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### **A manual of chemistry**

Physical and inorganic chemistry

**Watts, Henry**

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Part I. - Physics

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## PART I.—PHYSICS.

### OF DENSITY AND SPECIFIC GRAVITY.

It is of great importance to understand clearly what is meant by the terms *density* and *specific gravity*. By the *density* of a body is meant its *mass*, or *quantity of matter*, compared with the mass or quantity of matter of an *equal volume* of some standard body, arbitrarily chosen. *Specific gravity* denotes the *weight* of a body, —or the force with which it tends to fall to the earth—as compared with the weight of an equal bulk, or volume, of the standard body, which is reckoned as unity.\* In all cases of solids and liquids the standard of unity adopted in this country is pure water at the temperature of  $15.5^{\circ}\text{C}$ . ( $60^{\circ}\text{Fahr.}$ ). Anything else might have been chosen; there is nothing in water to render its adoption for the purpose mentioned indispensable: it is simply taken for the sake of convenience, being always at hand, and easily obtained in a state of perfect purity. An ordinary expression of specific weight, therefore, is a number expressing how many times the weight of an equal bulk of water is contained in the weight of the substance spoken of. If, for example, we say that concentrated oil of vitriol has a specific gravity equal to 1.85, or that perfectly pure alcohol has a density of 0.794 at  $15.5^{\circ}\text{C}$ ., we mean that equal bulks of these two liquids and of distilled water possess weights in the proportion of the numbers 1.85, 0.794, and 1; or 1850, 794, and 1000. It is necessary to be particular about the temperature, for, as will be hereafter shown, liquids are extremely expansible by heat; otherwise a constant bulk of the same liquid will not retain a constant weight. It will be proper to begin with the description of the mode in which the specific gravity of liquids is determined: this is the simplest case, and the one which best illustrates the general principle.

To find the specific gravity of any particular liquid compared with that of water, it is only requisite to weigh equal bulks at the standard temperature, and then divide the weight of the liquid by

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\* In other words, density means comparative *mass*, and specific gravity comparative *weight*. These expressions, although really relating to distinct things, are often used indifferently in chemical writings, and without practical inconvenience, since mass and weight are directly proportional to each other.



the weight of the water; the quotient will be greater or less than unity, as the liquid experimented on is heavier or lighter than water. Now, to weigh equal bulks of two liquids, the simplest and best method is clearly to weigh them in succession in the same vessel, taking care that it is equally full on both occasions.

The vessel commonly used for this purpose is a small glass bottle provided with a perforated conical glass stopper, very accurately fitted by grinding. By completely filling the bottle with liquid, and carefully removing the portion of liquid which is displaced when the stopper is inserted, an unalterable measure is obtained. The least possible quantity of grease applied to the stopper greatly promotes the exact fitting.

When the chemist has only a very small quantity of a liquid at his disposal, and wishes not to lose it, the little glass vessel (fig. 2) is particularly useful. It is formed by blowing a bulb on a glass tube. On that portion of the tube which is narrowed by drawing

Fig. 1.

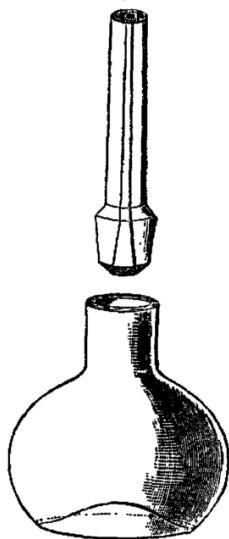


Fig. 2.



the tube out over a lamp, a fine scratch is made with a diamond. The bulb is filled up to this mark with the liquid whilst it stands in water, the temperature of which is exactly known. A very fine funnel is used for filling the bulb, the stem of the funnel being drawn out so as to enter the tube, and the upper opening of the funnel being small enough to be closed by the finger. The glass

stopper is wanted only as a guard, and does not require to fit perfectly.

Another form of apparatus for determining the specific gravity of liquids, devised by Dr. Sprengel, consists of an elongated U-tube (fig. 3), the ends of which terminate in the two capillary tubes, *a*, *b*,

Fig. 4

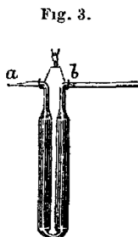
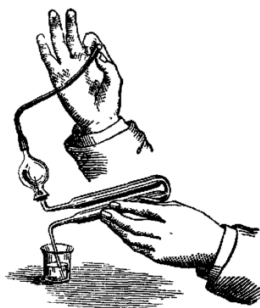


Fig. 3.



bent at right angles in opposite directions. The shorter one, *a*, is a good deal narrower (at least towards the end) than the longer one, the inner diameter of which is about half a millimeter. The horizontal part of this wider tube is marked near the bend with a fine line, *b*. The U-tube is filled by suction—the little bulb-apparatus (fig. 4) having been previously attached to the narrow capillary tube by a piece of india-rubber tubing—then detached from the bulb, placed in water almost up to the bends of the capillary tubes, left there till it has assumed the temperature of the water, and, after careful adjustment of the volume of the liquid up to the mark *b* in the wider capillary tube, it is taken out, dried, and weighed.

The determination of the specific gravity of a solid body is also made according to the principles above explained, and may be performed with the specific-gravity bottle (fig. 1). The bottle is first weighed full of water; the solid is then placed in the same pan of the balance, and its weight is determined; finally, the solid is put into the bottle, displacing an equal bulk of water, the weight of which is determined by the loss on again weighing. Thus, the weights of the solid and that of an equal bulk of water, are obtained. The former divided by the latter gives the specific gravity.

For example, the weight of a small piece of silver wire was found to be . . . . .	98.18 grains.
Glass bottle filled with water . . . . .	294.69 „
	<hr/>
	392.87 „
After an equal volume of water was displaced by the silver, the weight was . . . . .	383.54 „
	<hr/>
Hence the displaced water weighed . . . . .	9.33 „
From this the specific gravity of the silver wire is . . . . .	$\left. \begin{array}{l} 98.18 \\ 9.33 \end{array} \right\} = 10.523$ „

Another highly ingenious, but less exact method of determining the specific gravity of solids, is based on the well-known theorem of Archimedes, which may be thus expressed :

When a solid is immersed in a fluid, it loses a portion of its weight; and this portion is equal to the weight of the fluid which it displaces, that is, to the weight of its own bulk of that fluid.

Fig. 5.



This principle is applied as follows :—

Let it be required, for example, to know the specific gravity of a body of extremely irregular form, as a small group of rock-crystals : the first part of the operation consists in determining its absolute weight, or, more correctly speaking, its weight in air ; it is next suspended from the balance-pan by a fine horsehair, immersed completely in pure water at 15.5°, and again weighed. It now weighs less, the difference being the weight of the water it displaces, that is, the weight of an equal bulk. This being known, nothing more is required than to find, by division, how many times the latter number is contained in the former ; the quotient will be the density, water at the temperature of 15.5° being taken = 1. For example :—

The quartz-crystals weigh in air . . . . .	293.7 grains.
When immersed in water, they weigh . . . . .	180.1 „
	<hr/>
Difference, being the volume of an equal volume of water . . . . .	113.6 „

$$\frac{293.7}{113.6} = 2.59, \text{ the specific gravity required.}$$

The rule is generally thus written : “ Divide the weight in air by the loss of weight in water, and the quotient will be the specific gravity.” In reality it is not the weight in air which is required,

but the weight the body would have in empty space: the error introduced, namely, the weight of an equal bulk of air, is so trifling, that it is usually neglected.

Sometimes the body to be examined is lighter than water, and floats. In this case, it is first weighed, and afterwards attached to a piece of metal heavy enough to sink it, and suspended from the balance. The whole is then exactly weighed, immersed in water, and again weighed. The difference between the two weighings gives the weight of a quantity of water equal in bulk to both together. The light substance is then detached, and the same operation of weighing in air, and again in water, repeated on the piece of metal. These data give the means of finding the specific gravity, as will be seen by the following example:—

Light substance (a piece of wax) weighs in air . 133·7 grains.

Attached to a piece of brass, the whole now  
weighs . . . . . 183·7 ”  
Immersed in water, the system weighs . . . 38·8 ”

Weight of water equal in bulk to brass and wax. 144·9 ”

Weight of brass in air . . . . . 50·0 ”  
Weight of brass in water . . . . . 44·4 ”

Weight of equal bulk of water . . . . . 5·6 ”

Weight of bulk of water equal to wax and brass. 144·0 ”  
Weight of bulk of water equal to brass alone . 5·6 ”

Weight of bulk of water equal to wax alone . 139·3 ”

$$\frac{133\cdot7}{139\cdot3} = 0\cdot9598.$$

In all such experiments, it is necessary to pay attention to the temperature and purity of the water, and to remove with great care all adhering air-bubbles; \* otherwise a false result will be obtained.

Other cases require mention in which these operations must be modified to meet particular difficulties. One of these happens when the substance is dissolved or acted upon by water. This difficulty is easily overcome by substituting some other liquid of known density

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\* A simple plan of avoiding altogether the adhesion of air-bubbles, which often are not easily perceived, consists in heating the water to ebullition, and introducing the body which has been weighed in the air into the still boiling water, which is then allowed to cool to 15·5°, when the second weighing is performed.

which experience shows is without action. Alcohol or oil of turpentine may generally be used when water is inadmissible. Suppose, for instance, the specific gravity of crystallised sugar is required, we proceed in the following way :—The specific gravity of the oil of turpentine is first determined ; let it be 0·87 ; the sugar is next weighed in the air, then suspended by a horsehair, and weighed in the oil ; the difference is the weight of an equal bulk of the latter ; a simple calculation gives the weight of a corresponding volume of water :—

Weight of sugar in air . . . . .	400	grains.
Weight of sugar in oil of turpentine . . . . .	182·5	„
	<hr/>	
Weight of equal bulk of oil of turpentine . . . . .	217·5	„

$$87 : 100 = 217·5 : 250,$$

the weight of an equal bulk of water : hence the specific gravity of the sugar,—

$$\frac{400}{250} = 1·6.$$

If the substance to be examined consists of small pieces, or of powder, the method first described, namely, that of the specific gravity bottle, can alone be used.

By this method the specific gravities of metals in powder, metallic oxides, and other compounds, and salts of all descriptions, may be readily determined. Oil of turpentine may be used with most soluble salts. The crystals should be crushed or roughly powdered to avoid errors arising from cavities in their substance.

The specific gravity of a solid can also be readily found by immersing it in a transparent liquid, the density of which has been so adjusted that the solid body remains indifferently at whatever depth it may be placed. The specific gravity of the liquid must now be determined, and it will, of course, be the same as that of the solid. It is necessary that the liquid chosen for this experiment do not dissolve or in any way act upon the solid. Solutions of mercuric nitrate, or corrosive sublimate, can be used for bodies heavier than water, whilst certain oils, and essences, and mixtures of alcohol and water, can be conveniently employed for such substances as have a lower specific gravity than water. This method is not only adapted to the exact determination of specific gravities, but also serves in many cases as a means of readily distinguishing substances much resembling one another. Suppose, for instance, a solution of mercuric nitrate to have a specific gravity 3 ; a red amethyst (2·67) will then float upon, and a topaz of the same colour (3·55) will sink in this liquid.

*Hydrometers.*—The theorem of Archimedes affords the key to the general doctrine of the equilibrium of floating bodies, of which an

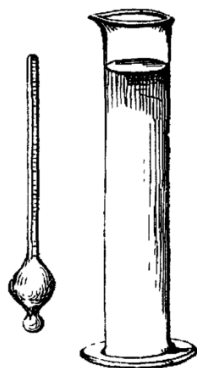
application is made in the common hydrometer,—an instrument for finding the specific gravities of liquids in a very easy and expeditious manner.

When a solid body is placed upon the surface of a liquid specifically heavier than itself, it sinks down until it displaces a quantity of liquid equal to its own weight, at which point it floats. Thus, in the case of a substance floating in water, whose specific weight is one-half that of the liquid, the position of equilibrium will involve the immersion of exactly one-half of the body, inasmuch as its whole weight is counterpoised by a quantity of water equal to half its volume. If the same body were put into a liquid of one-half the specific gravity of water, if such could be found, it would then sink beneath the surface, and remain indifferently in any part. A floating body of known specific gravity may thus be used as an indicator of the specific gravity of a liquid. In this manner little glass beads (fig. 6) of known specific gravities are sometimes employed in the arts to ascertain in a rude manner the specific gravity of liquids; the one that floats indifferently beneath the surface, without either sinking or rising, has of course the same specific gravity as the liquid itself; this is pointed out by the number marked upon the bead.

Fig. 6.



Fig 7.



The hydrometer (fig. 7) in general use consists of a floating vessel of thin metal or glass, having a weight beneath to maintain it in an upright position, and a stem above bearing a divided scale. The liquid to be tried is put into a small narrow jar, and the instrument floated in it. It is obvious that the denser the liquid, the higher will the hydrometer float, because a smaller displacement of liquid will counterbalance its weight. For the same reason, in a liquid of less density, it sinks deeper. The hydrometer comes to rest almost immediately, and then the mark on the stem at the fluid-level may be read off.

Very extensive use is made of instruments of this kind in the arts: they sometimes bear different names, according to the kind of liquid for which they are intended; but the principle is the same in all. The graduation is very commonly arbitrary, two or three different scales being unfortunately used. These may be sometimes reduced, however, to the true numbers expressing the specific gravity by the aid of tables of comparison drawn up for the purpose. (*See Appendix.*) Tables are likewise used to reduce the readings of the hydrometer at any temperature to those of the normal temperature.

It is much better, however, to use a hydrometer having the true scale of specific gravities marked upon its stem. To graduate such an instrument, a sufficient number of standard points may be determined by immersing it in liquids of known specific gravity, and the small interval between these points divided into equal parts.\*

The determination of the specific gravity of gases and vapours of volatile liquids is a problem of very great practical importance to the chemist: the theory of the operation is as simple as when liquids themselves are concerned, but the processes are much more delicate, and involve certain corrections for differences of temperature and pressure, founded on principles yet to be discussed. It will be proper therefore to defer the consideration of these matters for the present.

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\* For an accurate method of dividing the hydrometer scale when only a few points are determined by actual observation, see the article "Hydrometer," by the late Professor Jevons, in Watts's *Dictionary of Chemistry*, vol. iii, p. 206.

## THE PHYSICAL CONSTITUTION OF THE ATMOSPHERE, AND OF GASES IN GENERAL.

It requires some little abstraction of mind to realise completely the condition in which all things at the surface of the earth exist. We live at the bottom of an immense ocean of gaseous matter, which envelopes everything, and presses upon everything with a force which appears, at first sight, perfectly incredible, but whose actual amount admits of easy proof.

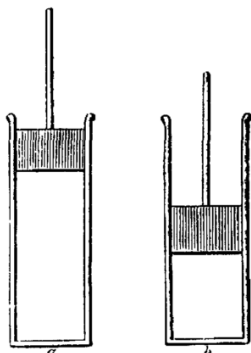
Gravity being, so far as is known, common to all matter, it is natural to expect that gases, being material substances, should be acted upon by the earth's attraction, as well as solids and liquids. This is really the case, and the result is the weight or pressure of the atmosphere, which is nothing more than the effect of the attraction of the earth on the particles of air.

Before describing the leading phenomena of the atmospheric pressure, it is necessary to notice one very remarkable feature in the physical constitution of gases, upon which depends the principle of the air-pump.

Gases are in the highest degree elastic; the volume or space which a gas occupies depends upon the pressure exerted upon it. Let the reader imagine a cylinder, *a*, closed at the bottom, in which moves a piston air-tight, so that no air can escape between the piston and the cylinder. Suppose now the piston be pressed downwards with a certain force; the air beneath it will be compressed into a smaller bulk, the amount of this compression depending on the force applied; if the power be sufficient, the bulk of the gas may be thus diminished to one hundredth part or less. When the pressure is removed, the elasticity or *tension*, as it is called, of the included air or gas, will immediately force up the piston until it arrives at its first position.

Again, take fig. 8, *b*, and suppose the piston to stand about the middle of the cylinder, having air beneath in its usual state. If the piston be now drawn upwards, the air below will expand, so as to fill completely the increased space, and this to an apparently unlimited extent. A volume of air, which, under ordinary circumstances, occupies the bulk of a cubic inch, might, by the removal of the pressure upon it, be made to expand to the capacity of a whole

Fig. 8.

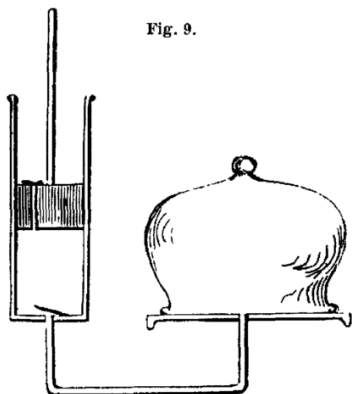




room, while a renewal of the former pressure would be attended by a shrinking down of the air to its former bulk. The smallest portion of gas introduced into a large exhausted vessel becomes at once diffused through the whole space, an equal quantity being present in every part; the vessel is *full* although the gas is in a state of extreme tenuity. This power of expansion which air possesses may have, and probably has, in reality, a limit; but the limit is never reached in practice. We are quite safe in the assumption, that for all purposes of experiment, however refined, air is perfectly elastic.

*The Air-pump.*—The ordinary air-pump, shown in section in fig. 9, consists essentially of a metallic cylinder, in which moves a tightly-fitting piston, by the aid of its rod. The bottom of the cylinder communicates with the vessel to be exhausted, and is furnished with a valve opening upwards. A similar valve, also

Fig. 9.



opening upwards, is fitted to the piston: these valves are made with slips of oiled silk. When the piston is raised from the bottom of the cylinder, the space left beneath it must be void of air, since the piston-valve opens only in one direction; the air within the receiver having on that side nothing to oppose its elastic power but the weight of the little valve, lifts the latter, and escapes into the cylinder. So soon as the piston begins to descend, the lower valve closes, by its own weight, or by the pressure transmitted from above, and communication with the receiver is cut off. As the descent of the piston continues,

the air enclosed in the cylinder becomes compressed, its elasticity is increased, and at length it forces open the upper valve, and escapes into the atmosphere. In this manner a cylinder full of air is removed from the receiver at every stroke of the pump. During the descent of the piston, the upper valve remains open, and the lower closed, and the reverse during the opposite movement.

In practice, it is very convenient to have two such barrels or cylinders, arranged side by side, the piston-rods of which are formed into racks, having a pinion or small-toothed wheel between them, moved by a winch. By this contrivance the operation of exhaustion is much facilitated, and the labour lessened. The arrangement is shown in fig. 10.

Fig. 11.

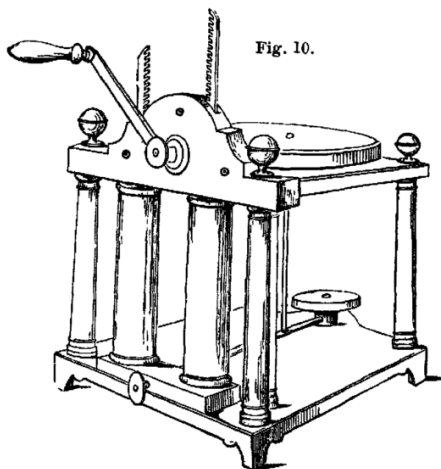


Fig. 10.



**Atmospheric Pressure—The Barometer.**—Air has weight ; a light flask or globe of glass, furnished with a stop-cock and exhausted by the air-pump, weighs considerably less than when full of air. If the capacity of the vessel be equal to 100 cubic inches, this difference may amount to nearly 30 grains.

After what has been said on the subject of fluid pressure, it will scarcely be necessary to observe that the law of equality of pressure in all directions also holds good in the case of the atmosphere. The perfect mobility of the particles of air permits the transmission of the force generated by their gravity. The sides and bottom of an exhausted vessel are pressed upon with as much force as the top.

If a glass tube of considerable length could be perfectly exhausted of air, and then held in an upright position, with one of its ends dipping into a vessel of liquid, the latter, on being allowed access to the tube, would rise in its interior until the weight of the

column balanced the pressure of the air upon the surface of the liquid. Now, if the density of this liquid were known, and the height and area of the column measured, means would be furnished for exactly estimating the amount of pressure exerted by the atmosphere. Such an instrument is the barometer. To construct it, a straight glass tube, 36 inches long, is sealed by the blowpipe flame at one end; it is then filled with clean, dry mercury, care being taken to displace all air-bubbles, the open end is stopped with a finger, and the tube is inverted in a basin of mercury. On removing the finger, the mercury falls away from the top of the tube, until it stands at the height of about 30 inches above the level of that in the basin. Here it remains supported by, and balancing the atmospheric pressure, the space above the mercury in the tube being of necessity empty.

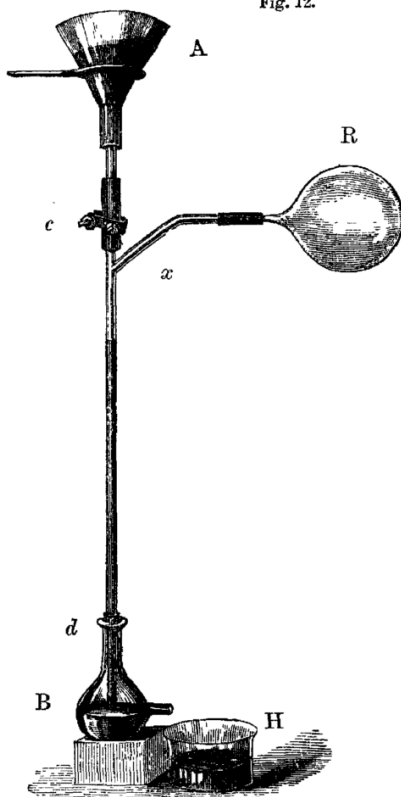
The pressure of the atmosphere is thus seen to be capable of sustaining a column of mercury 30 inches in height, or thereabouts. Now such a column, having an area of 1 inch, weighs between 14 and 15 lbs. : consequently such must be the amount of the pressure exerted by the air upon every square inch of the surface of the earth, and of the objects situated thereon, at least near the level of the sea. This enormous force is borne without inconvenience by the animal frame, by reason of its perfect uniformity in every direction; and it may be doubled, or even tripled, without injury.

A barometer may be constructed with other liquids besides mercury; but, as the height of the column must always bear an inverse proportion to the density of the liquid, the length of tube required will be often considerable; in the case of water it will exceed 33 feet. It is seldom that any other liquid than mercury is employed in the construction of this instrument. The Royal Society of London possessed a water barometer at their apartments at Somerset House. Its construction was attended with great difficulties, and it was found impossible to keep it in repair.

*Sprengel's Air-pump.*—If an aperture be made in the top of a barometer tube, the mercury will sink, and draw in air; and if the experiment be so arranged as to allow air to enter along with the mercury, and the supply of air is limited, while that of the mercury is unlimited, the air will be carried away and a vacuum produced. On this principle, Dr. Sprengel has contrived an apparatus by which a very complete exhaustion may be obtained. *cd* (fig. 12) is a glass tube longer than a barometer, open at both ends, and connected, by means of india-rubber tubing, with a funnel *A* filled with mercury, and supported on a stand. Mercury is allowed to fall through this tube at a rate regulated by a clamp at *c*; the lower end of the tube *cd* fits into the flask *B*, which has a spout at its side, a little higher than the lower end of the tube *cd*; the upper part of this tube has a branch at *x*, to which a receiver *R* can be tightly fixed. When the clamp at *c* is opened, the first portion of the mercury that runs out closes the tube and prevents air from entering below. As the mercury is allowed to run down, the exhaustion begins, and the

whole length of the tube from  $x$  to  $d$  is filled with cylinders of air and mercury having a downward motion. Air and mercury escape through the spout of the bulb B, below which is placed a basin H to receive the mercury; and this mercury is poured back from time to time into the funnel A, to be repassed through the tube till the exhaustion is complete. As this point is approached, the enclosed air between the mercury cylinders is seen to diminish, until the lower part of  $cd$  forms a continuous column of mercury about 30 inches high. The operation is complete when the column of mercury is quite free from air, and a drop of mercury falls on the top of it without enclosing the smallest air-bubble. The height of the column is then equal to that of the mercury in the barometer; in other words, the apparatus is a barometer whose vacuum is the receiver R. It may be advantageously combined with an exhausting syringe, which removes the greater part of the air, the exhaustion being then completed as above.

Fig. 12.



**Relations between Pressure, Elasticity, and Volume of Gases.**—It will

now be necessary to consider a most important law which connects the volume occupied by a gas with the pressure made upon it, and is thus expressed :—

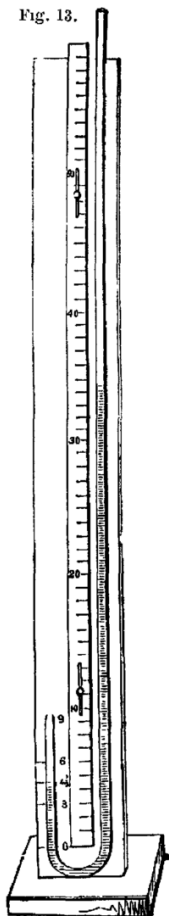
The volume of gas is *inversely* as the pressure; the density and elastic force are *directly* as the pressure, and *inversely* as the volume.

For instance, 100 cubic inches of gas under a pressure of 30 inches of mercury would expand to 200 cubic inches were the pressure reduced to one-half, and shrink, on the contrary, to 50 cubic inches

if the original pressure were doubled. The change of density must necessarily be in inverse proportion to that of the volume, and the elastic force follows the same rule.

This, which is usually called the law of Mariotte, though really discovered by Boyle (1661), is easily demonstrable by direct experiment. A glass tube about 7 feet long, is closed at one end, and bent into the form represented in fig. 13, the open limb of the syphon being the longer. It is next attached to a board furnished with a movable scale of inches, and enough mercury is introduced to fill the bend, the level being evenly adjusted, and marked upon the board. Mercury is now poured into the tube until the enclosed air is reduced to one-half of its former volume; and on applying the scale, it will be found that the level of the mercury in the open part of the tube stands very nearly 30 inches above that in the closed portion. The pressure of an additional "atmosphere" has consequently reduced the bulk of the contained air to one-half. If the experiment be still continued until the volume of air is reduced to a third, it will be found that the column measures 60 inches, and so in like proportion as far as the experiment is carried.

Fig. 13.



The above instrument is better adapted for illustration of the principle than for furnishing rigorous proof of the law. This has, however, been done. MM. Arago and Dulong published, in the year 1830, an account of experiments made by them in Paris, in which the law in question had been verified to the extent of twenty-seven atmospheres. With rarefied air also, of whatever degree of rarefaction, the law has been found true.

All gases are alike subject to this law, and all vapours of volatile liquids, when remote from their points of liquefaction.\* It is a matter of the greatest importance in practical chemistry, since it gives the means of making corrections for pressure, or determining by calculation the change of volume which a gas would suffer by any given change of external pressure.

Let it be required, for example, to solve the following problem: We have 100 cubic inches of

\* Near the liquefying point the law no longer holds; the volume diminishes *more rapidly* than the theory indicates, a smaller amount of pressure being then sufficient. (See further, p. 60.)

gas in a graduated jar, the barometer standing at 29 inches ; how many cubic inches will it occupy when the column rises to 30 inches ? Now the volume must be inversely as the pressure : consequently a change of pressure in the proportion of 29 to 30 must be accompanied by a change of volume in the proportion of 30 to 29, the 30 cubic inches of gas contracting to 29 cubic inches under the conditions imagined. Hence the answer—

$$30 : 29 = 100 : 96.67 \text{ cubic inches.}$$

The reverse of the operation will be obvious. The pupil will do well to familiarise himself with the simple calculations of correction for pressure.

**Collection, Transference, and Preservation of Gases.**—The management of gases is of great importance to the chemical student. We may illustrate it by describing the preparation of oxygen gas from the red oxide of mercury. This substance is placed in a short tube of hard glass, to which is fitted a perforated cork, furnished with a piece of narrow glass tube, bent as in fig. 14. The heat of a spirit-lamp or gas-lamp being applied to the substance, decomposition speedily commences, and globules of metallic mercury collect in the cool part of the wide tube, while gas issues in considerable quantity from the apparatus. This gas is collected and examined by the aid of the pneumatic trough, which consists of a vessel of water provided with a shelf, upon

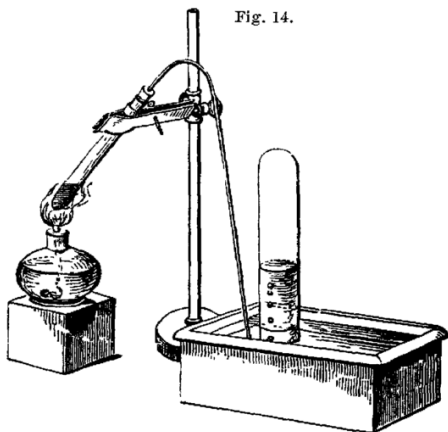


Fig. 14.

which stand the jars or bottles destined to receive the gas, filled with water and inverted. By keeping the level of the liquid

above the mouth of the jar, the water is retained in the latter by atmospheric pressure, and entrance of air is prevented. When the jar is brought over the extremity of the gas-delivery tube, the bubbles of gas, rising through the water, collect in the upper part of the jar, and displace the liquid. As soon as one jar is filled, it may be removed, still keeping its mouth below the water-level, and another substituted.

The water-trough is one of the most indispensable articles of the laboratory, and by its aid all experiments on gases are carried on when the gases themselves are not sensibly acted on by water. The trough is best constructed of japanned copper, the form and dimensions being regulated by the magnitude of the jars. It should have a firm shelf, so arranged as to be always about an inch below the level of the water, and in the shelf a groove should be made about half an inch in width and depth, to admit the extremity of the gas-delivery tube, which stands firmly on the shelf.

For gases which are easily soluble in water, such as hydrogen chloride and ammonia, a smaller trough is used, made of hard wood, and filled with mercury.

Gases are transferred from jar to jar with the utmost facility, by first filling the vessel into which the gas is to be passed, with water, inverting it, carefully retaining its mouth below the water-level, and then bringing beneath it the aperture of the jar containing the gas. On gently inclining the latter, the gas passes by a kind of inverted decantation into the second vessel. When the latter is narrow, a funnel may be placed loosely in its neck, by which loss of gas will be prevented.

A jar wholly or partially filled with gas at the pneumatic trough may be removed by placing beneath it a shallow basin, or even a common plate, so as to carry away enough water to cover the edge of the jar; and many gases, especially oxygen, may be so preserved for many hours without material injury.

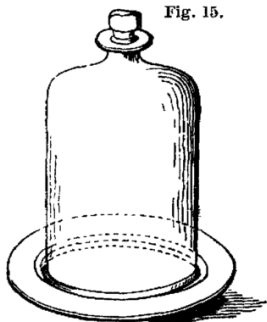


Fig. 15.

Gas-jars are often capped at the top, and fitted with a stop-cock for transferring gas to bladders or caoutchouc bags. When such a vessel is to be filled with water, it may be slowly sunk in an upright position in the well of the pneumatic trough, the stop-cock being open to allow the air to escape, until the water reaches the brass cap. The cock is then to be turned, and the jar lifted upon the shelf, and filled with gas in the usual way. If the trough be not deep enough for this method of proceeding, the mouth may be applied to the stop-cock, and the vessel filled by sucking out the air until the water rises to the cap. In all cases it is

proper to avoid as much as possible wetting the stop-cocks and other brass apparatus.

The late Mr. Pepys contrived an admirable piece of apparatus for storing and retaining large quantities of gas. It consists of a drum or reservoir of sheet copper, surmounted by a shallow trough or cistern, the communication between the two being made by a couple of tubes furnished with stop-cocks, one of which passes nearly to the bottom of the drum, as shown in fig. 16. A short wide open tube is inserted obliquely near the bottom of the vessel, into which a plug may be tightly screwed. A stop-cock near the top serves to transfer gas to a bladder or tube-apparatus. A glass water-gauge affixed to the side of the drum, and communicating with both top and bottom, indicates the level of the liquid within.

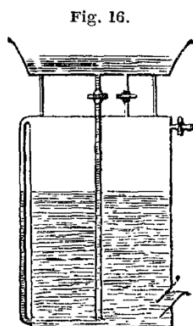
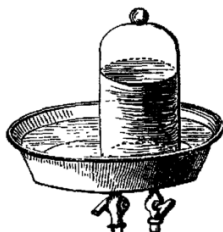


Fig. 16.

To use the gas-holder, the plug is first to be screwed into the lower opening, and the drum completely filled with water. All three stop-cocks are then to be closed and the plug removed. The pressure of the atmosphere retains the water in the gas-holder, and if no air-leakage occurs, the escape of water is inconsiderable. The extremity of the delivery-tube is now to be well pushed through the open aperture into the drum, so that the bubbles of gas may rise without hindrance to the upper part, displacing the water, which flows out in the same proportion into a vessel placed for its reception. When the drum is filled, or enough gas has been collected, the tube is withdrawn and the plug screwed into its place.

When a portion of the gas is to be transferred to a jar, the latter is to be filled with water at the pneumatic trough, carried by the help of a basin or plate to the cistern of the gas-holder, and placed over the shorter tube. On opening the cock of the neighbouring tube, the pressure of the column of water will cause compression of the gas, and increase its elastic force, so that, on gently turning the cock beneath the jar, it will ascend into the latter in a rapid stream of bubbles. The jar, when filled, may again have the plate slipped beneath it, and may then be easily removed.

Fig. 17





**HEAT.**

It will be convenient to consider the subject of heat under several sections, and in the following order :—

1. Expansion of bodies, or effects of variations of temperature in altering their dimensions.
2. Conduction, or transmission of heat.
3. Specific heat.
4. Change of state.
5. Sources of heat.
6. Dynamical theory of heat.

**Expansion.**

If a bar of metal of such magnitude as to fit accurately to a gauge, when cold, be heated considerably, and again applied to the gauge, it will be found to have become enlarged in all its dimensions. When cold, it will once more enter the gauge.

Again, if a quantity of liquid contained in a glass bulb furnished with a narrow neck, be plunged into hot water, or exposed to any

Fig. 18.

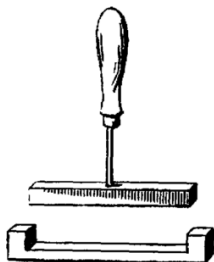


Fig. 19.



Fig. 20.



other source of heat, the liquid will mount in the stem, showing that its volume has been increased. The bulb, however, has likewise expanded by the heat, and its capacity has consequently been augmented. The rise of the liquid in the tube, therefore, denotes the difference between these two expansions.

Or, if a portion of air be confined in any vessel, the application of a slight degree of heat will suffice to make it occupy a space sensibly larger.

This most general of all the effects of heat furnishes in the outset a principle, by the aid of which an instrument can be constructed

capable of taking cognisance of changes of temperature in a manner equally accurate and convenient : such an instrument is the thermometer.

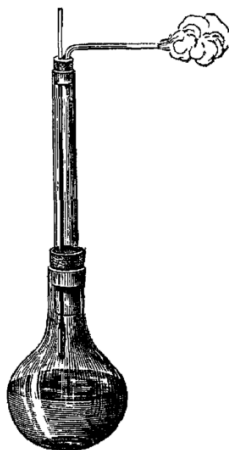
A capillary glass tube is chosen, of uniform diameter ; one extremity is closed and expanded into a bulb, by the aid of the blow-pipe flame, and the other somewhat drawn out, and left open. The bulb is now cautiously heated by a spirit-lamp, and the open extremity plunged into a vessel of mercury, a portion of which rises into the bulb when the latter cools, replacing the air which had been expanded and driven out by the heat. By again applying the flame, and causing this mercury to boil, the remainder of the air is easily expelled, and the whole space filled with mercurial vapour. The open end of the tube must now be immediately plunged into the vessel filled with mercury. As the metallic vapours condense, the pressure of the external air forces the liquid metal into the instrument, until finally the tube is completely filled with mercury. The thermometer thus filled is now to be heated until so much mercury has been driven out by the expansion of the remainder, that its level in the tube shall stand at common temperatures at the point required. This being satisfactorily adjusted, the heat is once more applied, until the column rises quite to the top ; and then the extremity of the tube is hermetically sealed by the blow-pipe. The retraction of the mercury on cooling now leaves an empty space, which is essential to the perfection of the instrument.

The thermometer has yet to be graduated ; and to make its indications comparable with those of other instruments, a scale, having at the least two fixed points, must be adapted to it.

It has been observed, that the temperature of melting ice, that is to say, of a mixture of ice and water, is always constant ; a thermometer, already graduated, plunged into such a mixture, always marks the same degree of temperature, and a simple tube filled in the manner described and so treated, exhibits the same effect in the unchanged height of the little mercurial column, when tried from day to day. The freezing point of water, or melting point of ice, constitutes then one of the invariable temperatures demanded.

Another is to be found in the boiling point of water, or, more accurately, in the temperature of steam which rises from boiling water. In order to give this temperature, which remains perfectly constant whilst the barometric pressure is constant, to the mercury of the thermometer, distilled water is made to boil in a glass vessel

Fig. 21.



with a long neck, when the pressure is at 30 inches (fig. 20). The thermometer is then so placed that all the mercury is surrounded with steam. It quickly rises to a fixed point, and there it remains as long as the water boils, and the height of the barometer is unchanged.

The tube having been carefully marked with a file at these two points, it remains to divide the interval into degrees: this division is entirely arbitrary. The scale now most generally employed is the Centigrade, in which the space is divided into 100 parts, the zero being placed at the melting point of ice. The scale is continued above and below these points, numbers below 0 being distinguished by the negative sign.

In England the division of Fahrenheit is still in use: the above mentioned space is divided into 180 degrees; but the zero, instead of starting from the melting point of ice, is placed 32 degrees below it, so that the temperature of ebullition is expressed by  $212^{\circ}$ .

The scale of Reaumur is nearly confined to a few places in the north of Germany and to Russia: in this scale the melting point of ice is made  $0^{\circ}$ , and the boiling point of water  $80^{\circ}$ .

It is unfortunate that a uniform system has not been generally adopted in graduating thermometers: this would render unnecessary the labour which now so frequently has to be performed of translating the language of one scale into that of another. To effect this, presents, however, no great difficulty. Let it be required, for example, to know the degree of Fahrenheit's scale which corresponds to  $60^{\circ}$  C.

$$100^{\circ} \text{ C.} = 180^{\circ} \text{ F.}; \text{ or } 5^{\circ} \text{ C.} = 9^{\circ} \text{ F.}$$

Consequently,

$$5 : 9 = 60 : 108.$$

But then, as Fahrenheit's scale commences with  $32^{\circ}$  instead of  $0^{\circ}$ , that number must be added to the result, making  $60^{\circ} \text{ C.} = 140^{\circ} \text{ F.}$

The rule, then, is the following:—To convert centigrade degrees into Fahrenheit degrees, multiply by 9, divide the product by 5, and add 32; to convert Fahrenheit degrees into centigrade degrees, subtract 32, multiply by 5, and divide by 9.

The reduction of negative degrees, or those below zero of one scale into those of another scale, is effected in the same way. For example, to convert  $-15^{\circ} \text{ C.}$  into degrees of Fahrenheit, we have—

$$-15 \times \frac{9}{5} + 32 = -27 + 32 = +5 \text{ F.}$$

In this work temperatures will always be given in centigrade degrees, unless the contrary is stated.

Mercury is usually chosen for making thermometers, on account of its regularity of expansion within certain limits, and because it is easy to have the scale of great extent, from the large interval between the freezing and boiling points of the metal. Other substances are sometimes used; alcohol is employed for estimating

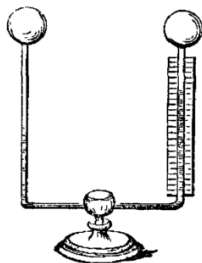
very low temperatures, because this liquid has not been frozen even at the lowest degree of cold which has been artificially produced.

Air-thermometers are also used for some few particular purposes; indeed, the first thermometer ever made was of this kind. There are two modifications of this instrument: in the first, the liquid into which the tube dips is open to the air; and in the second, shown in fig. 22, the atmosphere is completely excluded. The effects of expansion are in the one case complicated with those arising from changes of pressure, and in the other they cease to be visible at all when the *whole* instrument is subjected to alterations of temperature, because the air in the upper and lower reservoir,

Fig. 22.



Fig. 23.



being equally affected by such changes, no alteration in the height of the fluid column can occur. Accordingly, such instruments are called *differential* thermometers, since they serve to measure differences of temperature between the two portions of air, while changes affecting both alike are not indicated. Fig. 23 shows another form of the same instrument.

The air-thermometer may be employed for measuring all temperatures from the lowest to the highest; Pouillet described one by which the heat of an air-furnace could be measured. The reservoir of this instrument is of platinum, and it is connected with a piece of apparatus by which the increase of volume experienced by the included air is determined.

An excellent air-thermometer has been constructed and used by Rudberg, and more recently by Magnus and Regnault, for measuring the expansion of the air. Its construction depends on the law, that when air is heated and hindered from expanding, its tension increases in the same proportion in which it would have increased in volume if permitted to expand.

All bodies are enlarged by the application of heat, and reduced

by its abstraction, or, in other words, contract on being artificially cooled : this effect takes place to a comparatively small extent with solids, to a larger amount in liquids, and most of all in the case of gases.

Each solid and liquid has a rate of expansion peculiar to itself ; gases, on the contrary, expand nearly alike for the same increase of heat.

*Expansion of Solids.*—The actual amount of expansion which different solids undergo by the same increase of heat has been carefully investigated. The following are some of the results of the best investigations, more particularly those of Lavoisier and Laplace. The fraction indicates the amount of expansion in length suffered by rods of the undermentioned bodies in passing from  $0^{\circ}$  to  $100^{\circ}$  :—

Fir-wood*	$\frac{1}{2451}$	Tempered steel . . .	$\frac{1}{807}$
English flint glass . . .	$\frac{1}{1248}$	Soft iron . . . . .	$\frac{1}{819}$
Platinum . . . . .	$\frac{1}{1187}$	Gold . . . . .	$\frac{1}{882}$
Common white glass . . .	$\frac{1}{1160}$	Copper . . . . .	$\frac{1}{584}$
Common white glass . . .	$\frac{1}{1147}$	Brass . . . . .	$\frac{1}{353}$
Glass without lead . . .	$\frac{1}{1142}$	Silver . . . . .	$\frac{1}{324}$
Another specimen . . .	$\frac{1}{1090}$	Lead . . . . .	$\frac{1}{351}$
Steel untempered . . .	$\frac{1}{927}$	Zinc . . . . .	$\frac{1}{333}$

From the *linear* expansion, the *cubic* expansion (or measure of volume) may be calculated. When the expansion of a body in different directions is equal, as, for example, in glass, hammered metals, and generally in most uncrystallised substances, it will be sufficient as an approximation to triple the fraction expressing the increase in one dimension. This rule does not hold true for crystals belonging to irregular systems, for they expand unequally in the direction of the different axes.

Metals appear to expand pretty uniformly for equal increments of heat within the limits stated ; but above the boiling point of water the rate of expansion becomes irregular and more rapid.

The force exerted in the act of expansion is very great. In laying down railways, building iron bridges, erecting long ranges of steam-pipes, and in executing all works of the kind in which metal is largely used, it is indispensable to make provision for these changes of dimensions.

In consequence of glass and platinum having nearly the same amount of expansion, a thin platinum wire may be fused into a glass tube, without any fear that the glass will break on cooling.

A very useful application of expansion by heat, constantly practised in the laboratory for a great variety of purposes—is that of the cutting of glass by a hot iron. The glass to be cut is

---

\* In the direction of the vessels.

marked with ink in the required direction, and then a crack, commenced by any convenient method, at some distance from the desired line of fracture, may be led by the point of a heated iron rod along the latter with the greatest precision.

*Expansion of Liquids.*—The dilatation of a liquid may be determined by filling a thermometer with it, in which the relation between the capacity of the ball and that of the stem is exactly known, and observing the height of the column at different temperatures. It is necessary in these experiments to take into account the effects of the expansion of the glass itself, the observed result being evidently the *difference* of the two.

Liquids vary exceedingly in this particular. The following table is taken from Péclet's "*Éléments de Physique* :"—

*Apparent Dilatation in Glass between 0° and 100°.*

Water . . . . .		$\frac{1}{59}$
Hydrochloric acid, sp. gr. 1·137 . . . . .		$\frac{1}{27}$
Nitric acid, sp. gr. 1·4 . . . . .		$\frac{1}{9}$
Sulphuric acid, sp. gr. 1·85 . . . . .		$\frac{1}{17}$
Ether . . . . .		$\frac{1}{14}$
Olive oil . . . . .		$\frac{1}{12}$
Alcohol . . . . .		$\frac{1}{9}$
Mercury . . . . .		$\frac{1}{54}$

Most of these numbers must be taken as representing only mean results ; for there are but few liquids, which, like mercury, expand regularly between these temperatures. Even mercury above 100° shows an unequal and increasing expansion, if the temperature indicated by the air-thermometer be used for comparison. This is shown by the following abstract of a table given by Regnault :—

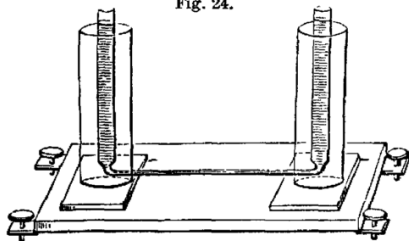
Reading of Air Thermometer.	Reading of Mercurial Thermometer	Temperature deduced from the Absolute Expansion of Mercury.
0°	0°	0°
100°	100°	100°
200°	200°	202·78°
300°	301°	308 34°
350°	354°	362·16°

The absolute amount of expansion of mercury is, for many reasons, a point of great importance ; it has been very carefully determined by a method independent of the expansion of the containing vessel. The apparatus employed for this purpose, first by Dulong and Petit, and later by Regnault, is shown in fig. 24, divested, however, of many of its subordinate parts. It consists of two upright glass tubes, connected at their bases by a horizontal tube of much smaller dimensions. Since a free communication exists between the two tubes, mercury poured into the one will rise to the same level in

the other, provided its temperature is the same in both tubes; when this is not the case, the hotter column will be the taller, because the expansion of the metal diminishes its specific gravity, and the law of hydrostatic equilibrium requires that the height of such columns should be inversely as their densities. By the aid of the outer cylinders, one of the tubes is maintained constantly at  $0^{\circ}$ , while the other is raised, by means of heated water or oil, to any required temperature. The perpendicular height of the columns may then be read off by a horizontal micrometer telescope, moving on a vertical divided scale.

These heights represent volumes of equal weight, because volumes of equal weight bear an inverse proportion to the densities of the liquids, so that the amount of expansion admits of being very easily calculated. Thus, let the column at  $0^{\circ}$  be 6 inches high, and that at  $100^{\circ}$ , 6.108 inches; the increase of height, 108 on 6000, or  $\frac{1}{55 \frac{1}{5}}$  part of the whole, will represent the absolute cubical expansion.

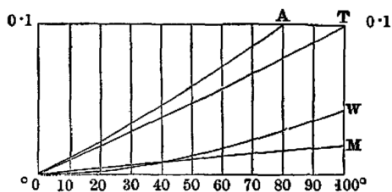
Fig. 24.



The indications of the mercurial thermometer are inaccurate when very high ranges of temperature are concerned, from the increased expansibility of the metal. The error thus caused is, however, nearly compensated, for temperatures under  $204.5^{\circ}$ , by the expansion of the glass tube. For higher temperatures a small correction is necessary, as the above table shows.

To what extent the expansion of different liquids may vary between the same temperatures is obvious from a glance at fig. 25, which represents the expansion of mercury (M), water (W),

Fig. 25.



oil of turpentine (T), and alcohol (A). A column of these several liquids, equalling at  $0^{\circ}$  the tenfold height of the line 0—0.1 in the diagram, would exhibit, when heated to a temperature of  $10^{\circ}$ ,  $20^{\circ}$ ,  $30^{\circ}$ , &c., an expansion indicated by the distances at which the perpendicular lines drawn over the numbers 10, 20, 30, &c., are intersected by the curves belonging to each of these liquids. Thus it is seen that oil of turpentine, between  $0^{\circ}$  and  $100^{\circ}$ , expands very nearly  $\frac{1}{10}$  of its volume, and that mercury between the same limits of temperature expands uniformly, while the rate of expansion of the other liquids increases with the rise of the temperature.

An exception to the regularity of expansion in liquid exists in the case of water; it is so remarkable, and its consequences so important, that it is necessary to advert to it particularly.

Let a large thermometer-tube be filled with water at the common temperature of the air, and then artificially cooled. The liquid will be observed to contract, until the temperature falls to about  $4^{\circ}$  C. ( $39.2^{\circ}$  F., or  $7.2^{\circ}$  above the freezing point.) After this a further reduction of temperature causes expansion instead of contraction in the volume of the water, and this expansion continues until the liquid arrives at its point of congelation, when so sudden and violent an enlargement takes place that the vessel is almost invariably broken. At the temperature of  $4^{\circ}$  water is at its maximum density; increase or diminution of heat produces upon it, for a short time, the same effect.

According to the latest researches of Kopp, the point of greatest density of water is  $4.08^{\circ}$  C. ( $39.34^{\circ}$  F.) According to the determinations of this physicist, the volume of water = 1 at  $0^{\circ}$  C. changes, when heated, to the following volumes :—

$2^{\circ}$ 0.99991	$16^{\circ}$ 1.00085	$35^{\circ}$ 1.00570	$70^{\circ}$ 1.02225
$4^{\circ}$ 0.99988	$18^{\circ}$ 1.00118	$40^{\circ}$ 1.00753	$75^{\circ}$ 1.02544
$6^{\circ}$ 0.99990	$20^{\circ}$ 1.00157	$45^{\circ}$ 1.00954	$80^{\circ}$ 1.02858
$8^{\circ}$ 0.99999	$22^{\circ}$ 1.00200	$50^{\circ}$ 1.01177	$85^{\circ}$ 1.03189
$10^{\circ}$ 1.00012	$24^{\circ}$ 1.00247	$55^{\circ}$ 1.01410	$90^{\circ}$ 1.03540
$12^{\circ}$ 1.00031	$25^{\circ}$ 1.00272	$60^{\circ}$ 0.01659	$95^{\circ}$ 1.03909
$14^{\circ}$ 1.00056	$30^{\circ}$ 1.00406	$65^{\circ}$ 1.01930	$100^{\circ}$ 1.04299

Sea-water has no point of maximum density above the freezing point. The more it is cooled, the denser it becomes, until it solidifies at  $-2.6^{\circ}$ .

The gradual expansion of pure water cooled below  $4^{\circ}$  must be carefully distinguished from the great and sudden increase of volume it exhibits in the act of freezing, in which respect it resembles many other bodies which expand on solidifying. The force thus exerted by freezing water is enormous. Thick iron shells, quite filled with water, and exposed with their fuse-holes securely plugged, to the cold of a Canadian winter night, have been found split on the following morning. The freezing of water in the joints and crevices of rocks is a most potent agent in their disintegration.



*Expansion of Gases.*—The principal laws relating to the expansion of gases are contained in the four following propositions:—

1. All gases expand nearly alike for equal increments of heat; and all vapours, when remote from their condensing points, follow the same law.
2. The rate of expansion is not altered by a change in the state of compression, or elastic force, of the gas itself.
3. The rate of expansion is uniform for all degrees of heat.
4. The actual amount of expansion is equal to  $\frac{1}{273}$  or  $\frac{11}{3000}$  or 0·003666 of the volume of the gas at 0° centigrade, for each degree of the same scale.\*

It will not be necessary to enter into any description of the methods of investigation by which these results have been obtained; the advanced student will find in Pouillet's "*Éléments de Physique*," and in the papers of Magnus and Regnault,† all the information he may require.

In the practical manipulation of gases, it very often becomes necessary to make a correction for temperature, or to discover how much the volume of a gas would be increased or diminished by a particular change of temperature; this can be effected with great facility. Let it be required, for example, to find the volume which 100 cubic inches of any gas at 10° would assume on the temperature rising to 20°.

The rate of expansion is  $\frac{1}{273}$  or  $\frac{11}{3000}$  of the volume at 0° for each degree; or 3000 measures at 0° become 3011 at 1°, 3022 at 2°, 3110 at 10°, and 3220 at 20°. Hence

$$\begin{array}{ccccccc} \text{Meas. at } 10^{\circ}. & & \text{Meas. at } 20^{\circ}. & & \text{Meas. at } 10^{\circ}. & & \text{Meas. at } 20^{\circ}. \\ 3110 & : & 3220 & = & 100 & : & 103\cdot537 \end{array}$$

If this calculation is required to be made on the Fahrenheit scale, it must be remembered that the zero of that scale is 32° below the melting-point of ice. Above this temperature the expansion for each degree of the Fahrenheit scale is  $\frac{1}{460}$  of the original volume.

This, and the correction for pressure, are operations of very frequent occurrence in chemical investigations, and the student will do well to become familiar with them.

The following formula includes both these corrections:—Let  $V$  and  $V'$  be the volume of a gas at the temperatures  $t$  and  $t'$  centigrade, and under the pressures  $p$  and  $p'$ , measured in millimeters of mercury: then

$$\frac{V}{V'} = \frac{1 + 0\cdot003666t}{1 + 0\cdot003666t'} \cdot \frac{p'}{p}$$

\* The fraction  $\frac{11}{3000}$  is very convenient for calculation.

† Poggendorff's *Annalen*, iv. 1—Ann. Chim. Phys. 3d series, iv. 5, and v. 52. See also Watts's *Dictionary of Chemistry*, art. Heat, vol. iii. p. 46; and Ganot's *Éléments de Physique*, translated by Dr. Atkinson, 4th edition, pp. 253—262.

The case which most frequently occurs is the reduction of a measured volume,  $V$ , of a gas at the temperature  $t$  and pressure  $p$  to the volume  $V_0$ , which it would occupy at  $0^\circ \text{C.}$ , and under a pressure of 760 mm. In this case, we have  $t' = 0$ , and  $p' = 760$ , therefore

$$\frac{V}{V_0} = (1 + 0.003666t) \cdot \frac{760}{p},$$

and

$$V_0 = \frac{V}{1 + 0.003666t} \cdot \frac{p}{760}.$$

If the barometric pressure is measured in inches, the number 30 must be substituted for 760.

*Note.*—Of the four propositions stated in the text, the first and second have recently been shown to be true within certain limits only; and the third, although in the highest degree probable, would be very difficult to demonstrate rigidly; in fact, the equal rate of expansion of air is assumed in all experiments on other substances, and becomes the standard by which the results are measured.

The rate of expansion for the different gases is *not* absolutely the same, but the difference is so small that for most purposes it may safely be neglected. Neither is the state of elasticity altogether indifferent, the expansion being sensibly *greater* for an equal rise of temperature when the gas is in a compressed state.

It is important to notice that the greatest deviations from the rule are exhibited by those gases which, as will hereafter be seen, are most easily liquefied, such as carbon dioxide, cyanogen, and sulphur dioxide; and that the discrepancies become smaller and smaller as the elastic force is lessened; so that, if means existed for comparing the different gases in states *equally distant* from their points of condensation, there is reason to believe that the law would be strictly fulfilled.

The experiments of Dalton and Gay-Lussac gave for the rate of expansion  $\frac{1}{267}$  of the volume at  $0^\circ$ : this is, no doubt, too high. Those of Rudberg give  $\frac{1}{274}$ , those of Magnus and of Regnault  $\frac{1}{273}$ .

### Conduction of Heat.

Different bodies possess very different conducting powers with respect to heat: if two similar rods, the one of iron, the other of glass, be held in the flame of a spirit-lamp, the iron will soon become too hot to be touched, while the glass may be grasped with impunity within an inch of the red-hot portion.

Experiments made by analogous but more accurate methods have established a numerical comparison of the conducting powers of many bodies. The following may be taken as a specimen:—

Silver . . .	1000	Steel . . .	116
Copper . . .	736	Lead . . .	85
Gold . . .	532	Platinum . . .	84
Brass . . .	236	German silver . . .	63
Tin . . .	145	Bismuth . . .	18
Iron . . .	119		

As a class the metals are by very far the best conductors, although much difference exists between them; stones, dense woods, and charcoal follow next in order; then liquids in general, and lastly gases, whose conducting power is almost inappreciable.

Under favourable circumstances, nevertheless, both liquids and gases may become rapidly heated; heat applied to the bottom of the containing vessel is very speedily communicated to its contents; this, however, is not so much by conduction, as by convection, or carrying. A complete circulation is set up; the portions in contact with the bottom of the vessel get heated, become lighter, and rise to the surface, and in this way the heat becomes communicated to the whole. If these movements be prevented by dividing the vessel into a great number of compartments, the really low conducting power of the substance is made evident; and this is the reason why certain organic fabrics, as wool, silk, feathers, and porous bodies in general, the cavities of which are full of air, exhibit such feeble powers of conduction.

The circulation of heated water through pipes is now extensively applied to the warming of buildings and conservatories; and in chemical works a serpentine metal tube containing hot oil is often used for heating stills and evaporating pans; the two extremities of the tube are connected with the ends of another spiral built into a small furnace at a lower level, and an unintermitting circulation of the liquid takes place as long as heat is applied.

### Specific Heat.

Equal weights of different substances having the same temperature require different amounts of heat to raise them to a given degree of temperature. If 1 lb. of water, at 100°, be mixed with 1 lb. at 40°, then, as is well known, a mean temperature of  $\frac{100 + 40}{2} = 70^\circ$  is obtained. In the same way the mean temperature is found when warm and cold oil, or warm and cold mercury, &c., are mixed together. But if 1 lb. of water at 100° be shaken with 1 lb. of olive oil at 40°, or with 1 lb. of mercury at 40°, then, instead of the mean temperature of 70°, the temperature actually obtained will be 80° in the first case, 98° in the second; 20 degrees of heat, which the water (by cooling from 100° to 80°) gave to the same weight of oil, were sufficient to raise the oil 40°, that is, from 40° to 80°; and 2°, which the water lost by cooling from 100° to 98°, sufficed to heat an equal quantity of mercury 58°, namely from 40° to 98°.

It is evident from these experiments that the quantities of heat which equal weights of water, olive oil, and mercury, require to raise their temperature to the same height, are unequal, and that they are in the proportion of the numbers  $1 : \frac{20}{40} : \frac{2}{58}$ , or  $1 : \frac{1}{2} : \frac{1}{29}$ .

These quantities of heat, expressed relatively to the quantity of heat required to raise the temperature of an equal weight of water from  $0^{\circ}$  to  $1^{\circ}$  C., are called the specific heats of the various substances: thus the experiments just described show that the specific heat of olive oil is  $\frac{1}{2}$ , that is to say, the quantity of heat which would raise the temperature of any given quantity of olive oil from  $0^{\circ}$  to  $1^{\circ}$  would raise that of an equal weight of water only from  $0^{\circ}$  to  $\frac{1}{2}^{\circ}$ , or of half that quantity of water from  $0^{\circ}$  to  $1^{\circ}$ .

The specific heats of bodies are sometimes said to measure their relative capacities for heat.

There are three distinct methods by which the specific heats of various substances may be estimated. The first of these is by observing the quantity of ice melted by a given weight of the substance heated to a particular temperature; the second is by noting the time which the heated body requires to cool down through a certain number of degrees; and the third is the method of mixture, on the principle illustrated; this last method is preferred as the most accurate.

The determination of the specific heat of different substances has occupied the attention of many experimenters; among these Dulong and Petit, and recently Regnault and Kopp, deserve especial mention.

From the observations of these and other physicists, it follows that each body has its peculiar specific heat, and that the specific heat increases with increase of temperature. If, for example, the heat which the unit of water loses by cooling from  $10^{\circ}$  to  $0^{\circ}$  be marked at  $10^{\circ}$ , then the loss by cooling from  $50^{\circ}$  to  $0^{\circ}$  will be, not 50, corresponding to the difference of temperature, but  $50 \cdot 1$ . By cooling from  $100^{\circ}$  to  $0^{\circ}$  it is  $100 \cdot 5$ , and rises to  $203 \cdot 2$  when the water is heated under great pressure to  $200^{\circ}$ , and afterwards cooled to  $0^{\circ}$ . Similar and even more striking differences have been found with other substances. It has also been proved that the specific heat of any substance is greater in the liquid than in the solid state. For example, the specific heat of ice is  $0 \cdot 504$ , that is, not more than half as great as that of liquid water.

It is remarkable that the specific heat of water is greater than that of all other solid and liquid substances, and is exceeded only by that of hydrogen. The specific heat of the solid parts of the crust of the globe is on an average  $\frac{1}{2}$ , and that of the atmosphere nearly  $\frac{1}{4}$  that of water.

If the specific heat of any body within certain degrees of temperature be accurately known, then from the quantity of heat which this body gives out when quickly dipped into cold water, the temperature to which the body was heated may be determined. Pouillet founded on this fact a method of measuring high temperatures,

and for this purpose, with the help of the air-thermometer, he determined the specific heat of platinum up to  $1600^{\circ}$ .

The determination of the specific heat of gases is attended with peculiar difficulties, on account of the comparatively large volume of small weights of gases. For many gases, however, satisfactory results have been obtained by the method of mixing.

When a gas expands, heat becomes latent, that is to say, insensible to the thermometer; in fact, the molecular motion which constitutes heat is converted into another kind of motion which overcomes the pressure to which the gas is subjected, and allows it to expand (see page 78). The amount of heat required, therefore, to raise a gas to any given temperature increases the more the gas in question is allowed to expand. The quantity of heat which the unit-weight of a gas requires in order to raise its temperature  $1^{\circ}$  without its volume undergoing any change (which can take place only by the pressure being simultaneously augmented) is called the specific heat of the gas *at constant volume*. The quantity of heat required by the unit-weight of a gas to raise its temperature  $1^{\circ}$ , it being at the same time allowed to dilate to such an extent that the pressure to which it is exposed remains unchanged, is called the specific heat of the gas *at constant pressure*. According to what has already been stated, the specific heat at constant pressure must be greater than that at constant volume. Dulong found, in the case of atmospheric air, of oxygen, of hydrogen, and of nitrogen, that the two specific heats are in the proportion  $1.421 : 1$ . For carbon monoxide, however, he obtained the proportion of  $1.423$ , for carbon dioxide  $1.337$ , for nitrogen dioxide  $1.343$ , and for olefiant gas  $1.24$  to  $1$ . The exact determination of these ratios is extremely difficult, and the results of different physicists by no means agree.

The first satisfactory comparison of the specific heat of air with that of water was made by Count Rumford; later comparisons of the specific heat of various gases have been made by Delaroche and Bérard, Dulong and Regnault.

The first researches of Delaroche and Bérard furnished the results embodied in the following table:—

	Equal volumes.		Equal weights.	
	The volumes constant.	The pressure constant.	Air = 1.	Water = 1.
Atmospheric air . . . .	1	1	1	0.2669
Oxygen . . . . .	1	1	0.9045	0.2414
Hydrogen . . . . .	1	1	14.4510	3.8569
Nitrogen . . . . .	1	1	1.0295	0.2748
Carbon monoxide . . . .	1	1	1.0337	0.2759
Nitrogen monoxide . . .	1.227	1.160	0.7607	0.2030
Carbon dioxide . . . .	1.249	1.175	0.7685	0.2051
Olefiant gas . . . . .	1.754	1.531	1.5829	0.4225

The latest and most trustworthy determinations are those of Regnault, given in the subjoined table, in the second column of

which the specific heats of the several gases and vapours are compared with that of an equal weight of water taken as unity, and in the third, with that of an equal volume of air referred to its own weight of water as unity. The latter series of numbers is obtained by multiplying the numbers in the second column by the specific gravities of the respective gases and vapours referred to air as unity :—

Gases.	Specific Gravity. Air = 1.	Specific Heat at Constant Pressure.	
		For equal weights. Water = 1.	For equal volumes.
Atmospheric air . . . . .	1	0.2377	0.2377
Oxygen . . . . .	1.1056	0.2175	0.2405
Nitrogen . . . . .	0.9713	0.2438	0.2368
Hydrogen . . . . .	0.0692	3.4090	0.2359
Chlorine . . . . .	2.4502	0.1210	0.2965
Bromine vapour . . . . .	5.4772	0.0555	0.3040
Carbon monoxide . . . . .	0.9670	0.2450	0.2370
Carbon dioxide . . . . .	1.5210	0.2169	0.3307
Nitrogen monoxide . . . . .	1.5241	0.2262	0.3447
Nitrogen dioxide . . . . .	1.0384	0.2317	0.2406
Olefiant gas . . . . .	0.9672	0.4040	0.4106
Marsh gas . . . . .	0.5527	0.5929	0.3277
Aqueous vapour . . . . .	0.6220	0.4805	0.2989
Sulphuretted hydrogen . . . . .	1.1746	0.2432	0.2857
Sulphur dioxide . . . . .	2.2112	0.1544	0.3414
Vapour of carbon bisulphide . . . . .	2.6258	0.1569	0.4122
Hydrochloric acid . . . . .	1.2596	0.1852	0.2333
Ammonia . . . . .	0.5894	0.5084	0.2996

The researches of Delaroche and Bérard led them to suppose that the specific heat of gases increased rapidly as the temperature was raised, and that for a given volume of gas it increased in proportion to the density or tension of the gas. Regnault found, however, the quantity of heat which a given volume of gas requires to raise it to a certain temperature, to be independent of its density ; and that for each degree between  $-30^{\circ}$  and  $225^{\circ}$  it is constant. Carbon dioxide, however, forms an exception to this rule, its specific heat increasing with the temperature. In the table mean values for temperatures between  $10^{\circ}$  and  $200^{\circ}$  have been given.

Several physicists have held that the specific heats of elementary gases, referred to equal volumes, are identical. The numbers which Regnault found for chlorine and bromine, however, show that the law does not hold good for all elementary gases.

It has been already stated that, when a gas expands, heat becomes latent. If a gas on expanding be not supplied with the requisite heat, its temperature will fall, on account of its own free heat becoming latent, that is to say, expended in overcoming pressure. On the other hand, if a gas be compressed, this latent heat becomes free,

and causes an elevation of temperature, which, under favourable circumstances, may be raised to ignition; syringes by which tinder is kindled are constructed on this principle.

### Change of State.

#### 1. *Fusion and Solidification.*

Solid bodies expand when heated; and many are liquefied, *i.e.*, they melt or fuse. The melting of solids is frequently preceded by a gradual softening, more especially when the temperature approaches the point of fusion. This phenomenon is observed in the case of wax or iron. In the case of other solids—of zinc and lead, for instance—and several other metals, this softening is not observed. Generally, bodies expand during the process of fusion; an exception to this rule is water, which expands during freezing (10 vol. of water produce nearly 11 vol. of ice), while ice when melting produces a proportionately smaller volume of water. The expansion of bodies during fusion, and at temperatures preceding fusion, or the contraction during solidification and further refrigeration, is very unequal. Wax expands considerably before fusing, and comparatively little during fusion itself. Wax, when poured into moulds, fills them perfectly during solidification, but afterwards contracts considerably. Stearic acid, on the contrary, expands very little before fusion, but rather considerably during fusion, and consequently pure stearic acid when poured into moulds solidifies to a rough porous mass, contracting little by further cooling. The addition of a little wax to stearic acid prevents the powerful contraction in the moment of solidification, and renders it more fit for being moulded.

The melting and solidifying point of each particular substance is constant under any given pressure, but those of different substances vary within very wide limits: thus sulphurous oxide ( $\text{SO}_2$ ) melts at  $-80^\circ$ , mercury at  $-40^\circ$ , bromine at  $-7.3^\circ$ , ice at  $0^\circ$ , phosphorus at  $+44^\circ$ , tin at  $235^\circ$ , silver at  $1000^\circ$ , platinum at  $2000^\circ$ .

The ordinary variations of atmospheric pressure have no perceptible influence on the melting points of bodies, but greater variations produce very appreciable effects: thus at pressures of 8.1 and 16.8 atmospheres, the melting point of ice is lowered by  $0.059^\circ$  and  $0.126^\circ$  respectively. Some bodies, on the other hand, have their melting points raised by pressure, as shown in the following table:—

Pressure in Atm	Melting Points.			
	Spermaceti.	Wax.	Sulphur.	Stearin.
1	51.1°	64.7°	107.2°	67.2
520	60.0	74.7	135.2	68.3
793	80.2	80.2	140.5	73.8

In general, those substances which expand on liquefying have their melting points raised by pressure; whereas those which, like water, contract on liquefying, have their melting points lowered by increased pressure.

Conversely, it has been shown by Dr. Carnelley\*, that ice, mercuric chloride, and certain other bodies, when subjected to pressures below a certain limit, called the "critical pressure," cannot be liquefied, however great may be the heat applied to them. Bodies under these conditions do not, however, appear to attain temperatures above their ordinary melting points, the whole of the heat applied to them being apparently absorbed as latent heat in the direct conversion of the solid body into vapour.

*Determination of Melting Points.*—The following is a convenient method for determining the melting points of bodies which fuse at moderate temperatures, such as commonly occur in the course of chemical investigations. Three or four glass tubes are drawn out until their sides become very thin and their bore nearly capillary, and into each is introduced a small quantity of the substance under investigation. They are then sealed at the bottom and placed in a glass vessel containing water (or paraffin or sulphuric acid if the substance melts above 100°), and standing in a small sand-bath by which the temperature can be slowly raised. The liquid is heated till the substance melts, then allowed to cool slowly to the solidifying point, and again warmed, these observations being repeated, and the temperatures of liquefaction and solidification being each time noted, until several nearly concordant results have been obtained. The mean of all these is taken as the true melting point of the substance.

For determining the melting points of bodies which melt at higher temperatures, such as metallic salts, a method has lately been given by Dr. Carnelley, depending on the following principle: When a small quantity of a salt is placed in a weighed platinum crucible suspended in the flame of a Bunsen burner or a blowpipe, and the crucible, at the instant when the salt fuses, is dropped into

\* Proceedings of the Royal Society, vol. xxxi. p. 284; Chem. Soc. Journal, xlii. 317.



a known weight of water of known temperature, the rise in temperature of the water being then noted, the temperature at which the fusion occurred may be found from the equation—

$$T = \theta + \frac{(W + w) r (\theta - t)}{Ms},$$

in which  $W$  denotes the weight of water in the calorimeter;  $w$  the thermal value of the calorimeter + mercury and glass of thermometer in grams of water;  $M$  the weight of the crucible;  $r$  the specific heat of water;  $s$  the specific heat of platinum (from  $0^\circ$  to  $T$ );  $t$  the initial, and  $\theta$  the final temperature of the water. Solidifying points may be determined in a similar manner, but with this difference, that when the salt has completely melted, the lamp is turned out, and the crucible dropped into the calorimeter at the instant when the salt begins to solidify.

The following table exhibits the melting and solidifying points of several salts determined in this manner;—

	M P.	S. P.	Difference.
Potassium nitrate . . .	353°	332°	21
„ chlorate . . .	372	351	21
„ chloride . . .	434	415	19
„ iodide . . .	639	622	17
„ bromide . . .	703	685	18
„ carbonate . . .	838	832	6

*Latent Heat of Fusion.*—During fusion bodies absorb a certain quantity of heat which is not indicated by the thermometer.

If equal weights of water at  $0^\circ$  and water at  $79^\circ$  be mixed, the temperature of the mixture will be the mean of the two temperatures, viz.,  $39.5^\circ$ ; but if the same experiment be made with snow or finely powdered ice at  $0^\circ$  and water at  $79^\circ$ , the temperature of the mixture will be only  $0^\circ$ , *but the ice will have been melted.*

$$\begin{aligned} & \left. \begin{array}{l} 1 \text{ lb. of water at } 0^\circ \\ 1 \text{ lb. of water at } 79^\circ \end{array} \right\} = 2 \text{ lb. water at } 39.5^\circ. \\ & \left. \begin{array}{l} 1 \text{ lb. of ice at } 0^\circ \\ 1 \text{ lb. of water at } 79^\circ \end{array} \right\} = 2 \text{ lb. water at } 0^\circ. \end{aligned}$$

In the last experiment therefore, as much heat has been apparently lost as would have raised a quantity of water equal to that of the ice through a range of 79 degrees.

The heat, thus become insensible to the thermometer in effecting the liquefaction of the ice, is called latent heat, or better, heat of fluidity.

Again, let a perfectly uniform source of heat be imagined, of such intensity that a pound of water placed over it would have its temperature raised  $5^\circ$  per minute. Starting with water at  $0^\circ$ , in rather less than 16 minutes its temperature would have risen  $79^\circ$ ; but the same quantity of ice at  $0^\circ$ , exposed for the same interval of time,

would not have its temperature raised a single degree. But, then, it would have become water, the heat received being exclusively employed in effecting the change of state.

This heat is not lost, for when the water freezes it is again evolved. If a tall jar of water, covered to exclude dust, be placed in a situation where it shall be quite undisturbed, and at the same time exposed to great cold, the temperature of the water may be reduced  $5^{\circ}$  or more below its freezing point without the formation of ice; \* but, if a little agitation be then communicated to the jar, or a grain of sand dropped into the water, a portion instantly solidifies, and the temperature of the whole rises to  $0^{\circ}$ ; the heat disengaged by the freezing of a small portion of the water is sufficient to raise the whole contents of the jar  $5^{\circ}$ .

This condition of instable equilibrium shown by the very cold water in the preceding experiment, may be reproduced with a variety of solutions which tend to crystallise or solidify, but in which that change is for a while suspended. Thus, a solution of crystallised sodium sulphate in its own weight of warm water, left to cool in an open vessel, deposits a large quantity of the salts in crystals. If, however, the warm solution be filtered into a clean flask, which when full is securely corked and set aside to cool undisturbed, no crystals will be deposited even after many days, until the cork is drawn and the contents of the flask are agitated. Crystallisation then rapidly takes place in a very beautiful manner, and the whole becomes perceptibly warm.

The law above illustrated in the case of water is perfectly general. Whenever a solid becomes a liquid, a certain fixed and definite amount of heat disappears, or becomes latent; and conversely, whenever a liquid becomes solid, heat to a corresponding extent is given out.

The following table exhibits the melting points of several substances, and their latent heats of fusion expressed in gram-degrees—that is to say, the numbers in the column headed “latent heat” denote the number of grams of water, the temperature of which would be raised  $1^{\circ}$  centigrade by the quantity of heat required to fuse one gram of the several solids :—

\* Fused bodies, when cooled down to or below their fusing point, frequently remain liquid, more especially when not in contact with solid bodies. Thus, water in a mixture of oil of almonds and chloroform, of specific gravity equal to its own, remains liquid to  $-10^{\circ}$ ; in a similar manner fused sulphur or phosphorus, floating in a solution of zinc chloride of appropriate concentration, retains the liquid condition at temperatures  $40^{\circ}$  below its fusing point. Liquid bodies, thus cooled below their fusing point, frequently solidify when touched with a solid substance, invariably when brought in contact with a fragment of the same body in the solid state. A body thus retained in the liquid state above its ordinary solidifying point, is said to be in a state of *surfusion* or *superfusion*.

Substance.	Melting Point.	Latent Heat.	Substance.	Melting Point.	Latent Heat.
Mercury . . .	-39°	2·82	Tin . . .	235°	14·25
Phosphorus . . .	+44	5·0	Silver . . .	1000	21·1
Lead . . .	332	5·4	Zinc . . .	433	28·1
Sulphur . . .	115	9·4	Calcium chloride } (CaCl <sub>2</sub> ,6H <sub>2</sub> O) }	28·5	40·7
Iodine . . .	107	11·7	Potassium nitrate.	339	47·4
Bismuth . . .	270	12·6	Sodium nitrate .	310·5	63·0
Cadmium . . .	320	13·6			

*Freezing Mixtures.*—When a solid substance can be made to liquefy by a weak chemical attraction, cold results, from sensible heat becoming latent. This is the principle of frigorific mixtures. When snow or powdered ice is mixed with common salt, and a thermometer plunged into the mass, the mercury sinks to 0° F. (-17·7° C.), while the whole after a short time becomes fluid; such a mixture is very often used in chemical experiments to cool receivers and condense the vapours of volatile liquids. Powdered crystallised calcium chloride and snow produce cold enough to freeze mercury. Even powdered potassium nitrate, or sal-ammoniac, or ammonium nitrate, dissolved in water, occasions a very notable depression of temperature; in every case, in short, in which solution is unaccompanied by energetic chemical action, cold is produced.

No relation can be traced between the actual melting point of a substance and its latent heat when in the fused state.

## 2. Vaporisation and Condensation.

A law of exactly the same kind as that above described affects universally the gaseous condition; change of state from solid or liquid to gas is accompanied by absorption of sensible heat, and the reverse by its disengagement. The latent heat of steam and other vapours may be ascertained by a mode of investigation similar to that employed in the case of water.

When water at 0° is mixed with an equal weight of water at 100°, the whole is found to have the mean of the two temperatures, or 50°; on the other hand, 1 part by weight of steam at 100°, when condensed in cold water, is found to be capable of raising 5·4 parts of the latter from the freezing to the boiling point, or through a range of 100°. Now  $100 \times 5·4 = 540°$ ; that is to say, steam at 100°, in becoming water at 100°, parts with enough heat to raise a weight of water equal to its own (if it were possible) 540° of the thermometer, or 540 times its own weight of water one degree. When water passes into steam the same quantity of sensible heat becomes latent.

The vapours of other liquids seem to have less latent heat than that of water. The following table, drawn up by Dr. Andrews of Belfast, serves well to illustrate this point. The latent heats are expressed, as in the last table, in gram-degrees :—

						Latent Heat.
Vapour of water	.	.	.	.	.	535·90°
„ alcohol	.	.	.	.	.	202·40
„ ether	.	.	.	.	.	90·45
„ ethyl oxalate	.	.	.	.	.	72·72
„ „ acetate	.	.	.	.	.	92·68
„ „ iodide	.	.	.	.	.	46·87
„ methyl alcohol	.	.	.	.	.	263·70
„ carbon bisulphide	.	.	.	.	.	86·67
„ tin tetrachloride	.	.	.	.	.	30·35
„ bromine	.	.	.	.	.	45·66
„ oil of turpentine	.	.	.	.	.	74·03

Boiling or Ebullition is occasioned by the formation of bubbles of vapour within the body of the evaporating liquid, which rise to the surface like bubbles of permanent gas. This occurs in different liquids at very different temperatures. Under the same circumstances, the boiling point is quite constant, and often becomes a physical character of great importance in distinguishing liquids which much resemble each other. A few cases may be cited in illustration :—

Substance.	Boiling Point.
Aldehyde . . . . .	22°
Ether . . . . .	35·6
Carbon bisulphide . . . . .	46·1
Alcohol . . . . .	78·4
Water . . . . .	100
Nitric acid (sp. gr. 1·414 at 15·5°) . . . . .	120·5
Oil of turpentine . . . . .	157
Sulphuric acid . . . . .	338
Mercury . . . . .	357

For ebullition to take place, it is necessary that the elasticity of the vapour should be able to overcome the cohesion of the liquid and the pressure upon its surface ; hence the extent to which the boiling point may be modified.

Water, under the usual pressure of the atmosphere, boils at 100° C. (212° F.); in a partially exhausted receiver or on a mountain-top it boils at a much lower temperature ; and in the best vacuum of an air-pump, over oil of vitriol, which absorbs the vapour, it will often enter into violent ebullition while ice is in the act of forming upon the surface.

On the other hand, water confined in a very strong metallic vessel may be restrained from boiling by the pressure of its own vapour to an almost unlimited extent ; a temperature of 177° or 204°

is very easily obtained, and, in fact, it is said that water may be made red-hot, and yet retain its liquidity.

The effect of diminished pressure in lowering the boiling point of a liquid may be illustrated by a very simple and beautiful experiment. A little water is made to boil for a few minutes in a flask or retort placed over a lamp, until the air has been chased out, and the steam issues freely from the neck. A tightly fitting cork is then inserted, and the lamp at the same moment withdrawn. When the boiling ceases, it may be renewed at pleasure for a considerable time by pouring cold water on the flask, so as to condense the vapour within, and occasion a partial vacuum.

The nature of the vessel, or, rather, the state of its surface, exercises an influence upon the boiling point, and this to a much greater extent than was formerly supposed. It has long been noticed that in a metallic vessel water boils, under the same circumstances of pressure, at a temperature one or two degrees below that at which ebullition takes place in glass; but by particular management a much greater difference can be observed. If two similar glass flasks be taken, the one coated in the inside with a film of shellac, and the other completely cleansed by hot sulphuric acid, water heated over a lamp in the first will boil at  $99.4^{\circ}$ , while in the second it will often rise to  $105^{\circ}$  or even higher; a momentary burst of vapour then ensues, and the thermometer sinks a few degrees, after which it rises again. In this state, the introduction of a few metallic filings, or angular fragments of any kind, occasions a lively disengagement of vapour, while the temperature sinks to  $100^{\circ}$ , and there remains stationary.

When out of contact with solid bodies, liquids not only solidify with reluctance, but also assume the gaseous condition with greater difficulty. Drops of water or of aqueous saline solutions floating on the contact-surface of two liquids, of which one is heavier and the other lighter, may be heated from 10 to 20 degrees above the ordinary boiling point; explosive ebullition, however, is instantaneously induced by contact with a solid substance.

A cubic inch of water in becoming steam under the ordinary pressure of the atmosphere expands into 1696 cubic inches, or nearly a cubic foot.

Steam, *not in contact with water*, is affected by heat in the same manner as the permanent gases; its rate of expansion and increase of elastic force are practically the same. When water is present, the rise of temperature increases the quantity and density of the steam, and hence the elastic force increases in a far more rapid proportion.

This elastic force of steam in contact with water, at different temperatures, has been very carefully determined by Arago and Dulong, and lately by Magnus and Regnault. The force is expressed in atmospheres; the absolute pressure upon any given surface can be easily calculated, allowing 14.6 lb. per square inch to each atmosphere. The experiments were carried to twenty-five

atmospheres—at which point the difficulties and danger became so great as to put a stop to the inquiry; the rest of the table is the result of calculations founded on the data so obtained :—

Pressure of Steam in Atmospheres.	Corresponding Temperature.	Pressure of Steam in Atmospheres	Corresponding Temperature.
1	100°	13	194°
1·5	112	14	197
2	122	15	200·5
2·5	129	16	203
3	135	17	207
3·5	140·5	18	209
4	145·5	19	212
4·5	149	20	214
5	153	21	217
5·5	157	22	219
6	160	23	222
6·5	163	24	224
7	167	25	226
7·5	169	30	236
8	172	35	245
9	177	40	253
10	182	45	255
11	186	50	266
12	190		

It is very interesting to know the amount of heat requisite to convert water of any given temperature into steam of the same or another given temperature. The most exact experiments on this subject are due to Regnault. He arrived at this result, that when the unit-weight of steam at the temperature  $t^\circ$  is converted into water of the same temperature, and then cooled to  $0^\circ$ , it gives out a quantity of heat  $T$ , represented by the formula :—

$$T = 606\cdot5 + 0\cdot305t.$$

This formula appears to hold good for temperatures both above and below the ordinary boiling point of water. The following table gives the values of  $T$ , corresponding to the respective temperatures in the first column :—

$t$ .	$T$ .
$0^\circ$	606·5°
50	621·7
100	637·0
150	652·2
200	667·5

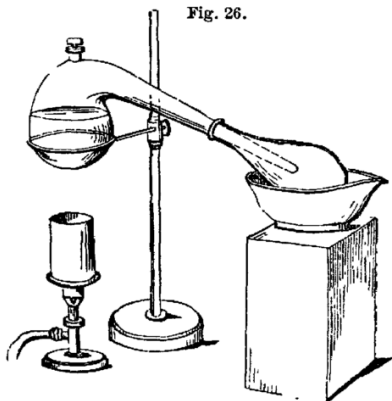
$T$  is called the total heat of steam, being the heat required to raise water from  $0^\circ$  to  $t^\circ$ , together with that which becomes latent by the transformation of water at  $t^\circ$  into steam at  $t^\circ$ . Regnault states, as a result of some very delicate experiments, that the heat neces-

sary to raise a unit-weight of water from  $0^{\circ}$  to  $t^{\circ}$  is not exactly denoted by  $t$ ; the discrepancy, however, is so small that it may be disregarded. Employing the approximate value, the latent heat of steam,  $L$ , at any temperature will be found by subtracting  $t$  from the total heat; or, according to the formula:—

$$L = 606.5 - 0.695t.$$

This equation shows us the remarkable fact that the latent heat of steam diminishes as the temperatures rises. Before Regnault's experiments were made, two laws of great simplicity were generally admitted, one of which, however, contradicted the other. Watt concluded, from experiments of his own, as well as from theoretical speculations, that the total heat of steam would be the same at all temperatures. Were this true, equal weights of steam passed into cold water would always exhibit the same heating power, no matter what the temperature of the steam might be. Exactly the same *absolute* amount of heat, and consequently the same quantity of fuel, would be required to evaporate a given weight of water *in vacuo* at a temperature which the hand can bear, or under great pressure and at high temperature. Watt's law, though agreeing well with the rough practical results obtained by engineers, is only approximately true; and the same may be said of the deductions which have just been made from it. The second law, in opposition to Watt's is that of Southern, stating the latent heat of steam to be

Fig. 26.



the same at all temperatures. Regnault's researches have shown that neither Watt's law ( $T$  constant) nor Southern's law ( $L$  constant) is correct.

*Distillation.*—The process of distillation is very simple: its object is either to separate substances which rise in vapour at different

temperatures, or to part a volatile liquid from a substance incapable of volatilisation. The same process applied to bodies which pass directly from the solid to the gaseous condition, and the reverse, is called *sublimation*. Every distillatory apparatus consists essentially of a boiler, in which the vapour is raised, and of a condenser, in which it returns to the liquid or solid condition. In the still employed for manufacturing purposes, the latter is usually a spiral metal tube immersed in a tub of water. The common retort and receiver constitute the simplest arrangement for distillation on the small scale; the retort is heated by a gas lamp, and the receiver is kept cool, if necessary, by a wet cloth, or it may be surrounded with ice (fig. 26).

Liebig's condenser (fig. 27) is a very valuable instrument in the laboratory; it consists of a glass tube tapering from end to end, fixed by perforated corks in the centre of a metal pipe, provided with tubes so arranged that a current of cold water may circulate through the apparatus. By putting ice into the little cistern, the water may be kept at  $0^{\circ}$ , and extremely volatile liquids condensed.

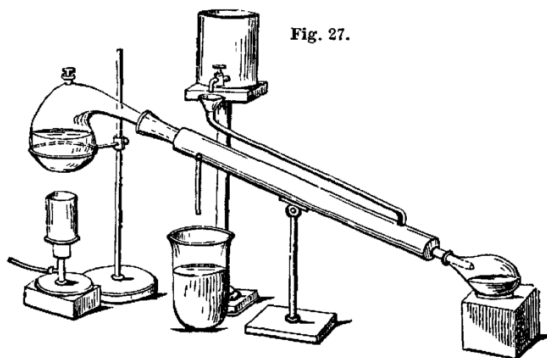


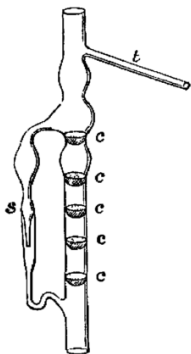
Fig. 27.

*Fractional Distillation.*—When a mixture of two liquids of different boiling points is distilled, the two always pass over together, the more volatile predominating in the earlier, and the less volatile in the later portions of the distillate. If the boiling points of the two liquids differ considerably, the earlier portions of the distillate will contain a large part of the more volatile liquid, but as the distillation proceeds, the boiling point of the remaining mixture gradually rises, and the less volatile passes over in larger and larger proportion; and it is only when the two liquids differ greatly in volatility, that anything approaching to complete separation can be effected by a single distillation; but on collecting separately the portions which distil between certain intervals of temperature, *e.g.*,  $5^{\circ}$  to  $10^{\circ}$ , the first will consist chiefly of the lower-boiling constituent,



and the last of the less volatile, while the intermediate fractions will be very similar in composition to the original mixture, and must all be subjected to similar treatment in order to obtain more complete separation. This series of operations being generally long and tedious, various contrivances have been adopted for facilitating the

Fig. 28.



separation, by causing the vapour of the less volatile constituent to condense in the upper part of the distilling apparatus, and run back again. One way of effecting this partial condensation is to surmount the flask or other distilling vessel with a vertical tube, having two or more bulbs blown on it, and a side-tube *t* (fig. 28) passing into the condenser; and still further separation may be effected by placing cups of platinum gauze *c c* in the vertical tube. The less volatile liquid then condenses in the meshes of these cups and the mixed vapour in passing through them is washed, as it were, by this condensed liquid, a further portion of which is dissolved out of the vapour by the portion already condensed. A side-tube *s* may also be attached to one of the bulbs to facilitate this running back of the liquid into the flask.

In some cases, however, the separation of the mixed liquids cannot be effected by fractional distillation. Wanklyn\* has shown that when a mixture of equal parts by weight of two liquids of different boiling point is distilled, the quantity of each constituent in the distillate is proportional to the product of its vapour-density and vapour-tension at the boiling point of the fraction. Hence, if the vapour-tensions and vapour-densities of the two liquids are proportional to one another, the mixture will distil unchanged. For example, a mixture of 91 parts carbon bisulphide (b. p.  $46^{\circ}$ ) and 9 parts ethyl alcohol ( $78.4^{\circ}$ ), distils without alteration at  $43^{\circ}$  to  $44^{\circ}$ ; and a mixture of equal volumes of carbon tetrachloride (b. p.  $76.6^{\circ}$ ) and methyl alcohol (b. p.  $65.2^{\circ}$ ) distils unaltered at  $55.6^{\circ}$  to  $59^{\circ}$ , that is to say, nearly  $10^{\circ}$  lower than the boiling point of the more volatile constituent.

*Tension of Vapours.*—Liquids evaporate at temperatures below their boiling points; in this case the evaporation takes place slowly from the surface. Water, or alcohol, exposed in an open vessel at the temperature of the air, gradually disappears; the more rapidly, the warmer and drier the air.

This fact was formerly explained by supposing that air and gases in general had the power of dissolving and holding in solution certain quantities of liquids, and that this power increased with the temperature; such an idea is incorrect.

\* Phil. Mag. [4], xlv. p. 129.

If a barometer-tube be carefully filled with mercury and inverted in the usual manner, and then a few drops of water passed up the tube into the vacuum above, a very remarkable effect will be observed,—the mercury will be depressed to a small extent, and this depression will increase with increase of temperature. Now, as the space above the mercury is void of air, and the weight of the few drops of water quite inadequate to account for this depression, it must of necessity be imputed to the vapour which instantaneously rises from the water into the vacuum; and that this effect is really due to the elasticity of the aqueous vapour, is easily proved by exposing the barometer to a heat of  $100^{\circ}$ , when the depression of the mercury will be complete, and it will stand at the same level within and without the tube; indicating that at that temperature the elasticity of the vapour is equal to that of the atmosphere—a fact which the phenomenon of ebullition has already shown.

By placing over the barometer a wide open tube dipping into the mercury below (fig. 29), and then filling this tube with water at different temperatures, the tension of the aqueous vapour for each degree of the thermometer may be accurately determined by its depressing effect upon the mercurial column; the same power which forces the latter *down* one inch against the pressure of the atmosphere, would of course *elevate* a column of mercury to the same height against a vacuum, and in this way the tension may be conveniently expressed. The following table was drawn up by Dalton, to whom we owe this method of investigation :—

Fig. 29.

Temperature.		Tension in Inches of Mercury.	Temperature.		Tension in Inches of Mercury.
F.	C.		F.	C.	
32°	0°	0·200	130°	54·4°	4·34
40	4·4	0·263	140	60	5·74
50	10	0·375	150	65·5	7·42
60	15·5	0·524	160	71·1	9·46
70	21·1	0·721	170	76·6	12·13
80	26·6	1·000	180	82·2	15·15
90	32·2	1·360	190	87·7	19·00
100	37·7	1·860	200	93·3	23·64
110	43·3	2·530	212	100	30·00
120	48·8	3·330			

Another table representing the tension of the vapour of water, drawn up by Regnault, is given in the Appendix to this volume.

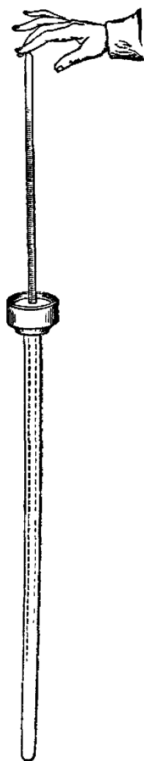
Other liquids tried in this manner are found to emit vapours of greater or less tension, for the same temperature, according to their different degrees of volatility; thus, a little ether introduced into the tube depresses the mercury 10 inches or more at the ordi-



nary temperature of the air ; oil of vitriol, on the other hand, does not emit any sensible quantity of vapour until a much greater heat is applied ; and that given off by mercury itself in warm summer weather, although it may be detected by very delicate means, is far too small to exercise any effect upon the barometer. In the case of water, the evaporation is quite distinct and perceptible at the lowest temperatures when the water is frozen to solid ice in the barometer-tube ; snow on the ground, or on a housetop, may often be noticed to vanish, from the same cause, day by day in the depth of winter, when melting is impossible.

There exists for each vapour a state of density which it cannot pass without losing its gaseous condition, and becoming liquid ; this is called the *condition of maximum density*. When a volatile

Fig. 30.



liquid is introduced in sufficient quantity into a vacuum, this condition is always reached, and then evaporation ceases. Any attempt to increase the density of this vapour by compressing it into a smaller space will be attended by the liquefaction of a portion, the density of the remainder being unchanged. If a little ether be introduced into a barometer-tube, and the latter slowly sunk into a very deep cistern of mercury (fig. 30) it will be found that the height of the column of mercury in the tube above that in the cistern remains unaltered until the upper extremity of the tube approaches the surface of the metal in the column, and all the ether has become liquid. It will be observed also, that, as the tube sinks, the stratum of liquid ether increases in thickness, but no increase of elastic force occurs in the vapour above it, and consequently, no increase of density : for tension and density are always, under ordinary circumstances at least, directly proportionate to each other.

The maximum density of vapours is dependent upon the temperature ; it increases rapidly as the temperatures rises. This is well shown in the case of water. Thus, taking the specific gravity of atmospheric air at  $100^{\circ} = 1000$ , that of aqueous vapour in its greatest state of compression for the temperature will be as follows :—

Temperature.		Specific Gravity.	Weight of 100 Cubic Inches.
F.	C.		
32°	0°	5·690	0·136 grains.
50	10	10·293	0·247 "
60	15·5	14·108	0·338 "
100	37·7	46·500	1·113 "
150	65·5	170·293	4·076 "
212	100	625·000	14·962 "

The last number was experimentally found by Gay-Lussac; the others are calculated from it by the aid of Dalton's table of tensions, on the assumption that steam, not in a state of saturation, that is, below the point of greatest density, obeys Boyle's law (which is, however, only approximately true), and that when it is cooled it contracts like the permanent gases.

Thus, there are two distinct methods by which a vapour may be reduced to the liquid form—*pressure*, by causing increase of density until the point of maximum density for a given temperature is reached: and *cold*, by which the point of maximum density is itself lowered. The most powerful effects are produced when the two are conjoined.

For example, if 100 cubic inches of vapour of water at 100° F., in the state above described, had its temperature reduced to 50° F., not less than 0.89\* grain of liquid water would necessarily separate, or very nearly eight-tenths of the whole.

Evaporation into a space filled with air or gas follows the same law as evaporation into a vacuum; as much vapour rises and the condition of maximum density is assumed in the same manner as if the space were perfectly empty; the sole difference lies in the length of time required. When a liquid evaporates into a vacuum, the point of greatest density is attained at once, while in the other case some time elapses before this happens: the particles of air appear to oppose a sort of mechanical resistance to the rise of the vapour. The ultimate effect is, however, precisely the same.

When to a quantity of perfectly dried gas confined in a vessel closed by mercury, a little water is added, the latter immediately begins to evaporate, and after some time as much vapour will be found to have risen from it as if no gas had been present, the quantity depending entirely on the temperature to which the whole is subjected. The tension of this vapour will add itself to that of the gas, and produce an expansion of volume, which will be indicated by an alteration of level in the mercury.

Vapour of water exists in the atmosphere at all times, and in all situations, and there plays a most important part in the economy of nature. The proportion of aqueous vapour present in the air is subject to great variation, and it often becomes important to determine its quantity. This is easily done by the aid of the foregoing principles.

*Dew-point.*—If the aqueous vapour be in its condition of greatest possible density for the temperature, or, as it is frequently but most incorrectly expressed, the air be saturated with vapour of water, the slightest reduction of temperature will cause the deposition of a portion in the liquid form. If, on the contrary, as is almost always in reality the case, the vapour of water is *below* its state of maximum

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\* 100 cub. inch. aqueous vapour at 100° F., weighing 1.113 grains, would at 50° F. become reduced to 91.07 cub. inch., weighing 0.225 grain.

density, that is, in an expanded condition, it is clear that a considerable fall of temperature may occur before liquefaction commences. The degree at which this takes place is called the dew-point, and it is determined with great facility by a very simple method. A little cup of thin tin-plate or silver, well polished, is filled with water at the temperature of the air, and a delicate thermometer inserted. The water is then cooled by dropping in fragments of ice, or dissolving in it powdered sal-ammoniac until moisture begins to make its appearance on the outside, dimming the bright metallic surface. The temperature of the dew-point is then read off upon the thermometer, and compared with that of the air.

Suppose, by way of example, that the latter were  $70^{\circ}$  F., and the dew-point  $50^{\circ}$  F., the elasticity of the watery vapour present would correspond with a maximum density proper to  $50^{\circ}$  F., and would support a column of mercury 0.375 inch high. If the barometer on the spot stood at 30 inches, therefore, 29.625 inches would be supported by the pressure of the dry air, and the remaining 0.375 inch by the vapour. Now, a cubic foot of such a mixture must be looked upon as made up of a cubic foot of dry air, and a cubic foot of watery vapour, occupying the same space, and having tensions indicated by the numbers just mentioned. A cubic foot, or 1728 cubic inches of vapour at  $70^{\circ}$  F., would become reduced by contraction, according to the usual law, to 1662.8 cubic inches at  $50^{\circ}$  F.; this vapour would be at its maximum density, having the specific gravity pointed out in the table: hence 1662.8 cubic inches would weigh 4.11 grains. The weight of the aqueous vapour contained in a cubic foot of air will thus be ascertained. In this country the difference between the temperature of the air and the dew-point seldom reaches  $30^{\circ}$  F. ( $16.6^{\circ}$  C.); but in the Deccan, with a temperature of  $90^{\circ}$  F. ( $32.2^{\circ}$  C.), the dew-point sinks as low as  $19^{\circ}$  F., making the degree of dryness  $61^{\circ}$  F.\*

*Liquefaction and Solidification of Gases.*—The perfect resemblance in every respect which vapours bear to permanent gases, led, very naturally, to the idea that the latter might, by the application of suitable means, be made to assume the liquid state, and this surmise has been verified. The first experiments in this direction were made by Faraday, who succeeded in liquefying eight gases previously regarded as permanent. The subjoined table shows the results of his first investigations, with the pressure in atmospheres, and the temperatures at which the condensation takes place.

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\* Daniell, Introduction to Chemical Philosophy, p. 154.

	Atmospheres.	Temperatures	
		F.	C.
Sulphur . . . . .	2	45°	7·2°
Hydrogen sulphide . . . . .	17	50	10
Carbon dioxide . . . . .	36	32	0
Chlorine . . . . .	4	60	15·5
Nitrogen monoxide . . . . .	50	45	7·2
Cyanogen . . . . .	3·6	45	7·2
Ammonia . . . . .	6·5	50	10
Hydrochloric acid . . . . .	40	50	10

The method of proceeding was very simple : the materials were sealed up in a strong narrow tube, together with a little pressure-gauge, consisting of a slender tube closed at one end, and having within it, near the open extremity, a globule of mercury. The gas being disengaged by heat, accumulated in the tube, and by its own pressure brought about condensation. The force required for this purpose was judged of by the diminution of volume of the air in the gauge.

Fig. 31.

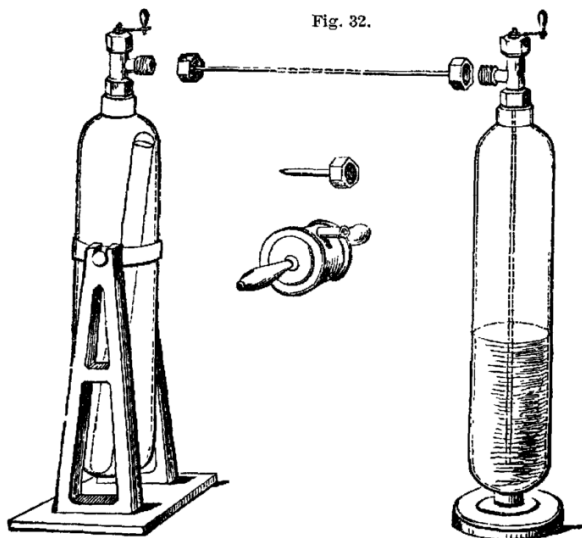


By the use of narrow green glass tubes of great strength, powerful condensing syringes, and an extremely low temperature, produced by means to be presently described, ethylene gas, hydriodic and hydrobromic acids, phosphoretted hydrogen, and the gaseous fluorides of silicon and boron, were successively liquefied. Oxygen, hydrogen, nitrogen, nitrogen dioxide, carbon monoxide, and marsh gas, refused to liquefy even at  $-166^{\circ}$  F. while subjected to pressures varying from 27 to 58 atmospheres.

Sir Isambard Brunel, and, more recently, M. Thilorier, of Paris, succeeded in obtaining liquid carbon dioxide (commonly called carbonic acid) in great abundance. Thilorier's apparatus (fig. 32) consists of a pair of extremely strong metallic vessels, one of which is destined to serve the purpose of a retort, and the other that of a receiver. They are made either of thick cast iron or gun metal, or, better, of the best and heaviest boiler-plate, and are furnished with stop-cocks of peculiar kind and excellent workmanship. The generating vessel or retort has a pair of trunnions upon which it swings in an iron frame. The joints are secured by collars of lead, and every precaution is taken to prevent leakage under the enormous pressure which the vessel has to bear. The receiver resembles the retort in every respect ; it has a similar stop-cock, and is connected with the retort by a strong copper tube and a pair of union screw-joints ; a tube passes from the stop-cock downwards, and terminates near the bottom of the vessel.

The operation is thus conducted :  $2\frac{3}{4}$  lb. of acid sodium carbonate, and  $6\frac{1}{2}$  lb. of water at  $100^{\circ}$  F., are introduced into the generator ; oil of vitriol to the amount of  $1\frac{1}{2}$  lb. is poured into a copper cylindrical vessel, which is lowered down into the mixture, and set upright ; the stop-cock is then screwed into its place, and forced home by a spanner and mallet. The machine is next tilted up on its trunnions, that the acid may run out of the cylinder and mix with the other contents of the generator ; and this mixture is favoured by swinging the whole backwards and forwards for a few minutes, after which it may be suffered to remain a little time at rest.

The receiver, surrounded with ice, is next connected with the generator, and both cocks are opened ; the liquefied carbon dioxide distils over into the colder vessel, and there again in part condenses. The cocks are now closed, the vessel is disconnected, the cock of the generator opened to allow the contained gas to escape ; and, lastly, when the issue of gas *has quite ceased*, the stop-cock itself is unscrewed, and the sodium sulphate turned out. This operation must be repeated five or six times before any considerable quantity of liquefied carbon dioxide will have accumulated in the receiver.



When the receiver thus charged has its stop-cock opened, a stream of the liquid is forcibly driven up the tube by the elasticity of the gas contained in the upper part of the vessel.

The experimenter incurs great personal danger in using this apparatus, unless the utmost care be taken in its management. A dreadful accident occurred in Paris by the bursting of one of the iron vessels.

Liquid carbon dioxide is also very frequently prepared by means of an apparatus constructed by Natterer, of Vienna, which enables the experimenter to work with less risk. The gas, disengaged by means of sulphuric acid from acid potassium carbonate, is pumped by means of a force-pump into a wrought-iron vessel, exactly as the air is pumped into the receiver of an air-gun. When a certain pressure has been reached, the gas is liquefied, and if the pressure be continued considerable quantities of the liquid carbon dioxide may be thus obtained. By this apparatus, nitrous oxide has been condensed to a liquid without the use of frigorific mixtures.

There still, however, remained six gases, viz., hydrogen, oxygen, nitrogen, nitrogen dioxide, carbon monoxide, and methane or marsh-gas, which down to the year 1877 had resisted all attempts to reduce them to the solid or liquid state; but towards the end of that year they were all liquefied by Cailletet\* and Pictet,† who employed methods exactly similar in principle to those used by Faraday, consisting in the application of cold and pressure, the gases being condensed in thick walled tubes of fine bore by means of forcing-pumps capable of producing a pressure of 300 to 1000 atmospheres, and at the same time subjected to the intense cold produced by a mixture of liquid sulphur dioxide and solid carbon dioxide.

*Complete Vaporisation of Liquids under great Pressures.*—When the temperature of a liquid is raised sufficiently high, vaporisation occurs under the highest pressure to which the substance can be subjected. Alcohol, ether, or rock-oil, enclosed in a tube of strong glass or iron, is completely converted into vapour, only when the space not occupied by the liquid is somewhat greater than the volume of the liquid itself. With rock-oil the empty space may be somewhat smaller than with alcohol, and with ether still less. Alcohol when thus heated acquires increased mobility, expands to twice its original volume, and is then suddenly converted into vapour. This change takes place at 207° C. (404·6° F.), when the alcohol occupies just half the volume of the tube; if the tube is more than half filled with alcohol, it bursts when heated. A glass tube one-third filled with water becomes opaque when heated, and bursts after a few seconds. If the chemical action of the water on the glass be diminished by the addition of a little carbonate of soda, the transparency of the glass will be much less impaired; and if the space occupied by the water be  $\frac{1}{4}$  of the whole tube, the liquid will be converted into vapour at about the temperature of

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\* Comptes rendus, lxxxv. pp. 1016, 1213, 1217, 1270.

† Ibid., lxxxv. pp. 1214, 1276; lxxxvi. pp. 37, 106.



melting zinc. These observations were made by Cagniard de Latour in 1822.

In like manner Dr. Andrews has observed that when liquid carbon dioxide is gradually heated in a sealed tube to  $31^{\circ}$ , the surface of demarcation between the liquid and gas becomes fainter, loses its curvature, and at last disappears. The space is then occupied by a homogeneous fluid, which exhibits, when the pressure is suddenly diminished, or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above  $31^{\circ}$  no apparent liquefaction of carbon dioxide or separation into two distinct forms of matter can be effected, even under a pressure of 300 or 400 atmospheres. Similar results are obtained with nitrous oxide.

It appears indeed that there exists for every liquid a temperature, called by Andrews the "critical point," above which no amount of pressure is sufficient to retain it in the liquid form; it is therefore not surprising that mere pressure, however intense, should fail to liquefy many bodies which usually exist in the form of gas.

Under the enormous pressures to which gases can be thus subjected, without liquefaction, they are found to deviate greatly from the laws of Boyle and Gay-Lussac (pp. 28, 40). Andrews has recently found that carbon dioxide, at  $60.7^{\circ}$  under a pressure of 223 atmospheres, is reduced to  $\frac{1}{4.47}$  of its original volume, or to less than one-half the volume it should occupy if it contracted according to Boyle's law. The co-efficient of expansion of the same gas by heat increases rapidly with the pressure; between  $6^{\circ}$  and  $64^{\circ}$  it is  $1\frac{1}{2}$  times as great under 22 atmospheres, and more than  $2\frac{1}{2}$  times as great at 40 atmospheres as at the pressure of 1 atmosphere.\*

*Cold produced by Evaporation.*—This effect has been already adverted to: it arises from the conversion of sensible heat into latent by the rising vapour, and may be illustrated in a variety of ways. Ether dropped on the hand produces the sensation of great cold; and water contained in a thin glass tube, surrounded by a bit of rag, is speedily frozen when the rag is kept wetted with ether.

Ice-making machines and refrigerators are constructed on this principle. Harrison's apparatus for freezing water consists of a multitubular boiler containing about 10 gallons of ether and immersed in a trough of salt water. The boiler is connected with an exhausting pump, by the working of which the ether is rapidly volatilised, thereby cooling the boiler and the salt water surrounding it to about  $24^{\circ}$  F. ( $-4.45^{\circ}$  C.) This cold water is made to flow through a channel in which are placed a number of vessels containing the water to be frozen, and when its temperature has been thus raised to about  $28^{\circ}$ , it is pumped back again into the trough con-

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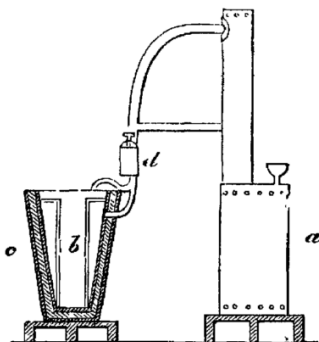
\* Journal of the Chemical Society, 1876, vol ii. p. 162.

taining the boiler, and then again cooled by the evaporation of the ether. In this manner a constant supply of cold salt water is kept up. The ether which is evaporated is condensed in a worm surrounded by cold water, and returned with very little loss to the boiler.\*

A simpler freezing apparatus is that of Carré, in which cold is produced by the rapid evaporation of liquefied ammonia-gas. It consists essentially of a cylindrical boiler *a*, fig. 33, holding about two gallons, filled to about three-fourths of its capacity with a strong aqueous solution of ammonia, and connected by pipes with a wrought-iron annular condenser or freezer *c*. The boiler is first placed in a furnace, and the freezer in water cooled to 12° C. (53.6° F.). The boiler is heated to 130° C., whereupon ammonia gas is given off, and condenses in the freezer, together with about one-tenth of its own weight of water. This operation being completed, the boiler is removed from the fire and immersed in cold water; the freezer, wrapped in very dry flannel, is placed outside, and the vessel containing the water to be frozen is placed in the cylindrical space *b*. As the boiler cools, the ammonia gas with which it is filled is redissolved, and the pressure being thus diminished, the ammonia which has been liquefied in *c* is again volatilised, and passes over towards *a*, to redissolve in the water which has remained in the boiler. This rapid evaporation of the ammonia causes a great absorption of heat, whereby the vessel *c* is reduced to a very low temperature, and the water contained in it is frozen. To obtain better contact between the sides of the vessel *b* and the freezer, alcohol is poured between them. This apparatus gives about 4 lb. of ice in an hour at the price of about a farthing a pound; but large continuously working apparatus have been constructed which produce as much as 800 lb. of ice in an hour.†

Another method of producing very low temperatures is by the rapid evaporation of methyl chloride,  $\text{CH}_3\text{Cl}$ , which is now prepared on the large scale from beetroot molasses (*see* vol. ii.). This compound is gaseous at ordinary temperatures and pressure, and when

Fig. 33.



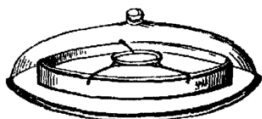
\* A figure of this apparatus is given in the *Pharmaceutical Journal*, vol. xvi. p. 477.

† See, Richardson and Watts's *Chemical Technology*, part v. p. 296.

liquefied boils at  $-23^{\circ}$ ; and by blowing air through this liquid, or better by placing it in connection with a good air-pump, its temperature may in a very short time be reduced to  $-55^{\circ}$ . Powerful refrigerating machines are now constructed on this principle.

Water may also be frozen by the cold resulting from its own evaporation. When a little water is put into a watch-glass, supported by a triangle of wire over a shallow glass dish of sulphuric acid placed on the plate of an air-pump, the whole covered with a low receiver, and the air withdrawn as perfectly as possible, the water is in a few minutes converted into a solid mass of ice. The absence of the air, and the rapid absorption of watery vapour by the oil of vitriol, induce such quick evaporation that the water has its temperature almost immediately reduced to the freezing point.

Fig. 34.



The same apparatus is constantly used in the laboratory for drying substances which cannot bear heating without decomposition. Frequently also the air-pump is dispensed with, and the substance to be dried is simply placed over a vessel containing strong sulphuric acid, quicklime, or some other substance which absorbs moisture very rapidly, and covered over with a bell-jar. Such an apparatus, with or without the air-pump, is called an *Exsiccator*. On the same principle a very powerful ice-making and refrigerating machine has lately been constructed, by which large quantities of ice can be rapidly and economically produced without the use of ether, or any other volatile liquid.\*

Still lower temperatures are produced by the evaporation of liquefied carbon dioxide, nitrogen monoxide, and other liquefied gases. When a jet of carbon dioxide is allowed to issue into the air from a narrow aperture, so intense a degree of cold is produced by the vaporisation of a part, that the remainder freezes to a solid, and falls in a shower of snow. By suffering this jet of liquid to flow into the metal box shown in fig. 32, a large quantity of the solid oxide may be obtained; it closely resembles snow in appearance, and when held in the hand occasions a painful sensation of cold, while it gradually disappears. When it is mixed with a little ether, and poured upon a mass of mercury, the latter is almost instantly frozen, and in this way pounds of the solidified metal may be obtained. The addition of the ether facilitates the contact of the carbon dioxide with the mercury.

The temperature of a mixture of solid carbon dioxide and ether in the air, measured by a spirit-thermometer, was found to be  $-106^{\circ}$  F.; when the same mixture was placed beneath the receiver of an air-pump, and exhaustion rapidly made, the temperature sank to  $-166^{\circ}$  F. This was the method of obtaining extreme cold em-

\* See Chemical News, Oct. 27th, 1882, vol. xlii. p. 192.

ployed by Faraday in his last experiments on the liquefaction of gases, and recently extended, as already observed, to the liquefaction and solidification of other gases previously regarded as permanent.

*Determination of the Specific Gravity of Gases and Vapours.*

To determine the specific gravity of a gas, a large glass globe is filled with the gas to be examined, in a perfectly pure and dry state, having a known temperature, and an elastic force equal to that of the atmosphere at the time of the experiment. The globe so filled is weighed. It is then exhausted at the air-pump as far as possible, and again weighed. Lastly, it is filled with dry air, the temperature and pressure of which are known, and its weight once more determined. On the supposition that the temperature and elasticity are the same in both cases, the specific gravity is at once obtained by dividing the weight of the gas by that of the air.

The globe or flask must be made very thin, and fitted with a brass cap, surmounted by a small but well-fitting stop-cock. A delicate thermometer should be placed in the inside of the globe, secured to the cap. The gas must be generated at the moment, and conducted at once into the previously exhausted vessel, through a long tube filled with fragments of pumice moistened with oil of vitriol, or some other extremely hygroscopic substance, by which it is freed from all moisture. As the gas is necessarily generated under some pressure, the elasticity of that contained in the filled globe will slightly exceed the pressure of the atmosphere; and this is an advantage, since, by opening the stop-cock for a single instant, when the globe has attained an equilibrium of temperature, the tension becomes exactly that of the air, so that all barometrical correction is avoided, unless the pressure of the atmosphere should vary sensibly during the time occupied by the experiment. It is hardly necessary to observe that the greatest care must also be taken to purify and dry the air used as the standard of comparison, and to bring both gas and air as nearly as possible to the same temperature, so as to obviate the necessity of a correction, or at least to reduce almost to nothing the errors involved by such a process.

**VAPOURS.**—1. *Dumas' Method.* This method consists in determining the weight of a given volume of the vapour at a known pressure and temperature. A glass globe about three inches in diameter, having its neck softened and drawn out in the blowpipe flame, is accurately weighed. About 6 or 7 grams of the volatile liquid are then introduced, by gently warming the globe and dipping the point into the liquid, which is then forced upwards by the pressure of the air as the vessel cools. The globe is heated in a bath of water, oil, or melted paraffin to a temperature from 30° to 50° above the boiling point of the liquid, in order to bring the vapour as nearly as possible into the state in which it obeys the laws of gaseous expansion and contraction by alteration of pressure and temperature.

The liquid is then rapidly converted into vapour, which escapes by the narrow orifice, chasing before it the air of the globe. When the

Fig. 35.



issue of vapour has wholly ceased, and the temperature of the bath appears nearly uniform, the open extremity of the point is sealed by a small blowpipe flame. The globe is removed from the bath, suffered to cool, cleansed if necessary, and weighed, after which the neck is broken off beneath the surface of water which has been boiled and cooled out of contact of air, or (better) under mercury. The liquid enters the globe, and, if the expulsion of the air by the vapour has been complete, fills it; if otherwise, an air-bubble is left, whose volume can be easily ascertained by pouring the liquid from the globe into a graduated jar, and then refilling the globe, and repeating the same observation, whereby also the capacity of the vessel is determined.

From these data the vapour-density ( $D$ ) may be calculated by means of the formula :

$$D = \frac{P + Vn_t}{(V - v)n'_t}.$$

$P$  = difference of weight (in grams) between the globe filled with air and when filled with vapour.

$V$  = capacity of globe in cubic centimeters.

$n_t$  = weight of one cubic centimeter of air at the temperature at which the globe filled with air was weighed.

$n'_t$  = weight of one cubic centimeter of air at the temperature of sealing the globe.

The values of  $n_t$  and  $n'_t$  (in grams) for every five degrees centigrade from  $0^\circ$  to  $300^\circ$  are given in the Appendix, Table VII.\*

In very exact experiments account must be taken of the change of capacity of the glass globe by the high temperature of the bath. When this correction is neglected, the density of the vapour will come out a little too high. The error of the mercurial thermometer at high temperatures is, however, in the opposite direction.

The preceding method is applicable to the determination of the vapour-densities of all substances whose boiling points are within the range of the mercurial thermometer, that is to say, not exceeding  $300^\circ$  C., and therefore to nearly all volatile organic compounds; indeed, there are but few such compounds which can bear higher temperatures without decomposition. But for mineral substances, such as sulphur, iodine, volatile metallic chlorides, &c., it is often

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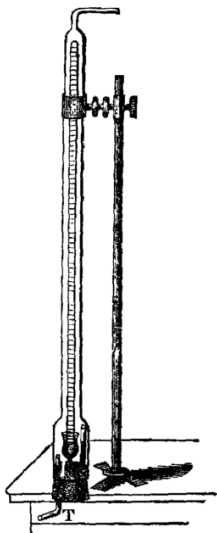
\* The table here referred to is an abstract of one drawn up by C. Greville Williams for every degree of temperature between the above limits. (See Watts's Dictionary of Chemistry, vol. v. p. 370.)

necessary to employ much higher temperatures; and for such cases a modification of the process has been devised by Deville and Troost. It consists in using a globe of porcelain instead of glass, heating it in the vapour of a substance whose boiling point is known and constant, and sealing the globe by the flame of the oxy-hydrogen blowpipe. The vapours employed for this purpose are those of mercury, which boils at  $350^{\circ}$ ; of sulphur, which boils at  $440^{\circ}$ ; of cadmium, boiling at  $860^{\circ}$ ; and of zinc, boiling at  $1040^{\circ}$ . The use of these liquids of constant boiling point obviates the necessity of determining the temperature in each experiment, which at such degrees of heat would be very difficult.

2. *Gay-Lussac's Method*.—This method consists in ascertaining the volume occupied by a given weight of a substance when converted into vapour at a known temperature and pressure. It is most readily performed with the apparatus contrived by Dr. A. W. Hofmann (fig. 36). A graduated glass tube about a meter long and 15 to 20 mm. wide, is filled with mercury and inverted in the little cup A, whereby a barometric vacuum 20 to 30 mm. high is formed at the top. The long tube is enclosed in another tube 30 to 40 mm. wide and 80 to 90 mm. long, drawn out at the top to a conducting tube of moderate width, which is bent at right angles, and connected with a glass or copper vessel in which water, aniline, or other liquid can be boiled. The lower part of the long tube is widened and rests upon a large cork, through which passes an escape tube T. By this arrangement, a stream of vapour of water, aniline, or other volatile liquid can be made to pass through the space between the two tubes, so as to keep the upper part of the barometer-tube at the temperature required for the determination. The substance whose vapour-density is to be determined, is introduced into the barometric vacuum in small glass tubes fitted with ground stoppers, which are forced out by the tension of the vapour. The great advantage of this method is that, under the very small pressure to which the enclosed vapour is subjected—which may be reduced to 20 or even 10 millimeters of mercury—the determinations may be made at comparatively low temperatures. Thus, in the case of liquids boiling under the ordinary pressure at  $120^{\circ}$  or even  $150^{\circ}$ , the vapour-density may be accurately determined at the temperature of boiling water.

By this mode of proceeding, we ascertain the volume which a known weight  $W'$  of substance occupies at a given temperature and

Fig. 36.



pressure; and dividing this by  $W$ , the weight of an equal volume  $V$  of air at the same pressure and temperature, which is given by the formula—

$$W = 0.001293 V \cdot \frac{1}{1 + 0.00367 T} \cdot \frac{P}{760},$$

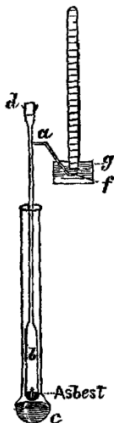
0.001293 being the weight in grams of a cubic centimeter of air at  $0^{\circ}\text{C}$ . and 760 mm. pressure, and 0.00367 the coefficient of the thermal expansion of gases,\* we obtain, for the density of the vapour, the expression—

$$D = \frac{W'}{W} = W' \frac{1 + 0.00367 T}{0.001293} \cdot \frac{760}{P}.$$

3. *V. and C. Meyer's Method.*†—This is a very simple method of determining vapour-densities, founded on the same principle as the last, and applicable to substances either of low or of high boiling point. Its simplicity consists in this, that it does not require the determination either of the temperature to which the vapour is heated, or of the volume of the vapour at that temperature—both these quantities being eliminated in the expression for the vapour-density—but only of the volume of air displaced by the vapour

evolved, this volume being measured at the atmospheric temperature. The apparatus (fig. 37) consists of a cylindrical glass bulb,  $b$ , having a capacity of about 100 c.c., to which is attached by fusion a tube 600 mm. long, terminating in a thimble-shaped enlargement, and having attached to it a side exit-tube  $a$ , by which the displaced air is transferred to a graduated tube standing in a small water-trough. For substances of boiling point not exceeding  $310^{\circ}$ , the bulb is heated in a glass tube, which terminates below in a bulb  $c$  containing various liquids, according to the volatility of the substance under experiment, viz., aniline (b. p.  $181.5^{\circ}$ ), toluidine ( $202^{\circ}$ ), ethyl benzoate ( $212^{\circ}$ ), amyl benzoate ( $261^{\circ}$ ), diphenylamine ( $310^{\circ}$ ). The mode of working is as follows:—The bulb, into which a little ignited asbestos has been introduced, is fixed in position in the bath, the end of the exit-tube  $a$  dipping into the water-trough below the mouth of the graduated tube, which is filled with water and inverted. A cork is now inserted into the top of the vertical tube at  $d$ , and the extremity

Fig. 37.



\* The values of the expression  $\frac{1}{1 + 0.00367 T}$  have been calculated by C. Greville Williams for all temperatures from  $1^{\circ}$  to  $150^{\circ}\text{C}$ . (See Table VIII. in the Appendix.)

† Berichte der deutschen chemischen Gesellschaft, 1877, p. 2253.

## SOURCES OF HEAT.

of the exit-tube  $a$  is watched, to see that the temperature in the bulb is uniform. The cork is now taken out, the small tube containing the substance is dropped in, and the cork is quickly replaced. The first few bubbles of air are suffered to escape, but immediately afterwards the inverted tube is placed quickly over the point of the delivery-tube  $a$ . The substance is soon volatilised and displaces air, which issues in a rapid stream into the graduated tube; and as soon as air ceases to come over, the cork is removed, and the air collected is cooled and measured.

The density of the vapour is calculated by the formula

$$\frac{S \cdot 760(1 + 0.00365t)}{(B - w)V \cdot 0.001293} \text{ or } \frac{S(1 + 0.00365t) \cdot 587780}{(B - w)V},$$

in which  $S$  denotes the weight of substance,  $t$  the temperature of the water,  $B$  the barometric pressure reduced to  $0^\circ$ ,  $w$  the tension of aqueous vapour, and  $V$  the volume of air displaced.

For temperatures above  $310^\circ$ , a bath of molten lead is employed; and for determining the vapour-densities of inorganic compounds which volatilise only at a red heat or at still higher temperatures, the glass vessel is replaced by one of porcelain or platinum heated in a gas-furnace.

For other recently proposed methods of determining vapour-densities, see Roscoe and Schorlemmer's *Treatise on Chemistry*, vol. iii. pp. 94—100; and Watts's *Dictionary of Chemistry*, vol. viii. p. 2096.

## Sources of Heat.

The first and greatest source of heat, compared with which all others are totally insignificant, is the sun. The luminous rays are accompanied by heat-rays, which, striking against the surface of the earth, raise its temperature; this heat is communicated to the air by convection, as already described, air and gases in general not being sensibly heated by the passage of the rays.

A second source of heat is supposed to exist in the interior of the earth. It has been observed that, in sinking mine-shafts, boring for water, &c., the temperature rises, in descending, at the rate, it is said, of about  $1^\circ$  F. ( $\frac{5}{9}^\circ$  C. for every 45 feet, or  $117^\circ$  F. ( $65^\circ$  C.) per mile. On the supposition that the rise continues at the same rate, the earth, at the depth of less than two miles, would have the temperature of boiling water; at nine miles, it would be red-hot; and at thirty or forty miles depth, all known substances would be in a state of fusion.\*

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\* The Artesian well at Grenelle, near Paris, has a depth of 1774.5 English feet; it is bored through the chalk basin to the sand beneath. The temperature of the water, which is exceedingly abundant, is  $82^\circ$  F.; the mean temperature of Paris is  $51^\circ$  F.; the difference is  $31^\circ$  F., which gives a rate of about  $1^\circ$  for 58 feet.



According to this idea, the earth must be looked upon as an intensely heated fluid spheroid, covered with a crust of solid badly conducting matter, cooled by radiation into space, and bearing somewhat the same proportion in thickness to the ignited liquid within, that the shell of an egg bears to its fluid contents. Without venturing to offer any opinion on this theory, it may be sufficient to observe that it is not positively at variance with any known fact; that the figure of the earth is really such as would be assumed by a fluid mass; and, lastly, that it offers the best explanation we have of the phenomena of hot springs and volcanic eruptions, and agrees with the chemical nature of their products.

Among the other sources of heat are chemical combination and mechanical work.

The disengagement of heat in the act of combination is a phenomenon of the utmost generality. The quantity of heat given out in each particular case is fixed and definite; its intensity is dependent upon the time over which the action is extended. Many admirable researches on this subject have been published; but their results will be more advantageously considered at a later part of this work, in connection with the laws of chemical combination.

*Heat produced by Mechanical Work.*—Heat and motion are convertible one into the other. The powerful mechanical effects produced by the elasticity of the vapour evolved from heated liquids afford abundant illustration of the conversion of heat into motion; and the production of heat by friction, by the hammering of metals, and in the condensation of gases (p. 50), shows with equal clearness that motion may be converted into heat.

In some cases the rise of temperature thus produced appears to be due to a diminution of heat-capacity in the body operated upon, as in the case of a compressed gas just alluded to. Malleable metals, also, as iron and copper, which become heated by hammering or powerful pressure, are found thereby to have their density sensibly increased, and their capacity for heat diminished. A soft iron nail may be made red hot by a few dexterous blows on an anvil; but the experiment cannot be repeated until the metal has been *annealed*, and in that manner restored to its former physical state.

But the amount of heat which can be developed by mechanical force is, in most cases, out of all proportion to what can be accounted for in this way. Sir H. Davy melted two pieces of ice by rubbing them together in a vacuum at the temperature of  $0^{\circ}$ ; and Count Rumford found that the heat developed by the boring of a brass cannon was sufficient to bring to the boiling point two and a half gallons of water, while the dust or shavings of metal cut by the borer weighed only a few ounces. In these and all similar cases the heat appears as a direct result of the force expended; the motion is converted into heat.

The connection between heat and mechanical force appears still more intimate when it is shown that they are related by an exact

numerical law, a given quantity of the one being always convertible into a definite amount of the other. The first approximate determination of this most important numerical relation was made by Count Rumford in the manner just alluded to. A brass cylinder enclosed in a box containing a known weight of water at  $60^{\circ}$  F. was bored by a steel borer made to revolve by horse power, and the time was noted which elapsed before the water was raised to the boiling point by the heat resulting from the friction. In this manner it was found that the heat required to raise the temperature of a pound of water by  $1^{\circ}$  F. is equivalent to 1034 times the force expended in raising a pound weight one foot high, or to 1034 "foot-pounds," as it is technically expressed. This estimate is now known to be too high, no account having been taken of the heat communicated to the containing vessel, or of that which was lost by dispersion during the experiment.

For the most exact determinations of the mechanical equivalent of heat, we are indebted to the careful and elaborate researches of Dr. J. P. Joule. From experiments made in the years 1840-43 on the relations between the heat and mechanical power generated by the electric current, Dr. Joule was led to conclude that the heat required to raise the temperature of a pound of water  $1^{\circ}$  F. is equivalent to 838 foot-pounds. This he afterwards reduced to 772; and a nearly equal result was afterwards obtained by experiments on the condensation and rarefaction of gases; but this estimate has since been found to be likewise too great.

The most trustworthy results are obtained by measuring the quantity of heat generated by the friction between solids and liquids. It was for a long time believed that no heat was evolved by the friction of liquids and gases; but in 1842 Meyer showed that the temperature of water may be raised  $22^{\circ}$  or  $23^{\circ}$  F. by agitating it. The warmth of the sea after a few days of stormy weather is also probably an effect of fluid friction.

The apparatus employed by Dr. Joule for the determination of this important constant, by means of the friction of water, consisted of a brass paddle-wheel furnished with eight sets of revolving vanes, working between four sets of stationary vanes. This revolving apparatus, of which fig. 38 shows a horizontal, and fig. 39 a vertical section, was firmly fitted into a copper vessel (see fig. 40) containing water, in the lid of which were two necks, one for the axis to revolve in without touching, the other for the insertion of a thermometer. A similar apparatus, but made of iron, and of smaller size, having six rotatory and eight

Fig. 38.

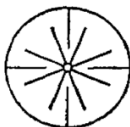
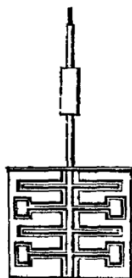
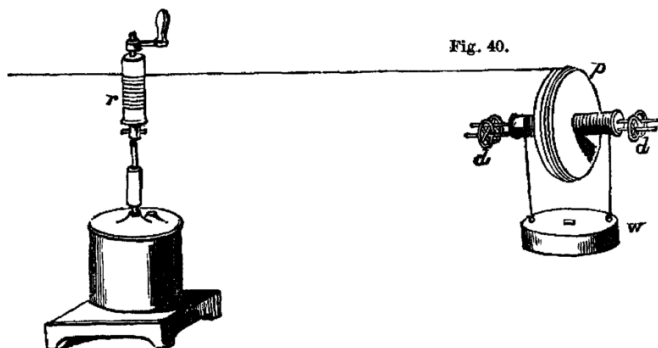


Fig. 39.



sets of stationary vanes, was used for the experiments on the friction of mercury. The apparatus for the friction of cast-iron consisted of a vertical axis carrying a bevelled cast-iron wheel, against which a bevelled wheel was pressed by a lever. The wheels were enclosed in a cast-iron vessel filled with mercury, the axis passing through the lid. In each apparatus motion was given to the axis by the descent of leaden weights *W* (fig. 40) suspended by strings from the axes of two wooden pulleys, one of which is shown at *p*, their



axes being supported on friction wheels *d d*, and the pulleys being connected by fine twine with a wooden roller *r*, which, by means of a pin, could be easily attached to or removed from the friction apparatus.

The mode of experimenting was as follows:—The temperature of the frictional apparatus having been ascertained, and the weights wound up, the roller was fixed to the axis, and the precise height of the weights ascertained; the roller was then set at liberty, and allowed to revolve till the weights touched the floor. The roller was then detached, the weights wound up again, and the friction renewed. This having been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the apartment was ascertained by observations made at the beginning, middle, and end of each experiment. Corrections were made for the effects of radiation and conduction; and, in the experiments with water, for the quantities of heat absorbed by the copper vessel and the paddle-wheel. In the experiments with mercury and cast-iron, the heat-capacity of the entire apparatus was ascertained by observing the heating effect which it produced on a known quantity of water in which it was immersed. In all the experiments, corrections were also made for the velocity with which the weights came to the ground, and for the friction and rigidity of the strings. The thermometers used were

capable of indicating a variation of temperature as small as  $\frac{1}{200}$  of a degree Fahrenheit.

The following table contains a summary of the results obtained by this method. The second column gives the results as they were obtained in air; in the third column the same results corrected for a vacuum:—

Material employed.	Equivalent in air.	Equivalent in vacuum.	Mean.
Water . . .	773·640	772·692	772·692
Mercurey . . .	773·762	772·814	774·083
	776·303	775·352	
	776·997	776·045	
Cast-iron . . .	774·880	774·930	774·987

In the experiments with cast-iron, the friction of the wheels produced a considerable vibration of the framework of the apparatus, and a loud sound; it was therefore necessary to make allowance for the quantity of force expended in producing these effects. The number 772·692, obtained by the friction of water, is regarded as the most trustworthy; but even this may be a little too high; because even in the friction of fluids it is impossible entirely to avoid vibration and sound. The conclusions deduced from these experiments are—

1. *That the quantity of heat produced by the friction of bodies, whether liquid or solid, is always proportional to the force expended.*

2. *That the quantity of heat capable of increasing the temperature of 1 lb. of water (weighed in vacuo, and between 55° and 60°) by 1° F., requires for its evolution the expenditure of a mechanical force represented by the fall of 772 lbs. through the space of 1 foot.*

*Or, the heat capable of increasing the temperature of 1 gram of water by 1° C., is equivalent to a force represented by the fall of 423·66 grams through the space of 1 meter. This is consequently the effect of "a unit of heat."*

Experiments made by other philosophers on the work done by a steam-engine, on the heat evolved by an electro-magnetic engine at rest and in motion, and on the heat evolved in the circuit of a voltaic battery and in a metallic wire through which an electric current is passing, have given values for the mechanical equivalent of heat very nearly equal to the above.

### Dynamical Theory of Heat.

For a very long time two rival theories have been held regarding the nature of heat: on the one hand, heat has been viewed as having a material existence, though differing from ordinary matter in being without weight, and in other respects; on the other hand, it has been regarded as a state or condition of ordinary matter, and generally as a condition of motion. From the latter part of the last

century, until the modern researches upon the mechanical equivalent, the former view had by far the greater number of adherents. Its popularity may be chiefly traced to the teaching of Black and Lavoisier. By the former of these philosophers, the various capacities for heat, or specific heats, of different bodies, seem to have been regarded as analogous to the various proportions of the same acid required to neutralise equal quantities of different bases, while the solid, liquid, and gaseous states were explained by Black as representing so many distinct proportions in which heat was capable of combining with ordinary matter. Very similar views were advocated by Lavoisier: he regarded all gases as compounds of a base characteristic of each, with *caloric*, and supposed that when, as the result of chemical action, they assumed the liquid or solid state, this caloric was set free, and appeared as sensible heat.

Heat was compared by these philosophers to a material substance, in order to explain its then known quantitative relations; and from this point of view the conception introduced by them had the great advantage of being more easily grasped than any which the advocates of the immaterial nature of heat had to offer in its place. It was much easier to conceive of definite quantities of an exceedingly subtle substance or fluid, than of definite quantities of motion, which was itself undefined as to its nature. It was a direct consequence of the material view, that heat should be considered as indestructible and as incapable of being produced, and therefore that the total quantity of heat in the universe should be regarded as at all times the same.

But, on the other hand, this hypothesis did not afford a satisfactory explanation of the production of heat by mechanical means. Here it was not easy to deny the actual generation of heat, or to explain the effects as depending merely on its altered distribution. Nevertheless, the evolution of heat by friction and percussion was generally considered, by the advocates of the material view, as in some way resulting from a diminution in the capacities for heat of the bodies operated upon; and this explanation derived considerable support from the remark, made by Black, that a piece of soft iron, which has been once made red hot by hammering (see p. 72), cannot be so heated a second time until it has been heated to redness in a fire and allowed to cool. In this case, certainly, it seemed as though the hammering forced out heat from the mass of iron, like water from a sponge, and that a fresh supply was taken up when the iron was put in the fire. This explanation, however, did not satisfy Rumford, who, in the investigation described above, made direct experiments upon the specific heat of the chips of metal detached by the friction, and found it to be identical with that of brass under ordinary circumstances. Still more decisive proof that the heat generated by friction cannot be ascribed to a diminution of specific heat in the substances operated on was afforded by Davy's experiment on the liquefaction of ice by friction; for in this case the ice was converted into a liquid having twice the specific heat of the

ice itself. Hence Davy\* drew the conclusion that, "the immediate cause of the phenomena of heat is motion, and the laws of its communication are precisely the same as the laws of the communication of motion."

The mechanical, or dynamical theory, which regarded heat as consisting in a state of molecular motion, cannot, however, be said to have been definitely established, until it also was made quantitative,—until it was shown that exact numerical laws regulate the production of heat by work or of work by heat, equally with its production during solidification and disappearance during fusion.

To illustrate the general nature of the dynamical theory of heat, we give an outline of the view of the constitution of gases, first put forward, in its present form, by Joule†; and subsequently developed by Kronig‡, and Clausius§, and of the explanation of the relations existing between solids, liquids, and gases, which has been deduced from it by the last-named philosopher.

First, then, it is assumed that the particles of all bodies are in constant motion, and that this motion constitutes heat, the kind and quantity of motion varying according to the state of the body, whether solid, liquid, or gaseous.

In gases, the molecules—each molecule being an aggregate of atoms—are supposed to be constantly moving forward in straight lines, and with a constant velocity, till they impinge against each other, or against an impenetrable wall. This constant impact of the molecules produces the expansive tendency or elasticity which is the peculiar characteristic of the gaseous state. The rectilinear movement is not, however, the only one with which the particles are affected. For the impact of two molecules, unless it takes place exactly in the line joining their centres of gravity, must give rise to a rotatory motion; and, moreover, the ultimate atoms of which the molecules are composed may be supposed to vibrate within certain limits, being, in fact, thrown into vibration by the impact of the molecules. This vibratory motion is called by Clausius *the motion of the constituent atoms*. The total quantity of heat in the gas is made up of the progressive motion of the molecules, together with the vibratory and other motions of the constituent atoms; but the progressive motion alone, which is the cause of the expansive tendency, determines the *temperature*. Now, the outward pressure exerted by the gas against the containing envelope arises, according to the hypothesis under consideration, from the impact of a great number of gaseous molecules against the sides of the vessel. But at any given temperature, that is, with any given velocity, the number of such impacts taking place in a given time must vary inversely as the volume of the given quantity of gas: hence *the pressure varies inversely as the volume, or directly as the density*, which is Boyle's law.

\* Elements of Chemical Philosophy, 1812, pp. 94, 95.

† Ann. Ch. Phys. [3], l. 381.

‡ Pogg. Ann. xcix. 315.

§ Ibid., 353.

When the volume of the gas is constant, the pressure resulting from the impact of the molecules is proportional to the sum of the masses of all the molecules multiplied into the squares of their velocities; in other words, to the so-called *vis viva* or *working force* of the progressive motion. If, for example, the velocity be doubled, each molecule will strike the sides of the vessel with a twofold force, and its number of impacts in a given time will also be doubled: hence the total pressure will be quadrupled.

Now, we know that when a given quantity of any perfect gas is maintained at a constant volume, it tends to expand by  $\frac{1}{273}$  of its bulk at zero for each degree centigrade. Hence the pressure or elastic force increases proportionally to the temperature reckoned from  $-273^{\circ}$  C.; that is to say, to the absolute temperature. Consequently, *the absolute temperature is proportional to the working force of the progressive motion.*

Moreover, as the motions of the constituent particles of a gas depend on the manner in which its atoms are united, it follows that in any given gas the different motions must be to one another in a constant ratio; and, therefore, the *vis viva* or *working force* of the progressive motion must be an aliquot part of the entire working force of the gas: hence also the absolute temperature is proportional to the total working force arising from all the motions of the particles of the gas.

From this it follows that the quantity of heat which must be added to a gas of constant volume in order to raise its temperature by a given amount is constant and independent of the temperature. In other words, the specific heat of a gas referred to a given volume is constant, a result which agrees with the experiments of Regnault, mentioned at p. 45. This result may be otherwise expressed, as follows:—*The total or working force of the gas is to the working force of the progressive motion of the molecules, which is the measure of the temperature, in a constant ratio.* This ratio is different for different gases, and is greater as the gas is more complex in its constitution; in other words, as its molecules are made up of a greater number of atoms. The specific heat referred to a constant pressure is known to differ from the true specific heat only by a constant quantity.

The relations just considered between the pressure, volume, and temperature of gases, presuppose, however, certain conditions of molecular constitution, which are, perhaps, never rigidly fulfilled: and accordingly the experiments of Magnus and Regnault show (p. 40) that gases do exhibit slight deviations from Gay-Lussac and Boyle's laws. What the conditions are which strict adherence to these laws would require will be better understood by considering the differences of molecular constitution which must exist in the solid, liquid, and gaseous states.

A movement of molecules must be supposed to exist in all three states. In the *solid state*, the motion is such that the molecules oscillate about certain positions of equilibrium, which they do not quit, unless they are acted upon by external forces. This vibratory

motion may, however, be of a very complicated character. The constituent atoms of a molecule may vibrate separately, the entire molecules may also vibrate as such about their centres of gravity, and the vibrations may be either rectilinear or rotatory. Moreover, when extraneous forces act upon the body, as in shocks, the molecules may permanently alter their relative position.

In the *liquid state*, the molecules have no determinate positions of equilibrium. They may rotate completely about their centres of gravity, and may also move forward into other positions. But the repulsive action arising from the motion is not strong enough to overcome the mutual attraction of the molecules, and separate them completely from each other. A molecule is not permanently associated with its neighbours, as in the solid state; it does not leave them spontaneously, but only under the influence of forces exerted upon it by other molecules, with which it then comes into the same relation as with the former. There exists, therefore, in the liquid state, a vibratory, rotatory, and progressive movement of the molecules, but so regulated that they are not thereby forced asunder, but remain within a certain volume without exerting any outward pressure.

In the *gaseous state*, on the other hand, the molecules are removed quite beyond the sphere of their mutual attractions, and travel onward in straight lines according to the ordinary laws of motion. When two such molecules meet, they fly apart from each other, for the most part with a velocity equal to that with which they came together. The perfection of the gaseous state, however, implies:—1. That the space actually occupied by the molecules of the gas be infinitely small in comparison with the entire volume of the gas; 2. That the time occupied in the impact of a molecule, either against another molecule or against the sides of the vessel, be infinitely small in comparison with the interval between any two impacts; 3. That the influence of the molecular forces be infinitely small. When these conditions are not completely fulfilled, the gas partakes more or less of the nature of a liquid, and exhibits certain deviations from Gay-Lussac and Boyle's laws. Such is, indeed, the case with all known gases; to a very slight extent with those which have not yet been reduced to the liquid state; but to a greater extent with vapours and condensable gases, especially near the points of condensation.

Let us now return to the consideration of the liquid state. It has been said that the molecule of a liquid, when it leaves those with which it is associated, ultimately takes up a similar position with regard to other molecules. This, however, does not preclude the existence of considerable irregularities in the actual movements. Now, at the surface of the liquid, it may happen that a particle, by a peculiar combination of the rectilinear, rotatory, and vibratory movements, may be projected from the neighbouring molecules with such force as to throw it completely out of their sphere of action, before its projectile velocity can be annihilated by the attractive



force which they exert upon it. The molecule will then be driven forward into the space above the liquid, as if it belonged to a gas, and that space, if originally empty, will, in consequence of the action just described, become more and more filled with these projected molecules, which will comport themselves within it exactly like a gas, impinging and exerting pressure upon the sides of the envelope. One of these sides, however, is formed by the surface of the liquid, and when a molecule impinges upon this surface, it will, in general, not be driven back, but retained by the attractive forces of the other molecules. A state of equilibrium, not static, but dynamic, will therefore be attained, when the number of molecules projected in a given time into the space above is equal to the number which in the same time impinge upon and are retained by the surface of the liquid. This is the process of vaporisation. The density of the vapour required to ensure the compensation just mentioned depends upon the rate at which the particles are projected from the surface of the liquid, and this again upon the rapidity of their movement within the liquid, that is to say, upon the temperature. It is clear, therefore, that the density of a saturated vapour must increase with the temperature.

If the space above the liquid is previously filled with a gas, the molecules of this gas will impinge upon the surface of the liquid, and thereby exert pressure upon it; but as these gas-molecules occupy but an extremely small proportion of the space above the liquid, the particles of the liquid will be projected into that space almost as if it were empty. In the middle of the liquid, however, the external pressure of the gas acts in a different manner. There also it may happen that the molecules may be separated with such force as to produce a small vacuum in the midst of the liquid. But this space is surrounded on all sides by masses which afford no passage to the disturbed molecules; and in order that they may increase to a permanent vapour-bubble, the number of molecules projected from the inner surface of the vessel must be such as to produce a pressure outwards equal to the external pressure tending to compress the vapour-bubble. The boiling point of the liquid will therefore, be higher as the external pressure is greater.

According to this view of the process of vaporisation, it is possible that vapour may rise from a solid as well as from a liquid; but it by no means necessarily follows that vapour must be formed from all bodies at all temperatures. The force which holds together the molecules of a body may be too great to be overcome by any combination of molecular movements, so long as the temperature does not exceed a certain limit.

The *production and consumption of heat* which accompany changes in the state of aggregation, or of the volume of bodies, are easily explained, according to the preceding principles, by taking account of the *work* done by the acting forces. This work is partly *external* to the body, partly *internal*. To consider first the *internal* work:

When the molecules of a body change their relative positions,

the change may take place either in accordance with or in opposition to the action of the molecular forces existing within the body. In the former case, the molecules, during the passage from one state to the other, have a certain velocity imparted to them, which is immediately converted into heat; in the latter case, the velocity of their movement, and consequently the temperature of the body, is diminished. In the passage from the solid to the liquid state, the molecules, although not removed from the spheres of their mutual attractions, nevertheless change their relative positions in opposition to the molecular forces, which forces have, therefore, to be overcome. In evaporation, a certain number of the molecules are completely separated from the remainder, which again implies the overcoming of opposing forces. In both cases, therefore, work is done, and a certain portion of the working force of the molecules, that is, of the heat of the body, is lost. But when once the perfect gaseous state is attained, the molecular forces are completely overcome, and any further expansion may take place without internal work, and, therefore, without loss of heat, provided there is no external resistance.

But in nearly all cases of change of state or volume, there is a certain amount of external resistance to be overcome, and a corresponding loss of heat. When the pressure of a gas, that is to say, the impact of its atoms, is exerted against a movable obstacle, such as a piston, the molecules lose just as much of their moving power as they have imparted to the piston, and, consequently, their velocity is diminished and the temperature lowered. On the contrary, when a gas is compressed by the motion of a piston, its molecules are driven back with greater velocity than that with which they impinged on the piston, and, consequently, the temperature of the gas is raised.

When a liquid is converted into vapour, the molecules have to overcome the atmospheric pressure or other external resistance, and, in consequence of this, together with the internal work already spoken of, a large quantity of heat disappears, or is rendered *latent*, the quantity thus consumed being, to a considerable extent, affected by the external pressure. The liquefaction of a solid not being attended with much increase of volume, involves but little external work; nevertheless the atmospheric pressure does influence, to a slight amount, both the latent heat of fusion and the melting point.

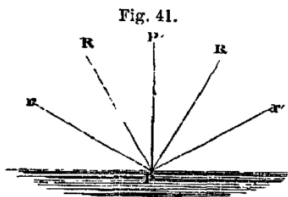
**LIGHT.**

Two views have been entertained respecting the nature of light. Newton imagined that luminous bodies emit, or shoot out, infinitely small particles in straight lines, which, by penetrating the transparent part of the eye and falling upon the nervous tissue, produce vision. Other philosophers drew a parallel between the properties of light and those of sound, and considered that, as sound is certainly the effect of undulations, or little waves, propagated through elastic bodies in all directions, so light might be nothing more than the consequence of similar undulations transmitted with inconceivable velocity through a highly elastic medium, of excessive tenuity, filling all space, and occupying the intervals between the particles of material substances. To this medium they gave the name of *ether*. The wave hypothesis of light is at present generally adopted. It is in harmony with all the known phenomena discovered since the time of Newton, not a few of which were first deduced from the undulatory theory, and afterwards verified by experiment. Several well-known facts are in direct opposition to the theory of emission.

A ray of light emitted from a luminous body proceeds in a straight line, and with extreme velocity. Certain astronomical observations afford the means of approximating to a knowledge of this velocity. The satellites of Jupiter revolve about the planet in the same manner as the moon about the earth, and the time of revolution of each satellite is exactly known from its periodical entry into or exit from the shadow of the planet. The time required by one is only 42 hours. Römer, the astronomer of Copenhagen, found that this period appeared to be longer when the earth, in its passage round the sun, moved from the planet Jupiter; and, on the contrary, he observed that the periodic time appeared to be shorter when the earth moved in the direction towards Jupiter. The difference, though very small for a single revolution of the satellite, increases, by the addition of many revolutions, during the passage of the earth from its nearest to its greatest distance from Jupiter, that is, in about half a year, till it amounts to 16 minutes and 16 seconds. Römer concluded from this, that the light of the sun, reflected from the satellite, required that time to pass through a distance equal to the diameter of the orbit of the earth; and since this space is little short of 200 millions of miles, the velocity of light cannot be less than 200,000 miles in a second of time. It will be seen hereafter that this rapidity of transmission is rivalled by that of electricity. Another astronomical phenomenon, observed and correctly explained by Bradley, the aberration of the fixed stars, leads to the same result. Physicists have, moreover, succeeded in measuring the velocity of light for terrestrial, and indeed comparatively small distances; the results of these experiments essentially correspond with those given by astronomical observations.

**REFLECTION.**—When a ray of light falls upon a boundary between two media, a part of it, and, in exceptional cases, the whole, is reflected into the first medium, whilst the other part penetrates into the second medium.

The law of regular reflection is extremely simple. If a line be drawn perpendicular to the surface upon which the ray falls, and the angle contained between the ray and the perpendicular be measured, it will be found that the ray, after reflection, takes such a course as to make with the perpendicular an equal angle on the opposite side of the latter. A ray of light,  $R$ , falling at the point  $P$ , will be reflected in the direction  $PR'$ , making the angle  $R'PP'$  equal to the angle  $RPP'$ ; and a ray from the point  $r$  falling upon the same spot will be reflected to  $r'$  in virtue of the same law. Further, it is to be observed, that the incident and reflected rays are always contained in the same normal plane.

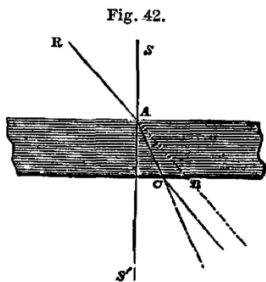


The same rule holds good if the mirror be curved, as a portion of a sphere, the curve being considered as made up of a multitude of little planes. Parallel rays cease to be so when reflected from curved surfaces, becoming divergent or convergent according as the reflecting surface is convex or concave.

Bodies with rough and uneven surfaces, the smallest parts of which are inclined towards each other without order, reflect the light diffused. The perception of bodies depends upon the diffused reflected light.

**REFRACTION.**—It has just been stated that light passes in straight lines; but this is true only so long as the medium through which it travels preserves the same density and the same chemical nature: when this ceases to be the case, the ray of light is bent from its course into a new one, or is said to be *refracted*.

Let  $R$  (fig. 42) be a ray of light falling upon a plate of some transparent substance with parallel sides, such as a piece of thick plate glass,—in short, any transparent homogeneous material which is either non-crystalline, or crystallises in the regular system; and let  $A$  be its point of contact with the upper surface. The ray, instead of holding a straight course and passing into the glass in the direction  $AB$ , will be bent downwards to  $C$ ; and, on leaving the glass, and issuing into the air on the other side, it will again be bent, but in the opposite direction, so as to make it parallel

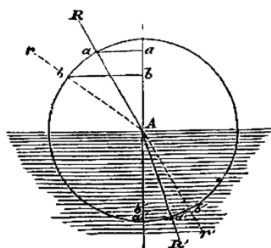


to the continuation of its former track, provided there be one and the same medium on the upper and lower side of the plate. The general law is thus expressed :—When the ray passes from a rare to a denser medium, it is usually refracted *towards* a line perpendicular to the surface of the latter ; and conversely, when it leaves a dense medium for a rarer one, it is refracted *from* a line perpendicular to the surface of the denser substance ; in the former case the angle of incidence is greater than that of refraction ; in the latter, it is less. In both cases the direction of the refracted ray is in the plane  $RAS$ , which is formed by the incident ray and the perpendicular  $SA$  drawn from the spot where the ray is refracted. The angle  $RAS = BAS'$ , is called the angle of incidence ; the angle  $CAS'$  the angle of refraction. The difference of these two angles, that is, the angle  $CAB$ , is the refraction.

The amount of refraction, for the same medium, varies with the obliquity with which the ray strikes the surface. When perpendicular to the latter, the ray passes without change of direction at all ; and in other positions, the refraction increases with the obliquity.

Let  $R$  (fig. 43) represent a ray of light falling upon the surface of a mass of plate glass at the point  $A$ . From this point let a perpendicular fall and be continued into the new medium, and around the

Fig. 43.



same point, as a centre, let a circle be drawn. According to the law just stated, the refraction must be towards the perpendicular ; in the direction  $AR'$  for example. Let the lines  $a-a'$ ,  $a'-a'$ , at right angles to the perpendicular, be drawn, and their length compared by means of a scale of equal parts, and noted : their length will, in the case supposed, be in proportion of 3 to 2. These lines are termed the *sines* of the angles of

incidence and refraction respectively.

Now let another ray be taken, such as  $r$  ; it is refracted in the same manner to  $r'$ , the bending being greater from the increased obliquity of the ray ; but what is very remarkable, if the sines of the two new angles of incidence and refraction be again compared, they will still be found to bear to each other the proportion of 3 to 2. The fact is expressed by saying, that so long as the light passes from one to the other of the same two media, the *ratio of the sines of the angles of incidence and refraction is constant*. This ratio is called the *index of refraction*.

Different bodies possess different refractive powers ; generally speaking, the densest substances refract most. Combustible bodies have been noticed to possess greater refractive power than their density would indicate, and from this observation Newton predicted

the combustible nature of the diamond long before anything was known respecting its chemical nature.

The method adopted for describing the comparative refractive power of different bodies, is to state the ratio borne by the sine of the angle of incidence in the first medium at the boundary of the second, to the sine of the angle of refraction in this second medium; this is called the *index of refraction* of the two substances; it is greater or less than unity, according as the second medium is denser or rarer than the first. In the case of air and plate glass the index of refraction is 1.5.

When the index of refraction of any particular substance is once known, the effect of the latter upon a ray of light entering it in any position can be calculated by the law of sines. The following table exhibits the indices of refraction of several substances, supposing the ray to pass into them from the air:—

Substances.	Index of refraction.	Substances.	Index of refraction.
Tabasheer*	1.10	Garnet	1.80
Ice	1.30	Glass with much oxide	
Water	1.34	of lead	1.90
Fluor spar	1.40	Zircon	2.00
Plate glass	1.50	Phosphorus	2.20
Rock-crystal	1.60	Diamond	2.50
Crysolite	1.69	Chromate of lead	3.00
Bisulphide of carbon	1.70	Cinnabar	3.20

When a luminous ray enters a mass of substance differing in refractive power from the air, and whose surfaces are not parallel, it becomes permanently deflected from its course and altered in its direction. It is upon this principle that the properties of prisms and lenses depend. To take an example.—

Fig. 44 represents a triangular prism of glass, upon the side of which the ray of light R may be supposed to fall. This ray will of course be refracted, on entering the glass, towards a line perpendicular to the first surface, and again, from a line perpendicular to the second surface on emerging into the air. The result is the deflection  $a c R$ , which is equal to the sum of the two deflections which the ray undergoes in passing through the prism.

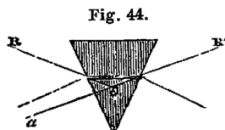


Fig. 44.

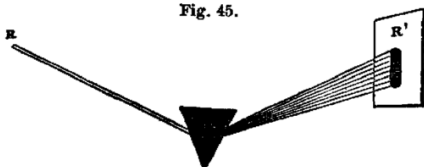
A convex lens is thus enabled to converge rays of light falling upon it, and a concave lens to separate them more widely; each separate part of the surface of the lens producing its own independent effect.

DISPERSION.—The light of the sun and of celestial bodies in general, as well as that of the electric spark and of all ordinary flames, is

\* A siliceous deposit in the joints of the bamboo.

of a compound nature. If a ray of light from any of the sources mentioned be admitted into a dark room by a small hole in a shutter, or otherwise, and suffered to fall upon a glass prism, in the manner shown in fig. 45, it will not only be refracted from its

Fig. 45.



straight course, but will be decomposed into a number of coloured rays, which may be received upon a white screen placed behind the prism. When solar light is employed, the colours are extremely brilliant, and spread into an oblong space of considerable length.

The prism being placed with its base upwards, as in fig. 45, the upper part of this image, or *spectrum*, will be violet and the lower red, the intermediate portion, commencing from the violet, being indigo, blue, green, yellow, and orange, all graduating imperceptibly into each other. This is the celebrated experiment of Sir Isaac Newton; from it he drew the inference that white light is composed of seven primitive colours, the rays of which are differently refrangible by the same medium, and hence capable of being thus separated. The violet rays are most refrangible, and the red rays least.\*

Bodies of the same mean refractive power do not always equally disperse or spread out the differently coloured rays to the same extent; because the principal yellow or red rays, for instance, are equally refracted by two prisms of different materials, it does not follow that the blue or the violet will be similarly affected. Hence, prisms of different varieties of glass, or other transparent substances, give, under similar circumstances, very different spectra,

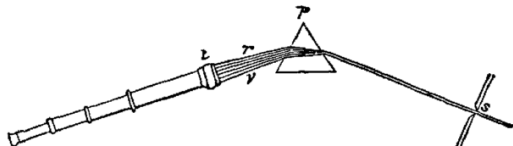
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\* The colours of natural objects are supposed to result from the power possessed by their surfaces of absorbing some of the coloured rays, while they reflect or transmit, as the case may be, the remainder of the rays. Thus an object appears red because it absorbs or causes to disappear the yellow and blue rays composing the white light by which it is illuminated. Any colour which remains after the deduction of another colour from white light, is said to be *complementary* to the latter. Complementary colours, when acting simultaneously, reproduce white light. Thus in the example already quoted, red and green are complementary colours. The fact of complementary colours giving rise to white light may be readily illustrated by mixing in appropriate quantities a rose-red solution of cobalt and green solution of nickel; the resulting liquid is nearly colourless.

both as respects the length of the image, and the relative extent of the coloured bands.

The appearance of the spectrum may also vary with the nature of the source of light: the investigation of these differences, however, involves the use of a more delicate apparatus. Fig. 46 shows the principle of such an apparatus, which is called a *spectroscope*.

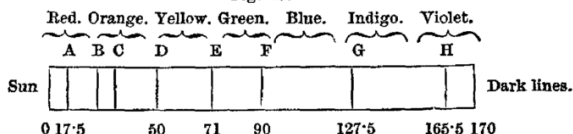
Fig. 46.



The light, passing through a fine slit, *s*, impinges upon a flint-glass prism, *p*, by which it is dispersed. The decomposed light emerges from the prism in several directions between *r* (red rays) and *v* (violet rays); and the spectrum thus produced is observed by the telescope *t*, which receives only part of it at once; but the several parts may be readily examined by turning slightly either the prism or the telescope.

If the solar spectrum be examined in this manner, numerous dark lines parallel with the edge of the prism are observed. They were discovered in 1802 by Dr. Wollaston, and subsequently more minutely investigated by Fraunhofer. They are generally known as Fraunhofer's lines. These dark lines, which exist in great numbers, and of very varying strength, are irregularly distributed over the whole spectrum. Some of them, in consequence of their peculiar strength and their relative positions, may always be easily recognised. Fig. 47 shows the relative positions of the more conspicuous lines on a scale divided into 170 equal parts (*see also the frontispiece to this volume*). The same dark lines, though paler, and much more difficult to recognise, are observed in the spectrum of

Fig. 47.



planets lighted by the sun; for instance, in the light emanating from Venus. On the other hand, the dark lines observed in the spectra which are produced by the light emanating from fixed stars—from Sirius, for instance—differ in position from those previously mentioned.

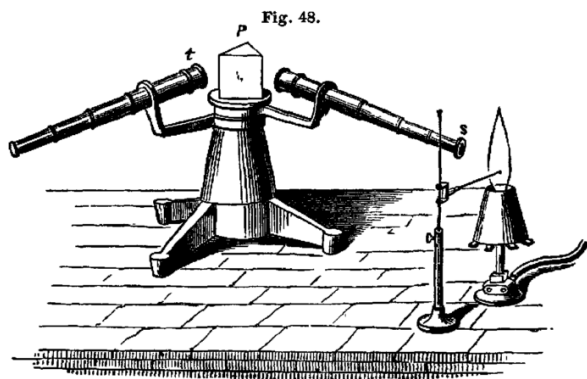
Sources of light which contain no volatile constituents—incan-



descent platinum wire, for example—furnish continuous spectra, exhibiting no such lines. But if volatile substances be present in the source of light, bright lines are observed in the spectrum, which are frequently characteristic of the volatile substances.

Professor Plücker, of Bonn, has investigated the spectra which are produced by the electric light when developed in very rarefied gases. He found the bright lines and the dark stripes between the lines to vary considerably with different gases. When the electric light was developed in a mixture of two gases, the spectrum thus obtained exhibited simultaneously the peculiar spectra belonging to the two gases of which the mixture consisted. When the experiment was made in gaseous compounds capable of being decomposed by the electric current, this decomposition was indicated by the spectra of the separated constituents becoming perceptible.

Many years ago the spectra of coloured flames were examined by Sir John Herschel, Fox Talbot, and W. A. Miller. More recently results of the greatest importance have been obtained by Kirchhoff and Bunsen, who have investigated the spectra furnished by the incandescence of volatile substances: these researches have enriched chemistry with a new method of analysis, the analysis by spectrum observations. In order to recognise one of the metals of the alkalis or of the alkaline earths, it is generally sufficient to introduce a minute quantity of a moderately volatile compound of the metal, on the loop of a platinum wire, into the edge of the very hot, but scarcely luminous flame, of a mixture of air and coal-gas, and to examine the spectrum which is furnished by the flame containing the vapour of the metal or its compound. Fig. 48 exhibits



the apparatus which is used in performing experiments of this description. The light of the flame in which the metallic compound is evaporated passes through the fine slit in the disc, *s*, into a tube,

the opposite end of which is provided with a convex lens. This lens collects the rays diverging from the slit, and throws them parallel upon the prism, *p*. The light is decomposed by the prism, and the spectrum thus obtained is observed by means of the telescope, which may be turned round the axis of the stand carrying the prism. Foreign light is excluded by an appropriate covering.

The limits of this elementary treatise do not permit us to describe the ingenious arrangements which have been contrived for sending the light from different sources through the same prism at different heights, whereby their spectra, the solar spectrum, for instance, and that of a flame, may be placed in a parallel position, the one above the other, and thus be compared.\* The spectra of flames in which different substances are volatilised frequently exhibit such characteristically distinct phenomena, that they may be used with the greatest advantage for the discrimination of these substances. Thus the spectrum of a flame containing sodium (Na) exhibits a bright line on the yellow portion, the spectrum of potassium (K) a characteristic bright line at the extreme limit of the red, and another at the opposite violet limit of the spectrum. Lithium (Li) shows a bright brilliant line in the red, and a paler line in the yellow portion; strontium (Sr) a bright line in the blue, one in the orange, and six less distinct ones in the red portion of the spectrum. The frontispiece exhibits the most remarkable of the dark lines of the solar spectrum (Fraunhofer's lines), and the position of the bright lines in the spectra of flames containing the vapours of compounds of the metals of the alkalis and alkaline earths, also of the metals thallium and indium.

The delicacy of these spectral reactions is very considerable, but unequal in the case of different metals. The presence of  $\frac{1}{200,000,000}$  grain of sodium in the flame is still easily recognisable by the bright yellow line in the spectrum. Lithium, when introduced in the form of a volatile compound, imparts to the flame a red colour; but this coloration is no longer perceptible when a volatile sodium compound is simultaneously present, the yellow coloration of the flame predominating under such circumstances. But when a mixture of one part of lithium and 1000 parts of sodium is volatilised in a flame, the spectrum of the flame exhibits, together with the bright yellow sodium line, likewise the red line characteristic of lithium. The observation of bright lines not belonging to any of the previously known bodies has led to the discovery of new elements. Thus, Bunsen and Kirchhoff, when examining the spectrum of the flame in which a mixture of alkaline salts was evaporated, observed some bright lines, which could not be attributed to any of the known elements, and were thus led to the discovery of the two new metals,

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\* See the article "Spectral Analysis," by Prof. Roscoe, in Watts's Dictionary of Chemistry, vol. v.

cæsium and rubidium. By the same method a new element, thallium, has been more recently discovered by Mr. Crookes ; another, called indium, by Reich and Richter ; a third, called gallium, by Lecoq de Boisbaudran ; and several new earth-metals, by Cleve, Delafontaine, Marignac, and Nilson.

For the examination of the bright lines in the spectra of metals, the electric spark may be conveniently employed as a source of light. Small quantities of the metal are invariably volatilised ; and the spectrum developed by the electric light exhibits the bright lines characteristic of the metal employed. These lines were observed by Wheatstone as early as 1835. This method of investigation is more especially applicable to the examination of the spectra of the heavy metals. The spark passes between two points of the metal or between two small cones of pure porous carbon impregnated with a solution of a compound of the metal.

By a series of theoretical considerations, Professor Kirchhoff has arrived at the conclusion that the spectrum of an incandescent gas is reversed—i.e., that the bright lines become dark lines—if there be behind the incandescent gas a very luminous source of light, which by itself furnishes a continuous spectrum. Kirchhoff and Bunsen have fully confirmed this conclusion by experiment. Thus a volatile lithium salt produces, as just pointed out, a very distinct bright line in the red portion of the spectrum ; but if bright sunlight, or the light emitted by a solid body heated to the most powerful incandescence, be allowed to fall through the flame upon the prism, the spectrum exhibits, in the place of this bright line, a black line similar in every respect to Fraunhofer's lines in the solar spectrum. In like manner the bright strontium line is reversed into a dark line. Kirchhoff and Bunsen have expressed the opinion that all the Fraunhofer lines in the solar spectrum are bright lines thus reversed. In their conception, the sun is surrounded by a luminous atmosphere, containing a certain number of volatilised substances, which would give rise in the spectrum to certain bright lines, if the light of the solar atmosphere alone could reach the prism ; but the intense light of the powerfully incandescent body of the sun which passes through the solar atmosphere, causes these bright lines to be reversed and to appear as dark lines on the ordinary solar spectrum. Kirchhoff and Bunsen have thus been enabled to attempt the investigation of the chemical constituents of the solar atmosphere, by ascertaining the elements which, when in the state of incandescent vapour, develop bright spectral lines, coinciding with Fraunhofer's lines in the solar spectrum. Fraunhofer's line D (fig. 47) coincides most accurately with the bright spectral line of sodium, and may be artificially produced by reversing the latter ; sodium would thus appear to a constituent of the solar atmosphere. Kirchhoff has proved, moreover, that sixty bright lines perceptible in the spectrum of iron correspond, both as to position and distinction, most exactly with the same number of dark lines in the solar spectrum, and, accordingly, he believes iron, in the state of vapour, to be present in

the solar atmosphere. In a similar manner this physicist has endeavoured to establish the presence of several other elements in the solar atmosphere.

*Absorption Spectra.*—The relative quantities of the several coloured rays absorbed by a coloured medium of given thickness may be observed by viewing a line of light through a prism and the coloured medium; the spectrum will then be seen to be diminished in brightness in some parts, and perhaps cut off altogether in others. This mode of observation is often of great use in chemical analysis, as many coloured substances when thus examined afford very characteristic spectra, the peculiarities of which may often be distinguished, even though the solution of the substance under examination contains a sufficient amount of coloured impurities to change its colour very considerably. The following method of making the observation is given by Professor Stokes.\*

A small prism is to be chosen of dense flint glass, ground to an angle of  $60^\circ$ , and just large enough to cover the eye comfortably. The top and bottom should be flat, for convenience of holding the prism between the thumb and fore-finger, and laying it down on a table, so as not to scratch or soil the faces. A fine line of light is obtained by making a vertical slit in a board six inches square, or a little longer in a horizontal direction, and adapting to the aperture two pieces of thin metal. One of the metal pieces is movable, to allow of altering the breadth of the slit. About the fiftieth of an inch is a suitable breadth for ordinary purposes. The board and metal pieces should be well blackened.

On holding the board at arm's length against the sky or a luminous flame, the slit being, we will suppose, in a vertical direction, and viewing the line of light thus formed through the prism held close to the eye, with its edge vertical, a pure spectrum is obtained at a proper azimuth of the prism. Turning the prism round its axis alters the focus, and the proper focus is got by trial. The whole of the spectrum is not, indeed, in perfect focus at once, so that in scrutinising one part after another, it is requisite to turn the prism a little. When daylight is used, the spectrum is known to be pure by its showing the principal fixed lines; in other cases the focus is got by the condition of seeing distinctly the other objects, whatever they may be, which are presented in the spectrum. To observe the absorption spectrum of a liquid, an elastic band is put round the board near the top, and a test-tube containing the liquid is slipped under the band, which holds it in its place behind the slit. The spectrum is then observed just as before, the test-tube being turned from the eye.

To observe the whole progress of the absorption, different degrees of strength must be used in succession, beginning with a

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\* Chem. Soc. Jour. xvii. 306.

strength which does not render any part of the spectrum absolutely black, unless it be one or more very narrow bands, as otherwise the most distinctive features of the absorption might be missed. If the solution be contained in a wedge-shaped vessel instead of a test-tube, the progress of the absorption may be watched in a continuous manner by sliding the vessel before the eye. Some observers prefer using a wedge-shaped vessel in combination with the slit, the slit being perpendicular to the edge of the wedge. In this case each element of the slit forms an elementary spectrum corresponding with a thickness of the solution which increases in a continuous manner from the edge of the wedge, where it vanishes. This is the mode of observation adopted by Gladstone.\*

Fig. 49 represents the effect produced in this way by a solution of chromic chloride, and fig. 50 that produced by a solution of potassium permanganate.

Fig. 49.

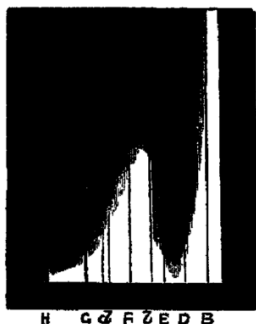
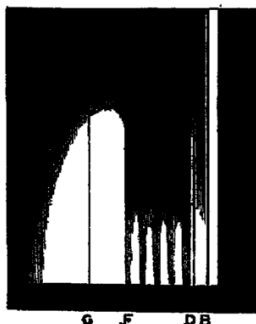


Fig. 50.



The right hand side of these figures corresponds with the red end of the spectrum ; the letters refer to Fraunhofer's lines. The lower part of each figure shows the pure spectrum seen through the thinnest part of the wedge ; and the progress of the absorption, as the thickness of the liquid increases, is seen by the gradual obliteration of the spectrum towards the upper part of the figures.

*Fluorescence.*—An examination into a peculiar mode of analysis of light, discovered by Sir John Herschel, in a solution of quinine sulphate, has within the last few years led to the discovery of a most remarkable fact. Professor Stokes has observed that light of certain refrangibility and colour is capable of experiencing a peculiar influence in being dispersed by certain media, and of undergoing

\* Chem. Soc. Journ. x. 79.

thereby an alteration of its refrangibility and colour. This curious change, called fluorescence, can be produced by a great number of bodies, both liquid and solid, transparent and opaque. Frequently the change affects only the extreme limits; at other times larger portions; and in a few cases even the whole, or, at all events, the major part of the spectrum. A dilute solution of quinine sulphate, for instance, changes the violet and the dark-blue light to sky-blue; by a decoction of madder in a solution of alum all rays of higher refrangibility than yellow are converted into yellow; by an alcoholic solution of the colouring matter of leaves, all the rays of the spectrum become red. In all cases in which this peculiar phenomenon presented itself in a greater or less degree, Stokes observed that it consisted in a diminution of the refrangibility. Thus, rays of so high a degree of refrangibility, that they extend far beyond the extreme limits of the spectrum visible under ordinary circumstances, may be rendered luminous, and converted into blue and even red light.

**DOUBLE REFRACTION AND POLARISATION.**—A ray of common light made to pass through certain crystals of a particular order is found to undergo a very remarkable change. It becomes split or divided into two rays, one of which follows the general law of refraction, while the other takes a new and extraordinary course, dependent on the position of the crystal. This effect, which is called double refraction, is beautifully illustrated in the case of Iceland spar, or crystallised calcium carbonate. On placing a rhomb of this substance on a piece of white paper on which a mark or line has been made, the object will be seen double.

Again, if a ray of light be suffered to fall on a plate of glass at an angle of  $56^{\circ} 45'$ , the portion of the ray which suffers reflection will be found to have acquired properties which it did not before possess; for on throwing it, at the same angle, upon a second glass plate, it will be observed that there are two particular positions of the latter, namely, those in which the planes of incidence are at right angles to one another, when the ray of light is no longer reflected, but entirely refracted. Light which has suffered this change is said to be *polarised*.

The light which passes through the first or polarising plate is also, to a certain extent, in this peculiar condition, and by employing a series of similar plates held parallel to the first, this effect may be greatly increased; a bundle of fifteen or twenty such plates may be used with great convenience for the experiment. It is to be remarked, also, that the light polarised by transmission in this manner is in an opposite state to that polarised



by reflection ; that is, when examined by a second or *analysing* plate, held at the angle before mentioned, it will be seen to be reflected when the other is transmitted, and to be dispersed when the first is reflected.

It is not every substance that is capable of polarising light in this manner ; glass, water, and certain other bodies bring about the change in question, each having a particular polarising angle at which the effect is greatest. For each transparent substance the polarising angle is that at which the reflected and refracted rays are perpendicular to each other. Metals can also polarise light, by reflection, but they do so very imperfectly.

The two rays into which a pencil of common light divides itself in passing through a doubly-refracting crystals are found on examination to be completely polarised, and also transversely, the one being capable of reflection when the other vanishes or is transmitted. The two rays are said to be polarised in opposite directions. With a rhomb of transparent Iceland spar of tolerably large dimensions, the two oppositely polarised rays may be widely separated and examined apart.

Certain doubly refracting crystals absorb one of these rays, but not the other. Through a plate of such a crystal one ray passes and becomes entirely polarised ; the other, which is likewise polarised, but in another plane, is removed by absorption. The best known of these media is tourmaline. When two plates of this mineral, cut parallel to the axis of the crystal, are held with their axes parallel, as in fig. 52, light traverses them both freely ; but when one of them is turned round in the manner shown in fig. 53, so as to make the axes cross at right angles, the light is almost wholly stopped, if the tourmalines are good. A plate of the mineral thus becomes an excellent test for discriminating between polarised light and that which has not undergone the change.

Fig. 52.

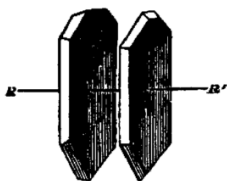
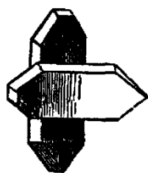


Fig. 53.



Instead of the tourmaline plate, which is always coloured, frequent use is made of two Nicol's prisms, or conjoined prisms of calcium carbonate, which, in consequence of a peculiar cutting and combination, possess the property of allowing only one of the oppositely polarised rays to pass. A more advantageous method of cutting and combining prisms has been given by M. Foucault. His prisms are as serviceable as those of Nicol and less expensive.

If two Nicol's or Foucault's prisms be placed one behind the other in precisely similar positions, the light polarised by the one goes through the other unaltered. But when one prism is slightly turned round in its setting, a cloudiness is produced; and by continuing to turn the prism, this increases until perfect darkness ensues. This happens, as with the tourmaline plates, when the two prisms cross one another. The phenomenon is the same with colourless as with coloured light.

*Circular Polarisation.*—Supposing that polarised light, coloured, for example, by going through a plate of red glass, has passed through the first Nicol's prism, and been altogether obstructed in consequence of the position of the second prism, then, if between the two prisms a plate of rock-crystal, formed by a section at right angles to the principal axis of the crystal, be interposed, the light polarised by the first prism will, by passing through the plate of quartz, be enabled partially to pass through the second Nicol's prism. Its passage through the second prism can then again be interrupted by turning the second prism round to a certain extent. The rotation required varies with the thickness of the plate of rock-crystal, and with the colour of the light employed. It increases from red in the following order :—yellow, green, blue, violet.

This property of rock-crystal was discovered by Arago. The kind of polarisation has been called circular polarisation. The direction of the rotation is with many plates towards the right hand; in other plates it is towards the left. The one class is said to possess right-handed polarisation, or to be *dextrorotatory* or *dextrogyrate*; the other class to possess left-handed polarisation, or to be *levorotatory* or *levogyrate*. For a long time quartz was the only solid body known to exhibit circular polarisation. Others have since been found which possess this property in a far higher degree. Thus, a plate of cinnabar acts fifteen times more powerfully than a plate of quartz of equal thickness.

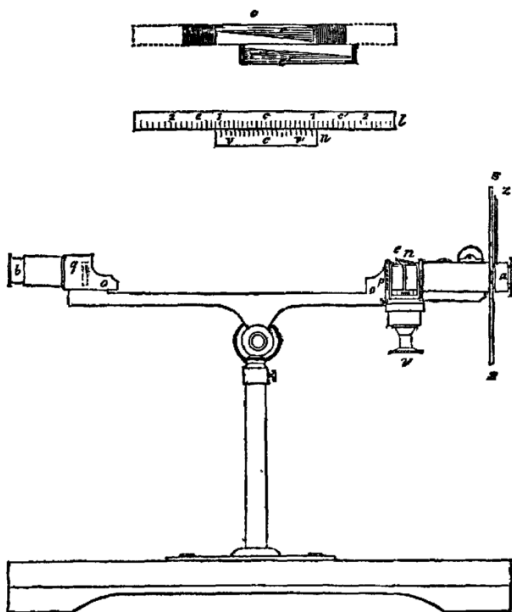
Biot observed that many solutions of organic substances exhibit the property of circular polarisation, though to a far less extent than rock-crystal. Thus, solutions of cane-sugar, glucose, and tartaric acid, possess right-handed polarisation; whilst albumin, uncrystallisable sugar, and oil of turpentine, are left-handed. In all these solutions the amount of circular polarisation increases with the concentration of the liquid, and the thickness of the column through which the light passes. Hence circular polarisation is an important auxiliary in chemical analysis. In order to determine the amount of polarisation which any liquid exhibits, it is put into a glass tube not less than from ten to twelve inches long, which is closed with glass plates. This is then placed between the two Nicol's prisms, which have previously been so arranged with regard to each other that no light could pass through. An apparatus of this description, the saccharimeter, is used for determining the concentration of solutions of cane-sugar.

The form of this instrument is shown in fig. 54. The two



Nichol's prisms are enclosed in the corresponding fastenings *a* and *b*. Between the two there is a space to receive the tube, which is filled with the solution of sugar. If the prisms are crossed in the way above-mentioned before the tube is put in its place, that is, if they are placed so that no light passes through them, then, by the action of

Fig. 54.



the sugar-solution, the light is enabled to pass, and the Nichol's prism, *a*, must be turned through a certain angle before the light is again perfectly stopped. The magnitude of this angle is observed on the circular disk *s s*, which is divided into degrees, and upon which, by the turning of the prism, an index *z* is moved along the division. When the tube is exactly ten inches long, and closed at both ends by flat glass plates, and when it is filled with a solution containing 10 per cent. by weight of cane-sugar, and free from any other substance possessing an action on light, the angle of rotation for the middle yellow ray is  $19.6^\circ$ . Now, the magnitude of this angle is directly proportional to the length of the column of liquid, and also to the quantity of sugar in solution. If, therefore, a solution containing

$z$  per cent. by weight of sugar in a tube  $l$  inches long, produce a rotation equal to  $\alpha$  degrees, the percentage of sugar will be given by the equation—

$$\frac{\alpha}{19.6} = \frac{l}{10} \cdot \frac{z}{10},$$

whence

$$z = \frac{100 \alpha}{19.6 l}.$$

This process is not sufficient when the solution contains cane-sugar and uncrystallisable sugar; for the latter rotates the ray to the left; in that case only the difference of the two actions is obtained. But if the whole quantity of sugar be changed into uncrystallisable sugar, and the experiment be repeated, then from the results of the two observations the quantity of both kinds of sugar can easily be calculated.

It is difficult to find exactly that position of the Nichol's prisms in which the greatest darkness prevails. To make the measurements more exact and easy, Soleil has made some additions to the apparatus. At  $q$ , before the prism  $b$ , a plate of rock-crystal cut at right angles to the axis is placed. It is divided in the centre of the field of vision, half consisting of quartz rotating to the right hand, and half of the variety which rotates to the left; it is 0.148 inch (3.75 millimeters) thick, this thickness being found by experiment to produce the greatest difference in the colour of the two halves, when one prism is slightly rotated. The solution of sugar has precisely the same action on the rotation, increasing the action of the half which has a right-handed rotation, and lessening that of the half which rotates to the left. Hence the two halves will assume a different colour when the smallest quantity of sugar is present in the liquid. By slightly turning the Nichol's prism  $a$ , this difference can be again removed. Soleil has introduced another more delicate means of effecting this, at the part  $l$ , which he calls the compensator. The most important parts of this are separately represented in fig. 54. It consists of two exactly equal right-angled prisms, of left-handed quartz, whose surfaces,  $c$  and  $c'$ , are cut perpendicular to the optic axis. These prisms can, by means of the screw  $v$  and a rack and pinion, be made to slide on one another, so that, when taken together, they form a plate of varying thickness, bounded by parallel surfaces. One of the frames has a scale  $l$ , the other a vernier  $n$ . When this points to zero of the scale, the optical action of the two prisms is exactly compensated by a right-handed plate of rock-crystal, so that an effect is obtained as regards circular polarisation, as if the whole system were not present. As soon, however, as the screw is moved, and thus the thickness of the plate formed by the two prisms is changed (we will suppose it increased), then a left-handed action ensues, which must be properly regulated, until it compensates the opposite action of a solution of sugar. Thus a convenient method is obtained of render-

ing the colour of the double plate uniform, when it has ceased to be so by the action of the sugar.

Faraday made the remarkable discovery that, if a very strong electric current be passed round a substance which possesses the property of circular polarisation, the amount of rotation is altered to a considerable degree.

**HEATING AND CHEMICAL RAYS OF THE SOLAR SPECTRUM.**—The luminous rays of the sun are accompanied, as already mentioned, by others which possess heating powers. If the temperature of the different-coloured spaces in the spectrum be tried with a delicate thermometer, it will be found to increase from the violet to the red extremity, and when the prism is of some particular kinds of glass, the greatest effect will be manifested a little beyond the visible red rays. The position of the greatest heating effect in the spectrum materially depends on the absorptive nature of the glass. Transparent though this medium is to the rays of light, it nevertheless absorbs a considerable quantity of the heat rays. Transparent rock-salt is almost without absorptive action on the thermal rays. In the spectrum obtained by passing the solar rays through prisms of rock-salt, the greatest thermal effect is found at a position far beyond the last visible red rays. It is inferred from this that the greater number of the heating rays are among the least refrangible components of the solar beam.

Again, it has long been known that chemical changes both of combination and of decomposition, but more particularly the latter, can be effected by the action of light. Chlorine and hydrogen combine at common temperatures only under the influence of light; and parallel cases occur in great numbers in organic chemistry. The blackening and decomposition of silver salts are familiar instances of the chemical powers of the same agent. Now, it is not always the luminous part of the ray which effects these changes; they are chiefly produced by certain invisible rays, which accompany the others, and are found most abundantly beyond the violet part of the spectrum. It is there that certain chemical effects are most marked, although the intensity of the light is exceedingly feeble. These chemically acting rays are sometimes called *actinic rays* (*aktis*, a ray), and the chemical action of sunlight is called *actinism*; but these terms are not very well chosen. The chemical rays are thus directly opposed to the heating rays in the common spectrum in their degree of refrangibility, since they exceed all the others in this respect. The luminous rays, too, under peculiar conditions, exert decomposing powers upon silver salts. The result of the action of any ray depends, moreover, greatly on the physical state of the surface upon which it falls, and on the chemical constitution of the body; indeed, for every kind of ray a substance may be found which under particular circumstances will be affected by it; and thus it appears that the chemical functions are by no means confined to any set of rays to the exclusion of the rest.

Upon the chemical changes produced by light is based the art of *photography*. In the year 1802 Mr. Thomas Wedgwood proposed a method of copying paintings on glass, by placing behind them white paper or leather moistened with a solution of silver nitrate, which became decomposed and blackened by the transmitted light in proportion to the intensity of the latter; and Davy, in repeating these experiments, found that he could thus obtain tolerably accurate representations of objects of a texture partly opaque and partly transparent, such as leaves and the wings of insects, and even copy with a certain degree of success the images of small objects obtained by the solar microscope. These pictures, however, required to be kept in the dark, and could be examined only by candle-light, otherwise they became obliterated by the blackening of the whole surface, from which the silver salt could not be removed. These attempts at light-painting attracted but little notice till the year 1839, when Mr. Fox Talbot published his plan of "photogenic drawing." This consisted in exposing in the camera a paper soaked in a weak solution of common salt, and afterwards washed over with a strong solution of silver nitrate; the image thus obtained was a *negative* one, the lights being dark and the shadows light, and the pictures were fixed by immersion in a solution of common salt.

Many improvements have been made in this process. In 1841 Fox Talbot patented the beautiful process known as the "Talbotype or Calotype process," in which the paper is coated with silver iodide by dipping it first in silver nitrate, then in potassium iodide. Paper thus prepared is not sensitive *per se* to the action of light, but may be rendered so by washing it over with a mixture of silver nitrate and gallic or acetic acid. If it be exposed to the camera for two or three minutes, it does not receive a visible image (unless the light has been very strong); but still the compound has undergone a certain change by the influence of the light: for on subsequently washing it over with the mixture of silver nitrate and acetic or gallic acid, and gently warming it, a negative image comes out on it with great distinctness. This image is *fixed* by washing the paper with sodium thiosulphate (commonly called hyposulphite), which removes the whole of the silver iodide not acted upon by the light, and thus protects the picture from further change by exposure to light. The negative picture thus obtained is rendered transparent by placing it between two sheets of blotting-paper saturated with white wax, and passing a moderately heated smoothing-iron over the whole. It may then be used for printing *positive pictures* by laying it on a sheet of paper prepared with chloride or iodide of silver, and exposing it to the sun.

A most important step in the progress of photography was the substitution of a transparent film of iodised collodion or albumin spread upon glass, for the iodised paper used in Talbot's process, to receive the negative image in the camera. The process is thus rendered so much more certain and rapid, and the positive pictures

obtained by transferring the negative to paper prepared with chloride or iodide of silver, are found to be so much sharper in outline than when the transference occurs through paper, as in the talbotype process, that this method is now universally employed. In this process, as in that of the Calotype, the image produced in the camera is a latent one, and requires development with substances such as pyrogallic acid, or ferrous sulphate, which, having a tendency to absorb oxygen, induce, in presence of silver nitrate, the reduction of the chloride or iodide to the metallic state. For a description of the best apparatus and latest processes used in the collodion method, the reader may consult Hardwich's "Manual of Photographic Chemistry," and Captain Abney's "Instruction in Photography."

Sir John Herschel showed that a great number of other substances can be employed in these photographic processes by taking advantage of the deoxidising effects of certain portions of the solar rays. Paper washed with a solution of ferric salt becomes capable of receiving impressions of this kind, which may afterwards be made evident by potassium ferricyanide, or gold chloride. Vegetable colours are also acted upon in a very curious and apparently definite manner by the different parts of the spectrum.

The *daguerreotype*, the announcement of which was first made in the summer of 1839, by M. Daguerre, who had been occupied with this subject from 1826, if not earlier, is another remarkable instance of the decomposing effects of the solar rays. A clean and highly polished plate of silvered copper is exposed for a certain time to the vapour of iodine, and then transferred to the camera obscura. In the most improved state of the process, a very short time suffices for effecting the necessary change in the film of silver iodide. The picture, however, becomes visible only by exposing it to the vapour of mercury, which attaches itself, in the form of exceedingly minute globules, to those parts which have been most acted upon, that is to say, to the lights, the shadows being formed by the dark polish of the metallic plate. Lastly, the plate is washed with sodium thio-sulphate, to remove the undecomposed silver iodide and render it permanent.

Since Daguerre's time this process has undergone considerable improvements; amongst these, we may mention the exposure of the plate to the vapour of bromine, by which the sensitiveness of the film is greatly increased, and the reduction of metallic gold upon the surface of the film during the process of fixing, by which the lights and shades of the picture are rendered more effective; but it is now completely superseded by photography.

Etching and lithographic processes, by combined chemical and photographic agency, promise to be of considerable utility. The earliest is that of Niépce: he applied a bituminous coating to a metal plate, upon which an engraving was superimposed. The light, being thus partially interrupted, acted unequally upon the varnish; a liquid hydro-carbon, *petroleum*, used as a solvent, removed the

bitumen wherever the light had not acted; the unprotected metal was bitten by an acid; and the plate could then be printed from in the usual way. Very successful results have also been obtained by M. Fizeau, who submits the daguerreotype to the action of a mixture of dilute nitric acid, common salt, and potassium nitrate, when the silver only is attacked, the mercurialised portion of the image resisting the acid; an etching is thus obtained following minutely the lights and shadows of the picture. To deepen this etching, the silver chloride formed is removed by ammonia, the plate is boiled in caustic potash and again treated with acid, and so on till the etching is of sufficient depth. Sometimes electro-gilding is resorted to, and an engraving acid is used to get still more powerful impressions.

Among recent results are those obtained by Mr. Talbot on steel plates: he uses a mixture of potassium bichromate and gelatin, which hardens by exposure to the light; the parts not affected are removed by washing. Platinum tetrachloride is used as an etching liquid: it has the advantage of biting with greater regularity than nitric acid.

The bitumen process of M. Nièpce has been applied to lithographic stone; and positives obtained from negative talbotypes have been printed off by a modification of the ordinary lithographic process. M. Nièpce finds that ether dissolves the altered bitumen, while petroleum or benzene attacks by preference the bitumen in its normal condition.

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### MAGNETISM.

A PARTICULAR species of iron ore has long been remarkable for its property of attracting small pieces of iron, and causing them to adhere to its surface; it is called loadstone, or magnetic iron ore.

If a piece of this loadstone be carefully examined, it will be found that the attractive force for particles of iron is greatest at certain particular points of its surface, while elsewhere it is much diminished, or even altogether absent. These attractive points are denominated poles, and the loadstone itself is said to be endowed with magnetic polarity.

If one of the pole-surfaces of a natural loadstone be rubbed in a particular manner over a bar of steel, its characteristic properties will be communicated to the bar, which will then be found to attract iron-filings like the loadstone itself. Further, the attractive force will appear to be greatest at two points situated very near the extremities of the bar, and least of all towards the middle. The bar of steel so treated is said to be magnetised, or to constitute an artificial magnet.

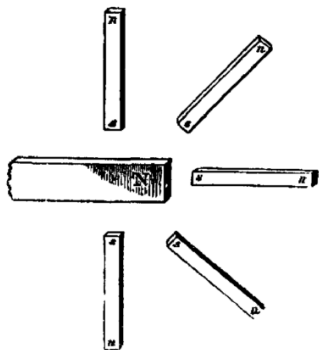
When a magnetised bar or natural magnet is suspended at its centre in any convenient manner, so as to be free to move in a hori-

zontal plane, it is always found to assume a particular direction with regard to the earth, one end pointing nearly north, and the other nearly south. This direction varies with the geographical position of the place, and is different also at the same place at different times. At London, in 1881, the needle pointed  $18^{\circ} 33'$  west of the astronomical north. If the bar be moved from this position, it will tend to reassume it, and, after a few oscillations, will settle at rest as before. The pole which points towards the astronomical north is usually distinguished as the north pole of the bar, and that which points southward as the south pole.

A magnet, either natural or artificial, of symmetrical form, suspended in the presence of a second magnet, serves to exhibit certain phenomena of attraction and repulsion which deserve particular attention. When a north pole is presented to a south pole, or a south pole to a north, attraction ensues between them; the ends of the bars approach each other, and, if permitted, adhere with considerable force; when, on the other hand, a north pole is brought near a second north pole, or a south pole near another south pole, mutual repulsion is observed, and the ends of the bars recede from each other as far as possible. *Poles of an opposite name attract, and poles of a similar name repel each other.* Thus, a small bar or needle of steel, properly magnetised and suspended, and having its poles marked, becomes an instrument fitted not only to discover the existence of magnetic power in other bodies, but to estimate the kind of polarity affected by their different parts.

A piece of soft iron brought into the neighbourhood of a magnet acquires itself magnetic properties: the intensity of the power thus conferred depends upon that of the magnet, and upon the space which divides the two, becoming greater as that space decreases, and greatest of all in actual contact. The iron, under these circumstances, is said to be magnetised by *induction* or influence, and the effect, which reaches its maximum in an instant, is at once destroyed by removing the magnet.

Fig. 55.



When steel is substituted for iron in this experiment, the inductive action is hardly perceptible at first, and becomes manifest only after the lapse of a certain time: in this condition, when the steel bar is removed from the magnet, it retains a portion of the induced polarity. It becomes, indeed, a permanent magnet, similar to the first, and retains its peculiar properties for an indefinite time. This resistance which steel always offers in a

greater or less degree both to the development of magnetism and to its subsequent destruction, is called *specific coercive power*.

The rule which regulates the induction of magnetic polarity in all cases is exceedingly simple, and most important to be remembered. The pole produced is always of the opposite name to that which produced it, a north pole developing south polarity, and a south pole north polarity. The north pole of the magnet figured in the sketch induces south polarity in all the nearer extremities of the pieces of iron or steel which surround it, and a state similar to its own in all the more remote extremities. The iron thus magnetised is capable of exerting a similar inductive action on a second piece, and that upon a third, and so to a great number, the intensity of the force diminishing as the distance from the permanent magnet increases. It is in this way that a magnet is enabled to hold up a number of small pieces of iron, or a bunch of filings, each separate piece becoming for the time a magnet by induction.

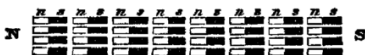
Magnetic polarity, similar in degree to that which iron presents, has been found only in some of the compounds of iron, in nickel, and in cobalt.

Magnetic attractions and repulsions are not in the slightest degree interfered with by the interposition of substances destitute of magnetic properties. Thick plates of glass, shellac, metals, wood, or of any substances except those above mentioned, may be placed between a magnet and a suspended needle, or a piece of iron under its influence, the distance being preserved, without the least perceptible alteration in its attractive power, or force of induction.

One kind of polarity cannot be exhibited without the other. In other words, a magnetic pole cannot be isolated. If a magnetised bar of steel be broken at its neutral point, or in the middle, each of the broken ends acquires an opposite pole, so that both portions of the bar become perfect magnets; and, if the division be carried still further, if the bar be broken into a hundred pieces, each fragment will be a complete magnet, having its own north and south poles.

This experiment serves to show very clearly that the apparent polarity of the bar is the consequence of the polarity of each individual particle, the poles of the bar being merely points through which the resultants of all these forces pass; the largest magnet is made up of an immense number of little magnets regularly arranged side by side, all having their north poles looking one way, and their

Fig. 56.



south poles the other. The middle portion of such a system cannot possibly exhibit attractive or repulsive effects on an external body, because each pole is in close juxtaposition with one of an opposite



name and of equal power. Hence their forces will be exerted in opposite directions, and neutralise each other's influence. Such will not be the case at the extremities of the bar; there uncompensated polarity will be found, capable of exerting its specific power.

This idea of regular polarisation of particles of matter in virtue of a pair of opposite and equal forces, is not confined to magnetic phenomena; it is the leading principle in electrical science, and is constantly reproduced in some form or other in every discussion involving the consideration of molecular forces.

Artificial steel magnets are made in a great variety of forms; such as small light needles, mounted with an agate for suspension upon a fine point; straight bars of various kinds; bars curved into the shape of a horse-shoe, &c. All these have regular polarity communicated to them by certain processes of rubbing or touching with another magnet, which require care, but are not otherwise difficult of execution. When great power is wished for, a number of bars may be screwed together, with their similar ends in contact, and in this way it is easy to construct permanent steel magnets capable of sustaining great weights. To prevent the gradual destruction of magnetic force, which would otherwise occur, it is usual to arm each pole with a piece of soft iron or keeper, which, becoming magnetised by induction, serves to sustain the polarity of the bar, and in some cases even increases its energy.

Magnetism is not peculiar to these substances which have more especially been called magnetic, such as iron, nickel, cobalt, but it is the property of all metals, though to a much smaller degree. Very powerful magnets are required to show this remarkable fact. Large horse-shoe magnets, made by the action of the electric current, are best adapted for the purpose. The magnetic action on different substances which are capable of being easily moved, differs not only according to the size, but also according to the nature of the substance. In consequence of this, Faraday divides all bodies into two classes. He calls the one magnetic, or, better, *paramagnetic*, and the other *diamagnetic*.

The matter of which a paramagnetic (magnetic) body consists is attracted by both poles of the horse-shoe magnet; on the contrary, the matter of a diamagnetic body is repelled. When a small iron bar is hung by untwisted silk between the poles of the magnet, so that its long diameter can easily move in a horizontal plane, it arranges itself axially, that is, parallel to the straight line which joins the poles, or to the magnetic axis of the poles, assuming at the end which is nearest the north pole, a south pole, and at the end nearest the south pole, a north pole. Whenever the little bar is removed from this position, it returns, after a few oscillations, to its previous position. The whole class of paramagnetic bodies behave in a precisely similar way under similar circumstances, but in the intensity of the effects great differences occur.

Diamagnetic bodies, on the contrary, have their long diameters placed equatorially, that is, at right angles to the magnetic axis

They behave as if at the end opposite to each pole of the magnet the same kind of polarity existed.

In the first class of substances, besides iron, which is the best representative of the class, we have nickel, cobalt, manganese, chromium, cerium, titanium, palladium, platinum, osmium, aluminium, oxygen, and also most of the compounds of these bodies, most of them even when in solution. According to Faraday, the following substances are also feebly paramagnetic (magnetic),—paper, sealing-wax, Indian ink, porcelain, asbestos, fluorspar, minium, cinnabar, binoxide of lead, sulphate of zinc, tourmaline, graphite, and charcoal.

In the second class are placed bismuth, antimony, zinc, tin, cadmium, sodium, mercury, lead, silver, copper, gold, arsenic, uranium, rhodium, iridium, tungsten, phosphorus, iodine, sulphur, chlorine, hydrogen, and many of their compounds. Also, glass free from iron, water, alcohol, ether, nitric acid, hydrochloric acid, resin, wax, olive oil, oil of turpentine, caoutchouc, sugar, starch, gum, and wood. These are diamagnetic.

When diamagnetic and paramagnetic bodies are combined, their peculiar properties are more or less neutralised. In most of these compounds, occasionally in consequence of the presence of a very small quantity of iron, the peculiar magnetic power remains more or less in excess. Thus green bottle-glass, and many varieties of crown glass, are magnetic in consequence of the iron they contain.

In order to examine the magnetic properties of liquids, they are placed in very thin glass tubes, the ends of which are then closed by melting; they are then hung horizontally between the poles of the magnet. Under the influence of poles sufficiently powerful, they begin to swing, and according as the fluid contents are paramagnetic (magnetic) or diamagnetic, they assume an axial or equatorial position.

Faraday tried the magnetic condition of gases in different ways. One method consisted in making soap-bubbles with the gas which he wished to investigate, and bringing these near the poles. Soap and water alone is feebly diamagnetic. A bubble filled with oxygen was strongly attracted by the magnet. All other gases in the air are diamagnetic, that is, they are repelled. But, as Faraday has shown, in a different way, this partly arises from the paramagnetic (magnetic) property of the air. Thus he found that nitrogen, when this differential action was eliminated, was perfectly indifferent, whether it was condensed or rarefied, whether cooled or heated. When the temperature is raised, the diamagnetic property of gases in the air is increased. Hence the flame of a candle or of hydrogen is strongly repelled by the magnet. Even warm air is diamagnetic in cold air.

For some time it had been believed that crystallised bodies exhibited a special and peculiar behaviour when placed between the poles of a magnet. It appeared as though the magnetic directing power of the crystal had some peculiar relation to the position of its

optic axis ; so that, independently of the magnetic property of the substance of the crystal, if the crystal were positively optical, it possessed the power of placing its optic axis parallel with the line which joined the poles of the magnet, while optically negative crystals tried to arrange their axes at right angles to this line. This supposition is disproved by the excellent investigation of Tyndall and Knoblauch, who showed that exceptions to the above law are furnished by all classes of crystals, and proved that the action, instead of being independent of the magnetic nature of the mass, was completely reversed where, in isomorphous crystals, a magnetic constituent was substituted for a diamagnetic one. Rejecting the various new forces assumed, Tyndall and Knoblauch referred the observed phenomena to the modification of the magnetic force by structure, and they imitated the effects exactly by means of substances whose structure had been modified by compression. In a later investigation Tyndall demonstrated the fundamental principle on which those phenomena depend, showing that the *entire mass* of a magnetic body is most strongly attracted when the attracting force acts parallel to the line of compression ; and that a diamagnetic substance is most strongly repelled when the repulsion acts along the same line. Hence when such a body is freely suspended in the magnetic field, the line of compression must set axially or equatorially, according as the mass is magnetic or diamagnetic. Faraday was the first to establish a differential action of this kind in the case of bismuth ; Tyndall extended it to several magnetic and diamagnetic crystals, and showed that it was not confined to them, but was a general property of matter. It was also proved that for a fixed distance the attraction of a magnetic sphere, and the repulsion of a diamagnetic sphere, followed precisely the same law, both being exactly proportioned to the square of the exciting current.

The phenomena of diamagnetism naturally suggest the inquiry, whether the repulsion exerted by a magnetic pole on diamagnetic bodies is a force distinct from that of magnetism as exerted upon iron and other bodies of the magnetic class ; or whether, on the other hand, the magnetic and diamagnetic conditions of matter are merely relative, so that all bodies are magnetic in different degrees, and the apparent repulsion of a diamagnetic body, such as bismuth, is merely the result of its being attracted by the magnet less than the particles of the surrounding medium, just as a balloon recedes from the earth because its weight is less than that of an equal bulk of the surrounding air. It is easy to show that the same body may appear magnetic or diamagnetic, according to the medium in which it is placed. Ferrous sulphate is a magnetic substance, and water is diamagnetic : hence it is possible, by varying the strength of an aqueous solution of this salt, to make it either magnetic, indifferent, or diamagnetic, when suspended in air. Again, a tube containing a solution of ferrous sulphate suspended horizontally within a jar also filled with a solution of the same salt, and placed between the poles of two powerful electro-magnets, will place itself axially or

equatorially, according as the solution contained in it is stronger or weaker than that in the jar. In the same manner, then, we may conceive that bismuth places itself equatorially between two magnetic poles, because it is less magnetic than the surrounding air. But the diamagnetism of bismuth and other bodies of the same class shows itself in a vacuum as well as in air: hence, if diamagnetism is not to be regarded as a distinct force, we must suppose that the *ether* is also magnetic, and occupies in the magnetic scale the place intermediate between magnetic and diamagnetic bodies.

That a body suspended in a medium of greater magnetic susceptibility than itself will recede from a magnetic pole in its neighbourhood, in consequence of the greater force with which the particles of the medium are impelled towards the magnet, is so obvious a consequence of mechanical laws, that we can scarcely avoid attributing the movements of diamagnetic bodies to the cause just mentioned; at least, when the body is suspended in air or other magnetic gas. There is, however, some difficulty in reconciling the above-described phenomena of compressed and crystallised bodies with this view; and, moreover, Tyndall has shown, by a method which we cannot here describe,\* that diamagnetic bodies possess opposite poles, analogous to those of magnetic bodies, each of these poles being attracted by one pole of a magnet, and repelled by the other. This polarity shows decidedly that the properties of diamagnetic bodies cannot be wholly due to the differential action above mentioned; for if they were, every part of a diamagnetic body would be repelled by either pole of a magnet. Diamagnetism must therefore, for the present at least, be regarded as a force distinct from magnetism.

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\* Phil. Trans, 1855 and 1856; see also Watts's Dictionary of Chemistry, vol. iii. p. 776.

**ELECTRICITY.**

WHEN glass, amber, or sealing-wax is rubbed with a dry cloth, it acquires the power of attracting light bodies, as feathers, dust, or bits of paper; this is the result of a new and peculiar condition of the body rubbed, called electrical excitation.

If a light downy feather be suspended by a thread of white silk, and a dry glass tube, excited by rubbing, be presented to it, the feather will be strongly attracted to the tube, adhere to its surface for a few seconds, and then fall off. If the tube be now excited anew, and presented to the feather, the latter will be strongly repelled.

The same experiment may be repeated with shellac or resin; the feather in its ordinary state will be drawn towards the excited body, and, after touching, again driven from it with a certain degree of force.

Now, let the feather be brought into contact with the excited glass, so as to be repelled by that substance, and let a piece of excited sealing-wax be presented to it: a degree of attraction will be observed far exceeding that exhibited when the feather is in its ordinary state. Or, again, let the feather be made repulsive for sealing-wax, and then the excited glass be presented: strong attraction will ensue.

The reader will at once see the perfect parallelism between the effects described and some of the phenomena of magnetism, the electrical excitement having a twofold nature, like the opposite polarities of the magnet. A body to which one kind of excitement has been communicated is attracted by another body in the opposite state, and repelled by one in the same state; the excited glass and resin being to each other as the north and south poles of a pair of magnetised bars.

To distinguish these two different forms of excitement, terms are employed which, although originating in some measure in theoretical views of the nature of the electrical disturbance, may be understood by the student as purely arbitrary and distinctive: it is customary to call the electricity manifested by glass rubbed with silk *positive* or *vitreous*, and that developed in the case of shellac, and bodies of the same class rubbed with flannel, *negative* or *resinous*. The kind of electricity depends in some measure upon the nature of the surface and the quality of the rubber; smooth and perfectly clean glass, rubbed with silk, becomes positive, but when ground or roughened by sand or emery, it acquires, under the same circumstances, a negative charge. Glass dried over a gas flame and rubbed with wool is generally also negative; and when dried over a fire of wood-charcoal it remains positive.

The repulsion shown by bodies in the same electrical state is taken advantage of to construct instruments for indicating electrical

excitement and pointing out its kind. Two balls of elder pith hung by threads or very fine metal wires, serve this purpose in many cases: they open out when excited, in virtue of their mutual repulsion, and show by the degrees of divergence the extent to which the excitement has been carried. A pair of gold leaves suspended from

Fig. 57.

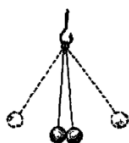
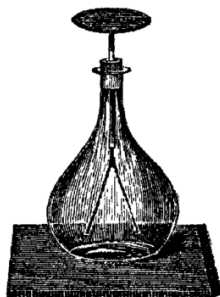


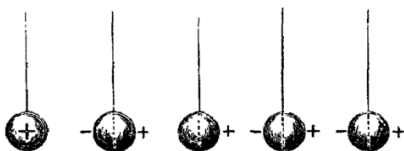
Fig. 58.



a metal rod having a brass plate on its upper end constitute a much more delicate arrangement, and one of great value in all electrical investigations. The rod should be covered with a thick coating of shellac, and must be fastened by means of a cork, air-tight, into a glass flask previously dried by warming. These instruments are called electroscopes: when excited by the communication of a known kind of electricity, they show, by an increased or diminished divergence, the state of an electrified body brought into their neighbourhood (fig. 58).

One kind of electricity can no more be developed without the other than one kind of magnetism: the rubber and the body rubbed always assume opposite states, and the positive condition on the surface of a mass of matter is invariably accompanied by a negative state in all surrounding bodies.

Fig. 59.



The induction of magnetism in soft iron has its exact counterpart in electricity: a body already electrified disturbs or polarises the particles of all surrounding substances in the same manner and

according to the same law, inducing a state opposite to its own in the nearer portions, and a similar state in the more remote parts. A series of globes suspended by silk threads, in the manner represented in fig. 59, will each become electric by induction when a charged body is brought near the end of the series, like so many pieces of iron in the vicinity of a magnet, the positive half of each globe looking in one and the same direction, and the negative half in the opposite one. The positive and negative signs are intended to represent the opposite states.

The intensity of the induced electrical disturbance diminishes with the distance from the charged body; if this be removed or discharged, all the effects cease at once.

So far, the greatest resemblance may be traced between these two sets of phenomena; but here it seems in great measure to cease. The magnetic polarity of a piece of steel can awaken polarity in a second piece in contact with it by the act of induction, and in so doing loses nothing whatever of its power: this is an effect completely different from the apparent transfer or discharge of electricity constantly witnessed, which in the air and in liquids often gives rise to the appearance of a bright spark of fire. Indeed ordinary magnetic effects comprise two groups of phenomena only, those, namely, of attraction and repulsion, and those of induction. But in electricity, in addition to phenomena very closely resembling these, we have the effect of *discharge*, to which there is nothing analogous in magnetism, and which takes place in an instant when any electrified body is put in communication with the earth by any one of the class of substances called conductors of electricity, all signs of electrical disturbance then ceasing.

These conductors of electricity, which thus permit discharge to take place through their mass, are contrasted with another class of substances called non-conductors or insulators. The difference, however, is only one of degree, not of kind; the very best conductors offer a certain resistance to the electrical discharge, and the best insulators permit it to a small extent. The metals are by far the best conductors; glass, silk, shellac, and dry gas, or vapour of any sort, the very worst; and between these there are bodies of all degrees of conducting power. Water is a moderately good conductor, and consequently the deposition of a film of moisture on the glass pillars and handles of electric apparatus greatly impairs their insulating power. The best way of preventing this inconvenience is to varnish such supports with an alcoholic solution of shellac. Supports made of this substance, or of baked wood, do not readily condense the moisture of the air.

In good conductors of sufficient size electrical discharges take place silently and without disturbance. But if the charge be very intense, and the conductor very small, or imperfect from its nature, it is often destroyed with violence. When a break is made in a conductor employed in effecting the discharge of a highly excited body, disruptive or spark-discharge takes place across the interven-

ing air, provided the ends of the conductor be not too distant. The electrical spark itself presents many points of interest in the modifications to which it is liable.

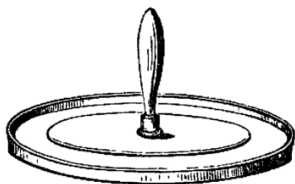
The time of transit of the electrical wave through a chain of good conducting bodies of great length is so minute as to be altogether inappreciable to ordinary means of observation, but the experiments of Wheatstone and of Foucault have shown that this velocity is measurable, and that in the passage of electricity through a copper wire, it far surpasses that of light.

Electrical excitation is manifested only upon the surfaces of conductors, or those portions directed towards other objects capable of assuming the opposite state. An insulated ball charged with positive electricity, and placed in the centre of the room, is maintained in that state by the inductive action of the walls of the apartment, which immediately become negatively electrified; in the interior of the ball there is absolutely no electricity to be found, although it may be constructed of open metal gauze, with meshes half an inch wide. Even on the surface the distribution of electrical force is not always the same; it depends upon the figure of the body itself, and its position with regard to surrounding objects. The polarity is always highest in the projecting extremities of the same conducting mass, and greatest of all when these are attenuated to points; in which case the inequality becomes so great that discharge takes place to the air, and the excited condition cannot be maintained.

By the aid of these principles, the construction and use of the common electrical machine, and other pieces of apparatus of great utility, will become intelligible.

The electrophorus (fig. 60) is a simple and ingenious instrument, enabling us to obtain by inductive action, an unlimited number of charges from one single charge. It consists of a round tray or dish about twelve inches in diameter, half an inch deep, and filled with melted shellac, the surface of which is rendered as even as possible. A brass disc, with rounded edge, of about nine inches diameter, is also provided, and fitted with an insulating handle. The resinous plate is excited by striking it with a dry, warm piece of fur or flannel, whereby it becomes charged with negative electricity. If the cover be then placed upon it, the positive electricity is drawn to the under surface of the metal nearest to the negatively charged resinous cake, while the negative electricity is repelled to the upper surface of the cover; on touching the cover with the finger, the negative electricity passes away to the earth, while an additional quantity of positive electricity is drawn into the plate; and if the

Fig. 60.



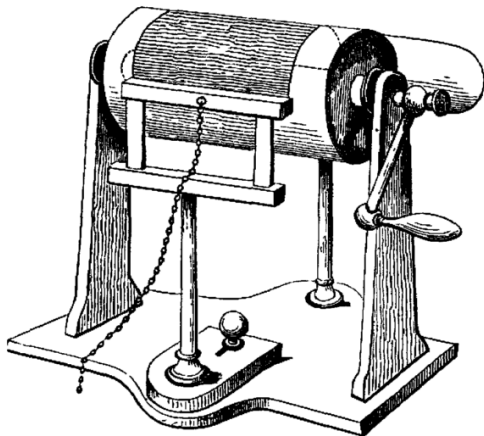


finger be removed and the cover then lifted by its insulating handle, it will be found so strongly charged by induction with positive electricity as to give a bright spark; and as the resin is not discharged by the cover, which merely touches it at a few points, sparks may be drawn as often as may be wished.

For obtaining electricity in larger quantity, Electrical Machines are used, consisting of a glass cylinder or plate, which is made to revolve and press against a leather cushion.

In the *Cylinder Machine* (fig. 61), the cushion is made to press by a spring against one side of the cylinder, while a large metallic con-

Fig. 61.



ductor armed with a number of points next the glass, occupies the other: both cushion and conductor are insulated by glass supports, and to the upper edge of the former a piece of silk is attached long enough to reach half round the cylinder. Upon the cushion is spread a quantity of soft amalgam of tin, zinc, and mercury,\* mixed up with a little grease: this substance is found by experience to excite glass most powerfully. The cylinder, as it turns, becomes charged by friction against the rubber, and as quickly discharged by the row of points attached to the great conductor; and as the latter is also completely insulated, its surface speedily acquires a charge of positive electricity, which may be communicated by contact to other

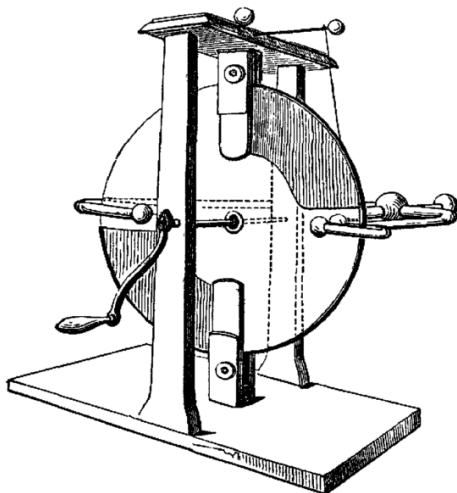
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\* 1 part tin, 1 zinc, and 6 mercury. An amalgam of permanent softness and great efficacy is obtained by mixing 65 parts mercury, 24 tin, and 11 zinc. It is better applied to silk than to leather.

insulated bodies. The maximum effect is produced when the rubber is connected by a chain or wire with the earth. If negative electricity be wanted, the rubber must be insulated and the conductor discharged.

Another form of the electrical machine consists of a circular plate of glass (fig. 62) moving upon an axis, and provided with two pairs

Fig. 62.

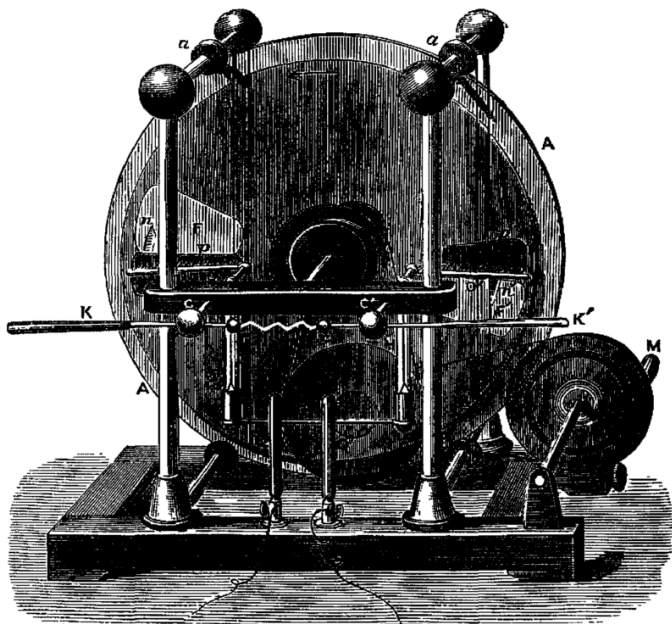


of cushions or rubbers, attached to the upper and lower parts of the wooden frame, and covered with amalgam, the plate moving between them with considerable friction. An insulated conductor, armed as before with points, discharges the plate as it turns, the rubber being at the same time connected with the ground by the woodwork of the machine, or by a strip of metal. This form of machine is preferred in all cases where considerable power is required; but for demonstrating the principles of the science, as in lecture-experiments, the cylinder machine is by far the more convenient form, as it affords the means of obtaining a positive or negative charge at pleasure.

A machine of much greater power than either of the preceding is that of Holtz, in which the development of the charge takes place much in the same manner as in the electrophorus. This machine, which may indeed be regarded as a revolving electrophorus, consists of two glass plates (fig. 63), one AA, fixed by means of four wooden rollers resting on glass axes and glass feet, while the other, BB, two inches less in diameter, turns on a horizontal glass axis passing

through the centre of the fixed plate, and is set in motion by a winch *M*, and a series of pulleys which give it a rotation of 12 to 15

Fig. 63.



turns in a second. The fixed plate *A* is perforated at the extremities of a diameter by two large apertures or windows, *F*, *F'*.

Two pieces of varnished paper, *p*, *p'*, are fastened to the back of the fixed plate below the window on the left, and above that on the right. These pieces of paper, or *armatures*, are furnished with narrow tongues which project forward through the windows towards the movable plate, and nearly touch it with their blunt points. The plate must rotate in the direction opposite to that in which the tongues point, as shown by the arrow. In front of the movable plate *B*, and at the height of the armatures, are two brass combs, *o*, *o'*, supported by two conductors of the same metal *C*, *C'*. At the front ends of these conductors are two brass knobs, through which pass two brass rods terminated by smaller knobs *r*, *r'*, and provided with wooden handles, *K*, *K'*. These rods, besides moving with gentle friction in the knobs, can also be turned so as to be more or less approached and inclined to each other.

To work the machine, the knobs  $r, r'$  are brought into contact, and a small initial charge is given by an electrophorus or a rubbed glass rod to one of the armatures. The plate B is then quickly rotated, and it is found that, after a few turns, the exertion required to keep up the rotation increases greatly; at the same time pale blue brushes of light are seen to issue from the points of the combs, and if one of the rods K, K' be then drawn back, a torrent of brilliant sparks will dart between the brass knobs. The mode of action is as follows.

Suppose a small positive charge to be given to the left armature  $p$ ; this charge acts inductively through the glass plates upon the brass comb, repelling positive electricity and attracting negative electricity, which is discharged by the points upon the front side of the movable plate, while the repelled positive electricity passes through the brass rods and balls, and is discharged through the right comb upon the front side of the plate. Here it acts inductively on the armature  $p'$ , attracting negative electricity into the part opposite to itself and repelling positive electricity into its farthest part, viz., into the tongue, which being bluntly pointed, slowly discharges a positive charge upon the back of the movable plate. If now the plate be turned in the direction indicated by the arrow, the positive charge on its back comes over from its right to its left side, and when it gets opposite the combs, it increases the inductive effect of the positive charge already existing on the armature  $p$ , and therefore repels more positive electricity through the brass rods and knobs into the right comb. Meanwhile the negative charge induced in the right armature has in its turn attracted positive electricity into the right comb, which has been discharged by the points upon the front of the moving plate, and has repelled negative electricity through the brass rods and knobs in the opposite direction, discharging it through the left comb upon the front of the same plate, there to neutralise the positive charge which is being conveyed over from the right on the front of the plate. These actions result in causing the upper half of the moving plate to be positively electrified on both sides, and the lower half negatively. The charges on the front serve, as they are carried round, to neutralise the electricities discharged from the points of the combs, while the charges on the back, induced in the neighbourhood of each of the armatures, serve, when the motion of the plate carries them round, to increase the inductive influence of the charge of the other armature. Hence a very small initial charge is speedily raised to a maximum, the limit being reached when the electrification of the armatures becomes so great that the loss of electricity at their surface equals the gain by convection and induction.

The power of the machine may be increased by suspending to the conductors C, C', two condensers or small Leyden jars H, H' (see page 117), having their external coatings connected by a conductor G. One of these jars H becomes charged with + electricity on the inside and - on the outside, the other H', - on the inside

and  $+$  on the outside. Becoming charged by the machine, and being discharged simultaneously with it by the knobs  $r, r'$ , they strengthen the spark and increase its length.

The current of the machine is utilised by placing on the frame two brass uprights  $Q, Q'$ , with binding screws in which are copper wires, then by means of the handles  $K, K'$ , inclining the rods which support the knobs  $r, r'$ , so as to bring them in contact with the uprights. The current being then directed by the wires, a battery can be quickly charged, water decomposed, a galvanometer deflected, and various other effects produced, as with the voltaic battery.

Very powerful electric excitation is produced by a jet of steam issuing at high pressure from a pipe provided with a nozzle of wood or metal, the effect being due, not to the pure steam itself, but to the friction of particles of condensed water against the inner surface of the exit-pipe. The steam is usually positive if the nozzle be constructed of wood or clean metal, but the slightest trace of oily matter produces a change of sign. The intensity of the charge increases, *ceteris paribus*, with the elastic force of the steam. A steam-boiler mounted on glass legs and provided with an exit-pipe, as above described, forms an electrical machine of very great power.

*Condensers and Accumulators.*—When the conductor of an electric machine is charged with electricity, it acts indirectly on all the surrounding conductors, in such a manner as to accumulate at their surfaces the electricity contrary to its own, producing the greatest effect on the conductor which is nearest to it and is in the best connection with the ground, whereby the electricity of the same kind as that of the machine may pass away. As the inducing electricity attracts the induced electricity of an opposite kind, so, on the other hand, is the former attracted by the latter. Hence, the electricity which the conductor receives from the machine must especially accumulate at that spot to which another good conductor of electricity is opposed. If a metal disc is in connection with the conductor of a machine, and if another similar disc, in good connection with the earth, is placed opposite to it, we have an arrangement by which tolerably large and good conducting surfaces can be brought close to one another, the positive condition of the first disc, as well as the negative condition of the other, being thereby increased in a very considerable degree. In this case, however, the limit is very soon reached, because the intervening air easily permits spark-discharge to take place through its substance; but with a solid insulating body, as glass or lac, this discharge takes place much less readily, even when the plate of insulating matter is very thin. It is on this principle that instruments for the *accumulation* of electricity depend, among which the Leyden jar is the most important.

A thin glass jar is coated on both sides with tinfoil, care being taken to leave several inches of the upper part uncovered (fig. 64); a wire, terminating in a metallic knob, communicates with the internal coating. When the outside of the jar is connected with

the earth, and the knob put in contact with the conductor of the machine, the inner and outer surfaces of the glass become respectively positive and negative, until a very great degree of intensity has been attained. On completing the connection between the two coatings by a metallic wire or rod, discharge occurs in the form of a very bright spark, accompanied by a loud snap : and if the human body be interposed in the circuit, the peculiar and disagreeable sensation of the electric shock is felt at the moment of its completion.

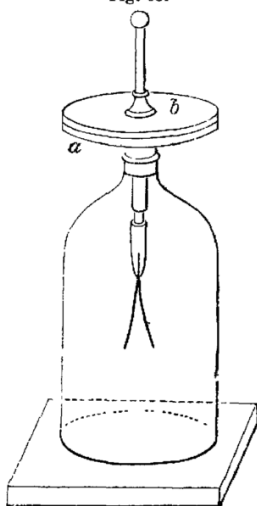
By enlarging the dimensions of the jar, or by connecting together a number of such jars in such a manner that all may be charged and discharged simultaneously, the power of the apparatus may be greatly augmented. By the discharge of such a combination—called an electric battery, thin wires of metal may be fused and dissipated ; pieces of wood may be shattered ; many combustible substances set on fire ; and all the well-known effects of lightning exhibited upon a small scale. The circumstances of a thunderstorm indeed exactly resemble those of the charge and discharge of a coated plate or jar, the cloud and the earth representing the two coatings, and the intervening air the conducting body, or *dielectric*. The polarities of the opposed surfaces and of the insulating medium between them become raised by mutual induction, until violent disruptive discharge takes place through the air itself, or through any other bodies which may happen to be in the interval. When these are capable of conducting freely, the discharge is silent and harmless ; but in other cases it often proves highly destructive. These dangerous effects may in a great measure be obviated by the use of lightning-rods attached to buildings. The masts of ships may be guarded in like manner by metal conductors. Sir W. Snow Harris devised a very ingenious plan for the purpose, which has been adopted, with complete success, in the Navy.

*Condensing Electroscopes.*—The delicacy of the gold-leaf electroscope may be greatly increased by laying on its cover a circular brass plate well polished ; and on this another brass plate provided with an insulating handle and covered on its lower surface with copal varnish to prevent metallic contact between the two.

Fig. 64.



Fig. 65.



Suppose now the lower plate  $a$  (fig. 65) to be connected with a source of electricity (say  $+E$ ) not strong enough to produce a sensible divergence in the gold leaves, and the upper plate to be touched with the finger. The  $+E$  in  $a$  will produce a charge of  $-E$  on the lower surface of  $b$ , and drive the  $+E$  of that plate into the ground. The  $-E$  will then draw more  $+E$  into the lower plate  $a$ , and this again will draw more  $+E$  into the lower surface of  $b$ , and so the action will go on till a quantity of  $+E$  will be accumulated on  $a$ , much larger than that which it would otherwise have acquired; and if the plate  $a$  be then disconnected with the source of electricity, and  $b$  be lifted up, the  $+E$  accumulated on  $a$  will diffuse itself equally through the electroscope, causing the gold leaves to diverge. In this way decided indications of electric action may often be obtained from sources too feeble to produce a deflection of the electroscope by direct communication. The apparatus is therefore called a *condenser*.

In all these forms of condensing and accumulating apparatus, the attainable degree of electric charge increases as the metallic surfaces are brought nearer together, or in other words, as the intervening thickness of air, glass or other insulator becomes less. It must not however be supposed that this intervening substance acts merely as an insulator; on the contrary, this medium itself becomes charged to a degree which for a given thickness is different for each particular substance; and this relative power or capability of receiving an electric charge is called the *Specific Inductive Capacity*, or better *Specific Inductivity*: the insulating medium itself is called a *Dielectric*.

The specific inductivity of different dielectrics was first observed in 1775 by Cavendish, afterwards, in 1837, by Faraday, who obtained the following values, the inductivity of air being taken for unity: sulphur, 2.26; shellac, 2.0; glass, 1.76 or more. Later observations by Gordon have given the following numbers:—

Air . . . . .	1	Gutta-percha . . . . .	2.462
Paraffin (solid) . . . . .	1.944	Sulphur . . . . .	2.58
Caoutchouc . . . . .	2.220 to 2.497	Shellac . . . . .	2.74
Ebonite . . . . .	2.284	Glass . . . . .	3.013 to 3.258

A comparison of these numbers with those of Faraday shows that the determination of specific inductivity is attended with considerable uncertainty. For liquids Gordon finds: turpentine, 2.16; petroleum, 2.03 to 2.07; carbon disulphide, 1.81. All gases appear to have the same or nearly the same specific inductivity as atmospheric air.

The consideration of these differences of inductivity in various media, together with that of other phenomena, has led to the idea that electric charge and discharge consist, not, as was formerly supposed, in the actual transference of a substance—the so-called “electric fluid”—from one conductor to another across the air or other intervening insulator, but rather that electric charge con-

sists in a state of strain or tension of the particles of an elastic medium pervading all space and interposed between the particles of bodies—in fact of the “ether,” the vibrations of which give rise to the phenomena of light (p. 82)\*,—and that *discharge* is effected by the relief or removal of that strain. The particles of bodies being surrounded by the ether, this strain is communicated to them, and its removal in the discharge occasions a more or less violent disturbance of those particles, sometimes resulting, in the case of solid dielectrics, in a rupture of the substance. Thus, when a Leyden jar is very highly charged, discharge sometimes takes place between the coatings through the substance of the glass, which is thereby cracked or perforated. The loud snap which accompanies the spark in air, and the rupture of wood and fusion of metallic wires by a powerful electric discharge, likewise indicate a violent disturbance of the particles of that medium.

*Various Sources of Electricity.*—As electric excitation is capable of producing disturbance in the particles of ponderable matter, so conversely is any disturbance in these particles, produced by mechanical or other causes, attended with development of electric power. The production of electricity by friction has been already considered. Other sources of electric excitation are :—

1. *Pressure.*—Solid bodies become oppositely electrified when simply pressed together (without friction) and afterwards separated. A slice of cork becomes positively electrified when pressed against caoutchouc, orange-peel, coal, amber, zinc, copper, silver, and heated Iceland spar; negative with dry animal substances, heavy spar, gypsum, fluorspar, and non-heated Iceland spar. Two pieces of the same substance do not become electrical by pressure unless one of them is heated, in which case the hotter becomes negative, the colder positive.

2. *Cleavage and Separation of Surfaces.*—When two laminæ of a crystal of mica are torn asunder, they appear oppositely electrified, and the separation is attended with a flash of light. Similar separation of electricities is exhibited in the cleavage of calcspar, fluorspar, and some other crystals, also when a playing card is torn into its two sheets, the separation being attended with sparks visible in the dark. Two sheets of paper stick fast together when rubbed with india-rubber, and on being pulled asunder appear strongly charged with opposite electricities. When melted sulphur is poured into a short conical glass vessel and a glass rod is inserted into it before it solidifies, no electricity is apparent so long as the sulphur remains in the glass, but on lifting it out by the glass handle, the sulphur appears positively, the inner surface of the glass negatively electrified. Similar effects are exhibited by chocolate and glacial phosphoric acid when left to solidify in glass vessels.

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\* See “Elementary Lessons in Electricity and Magnetism,” by Silvanus Thompson. London, 1882, p. 61.



3. *Vibration*.—The vibrations set up in a metal rod coated at one end with resin or sulphur, and made to slide through an insulated metallic ring, give rise to a separation of the two electricities at the surface of contact of the metal and the non-conducting body.

4. *Heat*.—(a.) In Crystals.—Pyro-electricity. Many hemihedral crystals,\* while being heated or cooled, exhibit contrary electricities at their opposite ends, those extremities or poles which are positive while the temperature of the crystal is rising, becoming negative as it falls. The effect depends entirely on change of temperature, no crystal exhibiting any electric polarity while its temperature remains constant. This effect was first observed in tourmaline, which has long been known to possess, when heated, the power of attracting light bodies. It has since been observed in boracite, zinc silicate or electric calamine, cane-sugar and Brazilian topaz, and in a lower degree by many other hemihedral crystals.

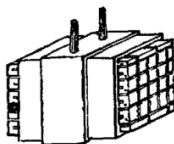
(b.) In Metals. Thermo-electricity.—When two pieces of different metals are joined together at each end, by soldering or otherwise, and one of the joints is more heated than the other, an electric current is set up, the strength of which appears to be in direct proportion to the difference of temperature between the two joints, while its direction depends upon the nature of the two metals. The metals may be arranged in a thermo-electric series, such that each metal when connected with another will transmit positive electricity across the heated junction to those on its right hand, and negative to those on its left,—and *vice versa* when the junction is cooled. The following is the thermo-electric series, according to Becquerel :—*Bismuth, platinum, lead, tin, gold, silver, copper, zinc, iron, antimony*. For a given difference of temperature, the current will be stronger the farther the two metals are separated in the series, the strongest combination being formed of bismuth and antimony ; but the current is always very feeble.

Greater power may however be obtained by combining a number of thermo-electric pairs into a *battery, chain or pile*, a number of bars of bismuth and antimony or of platinum and iron being alternately soldered together (figs. 66, 67) and heat applied to the first, third, fifth, &c., points of junction, while the alternate ones are kept cold.

Fig. 66.



Fig. 67.



\* See the chapter on Crystallography.

With this arrangement, the thermo-electric current produces, not only deflection of the magnetic needle, but also chemical decomposition and heating effects, so that even when one of the conducting wires of the battery is cooled by immersion in ice, the point of junction of that wire situated without the ice becomes sensibly warmed. Melloni's *Thermo-multiplier* or *Thermoscope* is a pile formed in this manner of bars of bismuth and antimony, and connected with a galvanometer. It is capable of indicating very slight changes of temperature, and has rendered excellent service in researches on radiant heat.

5. *Magnetism*.—When a magnet is moved, or when magnetism is either developed or destroyed, in the neighbourhood of a closed conducting circuit, a current of electricity is produced in that circuit, its direction depending upon the position of the magnetic poles relatively to the circuit (see page 126).

6. *Contact of Dissimilar Metals*.—If a bar made of two metals—zinc and copper for example—be held in the hand, and one end of it—say the zinc end—be made to touch the *lower* plate of a condensing electroscope (p. 117), the upper plate being at the same time touched with the hand, and if the hand be then removed, and the upper plate lifted up by its glass handle, the leaves of the electroscope will diverge with positive electricity, as may be shown by holding over the instrument a glass rod or tube excited by silk, which will increase the divergence. If a similar experiment be made with the copper end of the bar touching the lower plate of the condenser, the leaves will diverge with negative electricity. Here then it appears that a separation of the electricities has taken place, in consequence of mere contact of the zinc and copper, without any heating or cooling at the point of junction.

By experiments thus conducted it is found that the metals may be arranged in the following series, each metal becoming positive by contact with those which follow, negative with those which precede it.

+ Sodium.	Copper.
Magnesium.	Silver.
Zinc.	Gold.
Lead.	Platinum.
Tin.	- Carbon (graphite).
Iron.	

These results were first obtained by Volta, who attributed them solely to the contact of dissimilar metals. By other experimenters, however, this view has been disputed, especially by Faraday and De La Rive, who attributed the results obtained to the chemical action of water and acid vapours in the air on the zinc or other more oxidisable metal in the couple; and indeed their experiments led them to the conclusion that the more these causes of chemical action were got rid of, the smaller was the electrical effect produced and that with sufficient care it might be reduced almost to nothing

Hence they inferred that electricity is not developed by mere contact of dissimilar metals. Later experiments, however, made by Sir W. Thomson and by Messrs. Ayrton and Perry, with great care and extremely delicate apparatus, tend to confirm Volta's view, and to show that contact of metals does give rise to electric charge even when all extraneous causes of disturbance are removed. Moreover we may perhaps go so far as to say that, for the establishment of this point, no special experiments were required, the development of electric charge by the contact of dissimilar metals being sufficiently established by the phenomena of the thermo-electric circuit (p. 120), which in fact show that the development of electricity by such contact takes place *at all temperatures*, and in various degrees of intensity according to the temperature.

7. *Chemical Action.* Voltaic Electricity.—When two solid conducting bodies, generally metals, are immersed in a liquid which acts upon them unequally, the electric equilibrium is disturbed, the one acquiring the positive condition, and the other the negative. Thus, pieces of zinc and platinum put into dilute sulphuric acid, constitute an arrangement capable of generating electrical force: the zinc, which is the metal attacked, becomes negative; the platinum, which remains unaltered, assumes the positive condition; and on making a metallic communication in any way between the two plates, discharge ensues, evidenced by various electric phenomena, just as when the two surfaces of a coated and charged jar are put into connection. No sooner, however, has this occurred, than the disturbance is repeated; and as these successive charges and discharges take place through the fluid and metals with inconceivable rapidity, the result is an apparently continuous action, to which the term *electrical current* is given.

It is necessary, however, to guard against the idea, which this term naturally suggests, of an actual bodily transfer of something through the substance of the conductors, like water through a pipe: the real nature of these phenomena is not precisely known, but it probably consists in a movement or disturbance communicated from particle to particle throughout the whole chain. The word *current* is nevertheless convenient, and consecrated by long use; and with this caution, the very dangerous error of applying figurative language to describe an effect, and then seeking the nature of the effect from the common meaning of words, may be avoided.

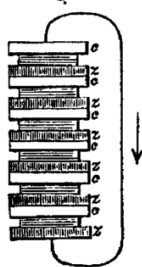
The original cause of the electric disturbance under the circumstances here considered is still a matter of dispute. Some authorities, following Volta, consider that the electricity is developed by the contact of the dissimilar metals, which, as already observed, is a real cause of electric excitement; others again ascribe it solely to the chemical action between one of the metals and the liquid. In favour of the contact theory it may be urged that when pure zinc or zinc amalgamated with mercury is used, no action whatever is observable so long as the two metals remain unconnected, but as soon as they are made to touch, or are connected by a wire,

hydrogen begins to escape at the surface of the copper or platinum plate, and the entire circuit exhibits signs of electric action. On the other side it is alleged that so slight a force as that which has been shown to be developed by the mere contact of metals can scarcely give rise to the powerful effects which are produced by the arrangements now under consideration; moreover that the electric activity of the circuit appears to be always in proportion to the intensity of the chemical action between the metal and the liquid, and that the direction of the current produced depends altogether upon the manner in which that action takes place. Thus when a plate of iron and a plate of copper connected together are immersed in dilute sulphuric acid, the current of positive electricity is directed from the iron through the liquid to the copper, and back again through the connecting wire to the iron; but if the plates be taken out, washed with water, and then immersed in a solution of an alkaline sulphide, the current will take the contrary direction, viz., from the copper through the liquid to the iron,—that is to say, in both cases its direction is from the metal chemically acted upon, through the liquid to the unattacked metal. This question cannot with advantage be further discussed at present, but its consideration will be resumed in a subsequent part of the work, after the subject of chemical action in general has been more fully treated.

The intensity of the electrical excitement developed by a single pair of metals and a liquid is too feeble to be detected excepting by a delicate condensing electroscope; but, by arranging a number of such alternations in a connected series, in such a manner that the direction of the current shall be the same in each, the intensity may be very greatly exalted. The two instruments invented by Volta, called the pile and crown of cups, depend upon this principle.

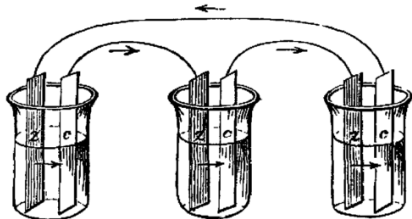
To construct a Voltaic pile, we lay upon a plate of zinc a piece of cloth, rather smaller than itself, steeped in dilute acid, or any liquid capable of exerting chemical action upon the zinc; upon this is placed a plate of copper, silver, or platinum; then a second piece of zinc, another cloth, and a plate of inactive metal, until a pile of about twenty alternations has been built up. If the two terminal plates be now touched with wet hands, the sensation of the electrical shock will be experienced; but, unlike the momentary effect produced by the discharge of a jar, the sensation can be repeated at will by repeating the contact, and with a pile of one hundred such pairs, excited by dilute acid, it will be nearly insupportable. When such a pile is insulated, the two extremities exhibit strong positive and negative states; and when connection is made between them by wires armed with points of hard charcoal or plumbago, the discharge takes place in the form of a bright enduring spark or stream of fire.

Fig. 68.



The second form of apparatus, or "crown of cups," is precisely the same in principle, although different in appearance. A number of cups or glasses are arranged in a row or circle, each containing a piece of active and a piece of inactive metal, and a portion of exciting

Fig. 69.



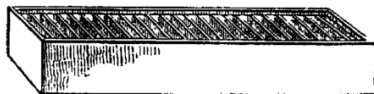
liquid—zinc, copper, and dilute sulphuric acid, for example. The copper of the first cup is connected with the zinc of the second, the copper of the second with the zinc of the third, and so to the end of the series. On establishing a communication between the first and last plates by means of a wire, or otherwise, discharge takes place as before.

When any such electrical arrangement consists merely of a single pair of conductors and an interposed liquid, it is called a "simple circuit;" when two or more alternations are concerned, the term "compound circuit" is applied: they are called also, indifferently, Voltaic batteries.

In every form of such apparatus, however complex it may appear, the direction of the current may be easily understood and remembered. When both ends of the series are insulated, the zinc end exhibits negative, the copper or platinum end positive electricity: consequently, when the two extremities or poles are joined by a conducting wire and a complete circuit formed, the current of positive electricity proceeds *without* the battery from the platinum or copper to the zinc, and *within* the battery, from the zinc to the copper or platinum, as indicated by the arrows—just as in the common electrical machine, when the positive conductor and the rubber are joined by a wire, the positive current proceeds from the conductor through the wire to the rubber, and thence along the surface of the glass cylinder or plate to the conductor again.

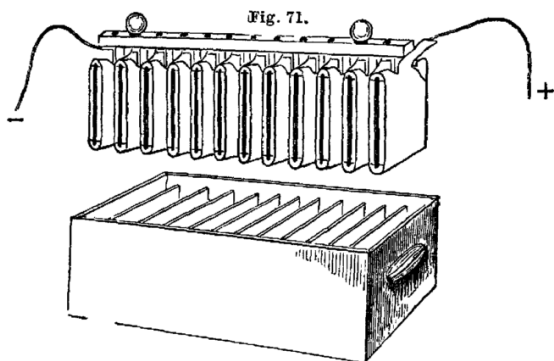
In the modification of Volta's original pile, made by Cruikshank,

Fig 70.



the zinc and copper plates are soldered together, and cemented water-tight into a mahogany trough, which thus becomes divided into a series of cells or compartments capable of receiving the exciting liquid. This apparatus (fig. 70) is well fitted to exhibit effects of *tension*, to act upon the electroscope, and give shocks: hence its advantageous employment in the application of electricity to medicine.

A form of battery more convenient for many purposes is that contrived by Wollaston (fig. 71). In this the copper is made completely to encircle the zinc plate, except at the edges, the two metals being kept apart by pieces of cork or wood. Each zinc is soldered to the preceding copper, and the whole screwed to a bar of dry



mahogany, so that the plates can be lifted into or out of the acid, which is contained in an earthenware trough, divided into separate cells. The liquid consists of a mixture of 100 parts water,  $2\frac{1}{4}$  parts oil of vitriol, and two parts commercial nitric acid, all by measure. A number of such batteries are easily connected together by strips of sheet copper, and admit of being put into action with great ease.

In this and other older forms of the voltaic battery, however, the power rapidly decreases, so that, after a short time, scarcely the tenth part of the original action remains. This loss of power depends partly on the gradual change of the sulphuric acid into zinc sulphate, but still more on other causes, which, together with the more modern forms of the battery contrived to obviate them, will be more easily understood at a subsequent part of the work, when we come to consider the nature and effects of electro-chemical decomposition.

The term "galvanism," sometimes applied to this branch of electrical science, is used in honour of Galvani, of Bologna, who, in 1790, observed that convulsions could be produced in the limbs of a

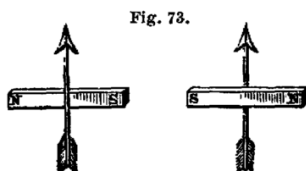
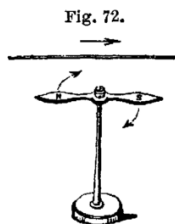
dead frog when certain metals were made to touch the nerve and muscle at the same moment. It was Volta, however, who pointed out the electrical origin of these motions; and his name is very properly associated with the invaluable instrument his genius gave to science.

#### ELECTRO-MAGNETISM.

Although the fact that electricity is capable, under certain circumstances, both of inducing and of destroying magnetism, has long been known from the effects of lightning on the compass-needle and upon small steel articles, as knives and forks, to which polarity has suddenly been given by the stroke, it was not until 1819 that the laws of these phenomena were discovered by Oersted, of Copenhagen, and shortly afterwards fully developed by Ampère.

If a wire conveying an electrical current be brought near a magnetic needle, the latter will immediately alter its position, and assume a new one as nearly perpendicular to the wire as the mode of suspension and the magnetism of the earth will permit. When the wire, for example, is placed directly over the needle, and parallel to its length, while the current it carries travels from north to south, the needle is deflected from its ordinary direction, and the north pole driven to the eastward. When the current is reversed, the same pole deviates to an equal amount towards the west. Placing the wire below the needle instead of above produces the same effect as reversing the current.

The direction which the needle will assume when placed in any particular position relatively to the conducting wire may be determined by the following rule:—*Let the current be supposed to pass through a watch from the face to the back: the motion of the north pole will be in the direction of the hands.* Or, let the observer imagine himself swimming in the direction of the current with his face towards the needle: the north pole of the needle will then be deflected towards his left hand.



If reference is often required, a little piece of apparatus (fig. 73) may be used, consisting of a piece of pasteboard, or other suitable material, cut into the form of an arrow for indicating the current, crossed by a magnet having its poles marked, and arranged in the

true position with respect to the current. The direction of the latter in the wire of the galvanoscope can at once be known by placing the representative magnet in the direction assumed by the needle itself.

When the needle is subjected to the action of two currents in opposite directions, the one above and the other below, they will obviously concur in their effects. The same thing happens when the wire carrying the current is bent upon itself, and the needle placed between the two portions as in fig. 74; and since every time the bending is repeated, a fresh portion of the current is made to act in the same manner upon the needle, it is easy to see how a current, too feeble to produce any effect when a simple straight wire is employed, may be made by this contrivance to exhibit a powerful action on the magnet. It is on this principle that instruments called *galvanometers*, *galvanoscopes*, or *multipliers*, are constructed; they serve not only to indicate the existence of electrical currents, but to show, by the effects upon the needle, the direction in which they are moving.

The delicacy of the instrument may be immensely increased by the use of a very long coil of wire, and by the addition of a second needle. The two needles are of equal size, and magnetised as nearly as possible to the same extent; they are then immovably fixed together parallel, and with their poles opposed, and hung by a long fibre of untwisted silk, with the lower needle in the coil, and the upper one above it. The advantage thus gained is twofold; the system is *astatic*, unaffected, or nearly so, by the magnetism of the earth; and the needles, being both acted upon in the same manner by the current, are urged with much greater force than one alone would be, all the actions of every part of the coil being strictly con-

Fig. 74.

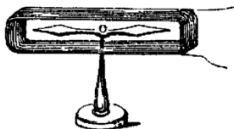
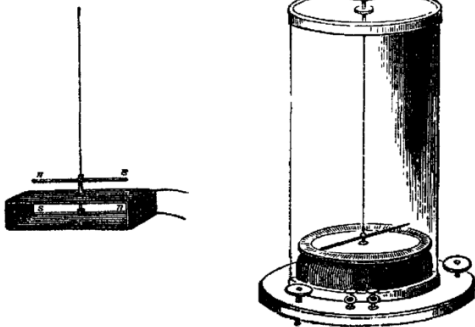


Fig. 75.





current. A divided circle is placed below the upper needle, by which the angular motion can be measured, and the whole is enclosed in a glass case, to shield the needles from the agitation of the air. The arrangement is shown in fig. 75.

The direction of the current which deflects the galvanometer-needle in a particular way is easily determined by the rules given on page 126, when we know the direction in which the wire is coiled round the frame. For this purpose it is necessary to distinguish between *right-handed* and *left-handed* coils or helices. Suppose the wire to be coiled round a cylinder beginning at the left hand; then if the turns in front of the cylinder proceed from below upwards, as in fig. 76, the coil is left-handed; if, on the contrary, they proceed in front from above downwards, as in fig. 77, the coil is right-handed.

Fig. 76.

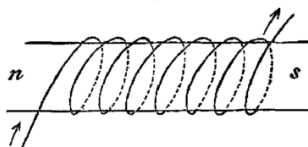
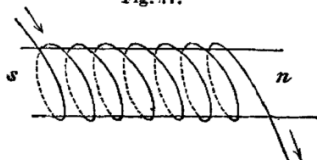


Fig. 77.



A magnetic needle placed with its centre in the axis of such a coil turns its north or south pole towards the end of the coil at which the current enters, according as the coil is left or right-handed.

The direction given to the needle is the same whether the coil is elongated, as in the above figures, or compressed, as in the galvanometer. As, however, in the galvanometer, when complete, it is not easy to see whether the coil is left or right-handed, it is best to determine by experiment, once for all, the direction taken by the needle when the current enters at one particular end of the coil.

*Action of the Magnet on the Electric Current.*—The action between the current and the magnet is mutual, so that if the conductor conveying the current is free to move, it is deflected in the direction opposite to that which the magnet takes under its influence; in short, if the magnet and conducting wire are both free to move, they place themselves at right angles to each other, the magnet moving in the manner indicated at page 126, and the wire in the opposite direction.

The action of the magnet on the current may be shown by means of Ampère's apparatus (fig. 78). On holding a bar-magnet below the rectangular wire, and parallel to its lower horizontal arm, the wire turns round and places itself at right angles to the magnet, the position of equilibrium being determined by the rule just alluded to.

A simpler apparatus for this purpose is De la Rive's floating battery, which consists of a pair of zinc and copper plates, contained

in a wide glass tube attached to a cork float, and connected together by a rectangular wire, or a flat coil, or elongated helix of covered wire (fig. 79).

Fig. 78.

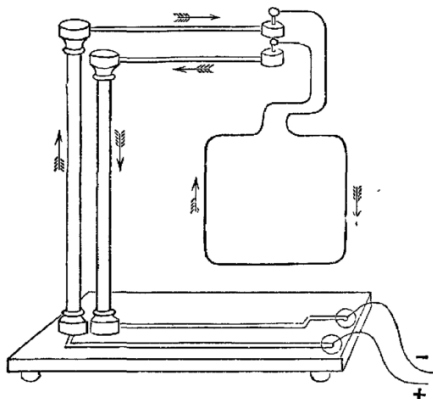
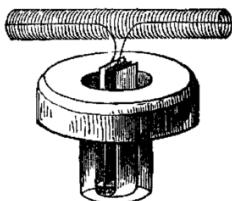


Fig. 79.



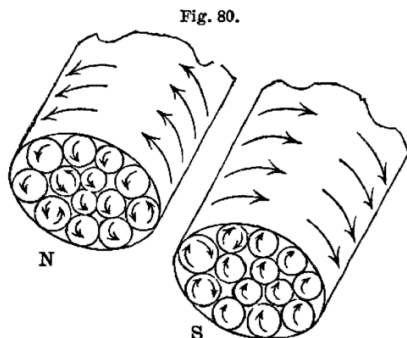
A movable electric current is deflected by the earth's magnetism in the same way as by an ordinary magnet. Thus the rectangular wire of Ampère's apparatus, or of a floating battery, when left to itself, will take up a position at right angles to the magnetic meridian; and remembering that the north magnetic pole of the earth is analogous to the south pole of an ordinary magnet, it is easy to see that, in the position of stable equilibrium, the direction of the current will be from east to west in the lower horizontal branch, and from below upwards on the western vertical side. If the wire has the form of a long helix, it will, in like manner, place itself with the turns of the helix at right angles to the magnetic meridian, and therefore with its axis parallel to that meridian, the ends pointing north and south, just like those of an ordinary magnetic needle. If the helix is left-handed, the end connected with the copper plate of the battery will point to the north.

*Mutual Action of Electric Currents.*—If a conducting wire connecting the poles of a voltaic battery be brought near the movable wire of Ampère's apparatus, or the wire of a floating battery, the movable wire will be attracted or repelled according to the relative direction of the two currents, the general law of the action being that, *electric currents moving in parallel lines attract one another if they move in the same direction, and repel one another if they move in opposite directions.* From this it is easy to see that if

a helix connecting the two poles of a battery be brought near the helix of a floating battery, and if the two helices are similar,—that is, both right or both left-handed,—their similar ends, *i.e.*, those by which the current enters or leaves the helix, will repel each other, and their dissimilar ends will attract each other, and consequently the movable helix will place itself parallel to the fixed helix with its poles or ends in the contrary direction to those of the fixed helix. In short, the two helices will act on one another exactly like two bar magnets; and if an ordinary bar magnet be substituted for the fixed helix, the effect will still be the same, each end of the movable helix being attracted by one pole of the magnet, and repelled by the other.

This striking resemblance between the mutual action of electric currents and that of magnets has led to the idea, suggested and developed by Ampère, that magnetism is actually produced by electric currents circulating round the molecules of a magnet all in the same direction. These currents may be supposed to pre-exist in all magnetic bodies, even before the development of magnetic polarity, but to be disposed without regularity, so that they neutralise each other. Magnetisation is the process by which these molecular currents are made to move in one direction, those situated at the surface yielding, as their resultant, a finite current circulating round the magnet, while the currents in the interior are neutralised by those in the next external layer, the contiguous portions of which

move in a direction opposite to their own. The resultant action of all these molecular currents is equivalent to that of a number of currents circulating round the magnet in planes perpendicular to its axis (fig. 80); and from what has been said about the mutual action of magnets and helices traversed by electric currents, it is easy to see that, on looking along the axis of a magnet with its *south* pole towards the observer, the current



moves in the direction of the hands of a watch, that is, upwards on the left side, and downwards on the right.

#### ELECTRO-DYNAMIC INDUCTION.

1. *Magnetisation by the Current.*—When an electro-current is passed through a wire placed at right angles to a bar of iron or steel the bar acquires magnetic polarity, temporary in the case of

soft iron, permanent in the case of hard iron or steel, the position of the poles being determined by the direction of the current, according to the laws already explained.

This effect is prodigiously increased by coiling the conducting wire in a helix round the bar. A piece of soft iron worked into the form of a horseshoe (fig. 81), and surrounded by a coil of wire covered with silk or cotton for the purpose of insulation, furnishes an excellent illustration of the inductive energy of the current in this respect: when the ends of the wire are put into communication with a small voltaic battery of a single pair of plates, the iron instantly becomes so highly magnetic as to be capable of sustaining a very heavy weight.

2. *Induction of Electric Currents by the action of Magnets, and of other Electric Currents.*—If the two extremities of the coil of the electro-magnet above described be connected with a galvanoscope, and the iron magnetised by the application of a permanent steel horse-shoe magnet to the ends of the bar, a momentary current will be developed in the wire, and pointed out by the movement of the needle. It lasts but a single instant, the needle, after a few oscillations, returning to a state of rest. On removing the magnet, whereby the polarity of the iron is at once destroyed, a second current or wave will become apparent, but in

Fig. 81.

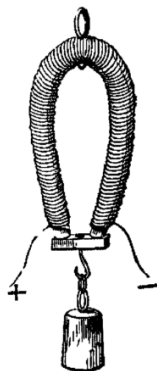
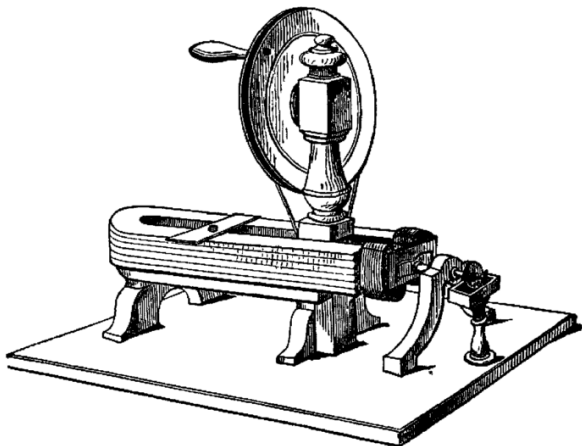


Fig. 82.



the opposite direction to that of the first. By employing a very powerful steel magnet, surrounding its iron keeper or armature with a very long coil of wire, and then making the armature itself rotate in front of the faces of the magnet, so that its induced polarity shall be rapidly reversed, magneto-electric currents may be produced, of such intensity as to give bright sparks and most powerful shocks, and exhibit all the phenomena of voltaic electricity. Fig. 82 represents a powerful arrangement of this kind.

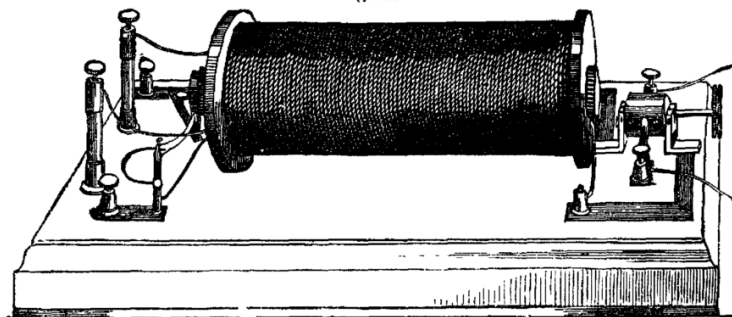
By using electro-magnets instead of permanent steel magnets, and rotating an armature between them by steam-power, very powerful machines, called "Dynamo-electric machines," are constructed, which are now extensively used for electric lighting and other applications of electricity. The light is produced by passing a strong current between two cylinders of hard carbon, whereby an arch of light of almost unendurable brilliancy is obtained—this is called the "Arc Light"—or by sending a current through a thin filament of carbon (prepared by heating cotton-thread or bamboo-fibre in a close vessel) placed in a glass vessel from which the air is exhausted by a Sprengel pump (p. 27), so that the carbon is made to glow without burning. This is called the "Incandescent Light." These, however, are matters the further discussion of which would be foreign to the object of this work. For information respecting them see Silvanus Thompson's "Elementary Lessons on Electricity and Magnetism," pp. 362—378.

*Induction-coils.*—When two covered wires are twisted together or laid side by side for some distance, and a current is transmitted through the one, a momentary electrical wave will be induced in the other in the reverse direction; and on breaking connection with the battery, a second single wave will become evident by the aid of the galvanoscope, in the same direction as that of the primary current. The same effects are produced if the wires are twisted, one above the other, round a hollow wooden cylinder, and the intensity of the induced currents may be enormously increased by inserting within the cylinder a bar of soft iron, or better, a bundle of iron wires, whereby magnetic and electric induction are made to cooperate. The more frequently contact is alternately made and broken, the greater will be the number of induced currents that follow each other, and the more powerful, within certain limits, will be the action. Instruments thus constructed are called induction-coils. The contact-breaker or commutator is usually made self-acting, an ordinary form consisting of a piece of thin steel which makes contact with a platinum point, and is drawn back by the attraction of the iron core on the passing of the current, and so makes and breaks circuit by vibrating backwards and forwards.

The most powerful form of induction-coil is that of Ruhmkorff (fig. 83), the cylinder of which is a foot or 18 inches long, and is surrounded by a coil of thick wire to convey the inducing current, and a much longer coil of thin wire for the development of the induced currents. The wires are insulated with resin. The direction

of the battery-current can be changed at pleasure by a commutator, by which the battery-poles are connected through the ends of the

Fig. 83.



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axis of a small ivory or ebonite cylinder to two cheeks of brass, which can be turned so as to place them either way in contact with two vertical springs, which are joined to the ends of the primary coil. This apparatus forms a very powerful electric machine, capable of yielding electricity of very high intensity, giving long sparks, and shocks of unendurable force. It is capable also of firing gunpowder and other inflammable materials, and has been used for exploding charges of gunpowder and other inflammable substances for mining, engineering, and military purposes. It is also frequently used in the chemical laboratory for firing gaseous mixtures.