed *ripples*, whereas those of greater length are termed *waves*.

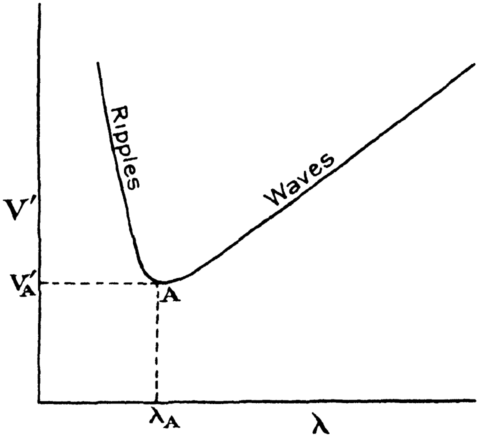

Fig. CV.

In the case of ripples the velocity of propagation is conditioned mainly by surface tension, for the influence of the term arising from the action of gravity in the equation for the velocity becomes of less and less importance the smaller the value of λ.

When, however, the value of λ is great, the term arising from surface tension becomes practically negligible in comparison with that due to gravity, so that the influence of gravity predominates in the propagation of large waves.

The equation for the velocity provides a means of determining the surface tension, T, if V′ and λ be known. In utilising the measurement of ripples for the determination of surface tension Lord Rayleigh employed an electrically driven tuning-fork by means of which a regular train of ripples could be generated. The number of ripples in a given length was then counted by viewing them by intermittent light, the period of the intermittent illumination being the same as that of the ripples. The value of λ was thus obtained. The value of the velocity, V', could then be determined from the relation $V' = n . \lambda$, the frequency, n, of the tuning-fork being known.

By substituting $n . \lambda$ for V' in the equation for the velocity the surface tension, T, could be calculated from the relation—

$$T = \rho . \left(\frac{\lambda^3 . n^2}{2\pi} - \frac{\lambda^2 . g}{4\pi^2}\right).$$

It has been shown that the minimum value of the velocity, V'_A (Fig. CV.) is given by the equation—

$$V'_A = \sqrt{2} . \left(\frac{T . g}{\rho}\right)^{\frac{1}{4}}.$$

For water at 15° C., T is approximately 73 dynes/cms., and we have—

$$V'_A = 23 \text{ cms./sec.}$$

This is, consequently, the minimum velocity with which a wave can travel over the surface of deep water. The corresponding value of the wave-length, λ_A, is 1·7 cms.

It follows that the stationary ripples which may frequently be observed on the surface of a stream flowing past an obstacle, such as a fishing-line, can only occur when the velocity of the stream exceeds 23 cms./sec.

The flow of the water against the line sets up ripples which travel up stream with a velocity corresponding to their wave-length (*vide* Fig. CV.).

The layer of water in actual contact with the line is at rest (*vide* § 48) —the velocity of the water increasing as we travel up stream—and a stationary ripple will therefore be produced when a point is reached at which both the velocity of propagation of the ripple and the velocity of the water are equal. Since the velocity of the water increases as we travel up stream (from the line) it is evident (Fig. CV.) that the wave-lengths of the ripples which appear to be stationary must become correspondingly shorter.

Experiment LXXIV.—Allow a stream of water to flow very slowly down a long metal trough and touch the surface of the water with a thin glass rod. No stationary pattern of ripples will be obtained. Now increase the rate of flow and observe the formation of a ripple-pattern, the crests of the ripples being closer together the further they lie up stream. On again reducing the rate of flow the ripples travel up stream and the pattern disappears.

By moving the glass rod across the surface of some water in a basin similar ripple-patterns can be obtained. The relative velocity between the water and the rod must, of course, be constant, and greater than 23 cms./sec., in order that the ripples may retain a fixed position relative to the rod and to one another.

103. Oscillation of a Spherical Drop.—It has been shown by Lord Rayleigh that the time of gravest vibration, S, of a spherical liquid drop, under the influence of surface tension alone, is given by the relation—

$$S = \frac{\pi}{\sqrt{2}} \cdot \left(\frac{a^3 . \rho}{T}\right)^{\frac{1}{2}},$$

where a is the radius of the spherical drop, ρ the density of the liquid, and T the surface tension.[1]

Thus a drop of water 2·5 cms. in radius would make, approximately, one vibration per second under the influence of surface tension, while a drop of water 0·00025 cm. in radius would vibrate a million times a second.

The oscillation of a drop was employed by Lenard for the measurement of surface tension, the time of vibration, S, being found by taking instantaneous photographs.

Experiment LXXV.[2]—Form a number of globules of olive oil in a mixture of alcohol and water of the same density, as in Experiment XLVII. Hit the globules on one side with a spatula so as slightly to deform them and observe that the larger globules vibrate more slowly than the smaller ones and take longer to recover their original spherical shape. Next blow several soap-bubbles and notice, as in the case of the oil globules, that the larger bubbles vibrate about the spherical shape more slowly than the smaller ones when slightly deformed by being struck with a piece of wood covered with baize.

It must be borne in mind that the time of vibration of a liquid drop when surrounded by a liquid of the same density is conditioned by the surface tension at the *inter-liquid* boundary. In order therefore to determine the surface tension for a liquid surface in contact

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[1] In order that the drop may vibrate under the sole influence of surface tension it must be surrounded by a fluid of the same density so that changes in the shape of the drop will not affect the potential energy due to gravity. In the case of very small drops, however, the potential energy due to gravity may be treated as negligible in comparison with that due to surface tension, so that the equation $S = \frac{\pi}{\sqrt{2}} \cdot \left(\frac{a^3 . \rho}{T}\right)^{\frac{1}{2}}$ may be applied even when the drops are not vibrating in a fluid medium of the same density.

When a drop is falling freely through the air the influence of gravity may also be neglected.

[2] Refer also to Experiments LXIII. and LXIV.

with air, the time of vibration of a drop must be found when the drop is falling freely through the air. The influence of gravity on the time of vibration is, in this case negligible.

The time of vibration, S, of a spherical liquid drop, under the influence of surface tension, may be shown by the "Method of Dimensions" to be given by the relation—

$$S = K . a^{\frac{3}{2}} . \rho^{\frac{1}{2}} . T^{-\frac{1}{2}},$$

where K is a numerical quantity having no dimensions. A proof of this relationship is given in Appendix C.

104. Surface Tensions of Different Liquids.—When one liquid is bounded by another, the surface tension at the inter-liquid boundary is different from that of either liquid when in contact with air. The interfacial surface tension is always less than the greater of the two air-liquid surface tensions, and may even fall below the value of the smaller. Thus, at 20° C., the surface tensions of water, benzene, and olive oil when in contact with air are, respectively, 72·3 dynes/cm., 28·8 dynes/cm., and 32 dynes/cm. The interfacial surface tensions, at the same temperature, for water-benzene and water-olive oil are, respectively, 33·6 dynes/cm. and 20·6 dynes/cm.

The first of the two following tables gives the surface tensions in dynes per centimetre for several liquids in contact with air, at 20° C.; the second table gives the surface tensions at a number of inter-liquid boundaries, at the same temperature.

Surface Tensions, at 20° C., for Liquids in Contact with Air.

Liquids.	Surface Tension.
	dynes/cm.
Benzene	28·8
Chloroform	26·7
Mercury	546
Olive Oil	32
Water	72·3

Surface Tensions, at 20° C., at Inter-liquid Boundaries.

Liquids.	Surface Tension.
	dynes/cm.
Water-benzene . . .	33·6
,, -chloroform. . .	29·5
,, -olive oil . . .	20·6
Mercury-water . . .	427
,, -chloroform . .	399

105. The Rise of a Liquid between two Parallel Vertical Plates.—The rise of a liquid in a capillary tube was investigated in Experiment LXIX., and the rise of a liquid between two parallel vertical plates partly immersed in the liquid and held close together may be treated in an analogous manner.

Thus, considering the equilibrium of the raised portion of a liquid bounded by two parallel glass plates and by two vertical planes at right angles to the plates at a distance δl apart, and equating the vertical component of the surface tension with the weight of the liquid supported, we have—

$$2\,.\,\delta l\,.\,\mathrm{T}\,.\,\cos\phi = d\,.\,\delta l\,.\left\{h + \frac{d(4-\pi)}{8}\right\}.\,\rho\,.\,g,$$

where T is the surface tension, ϕ the angle at which the liquid meets the plates, d the distance between the plates, and h the height of the liquid measured to the lowest part of the meniscus.[1]

Therefore—

$$\mathrm{T} = \frac{d}{2\cos\phi}\,.\left\{h + \frac{d(4-\pi)}{8}\right\}.\,\rho\,.\,g = \frac{d\,.\,\mathrm{H}\,.\,\rho\,.\,g}{2\cos\phi},$$

where H is written, for convenience, for the corrected height of the liquid.

For liquids that wet the glass, $\phi = 0°$, and $\cos\phi = 1$.

$$\therefore\ \mathrm{T} = \frac{d}{2}\,.\left\{h + \frac{d(4-\pi)}{8}\right\}.\,\rho\,.\,g = \frac{d\,.\,\mathrm{H}\,.\,\rho\,.\,g}{2}.$$

Adopting an alternative method of proof we may treat the curved liquid meniscus between the plates as sensibly cylindrical, so that the difference between the pressures on its two sides must equal $\frac{\mathrm{T}}{\mathrm{R}}$, where R is the radius of curvature of the meniscus (*vide* § 92).

Then, as in Experiment LXIX., we have—[2]

$$\frac{\mathrm{T}}{\mathrm{R}} = \left\{h + \frac{d(4-\pi)}{8}\right\}.\,\rho\,.\,g.$$

---

[1] If the plates be very close together, and if the liquid wet the glass, the liquid meniscus is sensibly hemicylindrical, so that the volume of liquid above the lowest part of the meniscus is practically equal to the difference between the volume of a rectangular right prism of base $d\,.\,\delta l$ and height $\frac{d}{2}$, and half the volume of a cylinder of length δl and radius $\frac{d}{2}$.

Since this difference in volume is equal to $\frac{d^2\,.\,\delta l}{8}\,.\,(4-\pi)$, the height measured to the lowest part of the meniscus must be increased by $\frac{d}{8}\,.\,(4-\pi)$.

If the liquid meet the plates at a finite angle, the height, h, must be increased by a somewhat smaller amount.

[2] See the preceding note.

But $$R \cos \phi = \frac{d}{2}.$$

$$\therefore T = \frac{d}{2 \cos \phi} \cdot \left\{ h + \frac{d(4 - \pi)}{8} \right\} \cdot \rho \cdot g,$$

which is the relationship previously obtained.

106. The Rise of a Liquid Between Two Vertical Plates Meeting at a Small Angle.—*Experiment LXXVI.*—Fasten together two rectangular pieces of plate glass by means of an india-rubber band, and insert a small strip of wood at one edge so that the plates may meet along the opposite edge at a small angle. Partly immerse the plates in water, with the common edge along which they meet in a vertical position, and observe that the water rises up between the plates until its surface forms a regular curve, ABC (Fig. CVI.).

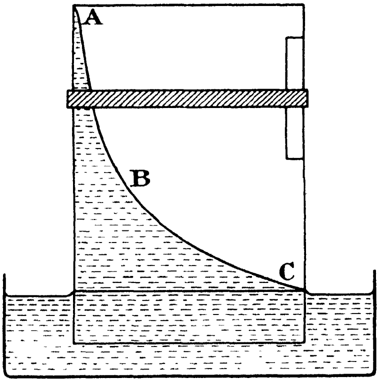

Fig. CVI.

It follows, from the preceding paragraph, that the height to which the water rises at any point B is given by the relation—

$$H' = \frac{2 . T}{d' . \rho . g},$$

where H′ is the corrected height of the liquid, and d' the distance between the plates at the point B.

$$\therefore H' . d' = \text{constant}.$$

Thus the rise of the water is inversely proportional to the distance separating the two plates. Since, however, d' is directly proportional to the horizontal distance x' between B and the vertical common edge of the plates, it follows that

$$H' . x' = \text{constant}.$$

The surface of the water thus forms a rectangular hyperbola.

107. Forces between Parallel Vertical Plates when Partly Immersed in a Liquid.—The rise of a liquid between two parallel vertical plates was considered in § 105, and it was shown that

$$H = \frac{2 . T . \cos \phi}{d . \rho . g}.$$

For liquids that wet the plates, $\phi = 0°$, and $\cos \phi = 1$.

$$\therefore H = \frac{2 . T}{d . \rho . g}.$$

It follows, in any such case, that H is positive, and the liquid therefore rises between the plates as in Fig. CVII. *a*.

Now, the *horizontal* forces acting upon the liquid in a meniscus such as ABC (Fig. CVII. *a*) are the surface tension, T, at A, the horizontal component, p_1, of the atmospheric pressure over the curved surface AB, and the force, p_2, exerted by the plate on the liquid over BC.

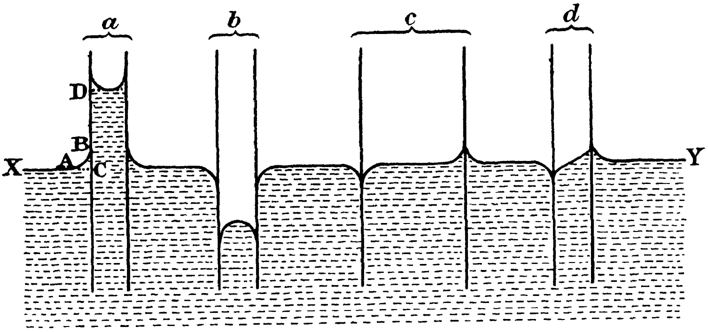

FIG. CVII.

The horizontal component, p_1, of the atmospheric pressure over the curved surface AB is, however, the same as the pressure which would be exerted by the atmosphere over BC if the meniscus were absent.

Since the liquid in the meniscus is in equilibrium, we have—

$$T - p_1 + p_2 = 0.$$
$$\therefore T - p_1 = - p_2.$$

Now, since p_2 is the force exerted by the plate on the liquid in the meniscus, $- p_2$ is the force exerted by the liquid in the meniscus on the plate, and this equals $T - p_1$, which is the force that would be exerted if the meniscus were absent and the liquid surface were continued horizontally along AC until it met the plate at C.

The same argument applies, of course, to the *horizontal* forces acting at any other meniscus, such as at D.

If, now, we consider the horizontal forces acting on one of the plates in Fig. CVII. *a*, it is clear that the plate is pulled equally, and in opposite directions, by the surface tension at A and D, but since the liquid is raised between the plates, the pressure in the raised portion of the liquid at any point must be less than the atmospheric pressure outside by an amount proportional to the height of the point above the level XY, the pressure at the level XY being, of course, that of the atmosphere. It follows, therefore, that the two plates are pushed together.

If the angle ϕ be greater than 0°, but less than 90°, cos ϕ will be less than 1 and greater than 0, and H will still be positive. In this case there will be an additional horizontal component of $-$ T sin ϕ acting at B upon the liquid in the meniscus ABC. The effect of this force will, however, be neutralised by an equal and opposite horizontal component exerted at the level at which the meniscus at D meets the plate, so that the two plates will still be forced together. The force of attraction will, however, be lessened in this case, owing to the liquid rising to a smaller height between the plates.

If the angle of contact ϕ be obtuse, cos ϕ is negative, and, in consequence, H is negative. The liquid will, therefore, be depressed between the plates below the level of the plane surface outside (Fig. CVII. *b*). It can be shown that, as in the previous case, the two plates are pushed together, for the pulls exerted by surface tension neutralise one another, while the pressure at any point in the liquid outside the plates is greater than the atmospheric pressure between the plates by an amount proportional to the depth of the point below the level XY.

When plates of different materials are employed, it may happen that the angle of contact is acute for one and obtuse for the other. If the plates be sufficiently far apart, a portion of the surface of the intervening liquid will be plane, and at the same level as XY (Fig. CVII. *c*). In this case there will be neither attraction nor repulsion between the plates. If, however, the plates be brought closer together, the intervening plane surface will become smaller and smaller until it finally vanishes, the vanishing point being represented by a *horizontal* tangent to the liquid surface at the point of inflexion. On bringing the plates still closer to the tangent the liquid surface at the point of inflexion will no longer be horizontal but will slope upwards to the plate for which the angle of contact is acute.[1]

In this case the level of the liquid between the plates where it

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[1] Since the curvature of the liquid surface vanishes at the point of inflexion, the pressure just below the surface at this point must be the same as the pressure just above, i.e. atmospheric. The point of inflexion will, consequently, be at the same level as XY.

meets the plate at an acute angle is lower than the level where it meets the same plate outside, whilst the level for the plate which the liquid meets at an obtuse angle is higher inside than outside (Fig. CVII. *d*).

If, now, we consider the horizontal forces acting on one of the plates, and, as in the previous cases, suppose that the liquid surfaces meet the plate horizontally, it is evident that the surface tension in the horizontal surface *between the plates* will be merely the horizontal component, at the point of inflexion, of the actual surface tension, so that the plate will be pulled outwards by the surface tension and inwards by this smaller horizontal component. It follows, therefore, that the two plates will be pulled apart.[1]

Experiment LXXVII.—Float two hollow glass spheres on the water in a trough and observe that they move together and also move up to the side of the trough. Small pieces of wood, or straw, when floating on the water in a pond will, similarly, collect together and gradually float up to the edge of the pond. In such cases the water wets the different bodies; i.e. $\phi = 0°$.[2]

Bubbles on the surface of a liquid collect together in a similar manner.

Now dip the glass spheres in melted paraffin wax and, after the thin coating of wax has solidified, again float them on the water. Since the angle of contact, ϕ, between the water and the wax is obtuse, the spheres will move together, but they will gradually float away from the side of the trough towards the centre.

If, now, a clean glass sphere and a sphere coated with paraffin wax be floated side by side they will move apart, the clean sphere gradually floating up to the side of the trough and the waxed sphere moving towards the centre. The same behaviour is exhibited when a dry needle is carefully placed on the surface of the water and a wet match is floated beside it.[3]

Next fill up the trough with water until the level of the latter is slightly higher than the edge of the trough. The surface of the water will now be convex near the edge of the trough while it is still concave near the wet match and glass sphere which have floated up to the side. The conditions therefore resemble the case illustrated in Fig. CVII. *d*, and consequently, the match and sphere float away towards the centre, while the waxed sphere and dry needle, as might be anticipated, now move up to the side of the trough, the needle probably falling over the edge.

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[1] When the plates are brought *very* close together the point of inflexion disappears, and the liquid rises between the plates, the latter being pushed together.

[2] If the glass spheres, for example, are not *quite* clean ϕ will not equal $0°$, but the water will meet the glass at a small angle. A slightly smaller attraction will therefore be exhibited between the spheres.

[3] A match coated with paraffin wax may be substituted for the needle. If a glass rod be dipped into the water the wet match will quickly float up to it, while the waxed match will be driven away.

108. The Surface Tension Exhibited by Exceedingly Thin Films.—It was shown, in Experiment XLV., that the surface tension of a liquid film was practically independent of the thickness—at any rate in the case of films which were not excessively thin. The surface tension of exceedingly thin soap-films was investigated by Rücker and Reinold, who found that when the thickness of the films became less than about $60\mu\mu$ the equilibrium became unstable and the films suddenly thinned down to approximately $12\mu\mu$ ($1\mu\mu = 10^{-6}$ mm.).

The thickness of the soap-films was determined either by measuring their electrical resistance, and assuming that their specific resistance was the same as that of the soap-solution, or by optical methods. It was found that the passage of the electric current up the films prevented them from draining and growing thinner. Rücker and Reinold found that when a portion of a soap-film has acquired a thickness of about $12\mu\mu$ there is an *abrupt* change in the thickness on passing from this portion to the thicker contiguous parts of the film. Fig. CVIII. illustrates a section of such a film, the thickness of the upper portion being $12\mu\mu$, and the thickness of the lower portion $60\mu\mu$ or more. Since the film is in equilibrium the surface tension in the two portions must be equal (*vide* § 110).

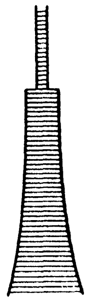

Fig. CVIII.

It has, further, been shown by Johonnott that a soap-film of $6\mu\mu$ thickness may exist contiguously to a film of $12\mu\mu$ thickness, there being an abrupt variation in the thickness on passing from one to the other.

These experimental results indicate that the variation in the surface tension may be represented by a curve such as that illustrated in Fig. CIX., where the ordinates correspond to the surface tension, T,

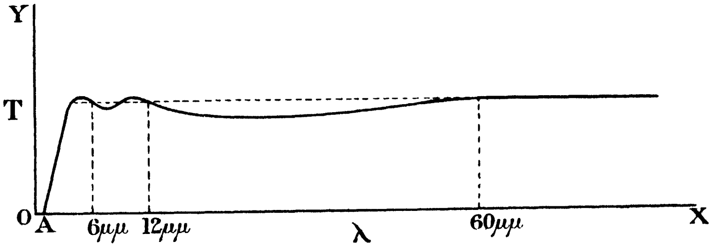

Fig. CIX.

and the abscissæ to the thickness, λ, of the soap-film. It is evident from the figure that films of $6\mu\mu$ and $12\mu\mu$ thickness would be in stable equilibrium when contiguous to films of a greater thickness than $60\mu\mu$, for any stretching of these thin films would raise—and any thickening lower—their surface tension. When the thickness of the films is reduced below $6\mu\mu$ the surface tension increases at first, and then diminishes down to zero value at a thickness corresponding to the point A in the figure.

Measurements of the thickness of exceedingly thin films furnish important corroborative evidence as to the approximate correctness of the molecular magnitudes previously deduced from the kinetic theory. Since no film can conceivably be of smaller thickness than the diameter of its molecules, this molecular diameter may be taken as corresponding to the point A at which the surface tension vanishes, and must evidently be less than $6\mu\mu$ (*vide* § 109).

109. Movements of Aniline, and Camphor, on Water.—*Experiment LXXVIII.*—Pour a small quantity of aniline on the surface of some water in a dish, and observe that the floating aniline globules are in a tremulous state, while minute particles become detached from the edges and spread out over the water, gradually dissolving in the latter. When the whole water surface has become covered with a film of aniline the action ceases, and the small globules of aniline remain floating quietly on the contaminated surface.

Next drop a number of small particles of camphor upon a clean water surface and observe that the particles dart about and rotate with great rapidity. Minute particles of soap behave in an analogous manner although the action is much less marked.

These actions are, in part, due to the substances dissolving in the water at the points of contact forming solutions having a smaller surface tension than the water. The surfaces of these solutions will, consequently, be pulled out by the surface tension of the contiguous water and the floating particles will be set in motion. It is probable, however, that other forces besides surface tension come into play during the process of solution.

If a small quantity of oil be placed upon the surface of the water while the camphor particles are darting about, their movement immediately ceases, since the oil film formed on the water reduces the surface tension below that of the camphor solution. Quantitative measurements of the variation in the surface tension of a water surface with the thickness of such a covering oil film were made by Lord Rayleigh who found that there was no appreciable change in the surface tension until the film had attained a thickness of approximately $1\mu\mu$.[1]

On further increasing the thickness of the oil film the surface tension diminished rapidly until a thickness of about $2\mu\mu$ was reached, beyond which point the tension diminished much more slowly, approximating gradually to that of the pure oil. These results are illustrated in Fig. CX., where the ordinates represent the surface tension, T, of the contaminated water surface, and the abscissæ the thickness, L, of the oil film ; the surface tension of clean water

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[1] The thickness of the film was ascertained by allowing a drop of oil of known weight to spread out over a known area.

corresponds to the value A, and that of the oil to the value B. Lord Rayleigh found that an oil film of about $2\mu\mu$ thickness was needed to stop the movement of camphor particles on a water surface; the point C (Fig. CX.), corresponding to this thickness, is consequently called the "Camphor Point." It was suggested by Lord Rayleigh that the thickness $1\mu\mu$ was equal to the diameter of a molecule of oil, but since Röntgen, in 1890, obtained layers of oil of only $0{\cdot}56\mu\mu$ thickness which held together, the molecular diameter must evidently be assigned a smaller value.

When the surface tension of the contaminated water surface lies between the values A and B (Fig. CX.), any increase in the thickness of the oil film will reduce the tension, whereas any decrease in the thickness will augment it. If, for example, a floating lath be drawn broadwise across such a contaminated surface, the oil will be heaped up in front of the lath whilst the surface immediately behind will be scraped clear of the oil film. This will make the surface tension behind the lath greater than in front, and there will, consequently, be a resultant force due to surface tension opposing the motion of the lath. Such a force, of course, could not arise in the case of a pure, uncontaminated liquid.

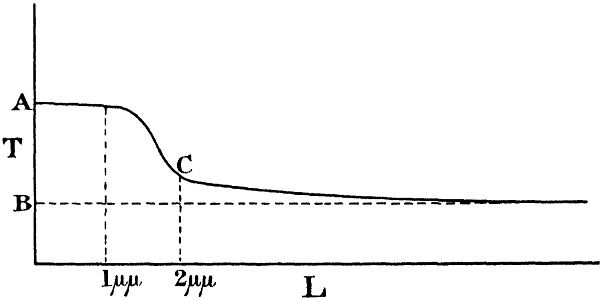

Fig. CX.

The calming of a rough sea by pouring oil over its surface may, similarly, be attributed to the action of surface tension. When the wind blows upon the contaminated surface it drives the film of oil forward, and heaps it up, leaving a cleaner water surface behind. The greater tension in this water surface, will, however, immediately come into play and oppose the motion, and will thus prevent, at any rate to a large extent, the heaping up of waves.

110. Durability of Liquid Films.—The surface tension exhibited by a film of a pure liquid has a constant value, provided the temperature remain constant and the film be not too thin. Such a film cannot exist unless the influence of gravity be eliminated, by surrounding the film, for example, with a fluid of the same density, for otherwise there would be no force to equilibrate the weight of the film. Thus, in Fig. CI., the tension in the upper part of the film B must be slightly greater than the tension in the lower portion for the film to remain in equilibrium. In the case of a pure liquid such a state of equilibrium would initially be attained by the stretching of the upper part of the film, the resulting cooling of the film producing an increase in its surface tension (*vide* § 91). This equilibrium would only be transient, for the film would soon warm up, and, ultimately, rupture at the top.[1]

If, however, the surface of the liquid were slightly contaminated a state of equilibrium could be much more readily maintained, for an extension of the surface at any point would produce a diminution in the degree of contamination at that point, and this would, in general, increase the surface tension and prevent further stretching of the film. Thus a vertical film of water when slightly contaminated with oil, could remain in equilibrium provided the covering oil film were not stretched thinner than $1\mu\mu$ (*vide* Fig. CX.). When a film is composed of a mixture of substances, its durability is largely conditioned by the relative volatility of the different constituents. A film made from soap-solution, for example, is much more stable than a water film, although its surface tension may be considerably less than that of water. In this case the vaporisation of the water at the surface of the film increases the concentration of the surface layer—which diminishes its surface tension. If, then, the film be stretched out at any point, the more dilute solution inside the film will be brought to the surface and will increase the surface tension, so that the film will contract and thicken again.

The instability of a film made from a mixture of alcohol and water may, on the other hand, be attributed to the greater volatility of the alcohol, for in this case the tension in the surface of the film will be *increased*, owing to vaporisation, and, consequently, any extension of the film will lower the surface tension and so cause the film to yield more readily to the stretching force.[2]

111. Vapour Pressure in Equilibrium with a Curved Liquid Surface. — We have seen that, in accordance with the kinetic theory, the evaporation of a liquid is due to the gradual escape of the molecules through the liquid surface, and that when the evaporation takes place into a closed space the molecules of vapour collect, a state of dynamic equilibrium being attained when as many molecules condense back into the liquid as escape from it in unit time.

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[1] It will, however, be seen from Fig. CIX. that in the case of very thin films the surface tension may *increase* with a diminution in the thickness. A vertical film of this nature could evidently exist in a state of stable equilibrium.

[2] Compare the phenomenon of "Tears in Wine" (§ 90).

Now, the number of molecules passing through a given area of a liquid surface, in unit time, *and escaping from the liquid*, will depend upon the curvature of the surface.

If the surface be concave (Fig. CXI. *a*), a rapidly moving molecule passing through the surface in the direction shown by the arrow may just fail to escape beyond the range of molecular attraction (cf. § 113). Such a molecule would, therefore, be drawn back again into the liquid, although it would have escaped into the surrounding space if the liquid had possessed the plane surface X.

If, on the other hand, the surface be convex (Fig. CXI. *b*), a molecule passing through the surface in the direction shown by the arrow may escape from the liquid, although it might have failed to do so had the surface been plane.

Thus, in the case of a concave surface, fewer molecules will escape from a given area in unit time, and the saturation pressure, which corresponds to the state of dynamic equilibrium, will, consequently, be less than that exerted over a plane surface at the same temperature, whereas the pressure in equilibrium with a convex surface will be greater than for one that is plane.

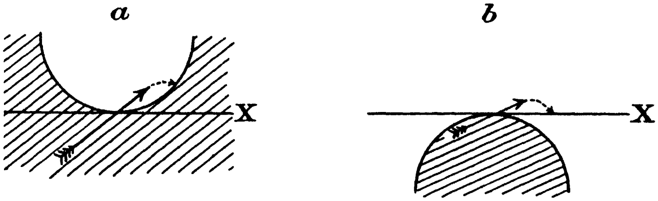

FIG. CXI.

We arrive at the same conclusion if we consider the changes in surface energy occasioned by vaporisation. Thus, in the case of a spherical drop, when vaporisation occurs there will be a diminution in the superficial area, with a consequent decrease in the potential energy due to surface tension, so that the surface tension will assist the vaporisation of the liquid, whereas vaporization at a plane surface, since it occasions no change in the area, will be unaided by surface tension. It may therefore be concluded that the saturation pressure exerted over a convex surface—such as the surface of a spherical drop—will exceed that exerted over a plane area at the same temperature.

The influence of the curvature of a liquid surface on the saturation vapour pressure was first deduced by Lord Kelvin in the following manner:—

Consider a vertical capillary tube partly immersed in the liquid and enclosed in a vessel from which the air has been exhausted (Fig. CXII.). Let the liquid rise in the capillary tube to a height, *h*, above the plane surface of the liquid outside. When a state of equilibrium has been attained the saturation vapour pressure, P_2, at the concave meniscus in the tube must equal the pressure of the surrounding vapour at the same level, and, consequently, must be less than the saturation vapour pressure, P_1, at the plane liquid surface outside by an amount equal to the hydrostatic pressure of a column of vapour of height h. If σ be the average density of the vapour throughout the height h, the hydrostatic pressure due to this column of vapour is $h \,.\, \sigma \,.\, g$, so that we have—

$$P_2 = P_1 - h \,.\, \sigma \,.\, g.$$

If ρ be the density of the liquid, the hydrostatic pressure due to the column of liquid of height h is $h \,.\, \rho \,.\, g$, so that the pressure just below the curved liquid meniscus in the capillary tube is equal to

$$P_1 - h \,.\, \rho \,.\, g.^1$$

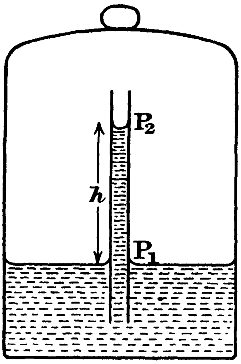

Fig. CXII.

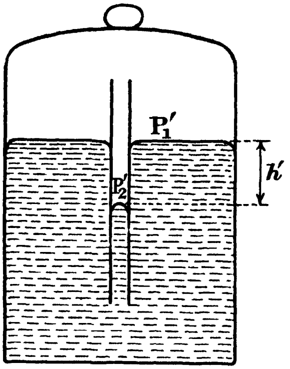

Fig. CXIII.

Thus the difference of pressure between the two sides of the curved meniscus is equal to $(P_1 - h \,.\, \sigma \,.\, g) - (P_1 - h \,.\, \rho \,.\, g)$; i.e. $(\rho - \sigma) \,.\, h \,.\, g$.

Since the curved liquid meniscus in a narrow capillary tube of circular cross-section is sensibly a portion of a hemisphere, the difference between the pressures on the two sides of the curved meniscus must equal $\frac{2T}{R}$, where R is the radius of curvature of the meniscus, and T the surface tension (§ 92).

Whence
$$(\rho - \sigma) \,.\, h \,.\, g = \frac{2T}{R}.$$

$$\therefore h \,.\, \sigma \,.\, g = \frac{2T}{R} \,.\, \left(\frac{\sigma}{\rho - \sigma}\right).$$

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[1] In the case of the plane liquid surface outside, the pressure, P_1, just above the surface is, of course, the same as the pressure just below.

Substituting this value in the equation $P_2 = P_1 - h \, . \, \sigma \, . \, g$, we have—

$$P_2 = P_1 - \frac{2T}{R} \, . \left(\frac{\sigma}{\rho - \sigma}\right).$$

Thus the saturation vapour pressure, P_2, at the concave hemispherical meniscus is less than the saturation vapour pressure, P_1, at the plane liquid surface by $\frac{2T}{R} \, . \left(\frac{\sigma}{\rho - \sigma}\right)$—the values of σ, ρ, and T being measured at the temperature of the liquid.

It follows that condensation will occur more readily on such a concave surface than on a plane liquid surface at the same temperature.

An analogous argument can be applied to the case where the liquid surface is convex. Let Fig. CXIII represent a vertical capillary glass tube partly immersed in mercury, or, alternatively, a similar tube coated with paraffin wax and immersed in water. The surface of the liquid within the tube will be depressed to a depth h' below the level of the plane surface outside, so that, using a similar notation to that previously employed, we have—

$$\begin{aligned} P'_2 &= P'_1 + h' \, . \, \sigma' \, . \, g, \\ &= P'_1 + \frac{2T'}{R'} \, . \left(\frac{\sigma'}{\rho' - \sigma'}\right). \end{aligned}$$

Thus the saturation vapour pressure, P'_2, at the convex hemispherical meniscus is greater than the saturation vapour pressure, P'_1, at the plane liquid surface by $\frac{2T'}{R'} \, . \left(\frac{\sigma'}{\rho' - \sigma'}\right)$.

Condensation will, therefore, occur more readily on a plane liquid surface than on a convex liquid surface at the same temperature.

112. The Formation of Clouds.—It was seen, in the preceding paragraph, that the vapour pressure in equilibrium with a curved liquid surface increases with the convexity of the surface, and that, in consequence, condensation takes place more readily the less the convexity of the surface. The increase in the saturation vapour pressure is, however, practically negligible until the radius of curvature of the liquid surface has become extremely small.

In order to gain information as to the magnitude of the effect produced when the radius of curvature is very small, we may calculate the saturation vapour pressure exerted at 0° C. by a drop of water of, say, 1 $\mu\mu$ radius.

In this case—

$$\begin{aligned} P'_2 &= P'_1 + \frac{2T'}{R'} \, . \left(\frac{\sigma'}{\rho' - \sigma'}\right), \\ &= (0{\cdot}458 \times 13{\cdot}596 \times 981) + \frac{2 \times 75{\cdot}2}{10^{-7}} \, . \left(\frac{48{\cdot}4 \times 10^{-7}}{0{\cdot}9999 - 48{\cdot}4 \times 10^{-7}}\right), \\ &= 6{,}121 + 7{,}280, \\ &= 13{,}401 \text{ dynes/cm}^2. \end{aligned}$$

Since P'_1 is equal to 6,121 dynes/cm^2, the saturation vapour pressure, at 0° C., over a drop of water 1 $\mu\mu$ in radius is seen to be approximately 2·2 times the saturation vapour pressure over a plane water surface at the same temperature.

It follows that such a minute drop would rapidly evaporate in a space which was saturated with respect to a plane water surface. In consequence, it is possible to cool water vapour considerably below the dew-point without condensation occurring, for the formation of very minute drops in the initial stage of the condensation cannot readily take place.

It was shown by Aitken, in 1880, that the presence of dust is, in general, necessary in order that condensation may proceed, for in this case the particles of dust serve as nuclei around which the water molecules are deposited, so that even in the initial stage of the condensation the drops possess sensible dimensions.

It was further shown by Wilson, in 1897, that gaseous ions can serve as nuclei for condensation at the ordinary dew-point, without the presence of dust particles of finite curvature[1] (cf. § 73).

Condensation can, however, be produced in the absence of electrical nuclei, and in dust-free air, provided a sufficient degree of supersaturation be attained. Thus Wilson showed that a dense mist was formed when saturated, dust-free air was suddenly allowed to expand to about 1·4 times its original volume. In this case the supersaturation is sufficient for the formation of drops which initially are very small. In the contaminated air of towns particles of smoke and dust furnish an enormous number of nuclei for the deposition of moisture, so that dense fogs are produced when condensation occurs. In the cleaner air of the country there are fewer dust particles, and, consequently, fewer centres of condensation, so that a larger amount of water is deposited around each particle of dust, the resulting drops being larger and farther apart, and constituting what is commonly called a "Scotch Mist." Since the wee drops in a "Scotch Mist" are larger than the very minute drops present in a fog it follows, in accordance with Stokes' Law (§ 73), that they will fall more rapidly through the air. At great altitudes where the air is, in general, very clean the formation of clouds is probably largely facilitated by the presence of gaseous ions. Since condensation takes place more readily the less the convexity of a liquid surface, it follows that, in a mist or fog, the larger drops, which possess a lower saturation vapour pressure, will tend to grow at the expense of the smaller ones, which possess a greater saturation vapour pressure. The smaller drops will thus tend to diminish in size and disappear.

The effect of dust particles on the formation of mist and the change in the character of the mist condensation when the number of

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[1] The influence of the electrification of a body in partly neutralising the effect of curvature, and thus assisting the condensation of vapour on a convex surface was shown by J. J. Thomson, in 1888.

solid nuclei which serve as condensation centres is made smaller and smaller can be demonstrated by means of the following experiment:—

Experiment LXXIX.—Connect an aspirator, A, to a round-bottomed flask, B, by means of a long flexible tube (Fig. CXIV.), and insert a straight tube, C, through the rubber stopper that closes the mouth of the flask. The tube C has a short length of rubber tubing, and a clip, D, fitted to its lower end. Open the clip and pour water into the aspirator until the water fills the lower part of the flask. Then close the clip and raise the aspirator above the level of the flask so that water may flow into B and compress the enclosed air. Allow the apparatus to stand until the air in B has become saturated with water-vapour at the temperature of the room, and then lower the aspirator again. Water will run out from the flask, and the saturated air will expand and cool, the cooling producing a state of super-saturation so that a dense mist will be formed inside the flask. This mist will gradually settle down on the water in the lower part of the flask, carrying with it many of the dust particles that served as nuclei for condensation. If the process be repeated several times it will be observed that, as the dust particles become fewer, the drops formed by the condensation become larger and farther apart, so that the mist inside the flask settles much more rapidly. After a sufficient number of expansions the air inside the flask will be freed from dust particles and subsequent expansion of the clean air will fail to produce a mist condensation. If, now, some dust be drawn into the flask—by holding a piece of smouldering filter-paper, for example, beneath the lower end of the tube C, opening the clip D, and lowering the aspirator—it

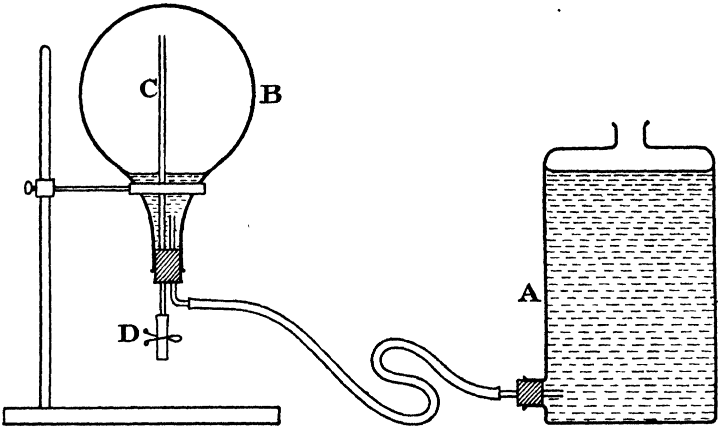

Fig. CXIV.

will be found that the next expansion of the saturated air causes the formation of a dense mist.

When clouds are formed in the atmosphere the minute globules of water of which they are composed fall, relatively to the air, with a terminal velocity which may be deduced from Stokes' Law (§ 73). A cloud may, however, rise, relatively to the earth, if an upward current of air be present.

If the minute water globules fall through a warmer layer of dry air they will evaporate and the cloud will gradually disappear. If, on the other hand, they fall through a warmer but saturated region, further condensation will take place on their surface—since the globules are colder than the surrounding air—so that they will increase in size and velocity, and may fall to the earth as rain.

It has been pointed out that the larger drops in a mist tend to grow at the expense of the smaller ones, so that the latter gradually diminish in size and disappear. The very large drops of rain which occur in a thunderstorm are, however, mainly the result of electrical action, the effect of which is to cause the different drops to attract one another so that when they come in contact they coalesce. It must also be borne in mind that, in a thunderstorm, the drops usually fall through a saturated region of considerable depth before reaching the ground. Since the lower layers of air are, in general, warmer than those at a greater height, a considerable amount of condensation will take place during the fall, and large raindrops will therefore be formed.

The union of drops of water to form larger drops under the influence of an electrified body may be readily demonstrated by the following experiment:—

Experiment LXXX.—Allow a jet of water to issue nearly vertically from a small nozzle, and let the water fall upon a sheet of paper placed on the floor. The jet, as pointed out in paragraph 94, scatters irregularly over the paper, for many of the separate drops into which the jet breaks bounce together and rebound from one another. Now bring an electrified ebonite rod into the vicinity of the jet, and observe that the drops fall on the paper with a loud pattering sound. This is due to the fact that the drops no longer rebound from one another on collision but coalesce instead into larger drops.

A similar action can be shown by allowing two nearly horizontal jets of clean water to collide and bounce apart. If the electrified ebonite rod be brought into the neighbourhood the jets immediately coalesce.

The presence of a trace of oil will immediately cause the jets to unite and they will also do so if the air be very dusty. In the same way the drops in the jet of falling water will coalesce and form much larger drops if a very small quantity of oil be introduced into the jet.

The union of the drops in this case may be attributed to the reduction in the surface tension occasioned by the oil.

113. Laplace's Theory of Capillarity.—It has already been pointed out that the only essential difference between a gas and a liquid is the possession by the latter of a definite surface due to surface tension.

Laplace developed a theory of capillarity in accordance with which we may assume that the attractive force between two molecules in a liquid becomes negligibly small when the distance between the molecules exceeds a certain very small value known as the *range of molecular action.*

It must again be pointed out that the magnitude of the cohesive forces in a gas at the ordinary temperature and pressure is quite small, for it is only when the gaseous density is very high that the curved paths traversed by the molecules while casually within the sphere of action of other molecules bears a sensible ratio to their mean free path. In a liquid, on the other hand, the molecules are very much closer together and the molecular attractive forces give rise to very considerable cohesion.

It follows that a molecule of a liquid situated at the surface of separation between the liquid and its vapour is acted upon mainly by forces from the liquid side of the surface, since few, if any, of the molecules on the vapour side are within the range of molecular action; and this lack of symmetry in the distribution of the attractive forces gives rise to the phenomenon of surface tension.

In the interior of a liquid the molecular attractive forces are, on the average, symmetrically distributed, and, consequently, the average resultant attractive force exerted on a molecule is zero. There is thus neither gain nor loss of energy when a molecule moves from one position to another in the interior of a liquid. If, on the other hand, the surface of a liquid be increased in area, the molecules which come from the interior of the liquid to form the new surface must do work against molecular attraction in moving up to the surface. It follows, therefore, that when a liquid surface is enlarged adiabatically the liquid will grow colder (cf. § 91).

Since work must be done in bringing a molecule from the interior of a liquid up to the surface, the potential energy possessed by the surface molecules must be greater than that of the molecules in the interior. A mechanical system is, however, in equilibrium when its potential energy is a minimum, and it therefore follows that the surface of a liquid will tend to become as small as possible (cf. § 89).

We have seen that the phenomenon of surface tension may be attributed to the lack of symmetry in the distribution of the attractive forces which occurs at a surface of separation between a liquid and its vapour. When, however, a liquid and its vapour are heated together in a closed vessel to the critical temperature the molecular attraction becomes equal throughout both phases, and, since there is no longer any lack of symmetry, the surface of separation disappears and the two phases become identical. Now we are ignorant of the exact manner in which the attractive force between two molecules varies with the distance between them. Nevertheless, we can, as was shown by Laplace, deduce a number of important quantitative relations if we assume that the attractive force may be treated as negligible when the distance between the molecules exceeds a certain very small value, *c*, which is called the range of molecular action.

Thus, let XY (Fig. CXV.) represent the surface of separation between a liquid and its vapour. Consider a molecule, M, of the liquid situated at a depth, *d*, below the surface.

It is evident that, at any instant, molecular attractive forces will be exerted on M only by those molecules which are enclosed within a sphere of radius *c* and with M as centre. If *d* be less than *c* (Fig. CXV.), part of this sphere will lie above the surface XY, and this part of the sphere will contain practically no attracting molecules provided the temperature be sufficiently far below the critical temperature of the given fluid. Now, if AB represent a plane surface parallel to the surface XY and at a depth 2*d* below the latter it follows, from considerations of symmetry, that the average resultant attractive force exerted on the molecule M by the molecules of the liquid lying between AB and XY is zero.

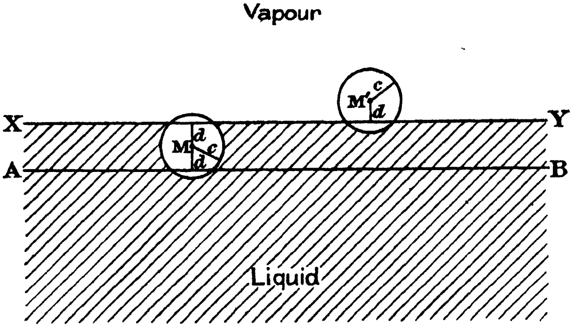

FIG. CXV.

Thus the resultant attractive force acting on the molecule M is due to those molecules of the liquid within its sphere of action which lie below the plane surface AB. It is thus evident that all molecules which do not lie at a greater depth than *c* below the surface XY are attracted towards the interior of the liquid, the attractive force being a maximum for those molecules situated at the liquid surface and becoming vanishingly small at a depth, *c*, equal to the range of molecular action.[*] We may, similarly, conclude that a molecule of vapour, M′ (Fig. CXV.), situated at a height *d* above the surface XY is attracted towards the liquid only by those molecules below XY which lie within its sphere of action. If, then, neither molecular dissociation nor polymerisation occur, on passing from the liquid to the vapour state, it follows that the resultant attractive force acting on a molecule of liquid, M, at a depth, *d*, below the surface XY is equal to that acting on a molecule of vapour, M′, at an equal distance above the surface. Thus the same amount of work must be expended in bringing a molecule from the interior of the liquid to the surface XY as in transporting it from the surface, into the vapour, to a point beyond the range of action of the liquid molecules.

The work done in transporting a molecule from the interior to the outside of a liquid may be calculated in the following manner:—

Let WXYZ (Fig. CXVI.) represent a disc of the liquid of thickness r and diameter $2r$, where r is greater than the range of molecular action, c. The attraction exerted by the disc on a molecule of the fluid, of mass m, situated at a point on the axis of the disc at a height x above the plane surface XY, will be $m \,.\, \rho \,.\, \phi(x)$, where ρ is the density of the liquid. The work done in moving the molecule a very small distance, δx, along the axis will therefore be $m \,.\, \rho \,.\, \phi(x) \,.\, \delta x$.

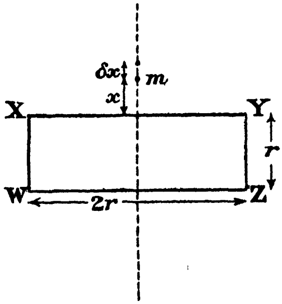

FIG. CXVI.

Now we are ignorant of the actual nature of the function $\phi(x)$, but it must evidently vanish for values of x greater than c. It follows, therefore, that the work done in transporting the molecule, of mass m, from the surface XY to a point beyond the range of molecular action of the liquid in the disc, is given by the expression—

$$m \,.\, \rho \int_0^c \phi(x) \,.\, dx.$$

This result is equally valid for a plane liquid surface of infinite extent when the depth of the liquid is greater than c.

An equal amount of work must, however, be expended in bringing a molecule from the interior of a liquid up to the surface, so that the total work done in transporting a molecule from the interior to the outside of a liquid is equal to—

$$2 \,.\, m \,.\, \rho \,.\int_0^c \phi(x) \,.\, dx.$$

Let K units of work be expended in transporting n molecules from the surface of a liquid to a distance exceeding the range of molecular action, *where n is the number of molecules contained in unit volume of the liquid.*

Then
$$K = n \,.\, m \,.\, \rho \,.\, \int_0^c \phi(x) \,.\, dx,$$
$$= \rho^2 \,.\, \int_0^c \phi(x) \,.\, dx, \text{ since } n \,.\, m \,. = \rho.$$

The total work done in transporting n molecules from the interior to the outside of the liquid will be 2K, and will therefore be equal to

$$2\rho^2 \,.\, \int_0^c \phi(x) \,.\, dx.$$

114. Latent Heat of Vaporisation.—The latent heat of vaporisation, L, of a liquid at any given temperature is defined as the quantity of heat required to vaporise unit mass of the liquid at that temperature, and in order to vaporise unit volume of the liquid $L \,.\, \rho$ heat units will be needed, where ρ is the density of the liquid.

This quantity of heat, which is required to vaporise unit volume of the liquid, must be equivalent to the total work done in transporting n molecules from the interior to the outside of the liquid (where n is the number of molecules contained in unit volume), *plus the external work done in pushing out the surrounding atmosphere.*

We may therefore write—
$$L \,.\, \rho \,.\, J = 2\rho^2 \,.\, \int_0^c \phi(x) \,.\, dx + W,$$
$= 2K + W$, where J is the mechanical equivalent of heat (*vide* Cap. I.), and W the work done in expanding against the atmospheric pressure.

In the case of water, at 100° C., we have—

$$L = 539 \text{ gm.-calories per gm.}$$
$$\rho = 0{\cdot}96 \text{ gm. per c.c.}$$
$$W = 1{\cdot}67 \times 10^9 \text{ ergs.}$$[1]

Whence—

$$2K = (539 \times 0{\cdot}96 \times 4{\cdot}19 \times 10^7) - (1{\cdot}67 \times 10^9) \text{ ergs/c.c.},$$
$$= (21{\cdot}68 \times 10^9) - (1{\cdot}67 \times 10^9) \text{ ergs/c.c.},$$
$$= 20{\cdot}01 \times 10^9 \text{ ergs./c.c.}$$
$$\therefore K = 1{\cdot}00 \times 10^{10} \text{ ergs/ c.c.}$$

115. The Tensile Strength of a Liquid.—It was pointed out in § 63 that liquids possess very considerable cohesion, and, consequently, can support a very large tension without rupture.

The tensile strength of a liquid may be readily calculated from the standpoint of Laplace's theory of capillarity.

Thus, let AB (Fig. CXVII.) represent the section of an imaginary

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[1] 1 c.c. of water at 100° C. forms 1647 c.cs. of saturated steam at the same temperature. The work done in expanding against the atmospheric pressure is, therefore, equal to 76 × 13·596 × 981 × 1646 ergs ; i.e. 1·67 × 10^9 ergs.

plane in the interior of a liquid, and let the liquid above the plane be divided up into very thin parallel layers of thickness δx. Consider a small element of one of these layers at a height x above AB. If the element be taken of unit area, and of thickness δx, its mass will be $\rho \, . \, \delta x$. The attractive force exerted on each unit of area of a layer at a height x above AB by the liquid below AB is therefore equal to $\rho^2 \, . \, \phi(x) \, . \, \delta x$; (cf. § 113).

Hence the total attractive force per unit area exerted by the liquid below AB on the liquid above AB is equal to $\rho^2 \, . \int_0^c \phi(x) \, . \, dx$; i.e. it is numerically equal to K.

This attractive force must be balanced by an internal or intrinsic pressure within the liquid which must also be numerically equal to K.

The total attractive force per unit area furnishes a measure of the tensile strength of the liquid, so that, in the case of water, at 100° C., the tensile strength is equal to $1{\cdot}00 \times 10^{10}$ dynes/cm.^{2}, or, approximately, 10,000 atmospheres.[1]

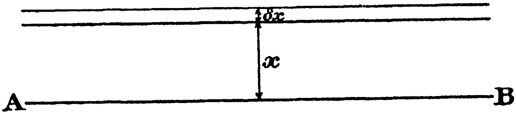

FIG. CXVII.

In the preceding investigation the influence of molecular motion has been neglected. Since, in accordance with the kinetic theory, the molecules of a liquid must be regarded as in a state of rapid motion, and undergoing incessant collisions with one another, it follows that these molecular collisions will give rise to an internal pressure which tends to neutralise the attractive force between the molecules, and thus diminishes the tensile strength of the liquid.

If the temperature be raised both the molecular velocity and the frequency of molecular collision will be increased, with a corresponding diminution in the tensile strength.

116. Molecular Escape from a Liquid Surface.—We have seen (§ 63) that in accordance with the kinetic theory the evaporation of a liquid is due to the gradual escape of the molecules through the liquid surface, and that since the more rapidly moving molecules escape more readily a cooling effect will be produced by the evaporation. Let a molecule, of mass m, leave the surface of a liquid normally with a velocity v. The work that must be done in transporting the molecule from the surface to a point beyond the range of molecular

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[1] The tensile strength of water is therefore approximately the same as that of ordinary steel wire.

action of the liquid is $m \,.\, \rho \int_0^c \phi(x) \,.\, dx$; i.e. $\frac{K \,.\, m}{\rho}$. The molecule will, consequently, escape if its translatory kinetic energy, $\frac{1}{2}m \,.\, v^2$, is greater than

$$\frac{K \,.\, m}{\rho}; \text{ i.e. if } v > \sqrt{\frac{2K}{\rho}}.$$

In the case of water, at 100° C., we have—

$$v > \sqrt{\frac{2{\cdot}00 \times 10^{10}}{0{\cdot}96}}.$$

i.e.

$$v > 1{\cdot}44 \times 10^5 \text{ cms./sec.}$$

It was shown (in § 18) that the mean molecular velocity, Ω, for oxygen at 0° C. was approximately $4{\cdot}25 \times 10^4$ cms./sec., so that at 100° C. the mean molecular velocity will be approximately $4{\cdot}96 \times 10^4$ cms./sec. Since, at a given temperature, the mean molecular velocities of two different gases are inversely proportional to the square roots of the molecular masses, it follows that the mean velocity of a molecule of water vapour, at 100° C., will be approximately $4{\cdot}96 \times 10^4 \times \sqrt{\frac{32}{18}}$ cms./sec., i.e. $6{\cdot}61 \times 10^4$ cms./sec. Thus at 100° C. a molecule of water must leave a plane water surface with a normal velocity more than double the mean velocity possessed by molecules of water vapour at the same temperature in order that it may escape from the liquid.

117. The Surface Energy of a Liquid.—It has been shown (§ 88) that the increase in the potential energy possessed by a liquid, per unit increase of area, is numerically equal to the surface tension, T.

If, then, we imagine that the liquid above the plane AB (Fig. CXVII.) be moved away from the liquid below AB to a distance exceeding the range of molecular action, c, the work done per unit area of AB will be numerically equal to 2T, since *two* new unit surfaces will have been produced.

Now we are ignorant of the manner in which the attractive force exerted on a molecule varies with its distance from the surface AB. We shall therefore assume, provisionally, that on starting from the surface the force remains constant throughout a normal displacement equal to the range of molecular action, c, and then falls suddenly to zero. When the liquid above the plane AB is displaced normally to that plane, work is done against molecular attraction until all the molecules initially present in a layer of thickness c above AB have been removed beyond the range of molecular action of the liquid below, and the *average* displacement of each of these molecules *while under the influence of the molecular attraction of the liquid below AB* is therefore equal to $\frac{c}{2}$

Now the total attractive force per unit area exerted by the liquid below AB on the liquid above is equal to $\rho^2 . \int_0^c \phi x . dx$, i.e. K; and since, in accordance with our provisional assumption, the attractive force acting on each molecule remains constant until the molecule passes beyond the range of molecular action, c, it follows that the total work expended per unit area of AB in separating the liquid above AB from the liquid below is equal to $K \times \frac{c}{2}$.

$$\therefore 2 . T = \frac{K . c}{2}.$$

$$\therefore c = \frac{4 . T}{K}.$$

It is almost certain, however, that the molecular attractive force is *not* constant throughout the range of molecular action. If we assume, instead, that the attractive force diminishes as the displacement increases, the range of molecular action, c, must be greater than $\frac{4 . T}{K}$ in order that the total work expended in separating the liquid may still be equal to 2 . T for each unit of area of AB. We can thus obtain—as was first pointed out by Young—an *inferior limit* for the range of molecular action.

In the case of water, at 100° C., we have—

$$c > \frac{4 \times 58{\cdot}4}{1{\cdot}00 \times 10^{10}} \text{ cms.}$$

$$\text{i.e. } c > 0{\cdot}23\mu\mu.$$

118. The Equation of van der Waals.—It was shown, in § 58, that the term $\frac{a}{V^2}$ which occurs in the van der Waals' equation corresponds to the diminution in the pressure exerted by a fluid on the boundary walls of a containing vessel owing to internal molecular cohesion.

If we consider any imaginary plane in the interior of the fluid, $\frac{a}{V^2}$ is the attractive force per unit area exerted by the fluid on one side of the plane on the fluid on the other side, so that, in the case of a liquid system, the term $\frac{a}{V^2}$ denotes the internal or intrinsic pressure and is numerically equal to K.

As was pointed out in § 58 the values of a, b and R in van der Waals' general equation can be obtained by substituting the corresponding values of P and V for the homogeneous fluid as experimentally determined at various temperatures.

Thus the volume of 1 gm. of saturated steam at 0° C. is 202,602 c.cs., its pressure being 0·47 cm. of mercury; and the volume of the same mass of saturated steam at 100° C., is 1672 c.cs., its pressure being 76 cms. of mercury.

Substituting these values in van der Waals' equation, and treating the volume b as negligible in comparison with the volume occupied by the vapour, we have—

$$\left(P + \frac{a}{V^2}\right)(V - b) = R.\theta.$$

$$\therefore \left(0{\cdot}47 \times 13{\cdot}596 \times 981 + \frac{a}{(202602)^2}\right).202602 = R.273,$$

and similarly—

$$\left(76 \times 13{\cdot}596 \times 981 + \frac{a}{(1672)^2}\right).1672 = R.373.$$

Solving for a we obtain the result—

$$a = 6{\cdot}1 \times 10^{10}.$$

Since the volume of 1 gm. of water at 100° C. is 1·04 c.c., we have—

$$\frac{a}{V^2} = \frac{6{\cdot}1 \times 10^{10}}{(1{\cdot}04)^2} = 5{\cdot}7 \times 10^{10} \text{ dynes/cms.}^2$$

Although it cannot be pretended that this result is in close agreement with the value of K deduced from the latent heat of vaporisation of water, yet it is evident that both Laplace's theory of capillarity and the equation of van der Waals lead to values for the internal pressure of a fluid which possess the *same order of magnitude.*

CHAPTER IX.

SOLIDS.

119. The Solid State of Matter.—The solid state has already been defined as that in which matter can permanently resist an applied tangential or shearing stress provided the latter be not too great in magnitude.

Now although solid bodies can, in general, preserve their shape for a very long time without any perceptible change, it must not be concluded that their molecules are therefore absolutely fixed relatively to one another. It was shown, for example, by Sir W. Roberts-Austen that gold diffuses through lead to an appreciable extent when the two metals are kept in contact at the atmospheric temperature, and other cases of solid diffusion have also been observed.

The vaporisation of solids, to which reference was made in § 75, also shows that the molecules of solid bodies are in a state of motion, the maximum or saturation vapour pressure for a solid corresponding to a state of dynamic equilibrium in which as many molecules land back upon the surface of the solid as escape from it in unit time.

The sublimation of a solid may be regarded as analogous to the distillation of a liquid, and, as was shown by Ramsay and Young, there is a definite "subliming-point" in the former case—corresponding to the boiling-point in the case of a liquid—at which the vapour pressure of the solid is equal to the atmospheric pressure.

In considering the properties of solids from the standpoint of the kinetic theory, it must be borne in mind that in solid systems the molecules are sufficiently close together to exert very considerable cohesion; the existence of cohesive forces being exhibited in the great resistance offered by solid bodies to changes of shape or volume.

120. Elasticity.—Gases, liquids, and solids all resist compression and thus possess *volume* or *bulk elasticity*, but solids alone possess *elasticity of shape*, for fluids, by definition (§ 62), yield continuously to applied tangential or shearing stresses, however small the magnitude of the latter may be, and thus offer no permanent resistance to changes of shape.

When the shape or volume of a body alters in any way, due to applied forces, the deformation of the body is termed a *strain*, the deforming forces being termed *stresses*.

The ratio of the applied stress to the resulting strain is termed a *modulus of elasticity* provided the applied stress be so small that the ratio is *constant.*

When the volume of a body alters due to a uniform pressure, the shape of the body remaining unchanged, the stress is measured by the pressure, i.e. by the normal force per unit area, and the strain by the ratio of the diminution of volume to the original unstrained volume, the ratio of stress to strain being termed the volume elasticity, or the *bulk modulus of elasticity.*

If, on the other hand, the shape of a body alters due to an applied shearing stress, the volume remaining unchanged, the stress is measured by the tangential force per unit area, and the strain by the angle of shear, the ratio of stress to strain being termed the shear modulus, or *modulus of rigidity.*

When a wire is stretched by an applied force acting along its length (while no forces act at right angles to the length), the longitudinal stress is given by the quotient of the applied force by the cross-section of the wire, and the longitudinal strain by the quotient of the increase in length by the original length of the unstrained wire. In this case the ratio of longitudinal stress to longitudinal strain is termed longitudinal elasticity, or *Young's Modulus.*

121. Isotropism and Æolotropism.—When every particle of a body possesses identical physical properties and chemical composition the body is said to be homogeneous. The term homogeneity is, however, employed in a less restricted sense to cover uniform mixtures of different substances. Thus a solution of sugar in water, a piece of glass, and a bronze coin are commonly regarded as homogeneous bodies.

A homogeneous body is said to be *isotropic* when it has similar properties in all directions. A well annealed piece of glass is, at any rate very approximately, both homogeneous and isotropic. The properties of many homogeneous bodies vary, however, in different directions. Such bodies are said to be *æolotropic.* Many crystalline bodies, for example, are æolotropic with regard to their thermal expansion and thermal conductivity. Wood, similarly, exhibits æolotropism, its tensile strength, for example, being considerably greater along the grain than at right angles to the latter.

122. Hooke's Law.—The general law of elasticity that strains are proportional to the deforming forces producing them was originally enunciated by Hooke in the form "*ut tensio, sic vis,*"[1] and was subsequently stated by Young in the modified form—*stress is proportional to strain.*

This law of the proportionality between stresses and strains only

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[1] Boyle's Law may be regarded as a particular case of this law.

holds good provided the applied stress be sufficiently small. If, for example, a vertical metal wire which is firmly fixed at its upper end be stretched by placing different weights in a scale-pan attached to its lower end, it is found that the elongation produced is proportional to the load per unit area of cross-section of the wire provided the load does not exceed a certain value. Up to this point the wire will recover its original length if the load be removed, and the corresponding extensions of the wire are therefore said to lie within the *range of perfect elasticity*, but for greater values of the load the wire is found to acquire a *permanent elongation* or *set* and is said to have been stretched beyond the *elastic limit*.

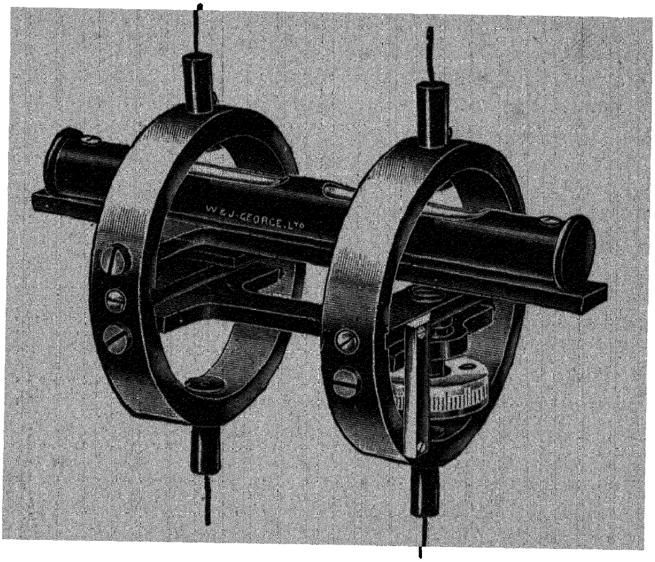

FIG. CXVIII.—Searle's Apparatus for determining Young's Modulus for a Wire.

After passing the elastic limit the elongation of the wire increases more rapidly than the load and Hooke's Law ceases to apply.

123. Determination of Young's Modulus from the Stretching of a Wire.—When a wire is stretched by a force acting along its length the ratio of the longitudinal stress to the longitudinal strain gives the value of Young's modulus for the material of which the wire is composed.

Experiment LXXXI.—Fig. CXVIII. illustrates an improved form of apparatus, devised by Searle, for determining Young's modulus for a wire.

Two long, similar wires of the given material are fixed at their upper ends to the same support, their lower ends being soldered into small brass swivels which pass through the tops of two circular brass frames. The wires are arranged parallel to each other, the swivels ensuring freedom from torsion. The circular frames (which are hinged together, so as to permit relative vertical motion), support the ends of a sensitive spirit level, one end of the latter being pivoted to the frame, while the other end rests on the point of a vertical micrometer screw, as shown in the figure.

Two shorter wires are soldered into brass swivels which pass through the bottoms of the circular frames, one of the wires carrying a scale-pan and the other a fixed mass. The weights of the scale-pan and the fixed mass must be sufficient to keep the two longer wires taut and free from kinks.[1]

The micrometer screw is initially adjusted so that one end of the bubble of the spirit level is at the zero mark. Different loads are then placed in the scale pan, and the bubble brought back to zero by means of the micrometer screw, the longitudinal extension of the wire, in each case, being given by the distance through which the screw has been moved.

Since the two wires are fixed at their upper ends to the same support, and since their coefficients of expansion may be assumed sensibly the same, even though the wires are subjected to different stresses, errors arising from the yielding of the support, and from variations of temperature, are practically eliminated.

The load in the scale-pan should be progressively increased by the addition of equal weights, and, subsequently, decreased by their removal, the micrometer screw being adjusted after each addition or removal and its reading noted. The mean of the two readings, with the load increasing and decreasing, for each particular load is then taken as the corresponding extension of the wire.

The weight of the scale-pan must, of course, be included in the value for the total load, and care must be taken that the maximum load employed is not sufficient to stretch the wire beyond the elastic limit.

The cross-section of the wire may be determined by measuring the diameter of the wire by means of a screw-gauge. Measurements should be made at a number of points, and, at each point, in two directions at right angles to one another, in order to make sure that the wire is of uniform section.

Instead of calculating the cross-section from measurements of the diameter of the wire, a more accurate method is to weigh a measured length of the wire in air and then in water. The volume of the wire is then readily calculated from the difference between the two weights

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[1] In carrying out a determination of Young's modulus the scale pan should be initially loaded, for a short time, to about one-half of the breaking load of the wire to ensure the wire being thoroughly straightened.

and from a knowledge of the density of the water at the temperature of the experiment. The cross-section is then found by dividing the volume of the wire by its length. The uniformity of the cross-section must initially be tested by means of a screw-gauge.

Let the original length of the wire between the fixed support and the point where it is soldered into the brass swivel be L cms., and its cross-section a cms.^{2}, and let the mean extension due to a load of W gms.-wt. be l cms.

Then Young's modulus, Y, is given by the relation—

$$Y = \frac{W \,.\, L}{a \,.\, l} \,.\, \text{gms.-wt./cm.}^2$$
$$= \frac{W \,.\, L \,.\, g}{a \,.\, l} \,.\, \text{dynes/cm.}^2$$

The following table gives the experimental values obtained for Young's modulus, for a number of different materials, in dynes per square centimetre :—[1]

Material.	Young's Modulus, Y.
Brass (*c.* 66 per cent. Cu, 34 per cent. Zn).	9·7-10·2 × 10″
Copper	12·4-12·9 × 10″
Iron (wrought)	19-20 × 10″
Silver	7·9 × 10″
Steel	19·5-20·6 × 10″

If, in Experiment LXXXI., the loads be plotted as ordinates and the corresponding extensions of the wire as abscissæ, we obtain at first an approximately straight line OA (Fig. CXIX.), showing that the extension is proportional to the load. If, however, the load be progressively increased, a point A is reached at which the extension increases more rapidly than the load, and the curve now takes the form AB. The point A represents the *elastic limit* of the material of which the wire is composed. Up to this point the wire will recover its original length if the load be removed, whereas for loads greater than that corresponding to the point A the wire requires a permanent elongation. On further increasing the load a point B is reached at which the curve becomes nearly horizontal, very large extensions being produced by any further small increments in the load. The point B is called the *yield-point*.

The maximum value, C, for the load arises from the diminution in

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[1] The values are those at the ordinary atmospheric temperature. In general, a substance becomes more plastic with rise in temperature, and more elastic when cooled. Thus a piece of lead when cooled in liquid air becomes highly elastic and rings clearly when struck.

the sectional area of the wire occasioned by the extension, any further elongation of the wire beyond the point C, *reducing* the value of the load which can be supported without rupture. The curve, therefore, slopes downwards from C until the *breaking-point* D is reached. In the neighbourhood of the point C, the wire begins to stretch out unevenly and the cross-section ceases to be uniform.

The curve OAEF (Fig. CXIX.) represents the relation between stress and strain, allowance being made for the diminution in the sectional area of the wire produced by the extension. After passing the elastic limit at A the strain increases more rapidly than the stress until a point E is reached where the longitudinal elasticity again becomes approximately constant, as is shown by the straight portion, EF, of the stress-strain curve. If, after passing the point E, the load be gradually removed, the wire will contract along the path EG, retaining a permanent elongation OG, when the whole load has been removed.[1]

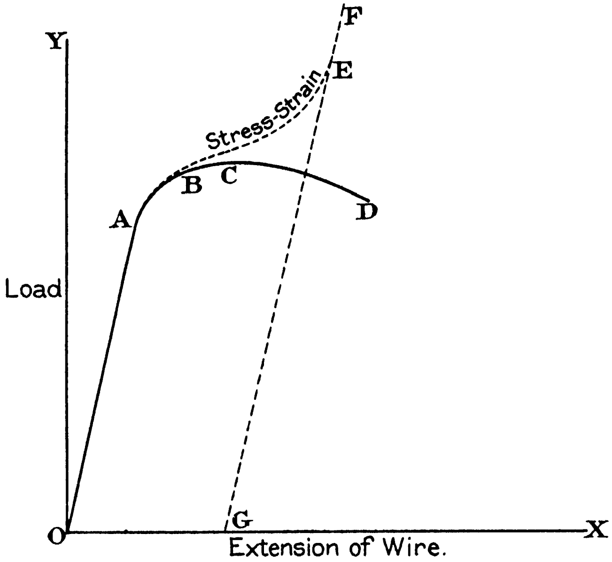

Fig. CXIX.

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[1] The fact that hard drawn copper wire, for example, has a considerably higher elastic limit than annealed copper wire may be explained in this manner. Microscopic examination of a section of a well annealed metal shows numerous crystalline aggregates with cleavage planes in definite directions. After straining the metal past the elastic limit it is found that relative motion has occurred amongst the crystals composing the aggregates, resulting in a more irregular distribution of the planes of cleavage. The metal, consequently, yields less readily to an applied stress in any given direction.

124. Elastic After-Effect and Elastic Fatigue.—It has been seen that a loaded wire will contract to its original length on removal of the load provided it has not been stretched beyond the elastic limit. Different materials, however, are found to take different times for the contraction, the delay in recovering the original length being termed the *Elastic After-Effect.*

A stretched steel wire, for example, recovers almost immediately, whereas a stretched glass fibre may take many hours. The period of delay is, in general, increased by leaving the wire loaded for a considerable time.

It was shown by Lord Kelvin that if a torsion pendulum were kept vibrating continuously for some time the rate at which the vibrations died away became greater and greater. This phenomenon is termed Elastic Fatigue. On allowing the torsion pendulum to remain stationary for some hours the period of vibration recovered its original value.

125. Poisson's Ratio.—When a cylindrical wire, for example, is stretched by the application of a longitudinal stress it extends longitudinally and, at the same time, undergoes a lateral contraction. Provided the applied longitudinal stress be sufficiently small it is found that, for isotropic substances, the ratio of the lateral contraction to the longitudinal extension is *constant.*

This ratio is termed *Poisson's Ratio.*

If the initial length of the unstrained wire be l, its diameter being d, and if a small longitudinal extension δl produce a lateral contraction δd, we have—

$$\sigma = \frac{\delta d}{d} \Big/ \frac{\delta l}{l}, \text{ where } \sigma \text{ is Poisson's ratio.}$$

In accordance with a molecular hypothesis developed by Poisson and Cauchy the value of σ for all isotropic bodies should be 0·25, but this conclusion is not supported by experimental evidence.

126. Deformation of an Isotropic Cube.—Consider a cube ABCDA′B′C′D′ (Fig. CXX.) of an isotropic solid. Let the faces ABCD and A′B′C′D′ be subjected to small normal tensile stresses of F_1 dynes per unit area. These stresses produce an extension proportional to F_1 in the direction AA′, and contractions proportional to F_1 in the directions AB and AD. The contractions in the directions AB and AD must be the same since the solid is isotropic. Let the extension in the direction AA′ be $\alpha . F_1$, and the contractions in the directions AB and AD be $\beta . F_1$. If the faces ABB′A′ and DCC′D′ of the cube were similarly subjected to small normal tensile stresses of F_2 dynes per unit area the extension in the direction AD would be $\alpha . F_2$, and the contractions in the directions AB and AA′ would be $\beta . F_2$. If, similarly, small normal tensile stresses of F_3 dynes per unit area were exerted on the faces ADD'A' and BCC'B', the extension in the direction AB would be $\alpha . F_3$, and the contractions in the directions AD and AA' would be $\beta . F_3$. If, now, the tensile stresses F_1, F_2, and F_3 be applied simultaneously, the resultant extension in the direction AA' is $\alpha . F_1 - \beta . F_2 - \beta . F_3$; the extension in the direction AD is $\alpha . F_2 - \beta . F_3 - \beta . F_1$; and the extension in the direction AB is $\alpha . F_3 - \beta . F_1 - \beta . F_2$.

Let the edge of the cube be, initially, of unit length, and let us consider the case where the tensile stresses F_1, F_2, and F_3 are all *equal*. Since each face of the cube is subjected to a small normal tensile stress of, say, F dynes, the length of each edge becomes—

$$1 + \alpha . F - 2\beta . F.$$

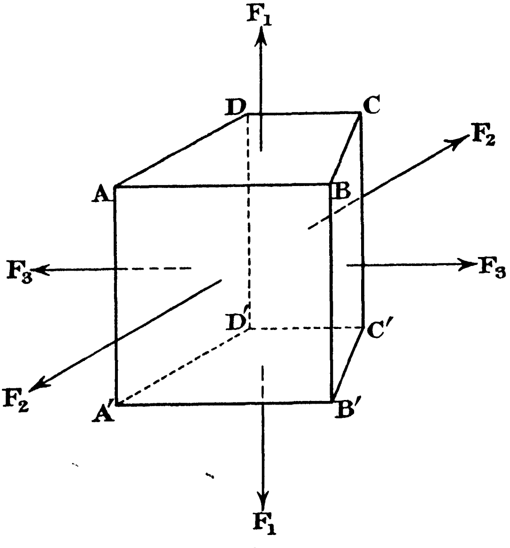

FIG. CXX.

The volume of the cube, therefore, becomes $\{1 + F(\alpha - 2\beta)\}^3$, i.e. $1 + 3F(\alpha - 2\beta)$, neglecting the terms containing the squares, cubes, and products of the very small quantities α and β. Thus the increase in the volume of a unit cube of an isotropic solid when each face is subjected to a small normal tensile stress, F, is $3F(\alpha - 2\beta)$.

127. The Bulk Modulus of Elasticity.—When the volume of a body alters due to a uniform pressure, the shape of the body remaining unchanged, the stress is measured by the pressure, i.e. by the normal force per unit area, and the strain by the ratio of the diminution of volume to the original unstrained volume, and the ratio of stress to strain is termed the Bulk Modulus of Elasticity. If, in the preceding investigation of the deformation of a unit isotropic cube, the normal tensile stress, F, exerted on each face be replaced by an equal normal compressive stress, we must change the sign of F in order to obtain the *increase* in the volume. Thus the *decrease* in the volume of a unit isotropic cube when subjected to a small hydrostatic pressure F is equal to $3F(\alpha - 2\beta)$.

It follows that—

$$K = \frac{F}{3F(\alpha - 2\beta)} = \frac{1}{3(\alpha - 2\beta)},$$

where K is the Bulk Modulus of Elasticity.

128. The Shear Modulus, or the Modulus of Rigidity.—When the shape of a body alters due to an applied shearing stress, the volume remaining unchanged, the stress is measured by the tangential force per unit area, and the strain by the angle of shear, and the ratio of stress to strain is termed the Shear Modulus or the Modulus of Rigidity.

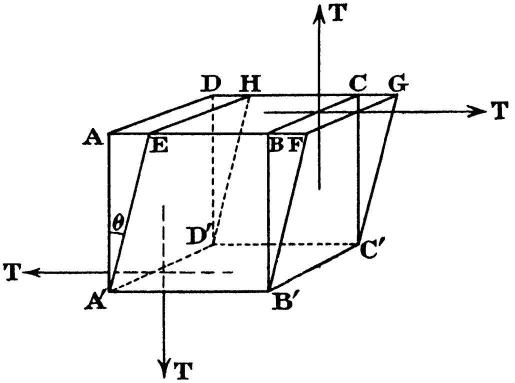

Fig. CXXI.

Thus let ABCDA′B′C′D′ (Fig. CXXI.) represent a cube, the edge of which is of unit length, and let it experience a uniform shear, so that it is deformed to the shape EFGHA′B′C′D′. In such a uniform shear all planes parallel to the fixed plane A′B′C′D′ remain undistorted, but experience a tangential displacement, relatively to each other, the displacement of any plane being proportional to its distance from the plane A′B′C′D′.

A uniform shear of this kind may be illustrated by placing a pack of playing cards on a table, so that the edges of the pack are vertical, and then sliding the cards forward, while the lowest card remains stationary, so that the ends of the pack remain plane but are no longer vertical. Any plane at right angles to the fixed plane A′B′C′D′ (Fig. CXXI.) and parallel to the direction of motion is called the *plane of* *the shear*, and the angle AA′E is termed the *angle of shear*. Let us next consider the forces that must be applied in order to produce this uniform shear parallel to the plane ABB′A′ in the unit cube ABCDA′B′C′D′ (Fig. CXXI.). Let a uniform tangential force, T, act on the face ABCD, from left to right, as shown in the figure, while an equal tangential force acts on the face A′B′C′D′ in the opposite direction. These forces constitute a couple tending to rotate the cube in a clockwise direction, and, in order to maintain equilibrium, let tangential forces equal to T act on the faces ADD′A′ and BCC′B′ tending to rotate the cube counter-clockwise.

These two couples will now be in equilibrium with one another, but will shear the cube as shown in the figure.

If we denote the angle of shear by θ, the tangential force acting on unit area being T, we have, in accordance with our previous definition—

$$n = \frac{T}{\theta}, \text{ where } n \text{ is the } \textit{Modulus of Rigidity.}$$

As in the case of other elastic moduli n is only sensibly constant provided the applied stress be sufficiently small.

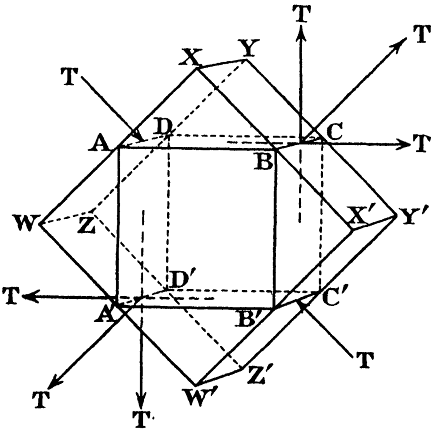

Fig. CXXII.

Now, it can be shown that a shear is the resultant of an extension in one direction and an equal contraction at right angles to that direction, and we shall therefore proceed to consider how a shearing stress is produced by mutually perpendicular tensile and compressive stresses.

Let our unit cube ABCDA′B′C′D′ be the centre portion of a rectangular block WXYZW′X′Y′Z′ (Fig. CXXII.), composed of the same isotropic solid, the faces ABB′A′ and DCC′D′ of the cube lying, respectively, in the faces WXX′W′ and ZYY′Z′ of the rectangular block, while the remaining faces of the cube cut the adjacent sides of the rectangular block at 45°, as shown in the figure.

Let the sides WXYZ and W′X′Y′Z′ of the rectangular block be subjected to small normal compressive stresses of T dynes per unit area, while equal normal tensile stresses, T, are exerted on the sides XX′Y′Y and WW′Z′Z.

Since the edge of the cube is of unit length, the length of the edge

AX of the triangular prism AXBDYC is $\frac{1}{\sqrt{2}}$, and the area of the face AXYD is $1 \times \frac{1}{\sqrt{2}}$. Hence the normal compressive force acting on the face AXYD is equal to $\frac{T}{\sqrt{2}}$ dynes. The normal tensile force acting on the face XBCY is, similarly, $\frac{T}{\sqrt{2}}$ dynes. The resultant of these two forces is equal to $2 \cdot \frac{T}{\sqrt{2}} \cdot \cos 45°$, i.e. T dynes, acting tangentially on the face ABCD, and since the area of ABCD is unity the shearing stress on this face of the cube is equal to T.

It follows, in a similar manner, that the faces BB'C'C, B'A'D'C', and A'ADD' of the cube are each acted upon by shearing stresses equal to T, as shown in the figure.

Thus the uniform shear due to the tangential stresses T, illustrated in Fig. CXXI., is that which would be produced if the cube were the centre portion of a rectangular block acted upon by mutually perpendicular compressive and tensile stresses, T, as shown in Fig. CXXII.

In general we may say that when an isotropic solid is subjected to mutually perpendicular compressive and tensile stresses of equal magnitude it undergoes a shear in a direction inclined at 45° to these stresses.

The tensile and compressive stresses, T, acting upon the rectangular block WXYZW'X'Y'Z' (Fig. CXXII.), produce an extension in the direction WX, and a contraction in the direction WW'. The magnitudes of the extension and contraction per unit length can be at once deduced from § 126, by putting $F_1 = T$, $F_2 = -T$, and $F_3 = 0$.

Thus the *extension* per unit length in the direction WX equals $T(\alpha + \beta)$, and the *contraction* per unit length in the direction WW' also equals $T(\alpha + \beta)$. Since the length of AB is unity, the length of WX, or of WW' is $\sqrt{2}$, and, consequently, the extension in the direction WX is $\sqrt{2} \cdot T \cdot (\alpha + \beta)$, the contraction in the direction WW' having an equal value.

Thus we may regard the shear of our unit cube ABCDA'B'C'D' as an extension of $\sqrt{2} \cdot T(\alpha + \beta)$ in the direction of the diagonal A'B combined with an equal contraction in the direction of the diagonal AB', i.e. in a direction at right angles to A'B.

Let ABB'A' (Fig. CXXIII.) represent the face of the unstrained unit cube, and EFB'A' the same face after the cube has experienced the small uniform shear. Draw the diagonals A'F and EB', intersecting at O.

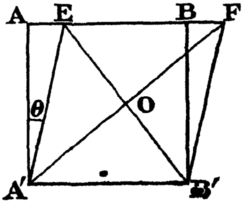

Fig. CXXIII.

Denoting the angle of shear, AA′E, by θ, expressed in circular measure, we have—

$$\frac{EB'}{A'F} = \frac{OB'}{A'O} = \tan OA'B' = \tan\left(\frac{\pi}{4} - \frac{\theta}{2}\right) = \frac{1 - \tan\frac{\theta}{2}}{1 + \tan\frac{\theta}{2}}.$$

But
$$\frac{EB'}{A'F} = \frac{\sqrt{2} - \sqrt{2}\,.\,T(\alpha + \beta)}{\sqrt{2} + \sqrt{2}\,.\,T(\alpha + \beta)} = \frac{1 - T(\alpha + \beta)}{1 + T(\alpha + \beta)}.$$

Whence
$$\frac{1 - T(\alpha + \beta)}{1 + T(\alpha + \beta)} = \frac{1 - \tan\frac{\theta}{2}}{1 + \tan\frac{\theta}{2}}.$$

$$\therefore T(\alpha + \beta) = \tan\frac{\theta}{2},$$

$$= \frac{\theta}{2},$$

provided the angle of shear be infinitesimally small.

Since $n = \frac{T}{\theta}$, we have—

$$T(\alpha + \beta) = \frac{T}{2n}.$$

$$\therefore n = \frac{1}{2(\alpha + \beta)}.$$

The extension per unit length of the rectangular block WXYZW′X′Y′Z′ (Fig. CXXII.), in the direction WX is thus equal to $\frac{\theta}{2}$, i.e. equals $\frac{T}{2n}$, the contraction per unit length in the direction WW′ having the same value.

129. Elastic Constants.—In the two preceding paragraphs the bulk modulus of elasticity, k, and the modulus of rigidity, n, were expressed in terms of α and β. We may now readily find expressions for Young's modulus and for Poisson's ratio in terms of k and n for any isotropic solid.

Consider the unit isotropic cube ABCDA′B′C′D′ (Fig. CXX.), and let the faces ABCD and A′B′C′D′ be subjected to small normal tensile stresses of F dynes, the remaining faces of the cube being free from stress. These stresses produce an extension αF in the direction AA′.

Then Young's modulus, Y, is given by the relation—

$$Y = \frac{F}{\alpha F} = \frac{1}{\alpha}.$$

It has, however, been shown that the bulk modulus of elasticity, k, and the modulus of rigidity, n, for the unit isotropic cube, are given by the respective equations—

$$k = \frac{1}{3(\alpha - 2\beta)},$$

$$n = \frac{1}{2(\alpha + \beta)}.$$

It follows, from the last two equations, that—

$$\alpha = \frac{3k + n}{9kn},$$

$$\beta = \frac{3k - 2n}{18kn}.$$

Whence $$Y = \frac{1}{\alpha} = \frac{9kn}{3k + n}.$$

Now the tensile stresses, F, exerted on the faces ABCD and A'B'C'D' of the unit isotropic cube produce a longitudinal extension αF in the direction AA', and lateral contractions βF in the directions AB and AD.

The ratio of the lateral contraction to the longitudinal extension has already been defined as Poisson's ratio, σ.

Thus $$\sigma = \frac{\beta F}{\alpha F} = \frac{3k - 2n}{2(3k + n)}.$$

130. Torsion of a Cylinder.—Let ABCA'B'C' (Fig. CXXIV.) represent a short element of a right circular cylinder of an isotropic solid, the parallel planes ABC and A'B'C' being at right angles to the axis of the cylinder, and l cms. apart. Let the upper face ABC of the element be fixed, and let a small couple whose axis is the axis of the cylinder be applied to the lower face A'B'C'.

The element, when subjected to this small uniform torsion, is twisted in such a manner that every cross-section of the element made by planes parallel to ABC is twisted in its own plane through an angle proportional to its distance from the fixed plane

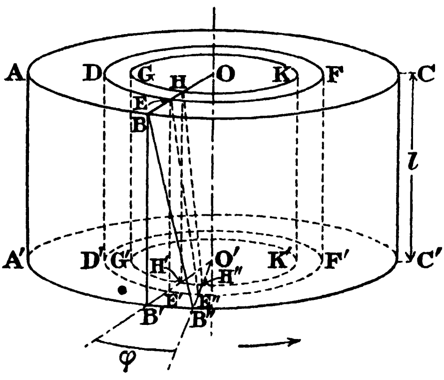

FIG. CXXIV.

ABC, while the axis OO′ of the element remains in the same straight line as before.

Consider the portion DEFD′E′F′GHKG′H′K′ of the element bounded by coaxial cylinders of radii OH and OE, respectively, and by the two parallel planes ABC and A′B′C′. Let OH = r, and OE = $r + \delta r$, where δr is very small.

Let OHEB and O′H′E′B′ be radii of the cylindrical element initially in the vertical plane OHEBB′E′H′O′ passing through the axis of the cylinder. When the element is subjected to the small uniform torsion, the radius O′H′E′B′ is twisted through an angle B′O′B″ proportional to the distance between the plane A′B′C′ and the fixed plane ABC. Let the angle B′O′B″ be equal to ϕ, expressed in circular measure.

If the cylindrical element were originally cut along the vertical plane OHEBB′E′H′O′ and the very thin annulus DEFD′E′F′GHKG′H′K′ removed and spread out flat, the latter would form a thin rectangular block EHE′H′$ehe'h'$ (Fig. CXXV.), the faces EHE′H′ and $ehe'h'$ of which were originally joined together.

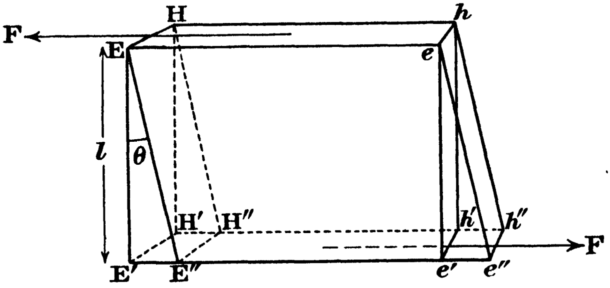

FIG. CXXV.

If, however, the annulus were removed and spread out *after twisting the cylindrical element*, a rectangular block would no longer be obtained, the effect of the uniform torsion being to shear the block to the shape EHE″H″$ehe''h''$, as shown in the figure.

Let the angle of shear, E′EE″ be equal to θ, expressed in circular measure.

Then $\theta = \dfrac{\text{E}'\text{E}''}{\text{EE}'}$, provided the angle of shear be infinitesimally small.

In order to produce this shear, a tangential force, F, must act on the face E′H′$e'h'$, from left to right, while an equal tangential force acts on the face EHeh in the opposite direction, as shown in the figure.[1]

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[1] Tangential forces must also act on the faces EHE′H′ and $ehe'h'$, but these may be disregarded in dealing with the equilibrium of the *annulus*

Then, if n be the modulus of rigidity, we have—

$$n = \frac{\frac{F}{E'H'e'h'}}{\theta} = \frac{\frac{F}{2\pi r \,.\, \delta r}}{\frac{E'E''}{EE'}}.$$

But $\frac{E'E''}{EE'} = \frac{H'H''}{HH'}$, provided δr be infinitesimally small; and $\frac{H'H''}{HH'} = \frac{r \,.\, \phi}{l}$.

$$\therefore n = \frac{\frac{F}{2\pi r \,.\, \delta r}}{\frac{r \,.\, \phi}{l}}.$$

Whence $$F = \frac{2\pi r^2 \,.\, \delta r \,.\, n \,.\, \phi}{l}.$$

Now in the case of the *annulus* DEFD'E'F'GHKG'H'K' (Fig. CXXIV.), the tangential forces acting on the faces DEFGHK and D'E'F'G'H'K' constitute equal but oppositely directed *torques* acting about the axis OO'. Thus the torque, δM, about the axis OO', due to the tangential force F acting on the face D'E'F'G'H'K' of the annulus, is given by—

$$\delta M = F \,.\, r,$$
$$= \frac{2\pi r^3 \,.\, \delta r \,.\, n \,.\, \phi}{l}.$$

The total torque, M, about the axis OO', that must be applied to the lower face A'B'C' of the cylindrical element in order to twist the face A'B'C' in its own plane through the angle ϕ, is therefore given by—

$$M = \int_0^R dM = \frac{2\pi n\phi}{l} \,.\, \int_0^R r^3 \,.\, dr = \frac{2\pi n\phi}{l} \,.\, \frac{R^4}{4} = \tfrac{1}{2}\pi n \frac{\phi}{l} \,.\, R^4,$$ where R is the radius of the cylindrical element.

An equal but oppositely directed torque must, of course, be exerted on the upper face ABC of the cylindrical element in order to keep this face fixed.

Now the angle of shear, θ, increases as the distance from the axis OO' increases, so that the shearing strain is greatest in the outside layers of the cylindrical element. It has, however, been tacitly assumed that even at the curved surface of the element the angle of shear, B'BB'', is very small, since otherwise the equation $M = \tfrac{1}{2}\pi n \frac{\phi}{l} R^4$ ceases to be strictly applicable. Provided, then, the angle of shear be

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DEFD'E'F'GHKG'H'K', since, in the annulus, the faces EHE'H' and *ehe'h'* are joined together, and the tangential force on each face is applied by the other.

small, we may apply the same argument to a long cylindrical wire of an isotropic solid, since the wire may be regarded as built up of a large number of short elements similar to ABCA′B′C′ (Fig. CXXIV.). In the case of a long wire fixed at its upper end, the angle ϕ through which its lower end is twisted may be fairly large without the angle of shear becoming too great.

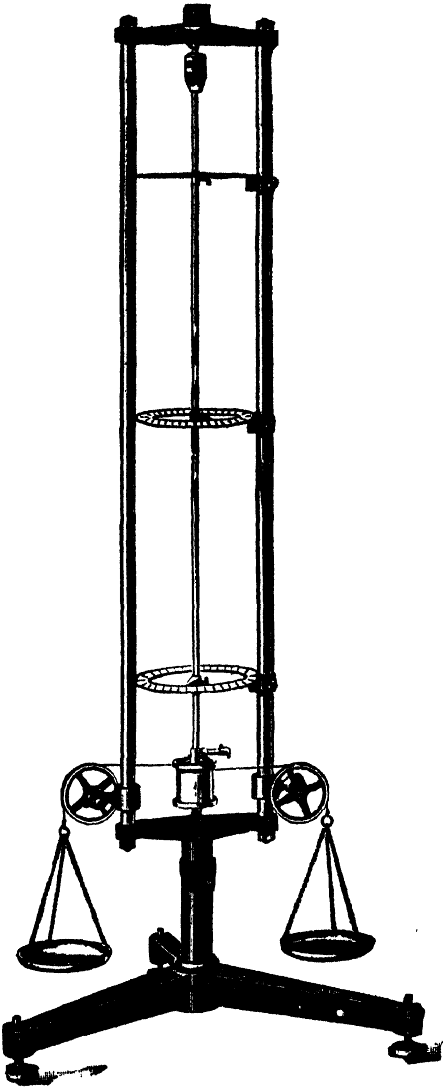

Fig. CXXVI.—Torsion of Wire Apparatus.

If instead of a solid cylinder we consider a hollow cylindrical shaft, the torque, M′, that must be applied in order to twist its lower end through an angle ϕ, when the upper end is fixed, is given by—

$$M' = \frac{2\pi n\phi}{l} \cdot \left(\frac{R_1^4}{4} - \frac{R_2^4}{4}\right),$$

$$= \tfrac{1}{2}\pi n\frac{\phi}{l} \cdot \left(R_1^4 - R_2^4\right),$$

where R_1 and R_2 are, respectively, the outer and inner radii of the shaft.

131. Statical Determination of the Modulus of Rigidity.—*Experiment LXXXII.*—Fig. CXXVI. illustrates a simple apparatus for determining the rigidity of the material of a wire. The wire, which should be of uniform circular cross-section, is firmly clamped at its upper end, its lower end being attached to a metal cylinder from the opposite sides of which two parallel strings pass over "frictionless" pulleys, and carry scale-pans, as shown in the figure.

Pointers are attached at different positions on the wire, and move over graduated circles, so that the angles of torsion corresponding to different lengths of the wire, and to various torsional couples, may be readily observed.

Let equal masses be placed in the scale-pans, and let the total mass, including the scale-pan, supported by each string be *m* gms. Then, if *a* be the radius of the cylinder in cms , the moment, M, of the torsional couple acting on the wire is equal to 2 *mga.* dynes/cms. If ϕ radians be the angle of torsion—corresponding to a length of *l* cms. of the wire—produced by this torsional couple, we have—

$$= \tfrac{1}{2}\pi n \frac{\phi}{l} . R^4 = 2mga,$$

where R is the radius of the wire, and *n* the modulus of rigidity for the material of which the wire is composed.

Whence—

$$n = \frac{4mgal}{\pi\phi R^4} \text{ dynes/cm.}^2$$

Since the radius, R, of the wire occurs to the fourth power in the expression for the rigidity it must be determined with very great care. The determination may be effected in a similar manner to that employed in Experiment LXXXI. for finding the cross-section of the wire.

A number of observations should be made of the angles of torsion corresponding to various loads, and the *mean* value of $\frac{m}{\phi}$ should be employed in the equation for the rigidity. Care must be taken not to employ too great a load, since ϕ is only proportional to *m*, provided the applied torsional couple does not strain the material of the wire beyond its elastic limit.[1]

132. Dynamical Determination of the Modulus of Rigidity.—*Experiment LXXXIII.*—The apparatus used in the preceding experiment may also be employed for the dynamical determination of the modulus of rigidity. The pointers, graduated circles, cylinder and scale-pans must be removed, and a vibration bar attached to the lower end of the wire. The vibration bar may, conveniently, be a metal cylinder, with its axis in line with the axis of the wire. A small white mark is made with a piece of chalk on the curved surface of the metal cylinder, and a telescope is adjusted so that this reference mark is accurately visually coincident with the cross-wires of the telescope. The wire is next set in torsional oscillation, by giving the metal cylinder a small rotation and then letting go, care being taken to avoid imparting any simple pendulous motion to the wire.

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[1] The proportionality between the angle of torsion and the moment of the applied torsional couple is utilised in various instruments, such as Coulomb's "Torsion-Balance," and Nernst's "Micro-Balance."

The time required for, say, a hundred oscillations is then observed by means of the telescope and a stop-watch, the mean of at least three observations being taken, and the time-period, T, of one oscillation is then calculated.

Now, since the torque exerted by the twisted wire is proportional to the angle of torsion, the metal cylinder will execute simple harmonic oscillations about its equilibrium position, the time-period, T, of the torsional oscillations being given by the relation—

$$T = 2\pi\sqrt{\frac{I}{C}},$$

where I is the moment of inertia of the cylinder about the axis of vibration, and C the torque exerted by the twisted wire per unit angle of torsion.

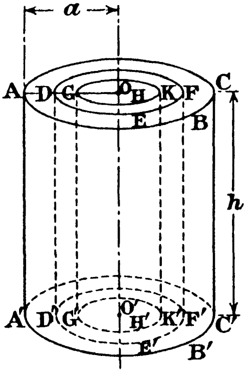

FIG. CXXVII.

Let ABCA′B′C′ (Fig. CXXVII.) represent the metal cylinder, and consider the very thin annulus DEFD′E′F′GHKG′H′K′.

Let the inner radius, OG, of the annulus be equal to x, the outer radius, OD, being equal to $x + \delta x$, where δx is very small. Then the mass of the annulus is equal to $2\pi x \,.\, \delta x \,.\, h \,.\, \rho$, where h is the length, and ρ the density, of the metal cylinder. The moment of inertia of the annulus about the axis of vibration, OO′, is therefore equal to $2\pi x \,.\, \delta x \,.\, h \,.\, \rho \,.\, x^2$, and the moment of inertia, I, of the whole cylinder ABCA′B′C′ about the axis, OO′ is therefore given by the relation—

$$\begin{aligned} I &= \int_0^a 2\pi x \,.\, dx \,.\, h \,.\, \rho \,.\, x^2, \\ &= 2\pi h\rho \int_0^a x^3 \,.\, dx, \\ &= 2\pi h\rho \,.\, \frac{a^4}{4}, \\ &= \pi a^2 h\rho \,.\, \frac{a^2}{2}, \\ &= M \,.\, \frac{a^2}{2}, \text{ where M is the mass, and } a \text{ the} \end{aligned}$$

radius, of the cylinder ABCA′B′C′.

Now, in accordance with § 130, the torque, C, exerted by the twisted wire per unit angle of torsion is given by the relation—

$$C = \frac{1}{2}\frac{\pi n R^4}{l},$$ where R is the radius, and l

the length, of the wire, and n the modulus of rigidity for the material of which the wire is composed.

Substituting for I and C in the equation for the time-period, we have—

$$T = 2\pi\sqrt{\frac{Ma^2 . 2l}{2 . \pi n R^4}},$$

$$= 2\pi\sqrt{\frac{Ma^2 l}{\pi n R^4}}.$$

Whence $$n = \frac{4\pi . Ma^2 l}{T^2 . R^4}.$$

As in the preceding experiment the radius, R, of the wire must be determined with very great accuracy; and care must also be taken that the magnitude of the torsional oscillation is not too great, since, otherwise, the material of the wire may be strained beyond its elastic limit.[1]

The dynamical method of determining n usually leads to a somewhat higher value than is obtained by the statical method. It is found—as might be anticipated from the standpoint of the kinetic theory—that the value *of n decreases* with rise in temperature.

133. Flexure of a Beam.—When a straight beam of uniform cross-section is bent into a curved form by applied forces, the material of the beam on the convex side of the curve is stretched—the material on the concave side being compressed.

Consider, for example, a rectangular beam of an isotropic solid, and let two equal and oppositely directed couples be applied at its ends, the plane of the couples passing through the centre of surface of each cross-section of the beam, and dividing each cross-section into two equal rectangles.

Under the action of these equal and opposite couples the rectangular isotropic beam will be bent into a circular arc, the convex side of the beam being stretched and the concave side compressed. There will, consequently, be a region within the beam which is neither in a state of tension nor of compression. This region is called the *neutral surface,* the line of intersection of the neutral surface and the plane of the couples being termed the *neutral axis.*

In the following elementary investigation on the flexure of beams it is assumed that the bending is so slight that the cross-section of the beam remains sensibly unaltered by the flexure.

Let ABCD (Fig. CXXVIII.) represent a vertical section through the middle of a rectangular isotropic beam fixed firmly at the end AD

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[1] It has been assumed that the restoring torque exerted by the twisted wire is independent of the longitudinal stress acting on the wire. Provided the weight of the metal cylinder, or vibration bar, be not too great this assumption is very approximately correct.

and carrying a small load, W, at the end BC—the breadth of the beam being at right angles to the vertical plane ABCD.

Such a beam is termed a cantilever. Let the length of the beam be l, its breadth b and its depth a. Let the beam be, initially, unloaded, and consider any two points, E and G, on AB at a very small distance, δx, apart. Since the small amount of bending due to the weight of the beam itself may, in general, be treated as negligible, we may draw EK and GL perpendicularly to AB, meeting DC, respectively, at K and L, EK and GL being parallel to one another. On applying the load, W, to the end BC, the fibres of the beam above the neutral surface, MN, are stretched—those below being compressed—so that EG is stretched to EG′, and KL compressed to KL′, EK and G′L′ being now inclined to one another at a very small angle, $\delta\theta$ (Figs. CXXVIII. and CXXIX. (i)).[1]

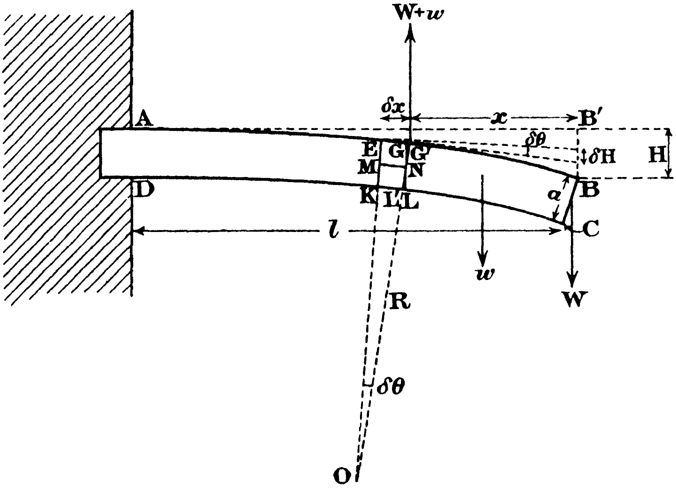

FIG. CXXVIII.

Let tangents be drawn to AB at E and G′ (Fig. CXXVIII.); these tangents will also be inclined to one another at the same angle $\delta\theta$.

Consider the equilibrium of the portion G′BCL′ of the beam. Provided the bending of the beam be very small, the section G′L′ will be sensibly vertical, and since the load, W, acts vertically downwards at the end BC, and the weight, w, of the portion G′BCL′ acts vertically downwards at the centre of gravity of G′BCL′, a shearing force equal to $W + w$ must act vertically upwards on G′BCL′ at the section G′L′.

---

[1] EG′ and KL′ (Fig. CXXIX. (i)), will only be *approximately* straight lines provided δx be taken sufficiently small, and provided the load, W, be not too great.

It follows from the equality of action and reaction that a force W + w must act vertically downwards on the portion AG′L′D of the beam at G′L′.

Now the vertical forces acting on the portion of the beam G′BCL′ form a couple, and, if the weight w of G′BCL′ be treated as negligible in comparison with the load W at the end of the beam, the torque acting on the portion G′BCL′ is equal to Wx, where x is the horizontal distance between the point of application of the load W and the cross-section G′L′.

This torque must be balanced by an equal and opposite torque acting on G′BCL′ across the section G′L′, and arising from the stretching of the fibres of the beam above the neutral surface, MN, and the compression of the fibres below that surface. This torque is termed the *bending torque* at the section G′L′.

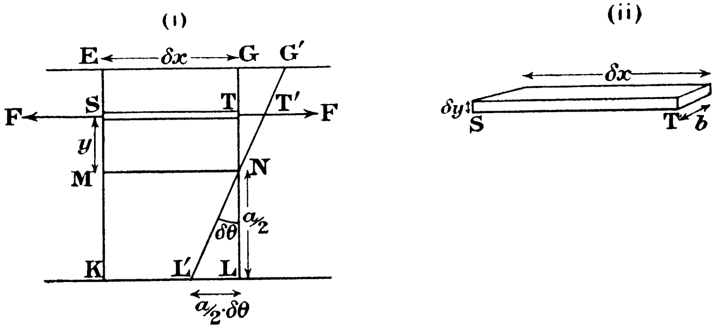

Fig. CXXIX.

Consider, now, an elementary filament such as ST (Fig. CXXIX. (i)), parallel to, and at a height y above, the neutral surface MN. Let the depth of the filament be δy, its length being δx, and its breadth b (Fig. CXXIX. (ii)). If F be the force stretching the filament from the length ST to the length ST′, we have—

$$Y = \frac{\dfrac{F}{b \,.\, \delta y}}{\dfrac{TT'}{\delta x}} = \frac{\dfrac{F}{b \,.\, \delta y}}{\dfrac{y \,.\, \delta\theta}{\delta x}},$$

where Y is Young's modulus for the material of which the beam is composed.

$$\therefore F = Y \,.\, \frac{y \,.\, \delta\theta}{\delta x} \,.\, b \,.\, \delta y.$$

Now, when the elementary filament is *above* the neutral surface, MN, the force, F, stretches the filament, and when the filament is *below* the neutral surface it is compressed by the force. Provided the bending of the beam be very small, all sections such as EK and G′L′ will be sensibly vertical, and since there is no resultant horizontal force acting across any of these sections tending to produce rectilineal translatory motion it follows that the algebraical sum of the forces acting across any section must be zero.

Thus, taking the algebraical sum of the forces acting across the section G′L′, we have—

$$\sum F = \frac{Y\,.\,\delta\theta}{\delta x}\,.\sum y\,.\,b\,.\,\delta y = 0,$$

$$\therefore \sum y\,.\,b\,.\,\delta y = 0.$$

But $b\,.\,\delta y$ is the area of the cross-section of each filament of the beam, and since the sum of the products of these areas by their respective distances from the neutral surface is zero, it follows that the centre of surface of the cross-section must lie in the neutral surface. A similar argument applies to all cross-sections of the beam, so that the line which joins the centres of surface of all the cross-sections is the neutral axis.

Now, the force F stretching the elementary filament exerts a torque equal to $F\,.\,y$ about the line through N, perpendicular to the plane of bending, in which the neutral surface cuts the cross-section G′L′. Integrating for all the filaments of the beam passing across the section G′L′ we obtain the total torque about the line in which the neutral surface cuts G′L′, and this torque is the bending torque at the cross-section and is equal to $W\,.\,x$.

Hence—

$$\int_{-a/2}^{a/2} F\,.\,y = Y\,.\,\frac{b\delta\theta}{\delta x}\int_{-a/2}^{a/2} y^2 dy = Y\,.\,\frac{b\delta\theta}{\delta x}\,.\,\frac{a^3}{12} = W\,.\,x.$$

$$\therefore \delta\theta = \frac{12\,.\,W\,.\,(x\,.\,\delta x)}{Y\,.\,b\,.\,a^3} = K\,.\,x\,.\,\delta x,$$

where K is a constant and is equal to $\frac{12W}{Y\,.\,b\,.\,a^3}$.

If R be the radius of curvature of the neutral axis at N (Fig. CXXVIII.), we have—

$$\frac{\delta x}{R} = \delta\theta = K\,.\,x\,.\,\delta x.$$

Whence $$R \propto \frac{1}{x}.$$

The radius of curvature of the neutral axis is therefore infinite when $x = 0$, and has a minimum value when $x = l$.

Since the bending of the beam is zero at the end BC, and has its maximum value at AD, the beam is not bent into a circular arc.[1]

Now, provided the small amount of bending due to the weight of the beam itself may be treated as negligible, the horizontal line AB′ (Fig. CXXVIII.) will represent the initial position of AB, and the depression B′B of the end B, due to the load W, will be sensibly vertical provided the bending be not too great. Let the vertical depression B′B of the end BC at which the beam is loaded be equal to H, and let the tangents to AB at E and G′ cut off a very small length δH from B′B.

Then the value of H is readily found by integrating the values of δH, corresponding to elements such as EG′, for the whole length, AB, of the beam.

For

$$\begin{aligned}\delta \mathrm{H} &\doteq x \,.\, \delta\theta,\\ &= \mathrm{K} \,.\, x^2 \,.\, \delta x.\end{aligned}$$

Whence

$$\mathrm{H} = \int_0^{\mathrm{H}} d\mathrm{H} = \mathrm{K}\int_0^{l} x^2 \,.\, dx = \mathrm{K} \,.\, \frac{l^3}{3}.$$

Substituting $\frac{12\mathrm{W}}{\mathrm{Y} \,.\, b \,.\, a^3}$ for K, we have—[2]

$$\mathrm{H} = \frac{4 \,.\, \mathrm{W} \,.\, l^3}{\mathrm{Y} \,.\, b \,.\, a^3}.$$

When the cross-section of the isotropic beam is not rectangular, the breadth, b, is not constant, but varies with the distance from the neutral surface. In this case, the bending torque at a cross-section such as G′L′ is given by the equation—

$$\mathrm{W} \,.\, x = \mathrm{Y} \,.\, \frac{\delta\theta}{\delta x}\int y^2 b\,dy.$$

The quantity $\int y^2 b\,dy$ represents the sum of the products of the cross-sections of all the filaments by the squares of their respective distances from the line in which the neutral surface cuts the cross-section G′L′ and is termed the moment of inertia of the cross-section

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[1] When such a uniform isotropic beam is bent by two equal and oppositely directed couples applied at its ends, it can be readily shown that the bending torque is constant for all cross-sections, and that R is, therefore, constant—so that the neutral axis is bent into an arc of a circle.

[2] Since two equal but oppositely directed forces, W + w, act tangentially to the section G′L′ of the beam, a shearing stress acts upon G′L′, the magnitude of the stress being $\frac{\mathrm{W} + w}{a \,.\, b}$. Neglecting the weight of the beam, the shearing stress will be the same at all cross-sections and equal to $\frac{\mathrm{W}}{a \,.\, b}$. If, however, the length, l, of the beam be very large in comparison with its depth, a, the vertical displacement due to shear may be treated as negligible in comparison with the vertical displacement due to the bending of the beam.

about that line. In the case of an isotropic beam of circular cross-section, for example, the moment of inertia of the circular cross-section, about a diameter, is equal to $\frac{\pi a^4}{4}$, where a is the radius, and the bending torque is given by—

$$W . x . = Y . \frac{\delta\theta}{\delta x} . \frac{\pi a^4}{4}.$$

134. Flexure of a Beam Supported at the Ends, and Loaded in the Middle.—Let Fig. CXXX. represent a rectangular isotropic beam supported at its ends on knife-edges in the same horizontal plane, and supporting a load W at the middle point.

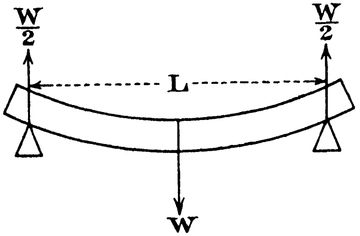

FIG. CXXX.

It is evident, from considerations of symmetry, that the tangent at the middle point is horizontal, and that the pressure exerted on each knife-edge is $\frac{W}{2}$. Thus we may regard either half of the beam as fixed in a horizontal position at the point of application of the load W, and acted upon by a vertical upward force $\frac{W}{2}$ at the knife-edge, and may calculate the vertical depression as in the preceding paragraph.

If, therefore, L be the distance between the knife-edges, the depression of the middle point of the beam is obtained by substituting $\frac{L}{2}$ for l, and $\frac{W}{2}$ for W, in the equation for H.

$$\text{Whence} \qquad H = \frac{4}{Y . b . a^3} . \frac{W}{2} . \left(\frac{L}{2}\right)^3 = \frac{W . L^3}{4 . Y . b . a^3}.$$

135. Determination of Young's Modulus from the Flexure of a Beam. *Experiment LXXXIV.*—Securely clamp a rectangular beam to a rigid support and insert a needle horizontally near the free end to serve as an index. Hang different weights from the beam by means of a loop of thread passed round the beam at the point where the needle is fixed, and read the position of the needle on a vertical scale, or, more accurately, by means of a cathetometer. The load, W, should be progressively increased, by the addition of equal weights, and, subsequently, decreased by their removal, the mean of the readings of the index, with the load increasing and decreasing, for each particular load being taken as the corresponding depression, H, of the beam.

Calculate the mean value of $\frac{H}{W}$. If the readings taken when removing the load differ appreciably from those obtained when the load was being increased, the beam has probably been loaded beyond its elastic limit. In this case the experiment should be repeated, using another beam of the same material, and employing a smaller maximum load.

Measure the distance, l, from the point of support to the needle, and the horizontal breadth, b, and the vertical depth, a, of the beam.

Young's modulus, Y, may then be obtained by substituting in the equation—

$$Y = \frac{4 . W . l^3}{H . b . a^3}.$$

Repeat the experiment, using a different length of the beam, and again calculate the value of Y.

The breadth, b, and depth, a, of the beam should be measured at a number of points at equal distances apart, and the mean values taken. Particular care must be exercised in measuring the depth, since it occurs to the third power in the expression for Y.

Experiment LXXXV.—In the preceding experiment Young's modulus was calculated from the vertical depression H, of the beam occasioned by a load W. An alternative method is to determine the angle through which the beam turns at the point where it is loaded.

Securely clamp one end of a rectangular beam to a rigid support, and fix a small mirror at, or near, the other end, the face of the mirror being perpendicular to the length of the beam.

Adjust a telescope, T, to which a vertical scale, S, is attached (Fig. CXXXI.), until the image of the scale in the mirror, M, is in the field of view. This adjustment is effected by mounting the telescope on blocks, so that its axis is on the same level as the mirror, and placing the telescope so that the beam produced roughly bisects the distance between the telescope and the scale (Fig. CXXXI.). Then focus the cross-wires in the eye-piece of the telescope, and focus the telescope on the mirror, M. Next slide the vertical scale, S, to right and left until the field of

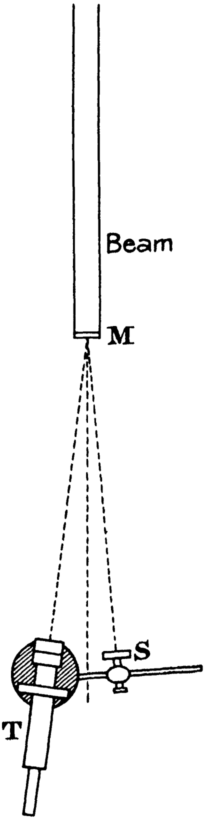

FIG. CXXXI.

view becomes white, and readjust the focus of the telescope until the scale figures are as sharp as possible.

Hang different weights from the beam by means of a loop of thread passed round the beam at the point where the mirror is fixed, and observe the scale reading which is coincident with the cross-wires of the telescope in each case. As in the preceding experiment, the load, W, should be progressively increased, by the addition of equal weights, and then decreased by their removal, the mean of the ascending and descending readings for each load being taken. These readings will not differ sensibly from one another if the maximum load employed be not too great.

Divide the means into two groups, and subtract each member of the first group from the corresponding member of the second group, and take the mean of all the values so obtained. This mean value represents the change of scale reading produced by increasing the load by a weight, W, where W is the difference between the load of any member of the second group and that of the corresponding member of the first group.[1]

Divide the mean value so obtained by twice the distance of the scale from the mirror, and let the quotient be θ. Then provided the bending of the beam be very small, θ is, with sufficient accuracy, the angular depression, in radians, of the beam at the point where the mirror is fixed.

Now, the tangents to AB at the points E and G′ (Fig. CXXVIII.) are inclined to one another at an angle $\delta\theta$, and the angle θ which the tangent at the point B makes with AB′ can be obtained by integrating the values of $\delta\theta$, corresponding to elements such as EG′, for the whole length AB.

Since $\delta\theta = \dfrac{12 \,.\, W \,.\, (x \,.\, \delta x)}{Y \,.\, b \,.\, a^3}$, we have—

$$\theta = \frac{12 \,.\, W}{Y \,.\, b \,.\, a^3}\int_0^l x \,.\, dx = \frac{12 \,.\, W}{Y \,.\, b \,.\, a^3} \cdot \frac{l^2}{2} = \frac{6 \,.\, W \,.\, l^2}{Y \,.\, b \,.\, a^3}.$$

Whence $Y = \dfrac{6 \,.\, W \,.\, l^2}{\theta \,.\, b \,.\, a^3}$, where l is the distance from the point of support to the point where the mirror is fixed and the weight, W, attached, and a and b are the vertical and horizontal dimensions of the cross-section of the beam.

Experiment LXXXVI.—Support a rectangular beam on knife-edges near its ends, and hang different weights from the middle of the beam by means of a loop of thread (Fig. CXXX.). Measure, by means of a cathetometer, the vertical depression of a needle-point

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[1] This method is a general one for calculating a mean value from a series of observations.

fixed at the middle of the beam, and calculate the mean depression, H, due to a load, W, as in the preceding experiments.

Measure the distance, L, between the knife-edges, and the breadth, *b*, and depth, *a*, of the beam, and calculate the value of Young's modulus by substituting in the equation—

$$Y = \frac{W \, . \, L^3}{4 \, . \, H \, . \, b \, . \, a^3}.$$

136. Determination of Young's Modulus, Y, and the Modulus of Rigidity, n, by Searle's Method.—In this method a uniform wire, AB, of the material for which Y and *n* are to be determined, is rigidly fixed at its ends into horizontal holes drilled through the middle points of two equal rectangular, or cylindrical, bars CD and EF (Fig. CXXXII.).

The bars are then suspended, by means of vertical silk threads, which are attached to hooks screwed into the middles of the respective bars at points adjacent to those where the wire AB is fixed, as shown in the figure.

The silk threads are made of equal length so that the wire AB, and the bars CD and EF, may be in the same horizontal plane, and since the threads are, sensibly, torsionless, the bars CD and EF, when at rest, hang parallel to one another, the wire AB being perpendicular to their length.

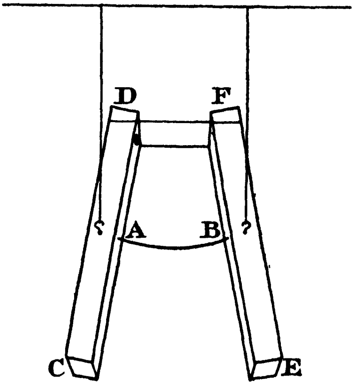

FIG. CXXXII.

The ends D and F of the bars are now drawn nearer together by means of a loop of cotton, as shown in Fig. CXXXII., and, on burning the cotton, the bars are set free and oscillate in a horizontal plane.

Provided the oscillations are very small, the wire AB will be bent to only a very small extent, so that the points A and B will remain, sensibly, at rest, the bent wire exerting a torque on each bar tending to bring it back to its equilibrium position, while each bar exerts an equal bending torque on the wire.

The period of oscillation, T, of either bar is given by the equation—

$T = 2\pi\sqrt{\frac{I}{C}}$, where I is the moment of inertia of the bar about the silk thread as axis, and C the torque per unit angle of twist (*vide* Expt. LXXXIII.). Since the wire AB is acted upon by two equal horizontal torques applied at its ends, the bending torque will be the same at all cross-sections, and the wire will consequently be bent into a horizontal circular arc.

If each of the bars, at any given moment, be twisted through an angle θ from the equilibrium position, the radius of curvature, R, of the wire, at the same moment, will be equal to $\frac{l}{2 . \theta}$, where l is the length of the wire; and the bending torque will be equal to

$$\frac{\mathrm{Y}}{\mathrm{R}}\int y^2 . b . dy \text{ (\textit{vide} § 133), i.e. equal to } \frac{\mathrm{Y} . 2\theta}{l}\int y^2 . b . dy.$$

Thus the bending torque, C, per unit angle of twist of each bar is equal to $\frac{2 . \mathrm{Y}}{l}\int y^2 . b . dy$.

If the wire AB be of circular cross-section, of radius a, we have—

$$\mathrm{C} = \frac{2 . \mathrm{Y}}{l} . \frac{\pi a^4}{4} \text{ (\textit{vide} § 133),}$$

$$= \frac{\pi . \mathrm{Y} . a^4}{2 . l}.$$

Substituting for C the value given by the equation $\mathrm{T} = 2\pi\sqrt{\frac{\mathrm{I}}{\mathrm{C}}}$, we have—

$$\frac{4 . \pi^2 . \mathrm{I}}{\mathrm{T}^2} = \frac{\pi . \mathrm{Y} . a^4}{2 . l} .$$

Whence $$\mathrm{Y} = \frac{8 . \pi . l . \mathrm{I}}{\mathrm{T}^2 . a^4}.$$

Next remove the silk threads and clamp the bar CD in a horizontal position, so that the wire AB is vertical, with the bar EF hanging horizontally at the end. Set the wire in torsional oscillation, by giving the bar EF a small rotation and then letting go, and calculate the time-period, t, of one oscillation, as in experiment LXXXIII.

Then $$t = 2\pi\sqrt{\frac{\mathrm{I} . 2l}{\pi . n . a^4}} \text{ (\textit{vide} Expt. LXXXIII.).}$$[1]

Whence $$n = \frac{8 . \pi . l . \mathrm{I}}{t^2 . a^4} .$$

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[1] The moment of inertia, I, of the bar about the axis of vibration AB will be the same as its moment of inertia about the silk thread as axis, since the cross-section of the bar is square, or circular.

CHAPTER X.

GRAVITY.

137. The Acceleration of Gravity.—When any body is dropped near the surface of the earth, it falls to the ground with nearly constant acceleration. It follows, therefore, that the *weight* of the body is, to the same extent, constant. The acceleration of a falling body at the surface of the earth, due to gravity, is termed the *acceleration of gravity*, and is denoted by the letter g.

The value of g is not rigidly constant, but varies, for example, with latitude, and with the height above sea-level, so that the weight of a body must also vary, and in the same proportion, since the *mass* of a body is assumed to be invariable.

It was originally surmised that different bodies fell to the ground at rates proportional to their respective weights, but, towards the end of the sixteenth century, Galileo contended that the rate of fall was the same for all bodies—provided gravity were the only force acting—and he attributed the slower rate of fall observed in the case of a light body to the resistance of the air, which exerted a relatively greater effect on a light body than on a heavy body of the same size and shape.

In support of this contention Galileo dropped different weights from the top of the leaning tower of Pisa and showed that they reached the ground in the same time. The effect due to the air resistance may be eliminated by dropping different bodies in a vacuum, as in the "guinea and feather" experiment, in which case the bodies fall at the same rate, the equality of the acceleration for both heavy and light bodies showing that the weight of a body is proportional to its mass.

Galileo also showed that spherical, and cylindrical, bodies rolled down an inclined plane with uniform accelerations, the acceleration having one value for the spheres, and another for the cylinders, but being independent, in both cases, of the masses of the rolling bodies.

Newton, and subsequently Bessel, proved that weight at any given place is proportional to mass by employing pendulums with hollow bobs, and showing that the time-period was the same whether the bobs were empty, or filled with different materials.

138. Experimental Determination of g.—The acceleration of gravity at any place is, in general, determined by means of the pendulum, the earlier types of apparatus, such as "Attwood's Machine," possessing merely an historic interest, since they are not susceptible of any great accuracy.

The following simple methods may, however, be employed to obtain an approximate value for g.

Experiment LXXXVII.—Smoke the surface of a glass or metal plate by holding the plate over burning turpentine or benzene. Suspend the plate, with the smoked face vertical, by means of a cotton thread, and then allow the plate to fall, by burning through the thread, at the same time lightly touching the smoked surface with a bristle fixed to the prong of a vibrating tuning-fork.[1]

Select three convenient points on the wave-line traced out by the bristle such that an equal number of complete wave-lengths separate the first point from the second and the second from the third, and measure the distances between the points by means of a cathetometer.

Let there be x complete wave-lengths between the first and second points, and let the frequency of the tuning-fork be n. The time taken in tracing out x wave-lengths is $\frac{x}{n}$, so that we have—

$$S_1 = u\left(\frac{x}{n}\right) + \tfrac{1}{2}g\left(\frac{x}{n}\right)^2,$$

where s_1 is the distance between the two points, and u the velocity of the plate at the instant the bristle was touching the first point.

Let s_2 be the distance between the second and third points, corresponding to an equal but subsequent time interval $\frac{x}{n}$.

$$\text{Then} \qquad S_1 + S_2 = u\left(\frac{2x}{n}\right) + \tfrac{1}{2}g\left(\frac{2x}{n}\right)^2.$$

$$\text{Whence} \qquad S_2 = u\left(\frac{x}{n}\right) + \tfrac{1}{2}g\left(\frac{x\sqrt{3}}{n}\right)^2.$$

$$\therefore S_2 - S_1 = \tfrac{1}{2}g\left(\frac{2x^2}{n^2}\right).$$

$$\therefore g = \left(S_2 - S_1\right) . \frac{n^2}{x^2}.$$

Experiment LXXXVIII.—Another method of determining the value of g is represented in Fig. CXXXIII. A small sphere, A, which may, conveniently, be of lead or brass, is held in position between a thin iron spring, B, and one arm of a bent brass rod, C, as indicated in the figure. The iron spring, B, is fixed at one end, and is connected to one of the terminals of the primary of an induction-

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[1] If a glass plate be employed it must be allowed to fall upon a suitable pad to avoid the risk of fracture. The tuning-fork should be suitably clamped to a stand.

coil, the other terminal of the primary coil being connected, through the battery, D, to a flat strip of metal, E. The metal strip, E—which must be placed vertically beneath the sphere, A—is hinged at one end, F, while the other end touches a brass pointer, G, which is in electrical connection with the brass rod, C. The terminals of the secondary coil are connected, respectively, to a tuning-fork, K, of known frequency, and to a metal drum, L, as shown in Fig. CXXXIII. An aluminium pointer is fixed to one prong of the tuning-fork, and a strip of smoked paper is fastened round the drum, so that when the tuning-fork is set in vibration, and the drum rotated by means of the handle, M, a wave-line is traced out on the smoked surface of the paper.

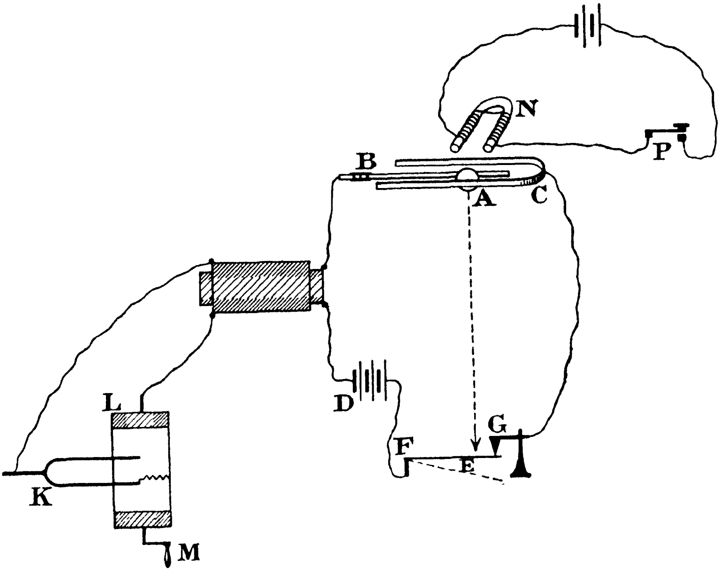

FIG. CXXXIII.

The sphere, A, is now released by depressing a key, P, and exciting an electro-magnet, N, which is placed horizontally beside the bent brass rod, C; the electro-magnet attracting the iron spring, B, and pulling it away from A into contact with C. At the instant the sphere is released, the primary circuit of the induction coil is broken, and a spark jumps the gap in the secondary circuit produced by the smoked paper, piercing the paper, and making a white spot on its smoked surface. When the iron spring comes into contact with the arm of the bent brass rod, C, the primary circuit is again closed, and another spark pierces the smoked paper on the rotating drum, making a second white spot on the wave line which the aluminium pointer is tracing out. The falling sphere, A, on striking the metal strip, E, breaks contact between the latter and the pointer, G, so that another spark pierces the smoked paper, producing a third white spot.

Before releasing the sphere, the vertical distance, S, between its lowest point and the upper surface of the metal strip, E, is measured by means of a cathetometer. The time, t, taken in falling this distance is obtained from the number of wave-lengths between the first and third white spot on the smoked paper, the frequency of the tuning-fork being known. Any fraction of a complete wave-length must be estimated as accurately as possible.

The acceleration of gravity is then calculated from the equation—

$$g = \frac{2 \cdot S}{t^2}.$$

139. Pendulum Methods of Determining "g": The Simple Pendulum.—In order to determine, with accuracy, the acceleration of gravity at any place, use is made of the pendulum. The two following experiments indicate how the determination may be effected, employing, respectively, a *simple* and a *reversible* pendulum.

Determination of "g" by means of the Simple Pendulum.—Experiment LXXXIX.—Attach a leaden sphere, of about 2000 gms. weight, to one end of a long thin wire, and securely clamp the other end of the wire to a rigid beam. The wire should be about 3 metres in length. Give a small pendulous motion to the suspended sphere of, say, 20 cms. on each side of its equilibrium position, and start a stop-watch as the sphere swings through its position of rest, counting "nought" at the same instant. Count each successive passage *in the same direction*, and stop the watch as the sphere swings through its position of rest when the count has reached "One Hundred." Make at least three such determinations, and calculate the mean value of the time-period, T, corresponding to one oscillation of the pendulum.

Measure the length of the pendulum wire, from the point of support to the point of attachment of the leaden sphere, by means of a measuring lath and a metre scale, and measure the diameter of the sphere with a calliper gauge.

Weigh the leaden sphere, and either weigh the suspension wire itself, or weigh a measured length of the same wire and then calculate the weight of the suspension wire from its known length.

Now, a simple pendulum may be regarded as consisting of a heavy particle attached to the end of a filament which is so thin that its mass may be treated as negligible, the other end of the filament being fixed. In accordance with the theory of the simple pendulum, the time-period, t, of a small oscillation is given by the relation—

$$t = 2\pi\sqrt{\frac{l}{g}},$$ where l is the length of the suspending filament, and g the acceleration of gravity.

Such a simple pendulum represents an ideal state of affairs, to which any real pendulum merely approximates more or less closely, for, in the case of any actual pendulum, the mass cannot be regarded as located at one point.

When a rigid body is suspended at a fixed point, and is displaced from its position of rest, we have a *physical* or *compound pendulum.*

In the case of a physical pendulum the time-period, T, of a small oscillation, is given by the relation—

$$\mathrm{T} = 2\pi\sqrt{\frac{\mathrm{I}}{\mathrm{M}\,.\,a\,.\,g}},$$ where I is the moment of inertia about the axis of rotation, M the mass of the pendulum, and a the distance of the centre of mass from the axis of rotation.

If, then, we assume that in our experiment the leaden sphere and the thin wire move as a *rigid* body, we can obtain a more accurate value for g by employing the formula for a physical pendulum, instead of the one for a simple pendulum.

Since our pendulum consists of a spherical bob at the end of a uniform straight wire, the time-period, T, of a small oscillation is given by—

$$\mathrm{T} = 2\pi\sqrt{\frac{m_1\{\frac{2}{5}r^2 + (l + r)^2\} + \frac{1}{3}m_2 l^2}{\{m_1(l + r) + \frac{1}{2}m_2 l\}\,.\,g}},$$ where m_1 is the mass, and r the radius, of the leaden sphere, and m_2 the mass, and l the length, of the suspension wire.

If m_1 be very large compared with m_2, and l be great compared with r, the time-period is, with sufficient accuracy, given by the relation—

$$\mathrm{T} = 2\pi\sqrt{\frac{l + r}{g}\left(1 - \frac{1}{6}\,.\,\frac{m_2}{m_1}\right)}.$$

It must, however, be noted that the assumption that the leaden sphere and the suspension wire form a rigid system is not strictly justifiable, for the inertia of the leaden sphere causes it to rotate—towards the end of each swing—through an angle greater than the angular deflection of the wire. In consequence, it is preferable to determine the value of g by employing a *rigid* body oscillating about a fixed axis. Thus, if a thin uniform metal rod, of length, l, be allowed to oscillate about an axis perpendicular to its length and passing through one end, we have—

$$\mathrm{T} = 2\pi\sqrt{\frac{\mathrm{I}}{\mathrm{M}\,.\,a\,.\,g}} = 2\pi\sqrt{\frac{\mathrm{M}\,.\,\frac{l^2}{3}}{\mathrm{M}\,.\,\frac{l}{2}\,.\,g}} = 2\pi\sqrt{\frac{2\,.\,l}{3\,.\,g}}.$$

140. Determination of "g" by means of Kater's Reversible Pendulum. —*Experiment XC.*—The value of g can be determined with very great accuracy by means of the reversible pendulum. In this method, a bar pendulum is employed, having two movable knife-edges, from each of which it may be suspended in turn.

The knife-edges are very firmly clamped, and a telescope is adjusted so that the edge of the pendulum is accurately visually coincident with the cross-wires of the telescope when the pendulum is suspended and at rest. The time-period about each knife-edge is then determined in a similar manner to that employed in the preceding experiment. The two time-periods will, in general, differ from one another, but by sliding one of the knife-edges along the bar, and making repeated trials, a position can be found for which the two-time periods are sensibly the same. If the time-periods *exactly* agree, the distance, l, between the knife-edges is the length of the equivalent simple pendulum, having the same time-period, t, *provided that the knife-edges lie on opposite sides of the centre of mass of the pendulum, and are not symmetrically situated with respect to the latter.*

In this case g can be determined from the equation—

$$t = 2\pi\sqrt{\frac{l}{g}}.$$

Exact accordance of the time-periods cannot, in general, be obtained, but, as was shown by Bessel, the formula can be transformed so that the value of g can be calculated with very great accuracy even when the time-periods about the two knive-edges are only approximately equal. Bessel's formula requires a knowledge of the distance of each knife-edge from the centre of mass of the pendulum. This may be obtained by balancing the pendulum length-wise on a narrow glass rod, and measuring with a metre scale from each knife-edge to the point of contact between the glass rod and the pendulum.

The distance between the knife-edges is then accurately measured with a metre scale, or, better, by means of a cathetometer.

In accordance with the theory of the physical or compound pendulum, the time-period, T, of a small oscillation about any axis of rotation is given by the relation—

$$T = 2\pi\sqrt{\frac{I}{M . a . g}},$$ where I is the moment of inertia about the same axis, M the mass of the pendulum, and a the distance of the axis from the centre of mass.

If K_0 be the spin-radius with respect to the centre of mass, we have—

$$I = M(K_0^2 + a^2).$$

Whence—

$$T = 2\pi\sqrt{\frac{K_0^2 + a^2}{a . g}}.$$

Now, let XY (Fig. CXXXIV.) represent a rigid body of any shape, and let C be its centre of mass, and S_1 and S_2 two parallel axes of rotation on opposite sides of C. If T_1 and T_2 be the respective time-periods about the axes S_1 and S_2, we have—

$$T_1^2 a_1 = \frac{4\pi^2}{g}(K_0^2 + a_1^2),$$

and $$T_2^2 a_2 = \frac{4\pi^2}{g}(K_0^2 + a_2^2),$$ where a_1 and a_2 are the respective distances of S_1 and S_2 from the centre of mass.

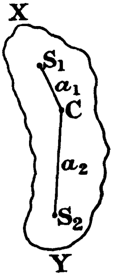

FIG. CXXXIV.

Eliminating K_0, we have—

$$T_1^2 a_1 - T_2^2 a_2 = \frac{4\pi^2}{g}(a_1^2 - a_2^2).$$

Now, let S_1 and S_2 be chosen so that $T_1 = T_2 =$ (say) T_ϵ.

Then, provided a_1 is *not equal* to a_2, we may divide both sides of our equation by $(a_1 - a_2)$, and it follows that—

$$T_\epsilon^2 = \frac{4\pi^2}{g}(a_1 + a_2).$$

If, further, S_1CS_2 (Fig. CXXXIV.) be a straight line, we have—

$$T_\epsilon^2 = \frac{4\pi^2}{g} \cdot (S_1S_2).$$

Whence $$T_\epsilon = 2\pi\sqrt{\frac{(S_1S_2)}{g}}.$$

Thus S_1S_2 is the length of a simple pendulum having the same time-period, T_ϵ, i.e. it is the length of the equivalent simple pendulum.

If the time-periods T_1 and T_2 be not equal, we may rewrite the equation

$$T_1^2 a_1 - T_2^2 a_2 = \frac{4\pi^2}{g}(a_1^2 - a_2^2)$$

in the equivalent form

$$\frac{T_1^2 + T_2^2}{2} \cdot (a_1 - a_2) + \frac{T_1^2 - T_2^2}{2} \cdot (a_1 + a_2) = \frac{4\pi^2}{g} \cdot (a_1^2 - a_2^2).$$

Whence—

$$\frac{T_1^2 + T_2^2}{2} + \frac{T_1^2 - T_2^2}{2} \cdot \left(\frac{a_1 + a_2}{a_1 - a_2}\right) = \frac{4\pi^2}{g} \cdot (a_1 + a_2).$$

This last equation is strictly accurate, but can only be satisfactorily employed when T_1 and T_2 are nearly equal, since the quantity $a_1 - a_2$ in the denominator cannot be measured with very great accuracy. Thus, in determining the value of g by means of Kater's pendulum, the time-periods about the two knife-edges should differ by less than 1 per cent. before the adjustment is considered satisfactory and Bessel's formula employed.

The quantity $a_1 + a_2$ is equal to the distance between the knife-edges, and can be measured with great exactness.

An alternative method is to plot the time-periods about each knife-edge against the respective distances between the latter, one knife-edge being kept fixed, while the position of the other is varied. The co-ordinates of the point of intersection of the two curves correspond, respectively, to the distance between the knife-edges when the time-period is the same about either, and to the value of that period, and g can then be determined from the equation—

$$t = 2\pi\sqrt{\frac{l}{g}}.$$

141. Corrections.—In the determination of g, by means of the pendulum, a number of corrections must be applied in all cases where great accuracy is required.

Thus, owing to the uniform rotation of the earth on its axis, bodies on its surface have a centripetal acceleration, which has a maximum value at the equator, and is zero at the poles, and, in consequence of this centripetal acceleration, the *apparent weight* of any body—as determined, for example, by means of a spring balance—is *less* than the gravitational force with which it is pulled towards the centre of the earth (i.e. is less than its *true weight*).

It follows that a determination of the acceleration of gravity at any place only gives the acceleration *relative to the surface of the earth at that place,* and not the value relative to the centre of the earth. It is therefore necessary to introduce a correction for the variation in the value of g occasioned by the difference in the centripetal acceleration in different latitudes.

Again, the earth is not truly spherical in form but is very nearly an oblate spheroid, the value of the ellipticity being nearly $\frac{1}{300}$. The equatorial radius therefore exceeds the polar radius by, approximately, thirteen miles, and, in consequence, a body at the equator is farther from the centre of mass of the earth, and experiences a smaller gravitational pull, than a body of equal mass situated near the poles.

The value of g also varies with the height above sea-level, the variation being inversely as the square of the distance from the centre of mass of the earth as soon as a height is reached at which the effect of local variations in the configuration of the surface can be neglected.

It was shown by Newton that the resultant gravitational force exerted on a unit mass inside a uniform spherical *shell* is zero, and that, in consequence, the gravitational attraction at any point inside a uniform sphere is directly proportional to the distance from the centre of mass. This result, however, will not apply to the earth, the density of which increases towards the centre, and it is found that, at first, the gravitational attraction also *increases* with the depth below the surface, being greater at the bottom of a mine, for example, than at the surface level.

In determining the value of g corrections must also be applied for the effect of the air on the motion of the pendulum; for the amplitude of the arc of swing; for the curvature of the knife-edges; and for the yielding of the support. The air effect itself may be regarded as the resultant of three separate actions. Thus, in accordance with the principle of Archimedes, the weight of the pendulum is effectively diminished by the weight of the air displaced. Again, as was shown by Du Buat, the pendulum carries along some of the surrounding air, so that the effective mass of the pendulum is increased. The viscosity of the air also slowly diminishes the amplitude of the arc of swing, but, in general, has a negligible effect on the time period.

Any variation in the temperature will, of course, affect the length of the pendulum, and also the magnitude of the corrections to be applied for the effect of the air. In the case of small pendulums, it is often convenient to enclose them in a chamber which can be exhausted and maintained at a constant temperature.

142. Gravitation.—It was shown by Newton that the gravitational force exerted on a unit mass at any point outside a sphere is the same as if the whole mass of the sphere were concentrated at the centre, provided the density of the sphere be uniform at all points equidistant from the centre. This result may be applied to the earth, since the latter is very approximately a sphere, the density of which may be assumed to be uniform at any constant distance from the centre.

Newton also proved, from a study of the motion of the moon, that the gravitational force with which a body at the surface of the earth is pulled towards the centre is merely a particular case of the general law of universal gravitation, in accordance with which "every particle in the universe attracts every other particle with a gravitational force in the line joining them proportional to the product of their masses and inversely proportional to the square of the distance between them." Thus, if m_1 and m_2 be the masses of any two particles, at a distance d from one another, the attractive force, F, on either is given by the equation—

$$\mathrm{F} = \mathrm{G} \,.\, \frac{m_1 m_2}{d^2},$$

where G is a constant, termed the Newtonian Constant of Gravitation.

It is evident that G is numerically equal to the attractive force on either of two unit masses at unit distance apart.

Since force is measured by the product of mass into acceleration, we have—

$$F = m_1 a_1 = G \cdot \frac{m_1 m_2}{d^2},$$

and, therefore

$$a_1 = G \cdot \frac{m_2}{d^2},$$

where a_1 is the acceleration of m_1 towards m_2.

If, then, m_2 be the mass of the earth, and m_1 the mass of any body dropped near its surface, we have—

$$g = G \cdot \frac{m_2}{r^2},$$

where g is the acceleration of gravity, and r the radius of the earth.

Knowing the dimensions of the earth, and the value of g, it only remains to determine one of the quantities G or m_2 in order to calculate the value of the other.

143. Determination of the Mass of the Earth.—The first attempt to compare the mass of the earth with that of some natural mass, such as a mountain, was made by Bouguer, who, in 1740, compared the horizontal attraction of Mount Chimborazo on a plumb-bob hung near the side of the mountain with the vertical attraction of the earth on the same body.

A similar investigation was carried out by Maskelyne, in 1774, at Mount Schiehallion in Perthshire. In the Schiehallion determination a telescope was erected first at a site on the southern slope of the mountain, and the angular distance of several stars from the zenith, when they crossed the meridian, was measured. The telescope employed for this purpose was a zenith sector, the telescope being pivoted about a horizontal east and west axis near the object-glass end, and carrying a graduated arc and plumb-line near the eye-piece end. The instrument was next moved to a site on the northern slope of Mount Schiehallion, and the angular distance of the same stars from the zenith, when they crossed the meridian, was again measured (Fig. CXXXV.).

Now, the direction of any given star, when crossing the meridian, was sensibly the same at both sides of the mountain. It followed that the difference between the angular distance of any star from the zenith, as observed on the northern and southern slopes, was *double* the deflection of the plumb-line at either side due to the attraction of the mountain, allowance being made for the change in the vertical on either side of the mountain occasioned by the curvature of the earth. The change in the vertical due to the curvature of the earth was obtained by measuring the distance between the northern and southern sites, and dividing this distance by the radius of the earth. In the Schiehallion determination, the curvature change was, approximately, 40 seconds of arc, whereas the observed deflection of a star, when viewed from the northern and southern sides of the mountain, was nearly 12 seconds greater, so that the deflection, θ, of the plumb-line on each side, due to the attraction of the mountain, was, approximately, 6 seconds of arc.

A careful survey of the mountain was next carried out, and the distribution of mass throughout the mountain estimated by means of a geological examination.

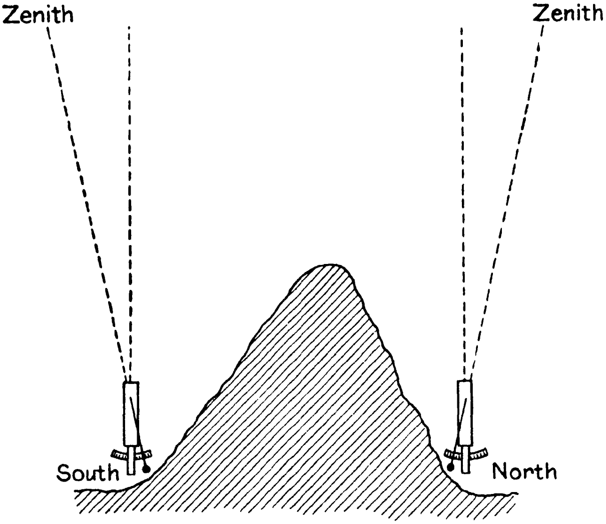

Fig. CXXXV.

It was then calculated, in accordance with the general law of gravitation, that the horizontal force, f, acting on the plumb-bob, due to the attraction of the mountain, was the same as if the whole mass, m_1, of the mountain were at a distance, d. The vertical force, F, due to the attraction of the earth, was the same as if the whole mass, m_2, of the earth were concentrated at its centre (*vide* § 142).

Whence $\tan\theta = \frac{f}{F} = \frac{\frac{m_1}{d^2}}{\frac{m_2}{r^2}}$, r being the radius of the earth.

The mass of the earth was then deduced, and its mean density found to be approximately 4·5 times that of water. A subsequent survey of Mount Schiehallion raised the value for the mean density of the earth to approximately 5 gms. per c.c.

Several other investigations have been carried out in which the mass of the earth has been compared with natural masses, such as mountains, or portions of the earth's crust. The density of such natural masses cannot, in general, be ascertained with much accuracy, so that only an approximate value for the mass of the earth can thus be deduced.

144. Determination of the Newtonian Constant of Gravitation; the Torsion Method.—The Rev. John Michell first suggested an experiment in which the attraction between two pairs of leaden spheres could be directly measured. He constructed an apparatus for this purpose, but died without having had an opportunity of carrying out the experiment.

Michell's apparatus was given to Cavendish, and the latter, after making certain modifications, carried out the experimental work in 1797 and the following year.

Cavendish employed a wooden torsion rod, 6 feet in length, from the ends of which were hung two small leaden spheres, 2 inches in diameter.

The torsion rod, which carried a vernier at each end, was suspended in a horizontal position by means of a torsion wire, approximately 39 inches in length, and was protected from air currents by a narrow wooden case. The verniers at each end of the rod moved close to fixed ivory scales, without touching the latter, the position of the torsion rod being observed by means of telescopes passing through holes in the walls of the room in which the apparatus was set up. This room was kept constantly closed in order that draughts might be avoided. Two heavy leaden spheres, 12 inches in diameter, were suspended by vertical copper rods from the ends of a horizontal beam. This beam was pivoted to the ceiling at a point in line with the axis of the torsion-wire, and could be rotated by means of ropes passing through holes in the walls of the room. The two heavy leaden spheres could thus be brought up on opposite sides of the small leaden spheres hanging from the ends of the torsion rod, and the length of the vertical copper rods was so adjusted that the centres of all the four leaden spheres were in the same horizontal plane.

In order to carry out a determination, the heavy leaden spheres were swung round until they were close to, and on opposite sides of, the small spheres, as shown at A and B in Fig. CXXXVI. The torsion rod carrying the small leaden spheres was allowed to oscillate through a very small angle, and its position of rest was deduced by observing the extent of the swings corresponding to three consecutive turning points, in a similar manner to that employed in weighing by oscillations.

The heavy leaden spheres were next swung round so as to occupy positions at the same distance from the small spheres, but on the other sides—as shown at A′ and B′ in the figure—and the new position of rest of the torsion rod determined.

The angular distance between the two positions of rest of the torsion rod, was equal to twice the angle of twist, θ, due to the attractions of the leaden spheres in either position. The torque, C, exerted by the torsion wire per unit angle of twist was determined from the moment of inertia and time of oscillation of the torsion rod (*vide* Experiment LXXXIII., § 132).

Let m_1 = the mass of each small leaden sphere,
m_2 = the mass of each large leaden sphere, and
d = the distance apart of the centres of the large and small spheres when the angular deflection of the torsion rod is θ.

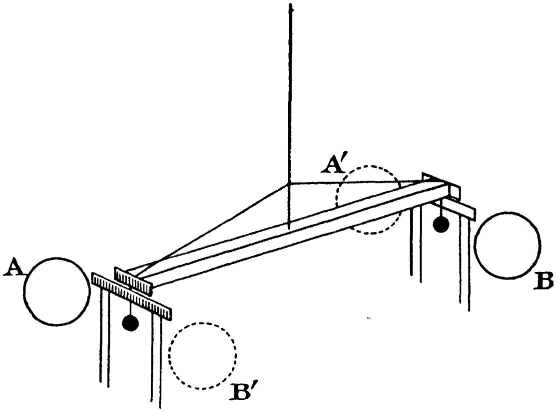

FIG. CXXXVI.

Then, the attractive force, F, acting on either a small or a large sphere is given by the equation—

$$F = G \, . \frac{m_1 \, . \, m_2}{d^2},$$ where G is the Newtonian constant of gravitation.

Let a = the distance between the centres of the two small leaden spheres.

Then, the torque applied to the torsion wire due to the attraction exerted by the pair of large spheres on the pair of small spheres is given by the equation—

$$F \, . \, a = G \, . \frac{m_1 \, . \, m_2 \, . \, a}{d^2}.$$

The torque exerted by the torsion wire when twisted through an angle θ is equal to $C \, . \, \theta$.

Whence $$C \cdot \theta = G \cdot \frac{m_1 \cdot m_2 \cdot a}{d^2}.$$

$$\therefore G = \frac{C \cdot \theta \cdot d^2}{m_1 \cdot m_2 \cdot a}.$$

After introducing various corrections, Cavendish, as the result of twenty-nine determinations, obtained the mean value—

$$G = 6{\cdot}562 \times 10^{-8}.$$

If m_2 be the mass of the earth, we have—

$$g = \frac{G \cdot m_2}{r^2},$$ where g is the acceleration of gravity, and r the radius of the earth (*vide* § 142).

If Δ be the mean density of the earth, we have—

$$m_2 = \frac{4}{3}\pi r^3 \cdot \Delta.$$

Whence—

$$g = \frac{4}{3} \cdot \pi \cdot r \cdot \Delta \cdot G.$$

$$\therefore \Delta = \frac{3 \cdot g}{4 \cdot \pi \cdot r \cdot G}.$$

Employing Cavendish's mean value for G, and substituting in the right-hand side of the last equation, we obtain a value of 5·448 gms./c.c. for the mean density of the earth.

The torsion method of Cavendish for determining the Newtonian constant of gravitation has been employed by several subsequent investigators; notably by Boys in 1895. Boys employed an exceedingly fine quartz fibre in place of the torsion wire used by Cavendish, and was thus able, without loss of sensitiveness, to reduce the whole torsion apparatus to a very much smaller size, which allowed it to be kept at a more uniform temperature, and so lessened the disturbance due to air currents. He obtained the mean value—

$$G = 6{\cdot}6576 \times 10^{-8}.$$

Whence $$\Delta = 5{\cdot}5270 \text{ gms./c.c.}$$

145. Determination of the Newtonian Constant of Gravitation by Means of the Common Balance.—The Newtonian constant of gravitation has also been determined by means of the common balance. The balance was first used for such a determination by von Jolly, in 1878, and, subsequently, by Poynting, in 1893, and by Richarz and Krigar-Menzel, in 1898.

Richarz and Krigar-Menzel employed a balance with two scale-pans suspended from each end of the beam, one scale-pan being near the beam while the other scale-pan hung a little more than two metres lower down. A spherical weight of one kilogramme was placed in the upper right-hand scale-pan, and an equal spherical weight in the lower left-hand scale-pan, and the deflection of the pointer was observed. The right-hand weight was then transferred from the upper to the lower right-hand scale-pan, and the left-hand weight from the lower to the upper left-hand scale-pan, and the deflection of the pointer was again observed.

It was found that the right-hand side gained 1·2453 mgm. in weight over the left-hand side on thus changing the positions of the spherical weights, so that a single kilogramme gained 0·6227 mgm. when lowered approximately 2 metres towards the centre of the earth.

A leaden parallelopiped, 2 metres in height, and 2·1 metres square, was next built up between the upper and lower scale-pans, narrow passages being left for the wires from which the lower scale-pans were suspended, and, on repeating the preceding observations with the 2 kilogrammes, it was found that the left-hand side gained 0·1211 mgm. in weight over the right-hand side, so that the attraction of the leaden parallelopiped produced a difference of 1·3664 mgm.

Since the attraction of the leaden parallelopiped acted in opposite directions on weights in the upper and lower scale-pans, it followed that the attraction on each of the kilogramme weights, due to the parallelopiped, was one-quarter of this difference, viz. 0·3416 mgm.

The mean density of the earth could then be calculated by comparing the attraction of the earth on a kilogramme (viz. 10^6 mgm.), with that exerted by the leaden parallelopiped, the mass of the parallelopiped and its distance from the kilogramme being known.

Richarz and Krigar-Menzel obtained the mean values—

$$G = 6{\cdot}685 \times 10^{-8};$$
$$\Delta = 5{\cdot}505 \text{ gms./c.c.}$$

146. The Properties of Gravitation.—Various investigations have been carried out on the properties of gravitation. These investigations indicate that gravitational attraction is quite independent of the chemical composition and physical condition both of the attracting masses and of the intervening medium, being solely conditioned by the masses of the attracting bodies and the distance between them.

APPENDIX A.

The Joule-Thomson Effect.—The thermal phenomena accompanying the free expansion of gases were investigated by Joule and Thomson in the following manner:—

A stream of gas, at constant pressure, was driven through a long copper spiral immersed in a constant temperature water-bath, and was then allowed to flow through a porous plug of cotton wool, or silk fibre—the wool, or fibre, being packed between two perforated brass discs inside a boxwood cylinder. After passing through the porous plug, the gas attained atmospheric pressure, and flowed round a sensitive thermometer, so that any change in the temperature of the gas could be directly observed.

Provided that the difference of pressure between the two sides of the porous plug were small, there was no sensible gain in the velocity of the stream of gas on flowing through the porous plug, and, therefore, no gain in kinetic energy arising from an increase in the translatory energy of the gas as a whole.

When, however, larger differences of pressure were employed, Joule and Thomson found that the temperature of the gas, after passing through the porous plug, was lower when measured near to the surface of the plug than when measured at points farther away. Under these circumstances the gas streamed through the porous plug with sensibly increased velocity, the corresponding increase in kinetic energy, due to the increase in the translatory energy of the gas as a whole, necessitating an equal decrease in the molecular kinetic energy of the gas, and a consequent fall in temperature. After passing the plug, the gas was soon reduced to a state of steady flow, owing to viscosity and to friction with the walls of the tube, the translatory energy of the stream being reduced to approximately its original value provided the difference of pressure between the two sides of the plug were not excessive. The cooling effect which occurred in the "rapids" near the surface of the porous plug, due to the increase in the translatory energy of the stream, was, consequently, eliminated at points farther away where a steady state of flow had been attained.

Joule and Thomson, however, found that there was an additional thermal effect accompanying free expansion— due, in part, to a change in the internal or *intrinsic* energy of the gas, and, in part, to the gas not strictly obeying Boyle's Law.

The nature of this thermal effect may be readily understood from the following simple illustration:—

Let AB (Fig. CXXXVII.) represent a long cylindrical pipe, of unit cross-section, closed at C by a diaphragm with a small aperture, D, and let air be forced through the aperture by the frictionless piston, E, the pressure of the air between E and C being constant and equal to P_1. After passing through the aperture let the air expand and push forward the frictionless piston, F, the pressure of the air, P_2, between F and C being constant and less than P_1.

If the volume of unit mass of air between E and C be V_1, the work done *on* unit mass of air in forcing it through the aperture, D, will be equal to P_1V_1. This work is expended in overcoming friction in the aperture, and, if the walls of the cylindrical pipe, AB, and the pistons, E and F, be assumed non-conductors of heat, the heat generated in the aperture will be absorbed by the air when a steady state of temperature has been attained.

If, now, the volume of unit mass of air between F and C be V_2, the work done *by* unit mass of air in expanding and pushing forward the piston, F, will be equal to P_2V_2.

In the case of any gas which obeys Boyle's Law, $P_1V_1 = P_2V_2$, and, consequently, the heat generated in the aperture and absorbed by the gas is equal to the heat withdrawn from the gas and converted into work during the expansion. In this case, therefore, the *total* energy possessed by the gas is unchanged by passing through the aperture and expanding from V_1 to V_2. If, then, the temperature of the gas (when measured at a sufficient distance from the "rapids" near the aperture D), be found the same on both sides of the diaphragm C, it follows that no heat energy has been absorbed during the expansion in doing work against internal molecular cohesive forces. If, on the other hand, the temperature of the gas be lowered by the expansion it follows that some work has been done against molecular cohesive forces—the gain in potential energy due to the increased distance between the molecules being accompanied by a corresponding decrease in the kinetic energy of molecular translation and a consequent fall in temperature.

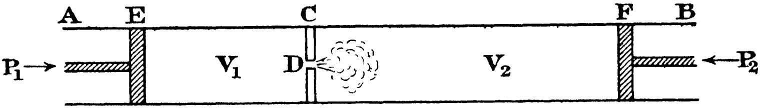

Fig. CXXXVII.

In the case of a gas which does not obey Boyle's Law, the product PV may either increase or decrease with decrease in the pressure, P.

If $P_1V_1 < P_2V_2$, the work done *on* the gas in forcing it through the aperture is less than the work done *by* the gas during the expansion, and, consequently, the total energy possessed by the gas is diminished, so that even if molecular cohesive forces be absent a cooling effect will be produced. If, in addition, work be done against molecular cohesion the cooling effect will be increased.

If $P_1V_1 < P_2V_2$, the total energy possessed by the gas is increased by passing through the aperture and expanding, so that, in the absence of cohesive forces, a heating effect will be produced. This heating effect will be reduced if work be done against molecular cohesion, and may even be replaced by a cooling effect [1]

Thus, the total cooling or heating effect observed is the algebraic sum of the cooling due to the work done against molecular cohesive forces, and the cooling or heating effect due to the variation in PV with the pressure.

Joule and Thomson found that with air, for example, a cooling effect of approximately 0·9° C. was obtained when the air, under a pressure of about

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[1] The same considerations apply, *mutatis mutandis*, if it be assumed that repulsive forces exist between the molecules; such molecular repulsion leading to a *diminution* in potential energy, and a corresponding increase in kinetic energy, on expansion.

130 inches of mercury, and at a mean temperature of 7° C., was forced through the porous plug, and allowed to attain the atmospheric pressure. Adopting Amagat's results for the increase in the product P.V. corresponding to this fall in pressure, it was calculated that the cooling effect *due to the increase in P.V.* was approximately 0·1° C., so that the additional cooling effect of about 0·8° C. was due to work done against molecular cohesive forces.

In the case of carbon-dioxide—(a less perfect gas)—a considerably greater cooling effect was obtained, which was shown to be mainly due to the work expended in separating the molecules farther apart.

With hydrogen a very small heating effect was obtained, of approximately the value calculated from Amagat's results for the *decrease* in the product PV corresponding to the given fall in pressure. In the case of hydrogen, therefore, at ordinary temperatures, the molecular cohesive forces must be very small.

Joule and Thomson also found that the cooling effect obtained with gases such as air and carbon-dioxide diminished with rise in temperature—(as was to be anticipated from the fact that the decrease in P.V. with rise in pressure becomes less marked as the temperature is raised)—and, further, that at a certain temperature the cooling effect disappeared, being replaced at higher temperatures by a heating effect. The temperature at which the transition occurs is known as the *temperature of inversion of the Joule-Thomson effect.*

It has been shown, in recent years, that there is for most, if not all, gases also a *minimum* temperature at which cooling is produced by expansion.

Thus Porter, in 1906, pointed out that the equations of state—such as those of van der Waals and Dieterici—indicated that, if there were any inversion effect at all, there should be *two* inversion temperatures for any one pressure, and, further, that above a certain pressure heating should result, when a gas expanded through a throttle or similar aperture, for all temperatures.

Jenkin and Pye, in 1913, showed that a minimum inversion temperature occurred, in the case of carbon-dioxide, between − 20·7° C. and − 31° C., and by plotting their data Porter showed that the temperature should correspond to approximately − 24° C., the pressure of the compressed carbon-dioxide being about half the critical pressure.

APPENDIX B.

The Theorem of Le Chatelier.—When the temperature of any system in a state of equilibrium is varied, a change takes place within the system which can be qualitatively foretold by means of van't Hoff's *Law of Mobile Equilibrium* (1884).

In accordance with this law we may state that "on raising the temperature of a system in chemical or physical equilibrium, that reaction takes place which is attended with an absorption of heat; whereas, on lowering the temperature, that reaction takes place which is attended with an evolution of heat."

It was shown by Robin (1879), that "on increasing the pressure exerted upon a system in chemical or physical equilibrium, that reaction takes place which is attended with a diminution in volume; whereas, on decreasing the pressure, that reaction takes place which is attended with an increase in volume."

These two laws, as was shown by Le Chatelier, are applicable to *all* systems; they are both covered by the more general *Theorem of Le Chatelier* (1888), which states that:—

"When any system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint, i.e. one by which its effect is partially destroyed."

The theorem of Le Chatelier is of the widest applicability, and covers all chemical and physical changes of equilibrium. Thus, a rise of temperature favours endothermal reactions, and a fall of temperature exothermal reactions, whereas change of temperature is without influence on the equilibrium of thermally neutral reactions. The dissociation of phosphorus pentachloride, for example, is accompanied by an absorption of heat (PCl_5 + 30,000 cals. $\rightleftarrows PCl_3 + Cl_2$), and the degree of dissociation is, accordingly, increased by raising the temperature.

Again, the solution of anhydrous sodium sulphate in water is attended with an evolution of heat, whilst hydrated sodium sulphate dissolves with an absorption of heat: in the former case the solubility diminishes with rise in temperature; whereas, in the latter case, the solubility increases. Thus, any substance which absorbs heat in dissolving will become more soluble as the temperature is raised.

As was pointed out in § 91, a liquid film when stretched adiabatically becomes colder, since the surface tension of any liquid diminishes with rise in temperature.

When ice melts, the water obtained occupies a smaller volume than the ice from which it was formed: it is found, in agreement with Le Chatelier's Theorem, that the melting-point of ice is lowered by an increase of pressure. Paraffin wax contracts on solidifying, and its melting-point is raised if the pressure be increased.

The degree of dissociation of the vapour of phosphorus pentachloride ($PCl_5 \rightleftarrows PCl_3 + Cl_2$) is increased by reducing the pressure, since the dissociation is accompanied by an increase in volume; the degree of dissociation may, similarly, be increased by diluting the vapour with any indifferent gas. A change of pressure will have no effect on the equilibrium of a system the volume of which is unaffected by a variation in the position of the equilibrium point. Thus the dissociation of hydrogen iodide into hydrogen and iodine ($2HI \rightleftarrows H_2 + I_2$) is unattended by any change in volume, and, in consequence, the equilibrium position is unaffected by variations of pressure.

APPENDIX C.

Units and Dimensions.—In order to describe any physical quantity we must specify the unit employed, and also the numerical ratio between the quantity and that unit.

It has been found sufficient, in the science of mechanics, to select three *fundamental* units, all other units being derived from these three, and being known, in consequence, as *derived* units.

The three fundamental units usually selected are Length, Mass, and Time, and all other units are defined in terms of these fundamental units. Thus, for example, unit volume is defined (arbitrarily) as the volume of a *cube* the edge of which is of unit length ; unit velocity as that possessed by a body which travels unit distance in unit time ; unit force as that which acting on unit mass imparts to it unit velocity in unit time ; unit work as that done by unit force when the point of application of the force moves unit distance in the direction of the force.

The magnitude of any derived unit will, evidently, depend upon the values assigned to the fundamental units. If, for example, the unit of length were *doubled*, the unit of area (defined, arbitrarily, as the area of a *square* having a side of unit length) would become four times as large, and the unit of volume eight times as large : if the units of length, mass, and time were *all* doubled, the units of velocity and force would remain unchanged in magnitude, but the unit of work would be doubled.

Since an area is of the same dimensions as the square of a length, it is said to be of the second dimension in length. This may be expressed, in the form of an equation, as follows :—

$$[\text{Area}] = [L^2].$$

The dimensions of a velocity are + 1 in length, and - 1 in time, since velocity is measured by *dividing* a length by a time, or :—

$$[\text{Velocity}] = [L\,.\,T^{-1}].$$

The dimensions of other derived units may, similarly, be written in equational form. Thus, to give merely a few examples :—

$$\begin{aligned}
[\text{Volume}] &= [L^3], \\
[\text{Acceleration}] &= [L\,.\,T^{-2}], \\
[\text{Force}] &= [M\,.\,L\,.\,T^{-2}], \\
[\text{Work}] &= [M\,.\,L^2\,.\,T^{-2}], \\
[\text{Young's Modulus}] &= [M\,.\,L^{-1}T^{-2}].
\end{aligned}$$

A knowledge of dimensions is often of use, both in checking the accuracy of formulæ, and in determining their form.

Consider, for example, the case of a beam, supported at its ends, and loaded in the middle (§ 134). Let us suppose that, in our previous investigation, we had erroneously obtained the equation

$$H = \frac{WL^3}{4Yb^3a^3}$$

for the depression, H, of the middle point of the beam.

Now, the dimensions of the two sides of the equation must be identical, i.e. :—

$$[L] = \left[\frac{M\,.\,L\,.\,T^{-2}\,.\,L^3}{M\,.\,L^{-1}\,.\,T^{-2}\,.\,L^3\,.\,L^3}\right],$$

$$\text{or} \qquad [L] = [L^{-1}].$$

The above equation for the depression, H, is, in consequence, incorrect.

The use of a knowledge of dimensions for *constructing* physical formulæ is commonly known as the "Method of Dimensions."

Let us, for example, construct the formula for the time of oscillation of a simple pendulum, and let us assume that the time-period, t, is only dependent upon the mass, m, of the pendulum bob, the length, l, of the suspending filament, the acceleration of gravity, g, and the angle, θ, of the arc of oscillation.

Now, since the circular measure of an angle is obtained by dividing a length by a length, θ is of *zero* dimensions.

We may, therefore, write—

$$t = k \,.\, m^x \,.\, l^y \,.\, g^z,$$

where k is a numerical quantity (having no dimensions), which may, or may not, be *constant*.

The dimensions of the two sides of this equation must be identical, i.e.:—

$$\begin{aligned}[\mathrm{T}] &= [\mathrm{M}^x \,.\, \mathrm{L}^y \,.\, (\mathrm{L} \,.\, \mathrm{T}^{-2})^z], \\ &= [\mathrm{M}^x \,.\, \mathrm{L}^{y+z} \,.\, \mathrm{T}^{-2z}].\end{aligned}$$

Since the dimensions of the left-hand side of the equation are + 1 in time, and zero in both mass and length, we have—

$$\begin{cases} x = 0, \\ y + z = 0, \\ -\ 2z = 1. \end{cases}$$

Whence, $z = -\frac{1}{2}$, and $y = +\frac{1}{2}$.

The formula for the time-period is, therefore—

$$t = k \,.\, l^{\frac{1}{2}} \,.\, g^{-\frac{1}{2}},$$

i.e.

$$t = k\sqrt{\frac{l}{g}}.$$

The method of dimensions, however, gives no information about the numerical factor, k, which, in this case, has the constant value 2π, provided the angle, θ, of the arc of oscillation be small.

As another example of the method of dimensions we will construct the formula for the time of vibration of a spherical liquid drop, under the influence of surface tension (§ 103).

If it be assumed that the time of vibration, S, is only dependent upon the radius, a, of the spherical drop, and upon the density, ρ, and surface tension, T, of the liquid, we may write—

$$\mathrm{S} = \mathrm{K} \,.\, a^x \,.\, \rho^y \,.\, \mathrm{T}^z,$$

where K is a numerical quantity without dimensions. Since the dimensions of the two sides of this equation must be the same, we have—[1]

$$\begin{aligned}[\mathrm{T}] &= [\mathrm{L}^x \,.\, (\mathrm{M} \,.\, \mathrm{L}^{-3})^y \,.\, (\mathrm{M} \,.\, \mathrm{T}^{-2})^z], \\ &= [\mathrm{L}^{x-3y} \,.\, \mathrm{M}^{y+z} \,.\, \mathrm{T}^{-2z}].\end{aligned}$$

---

[1] The dimensions of ρ are + 1 in mass and − 3 in length, since density is measured by dividing a mass by a volume; the dimensions of T are + 1 in mass and − 2 in time, since surface tension is measured by dividing a force by a length.

The dimensions of the left-hand side of the equation are + 1 in time, and zero in both mass and length, so that—

$$\begin{cases} x - 3y = 0, \\ y + z \;\;= 0, \\ \;\;\; - 2z = 1. \end{cases}$$

Whence, $z = -\frac{1}{2}$, $y = +\frac{1}{2}$, and $x = +\frac{3}{2}$.

The formula for the time of vibration is, therefore—

$$S = K \,.\, a^{\frac{3}{2}} \,.\, \rho^{\frac{1}{2}} \,.\, T^{-\frac{1}{2}},$$

i.e.

$$S = K \,.\, \left(\frac{a^3 \,.\, \rho}{T}\right)^{\frac{1}{2}}.$$

Lord Rayleigh showed that the time of gravest vibration, S, of a spherical liquid drop, under the influence of surface tension alone, was given by the relation—

$$S = \frac{\pi}{\sqrt{2}}\left(\frac{a^3 \,.\, \rho}{T}\right)^{\frac{1}{2}}.$$

It is evident that *all* quantities upon which the quantity under consideration is dependent must be carefully included when constructing a dimensional equation.

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