

VII. *On the Viscosity of Gases at High Exhaustions.*

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Received December 26, 1880,—Read February 17, 1881.

[PLATES 55–58.]

CONTENTS.

| | Par. | | Par. |
|---|------|--|------|
| Introduction | 635 | Repulsive force of radiation in carbonic an- | |
| The viscosity torsion apparatus | 638 | hydride | 680 |
| McLEOD's gauge for high vacua..... | 642 | Observations on the spectrum of carbonic | |
| Process of observation. Logarithmic decre- | | anhydride | 681 |
| ment | 645 | Viscosity of carbonic oxide gas | 682 |
| Precautions necessary before exhausting to | | Plotted curves of the viscosity of carbonic | |
| high points | 650 | oxide | 684 |
| Note on the viscosity of glass..... | 652 | Repulsive force of radiation in carbonic oxide | 685 |
| Viscosity of air..... | 653 | Observations on the spectrum of carbonic | |
| Repulsive force of radiation in air.. .. | 655 | oxide | 686 |
| Calculating the zero-point for the swing pro- | | Viscosity of hydrogen gas | 687 |
| duced by radiation | 656 | Plotted curves of the viscosity of hydrogen.. | 690 |
| Plotted curves of the viscosity of air..... | 658 | Repulsive force of radiation in hydrogen.... | 691 |
| Mean free paths of the molecules | 661 | Proportion between the viscosities of air and | |
| Resistance of air to the passage of an induc- | | hydrogen | 692 |
| tion spark | 663 | Influence of foreign gas on the viscosity of | |
| Viscosity of oxygen gas | 666 | hydrogen | 695 |
| Plotted curves of the viscosity of oxygen.... | 668 | Observations on the spectrum of hydrogen .. | 698 |
| Repulsive force of radiation in oxygen..... | 670 | Influence of aqueous vapour on the viscosity | |
| Viscosity of nitrogen gas..... | 671 | of air | 699 |
| Comparison of the air curves with those of | | Plotted curve of the viscosity of moist air .. | 701 |
| oxygen and nitrogen | 674 | Explanation of the action of aqueous vapour | 702 |
| Observations on the spectrum of nitrogen ... | 675 | Viscosity of kerosoline vapour | 705 |
| Repulsive force of radiation in nitrogen | 676 | Discussion of results | 706 |
| Viscosity of carbonic anhydride gas | 677 | The ultra-gaseous state of matter | 710 |
| Plotted curves of the viscosity of carbonic | | | |
| anhydride | 679 | | |

Note on the Reduction of Mr. CROOKES's Experiments on the Decrement of the Arc of Vibration of a Mica Plate oscillating within a Bulb containing more or less Rarefied Gas. By Professor G. G. STOKES, Sec. R.S..... page 435

MDCCLXXXI.

3 E



INTRODUCTION.

635.* By the viscosity or internal friction of a gas, is meant the resistance it offers to the gliding of one portion over another. In a paper read before the British Association in 1859, MAXWELL† gives the following explanation of the internal friction of gases :—

“Particles having the mean velocity of translation belonging to one layer of the gas, pass out of it into another layer having a different velocity of translation, and by striking against the particles of the second layer exert upon it a tangential force which constitutes the internal friction of the gas. The whole friction between two portions of gas separated by a plane surface, depends upon the total action between all the layers on the one side of that surface upon all the layers on the other side.”

The research here recorded commenced with experiments instituted to discriminate between the friction of the pivot supporting the fly of a radiometer and the viscosity of the residual gas. In the paper just quoted, MAXWELL presented the remarkable result that on theoretical grounds the coefficient of friction, or the viscosity, should be independent of the density of the gas, although at the same time he states that the only experiments he had met with on the subject did not seem to confirm his views.

An elaborate series of experiments were undertaken by MAXWELL to test so remarkable a consequence of a mathematical theory ; and in 1866, in the Bakerian lecture for that year,‡ he published the results under the title of “The Viscosity or Internal Friction of Air and other Gases.” He found the coefficient of friction in air to be practically constant for pressures between 30 inches and 0·5 inch ; in fact, numbers calculated on the hypothesis that the viscosity was independent of the density agreed very well with the observed values.

The apparatus used by MAXWELL was not of a character to admit of experiments with much lower pressures than 0·5 inch.

636. In the *Philosophical Magazine* for July, 1875, is a translation of a paper by MM. KUNDT and WARBURG, “On Friction and Heat Conduction in Rarefied Gases,” in which the laws theoretically discovered by MAXWELL were examined at higher exhaustions.

MAXWELL’S theory, that the viscosity of a gas is independent of the density, presupposes that the mean length of path of the molecules between their collisions is very small compared with the dimensions of the apparatus ; but inasmuch as the mean length of path increases directly with the expansion, whilst the distance between the molecules only increases with the cube root of the expansion, it is not difficult with the SPRENGEL pump to produce an exhaustion in which the mean free path is

* The research embodied in this paper is an outcome of work recorded in my various papers “On Repulsion resulting from Radiation,” Parts 1 to 6, “On the Illumination of Lines of Molecular Pressure, and the Trajectory of Molecules,” and “Contributions to Molecular Physics in High Vacua.” The paragraphs are therefore numbered in continuation of the last-named paper.

† *Phil. Mag.*, 4th ser., vol. xix., p. 31.

‡ *Phil. Trans.*, 1866, Part I., p. 249.

measured by inches, and even feet,* and at exhaustions of this degree it is probable that MAXWELL'S law would not hold good.

MM. KUNDT and WARBURG found that for pressures between 760 millims. and 1.5 millim. the coefficient of viscosity of air was constant, but at higher vacua it fell off. They, however, give no measurements of the amount of exhaustion obtained, simply speaking of Vacua I., II., III., and IV.

637. As I have had considerable experience in working in high vacua, and am accustomed to measure with accuracy exhaustions up to the ten-millionth of an atmosphere and even higher, it has been proposed that I should continue these experiments on viscosity of gases at high exhaustions, at the same time obtaining as many other data and measurements as the apparatus can be made to afford.

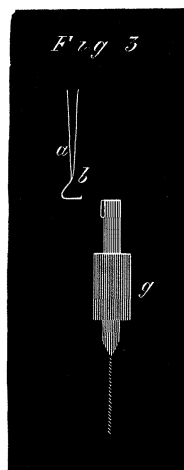
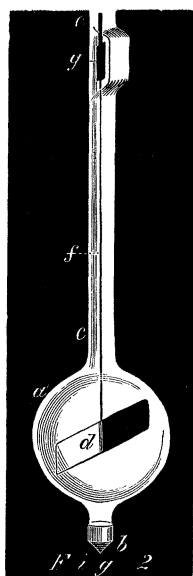
My experiments were commenced early in 1876, and have been continued to the present time. In November, 1876, I gave a note to the Royal Society on some preliminary results. Several different forms of apparatus have since been used one after the other, with improvements and complexities suggested by experience or rendered possible by the extra skill acquired in manipulation. The earlier observations are now of little value, but the time spent in their prosecution was not thrown away, as out of those experiments has grown the very complicated apparatus now finally adopted. I will therefore not occupy time in describing earlier forms of apparatus, but will proceed at once to the one finally adopted.

THE VISCOSITY TORSION APPARATUS.

638. Plate 55, fig. 1, shows the general construction, fig. 2 (p. 390) an enlarged view of the torsion beam, &c., the same references applying to either figure. *a* is a glass bulb, blown with a point at the lower end, *b*, and sealed on to a long narrow glass tube *c c*. In the bulb is suspended a plate of mica, *d*, by means of a fine fibre of glass, 26 inches long, which is sealed to the top of the glass tube *c c*, and hangs vertically along its axis. The plate of mica is ignited and lamp-blackened over one-half, as shown. The tube *c c* is pointed at the upper end, *e*; the points *e* and *b* are 46 inches apart, and are accurately in the prolongation of the axis of the tube. Sockets are firmly fixed at *b* and *e* to a solid support, so that when the tube and bulb are clamped between them

* Thus, supposing the mean free path of the molecules of air at the ordinary pressure is the $\frac{1}{100000}$ th of a millimetre, at an exhaustion of the ten-thousandth of an atmosphere, the mean free path will be 1 millim. At one-millionth of an atmosphere the mean free path will be 10 centims., and at an exhaustion of one hundred millionth—by no means a difficult point to attain with present appliances—the mean free path will be over 30 feet. This rarefaction corresponds to that of the atmosphere at a height above the earth of a little more than 90 miles, assuming that its density decreases in geometrical progression as its height increases in arithmetical progression, and neglecting the small corrections for diminished gravity and temperature. As the height above the earth increases, the length of the mean free path of the molecules of air rapidly approaches to planetary distances; at about 200 miles height the mean free path is 10,000,000 miles, whilst between 80 and 90 miles higher the rarity is such that the mean free path would extend from here to Sirius.

they are only able to move around the vertical axis. The upper socket is lined with cork and is pressed down by a spring. The lower socket is a steel cup, and a brass point is attached to the bottom of the bulb. This device is adopted because in the earlier apparatus the friction of glass against cork generated electricity, which interfered with the free movement of the torsion fibre. The glass fibre being only connected with the tube at *e*, rotating the tube on its axis communicates torsion to the fibre and sets the mica plate swinging on the same axis without giving it any pendulous movement. The mica plate *d* is not fastened direct to the suspending fibre, but through the intermediary of a twisted aluminium wire, *f*, about 12 inches long, with a mirror of platinised glass attached to it. The tube opposite the mirror is blown into the form of a thin cylinder of about double its original diameter, and the centre of curvature is made to coincide as closely as possible with the fibre, or centre of motion of the mirror. There are three reasons why the mirror is kept some distance above the mica plate, instead of being close to it:—1. There is much less distortion of the reflected index of light when passing through a cylinder than through a bulb. 2. The light falling on the mirror from the lamp might diffuse sufficiently to produce repulsion of the black surface. 3. The torsion bulb and plate can be completely packed in wool or immersed in water, to diminish variation of temperature.



The total weight of mica plate, mirror, and aluminium support is 5.69 grains. These are purposely made very light, and to render the effects of viscosity more apparent the glass fibre is as fine as it can be drawn consistent with safety. The diameter of the fibre is about 0.001 inch. The attachment of so thin a fibre at each end of the apparatus requires extreme care, or it will snap off at a joint when torsion is applied. The following plan has been found to answer best:—The fibre being

drawn from a piece of glass rod about 0·5 millim. in diameter is left attached at one end to the rod from which it was drawn, the other end being broken off to the right length. This broken end of the fine torsion fibre is inserted into the wider end of a fine, somewhat conical, glass tube *a*, fig. 3 (which must not be much larger than is necessary to allow the fibre to enter freely). A small flame applied at *b* melts the glass tube and fibre together. The lower part of the glass tube is bent, as shown in the figure, to allow the aluminium support for the mirror, *g*, and mica plate to be hooked on to it. The small piece of glass rod remaining attached to the upper part of the torsion fibre is then passed through, so as to project above the top of the glass tube *c c*, fig. 1, which has previously been drawn out to the right size, and held in position by an aluminium spring. When the instrument is held in a vertical position, the final adjustment can be made by moving the projecting end of the rod; the top aperture is then sealed, and the piece of rod carrying the fibre is likewise sealed in at the same time. The viscosity apparatus is connected to the pump by the arm *h*, and tubes *i*, *j*, *k*, *l*, *m*, *n*, and *o*. A flexible glass spiral is introduced at *i*, so as to allow the apparatus to rotate on the pivots *b*, *e*, and at the same time to be connected to the pump altogether with sealed glass joints. Another arm at *p*, working between metal stops, limits the rotation to the small angle only which is necessary. A spring keeps the arm pressed close to one of these stops.

639. The bulb of the viscosity apparatus is entirely enclosed in a box, packed with cotton-wool; in this box is a tube, *q*, opposite the black half of the mica plate, so that a candle at *r* will shine on it and produce a deflection. This tube is closed at each end with glass plates to keep out air-currents, and in front is a shutter to cut off or turn on the light of the candle, as desired. The position of the candle flame and its distance from the plate are always kept identical in the following manner:—A small lens, fixed at some distance from the candle, forms an image of the flame on a white screen, and it is so adjusted that when the flame shines direct on to the mica plate its image exactly overlaps a mark on the screen. A second system of lens and screen is fixed at right angles to the first, and thus the position of the flame can in a few moments be adjusted. To avoid unnecessary complication this arrangement is not shown in the figure.

In viscosity experiments when the deflection produced by the candle-flame is not measured—as, for instance, in exhaustions below one millimetre—the whole apparatus is immersed in a large copper vessel full of water surrounded by a double row of Winchester quart bottles, also full of water, and the spaces between them and the copper vessel are filled with cotton-wool. A cardboard case surrounds and covers the whole. A thermometer reading to tenths of a degree C. is in the water close to the bulb. This device, which I have long adopted, and found extremely useful, prevents the temperature of the apparatus during a long day's work from varying more than the tenth of a degree.

The torsional movement given to the mica plate, by the light of the candle shining

on it or by the rotation of the bulb and tube on its axis by the movement of the arm p between the stops, is measured by a beam of light from the lamp s , reflected from the mirror g to the graduated scale t .

640. The angle through which the apparatus is rotated is small. The distance of the scale from the mirror is 4 feet, and the amplitude of swing carries the line of light between 100 and 200 divisions of the scale. 100 divisions of the scale = 62 millims., so that the deflection of the line of light is never more than about 10 degrees. As the scale forms the tangent of a circle a small correction is required for the scale-reading. Let S be the scale-reading; R the radius or distance of mirror (centre of motion) from the scale; S' what would be the scale-reading if it were curved in a circle of radius, R ; then—

$$S' = S \left\{ 1 - \frac{1}{3} \left(\frac{S}{R} \right)^2 + \frac{1}{5} \left(\frac{S}{R} \right)^4 - \&c. \right\}$$

The ratio of S to R is, however, so small as to make $\frac{1}{5} \frac{S^5}{R^4}$ and the succeeding terms insensible. The correction therefore is simply—

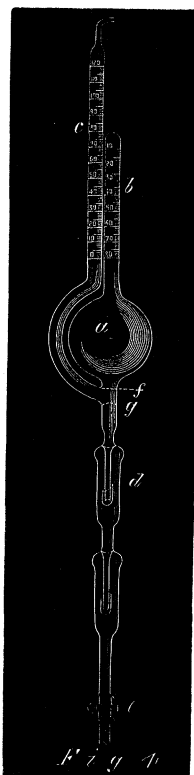
$$-\frac{1}{3} \frac{S^3}{R^2}.$$

Except in special cases this correction was not applied, for unless the amplitudes were very long the amount to be deducted was less than the average error of each observation.

641. Air is introduced into the apparatus through a very fine glass tube drawn out to almost the fineness of a hair, and projecting from the connecting tubes at A . A momentary contact with a spirit flame seals up the point, and when air is to be admitted the tip of the tube is broken off, and the air slowly enters, passing through the drying-tubes, m , before it reaches the apparatus.

Gases other than atmospheric air are introduced into the apparatus through the tubes u and v . The tubes u and v are only open when actually in use, and when the apparatus has been filled with a pure gas and exhausted a sufficient number of times, they are sealed off at u or at v , as the case may be, and when required are again attached for another gas. This prevents the apparatus when actually at work having any mercury joints, blown joints being used in all other cases. At m is a system of six tubes, for the double object of drying the gas and of keeping mercury vapour out of the torsion bulb. The tube nearest the pump contains pure sulphur which has been fused, then finely powdered, and introduced while warm into the tube. The next tube contains finely-divided copper reduced by hydrogen from the oxide, and the four remaining tubes contain phosphoric anhydride. The phosphoric anhydride must be tightly packed in the tubes, so as to force the air to pass through, and not merely over it, or the last traces of water will not be removed. The sulphur tube stops mercury vapour, and in the course of some months becomes darkened at the end nearest

the pump. A tube packed with gold-leaf was used in the early experiments, but as it did not entirely stop the passage of mercury vapour, it was discarded in favour of sulphur, which, whilst not quite perfect, answers fairly well. As it was thought possible that sulphur vapour might be given off, the copper tube was interposed: at first a tube of oxide of lead was used for this purpose, but copper seems to answer better. At *w* a similar system of six tubes is interposed in the path of the entering gas. These will be further alluded to when the experiments with gases other than air are described. The tube *o* is the phosphoric anhydride reservoir belonging to the pump; *x* is the McLEOD measuring apparatus; *y* is a small radiometer, having a standard candle at a fixed distance from it; *k* is a spectrum tube with capillary bore furnished with aluminium poles; *l* is a resistance tube having aluminium terminals with ends 4 millims. apart (663, 664, 665). At *z* a series of spectrum tubes is attached, so that in course of experiment one tube can be sealed off at any particular pressure for further reference.



642. The pump employed has already been described (355). The measuring apparatus is similar to that described by Professor McLEOD* before the Physical Society, June 13th, 1874. As it contains several improvements shown by experience to be necessary when working at very high vacua, a detailed description may be useful. The instrument shown in fig. 4 consists essentially of a globe, *a*, a volume tube, *b*,

* Philosophical Magazine, vol. xlviii., p. 110, August, 1874.

and a pressure tube, *c*. The upper part of *c* communicates with the exhaust arm of the pump, and the tube *e* communicates with the upper mercury reservoir by means of a screw tap. The pressure and volume tubes are from the same piece, accurately of the same internal diameter, and are graduated in millimetres. The divisions in the pressure tube are numbered from below upwards, and extend to some height above the volume tube; and the divisions of the volume tube are numbered from above downwards, the lowest division, 80, being on a level with the 0 of the pressure tube. The proportion between the contents of the volume tube and the globe was ascertained in the manner directed by Professor McLEOD, and it was found that the globe, &c., from the point *f* had 111·8 times the capacity of the volume tube down to the 80th division. The action of the instrument is as follows:—Before the viscosity apparatus on the pump is exhausted the tap *e* is closed, in order to exclude mercury from the measuring instrument, the upper part being in communication with the pump and viscosity apparatus. The pump is now set to work, and the exhaustion in the globe keeps pace with that in the apparatus, there being free passage from one to the other. When the exhaustion is good it is advisable carefully to unscrew the tap *e* a little, to allow mercury to fill the two air-traps, *d d*, and rise in the tube as far as *g*. The tap *e* is then tightly closed, and the exhaustion continued. When it is desired to make a measurement of the pressure, the tap *e* is opened, and the mercury allowed slowly to rise. When it reaches the point *f* it cuts off communication between the globe *a* and the rest of the apparatus. The globe *a* now contains an accurately measured volume of highly rarefied gas of exactly the same exhaustion as that in the viscosity apparatus. The mercury continuing to rise, part ascends the pressure tube *c*, and part fills the globe, compressing the rarefied gas, until, when it reaches the lowest division, 80, of the volume tube, the gas is condensed to 111·8 times its original volume. I now quote from Professor McLEOD's description:—"Ultimately the whole of the gas in the globe is condensed into the volume tube; and its tension is then found by measuring the difference of level between the columns of mercury in the volume and pressure tubes. On dividing this difference by the ratio between the capacities of the globe and volume tube, a number is obtained which is approximately the original pressure of the gas: this number must now be added to the difference between the columns, since it is obvious that the column in the pressure tube is depressed by the tension of the gas in the remaining part of the apparatus: on dividing this new number once more by the ratio between the volumes, the exact original tension is found. . . . The relations existing between the contents of the other divisions of the volume tube and the total contents of the globe were determined by measuring the tensions of the same quantity of gas when compressed into the different volumes." In this way a table has been constructed giving the value of each millimetre in the volume tube from 1 to 80. I generally make several readings at different heights of the volume tube, and take the mean. The McLEOD gauge will not show the presence of mercury vapour. I have, however, entirely failed to detect the presence of mercury vapour at

any great distance from the mercury in the pump; and the tube packed with gold-leaf, which I formerly interposed between the pump and the apparatus, showed no trace of bleaching, and exerted no appreciable effect one way or the other on the results. The chief improvements in this instrument over Professor McLEOD's original design consist in the entire absence of joints; the tubes and bulbs are all soldered together in one piece; and the two air-traps, *d d*, which obviate the inconvenience at first encountered, of traces of air rising with the mercury and spoiling the vacuum in *a*. The globe *a* is also larger in proportion to the volume tube, and this tube is longer. These improvements are mere details, and in no way detract from the great beauty and merit of Professor McLEOD's valuable instrument.

643. In the case of a body moving quickly through air of ordinary density the "work" is almost wholly represented by a wake of eddies left behind. The smaller the velocity of the body and the rarer the gas the less is the work spent in producing eddies compared with the work spent in *directly* overcoming friction. In these experiments the motion is so slow that even at full pressure the effect of eddies is well nigh or altogether invisible, and it is utterly insensible at even moderate exhaustions. The molar *vis viva* is rapidly converted by internal friction or viscosity into molecular *vis viva* (heat, thermometric—not radiant), and this is too rapidly dissipated to interfere with the observations.

644. Before taking an observation the arm *p* (fig. 1) remains pressed against one of the stops. In this position the index line of light stands in the middle of the scale at 0, the divisions counting on each side from 0 upwards. The arm is then moved over to the other stop, and in a few seconds allowed to return to its original position by the action of the spring. This movement rotates the viscosity apparatus through a small angle, and sets the mica plate vibrating, the reflected line of light traversing from one side of the scale to the other in arcs of diminishing amplitude till it finally settles down once more at *zero*. The amplitude depends on the manipulation, a slower turn being more effective in producing motion than a very quick one. Even if the arm *p* is turned at the same rate, in experiments with different degrees of exhaustion there will be no simple relation between the arc swung through and the viscosity. What is simply related to the viscosity is the logarithmic decrement of the arc of oscillation. The logarithmic decrement will of course involve the viscosity of the glass; but glass is so nearly perfectly elastic, and the fibre is so very thin, that this will be practically insensible except at the very highest exhaustions (652).

The observer watching the moving index of light records the scale number reached at the extremity of each arc. The numbers being alternately on one and the other side of zero are added two by two together, to get the value of each oscillation. The logarithms of these values are then found, and their differences taken; the mean of these differences is the logarithmic decrement per swing of the arc of oscillation.

The following illustration will render this plain. The observation is supposed to be taken with air at the pressure of 760 millims. :—

| Readings. | Arcs. | Log. arcs. | Diff. |
|-----------|----------------|------------|--------|
| 113·0 | | | |
| | 200·0 | 2·3010 | |
| 87·0 | | | 0·1124 |
| | 154·4 | 2·1886 | |
| 67·4 | | | 0·1123 |
| | 119·2 | 2·0763 | |
| 51·8 | | | 0·1116 |
| | 92·0 | 1·9647 | |
| 40·2 | | | 0·1134 |
| | 71·0 | 1·8513 | |
| 30·8 | | | 0·1125 |
| | 54·8 | 1·7388 | |
| 24·0 | | | 0·1125 |
| | 42·3 | 1·6263 | |
| 18·3 | | | |
| | Mean | | 0·1124 |

The logarithmic decrement for the oscillation comes out 0·1124.

645. The actual number obtained varies with each apparatus. The number does not represent an absolute, but a relative, quantity, to be compared only with the results obtained with the same apparatus at other pressures or with other gases.

The first swing is seldom found to be in regular series. It is better to start an oscillation greater than is intended to be observed, so that the oscillation shall be fairly established when beginning to preserve the scale-readings.

On comparing a large number of observations there appears to be a tendency for the logarithmic decrements to come alternately greater and less than the mean. It is quite conceivable that this may be real, and not accidental, as the body is moving opposite ways—just as the resistance to a ship would be different according as she went prow foremost or stern foremost. Therefore it is well to take an *odd* number of arcs for final discussion, leaving an *even* number of intervals, so that the difference, if any, between fore and aft motion should be eliminated.

646. Instead of taking the whole number of arcs it comes to the same thing to use the initial and final arc only, except for the sake of comparing the individual results with the mean of the whole. To take a particular instance,—say there are 7 arcs, $a_1, a_2,$ to a_7 , The mean logarithmic decrement is—

$$\frac{1}{6}\{(\log a_1 - \log a_2) + (\log a_2 - \log a_3) + (\log a_3 - \log a_4) + (\log a_4 - \log a_5) + (\log a_5 - \log a_6) + (\log a_6 - \log a_7)\}$$

which is the same thing as $\frac{1}{6}(\log a_1 - \log a_7)$, and the same is evidently true whatever be the number of arcs.

For instance, in the illustration already given much time will be saved by taking the observation thus :—

| Readings. | Arcs. | Log. arcs. |
|-----------|-------|------------|
| 113.0 | | |
| | 200.0 | 2.3010 |
| 87.0 | | |
| .. | | |
| .. | | |
| .. | | |
| .. | | |
| 24.0 | | |
| | 42.3 | 1.6263 |
| 18.3 | | |
| | | ----- |
| | | 6)0.6747 |
| | | ----- |
| | | 0.1124 |

647. In deducing the logarithmic decrement from the initial and final arcs it is advisable not to wait until the final arc has fallen very low, for then an error in the reading of the arc tells too much. In taking a long series a good plan is to group them into intervals of, say, 4 arcs, and take the logarithmic decrements for comparison with one another. Thus, let a_1, a_2, a_3, \dots be the arcs; we may then take

$$\begin{aligned} & \frac{1}{4} (\log a_1 - \log a_5) \\ & \frac{1}{4} (\log a_5 - \log a_9) \\ & \frac{1}{4} (\log a_9 - \log a_{13}) \\ & \frac{1}{4} (\log a_{13} - \log a_{17}), \end{aligned}$$

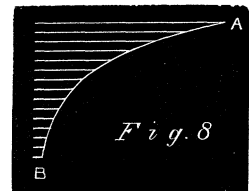
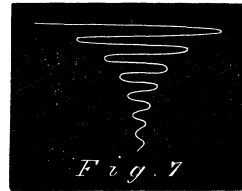
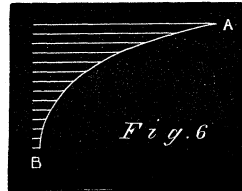
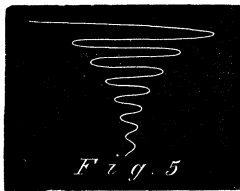
and compare them with each other. They will be more regular than the logarithmic decrements for single intervals only, as the errors of observation will be divided by 4.

648. The *proportional* error of observation of a small arc is of course much greater than that of a large one, but the *absolute* error, if anything, is rather less. Assuming the absolute errors to be the same in each case, the best arc to stop with so that a given error in the observation of the small arc shall produce a minimum error in the deduced logarithmic decrement, we find it (the last arc) should be $\frac{1}{e}$ -th part of the first arc used in the computation, e being the base of the Napierian logarithms, namely, 2.71828 As the small arcs can be observed a little better than the large arcs, on account of the slowness of the motion, we may go a little lower, say to $\frac{1}{3}$ rd of the first arc preserved for calculation.

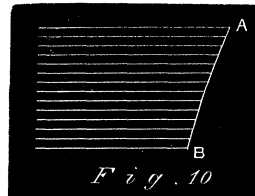
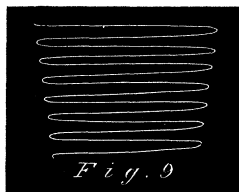
649. The slight diminution in the log. dec. of air between pressures of 760 millims. and 1 millim. is clearly shown in figs. 5, 6, 7, and 8. The curved lines are copied from photographic traces made on a sensitive surface by the index ray of light.

The experiments in which photography was employed will be described later on.

The successive diminutions of arc are caused by the resistance or the viscosity of the air. Fig. 5 shows the damping action at 760 millims., and fig. 7 that at 1 millim. Figs. 6 and 8 show the diminution in length of the successive arcs at the same two pressures, the line A B joining the extremities being the logarithmic curve.



In figs. 9 and 10 I give the curves representing the successive diminutions of the arc of vibration at high exhaustions due to viscosity. Fig. 9 is copied from a photograph, and shows the damping action at 0.02 M. The diminution in length of the arcs and the logarithmic curve—now nearly straight—are given in fig. 10. It is interesting to compare these figures with figs. 5, 6, 7, and 8, which show similar results at low exhaustions.



A very large number of experiments have been made on the viscosity of air and other gases. To reduce the results within convenient limits I will first take the case of dry air between the ordinary atmospheric pressure and the $\frac{1}{10000}$ th of an atmosphere, and will then describe the results obtained between the $\frac{1}{1000}$ th and the $\frac{1}{1,000,000}$ th of an atmosphere, and higher. I have taken observations at as high an exhaustion as 0.02 M, but at these high points they are not sufficiently concordant to be trustworthy. The pump will exhaust to this point without difficulty if a few precautions are taken, but at this low pressure the means of measuring fail in accuracy.

650. It may be useful if I here give some of the precautions which experience shows to be necessary when exhausting to the highest points. In the first place, the mercury must be pure. If it contains metals more easily oxidisable than itself, there is a tendency, if acids, or even water, come in contact with the mercury, for hydrogen to be liberated. This hydrogen is in part absorbed by the mercury, and, carried by it through the pump, is slowly liberated at low pressure. The consequence is that the highest exhaustions cannot be obtained, whilst the results are due to hydrogen rather

than to air. Before this discovery many months were wasted in taking useless observations, owing to the presence of hydrogen as impurity, and several pieces of viscosity apparatus and pumps were taken to pieces to find out a supposed leakage.

The best way to purify mercury is to violently agitate it with a solution of perchloride of iron. The mercury is thus rapidly converted into a pasty mass of metallic globules in so fine a state of division as to be invisible to the naked eye. The globules are washed, and then dried by squeezing first through a cloth, then through chamois leather. In these operations the minute globules coalesce, and the metal reassumes its fluidity.

651. When the high exhaustions are first approached in the apparatus another precaution is necessary. The pump is kept going till an exhaustion of about 0.5 M is attained, and the whole apparatus, including the connecting-tubes and those belonging to the pump, are heated to between 300° and 400°, by passing over them the flame of a BUNSEN burner. The apparatus itself is then kept at a temperature of about 300° for half an hour or more, and the pump is worked the whole time. Glass condenses on its surface a certain amount of permanent gas which is let out very slowly and incompletely in a vacuum; but the gas is driven off, in quantity sufficient to depress the gauge, when the temperature of apparatus and pump is quickly raised to 300° or 400°.

The relation between the viscosity and pressure in the apparatus after this heating is not quite the same as before, showing that the gas liberated has not quite the composition of atmospheric air. It is therefore necessary to exhaust again to a very high point, and then to add a little air (some should always be retained in the air-traps for this purpose) and again exhaust. After this treatment it is practicable to attain much higher exhaustions.

Another very necessary precaution is to allow a sufficient time to elapse, after the pump has stopped, before the observations are taken. At low exhaustions the pressure in the apparatus equalises in a few minutes; but when the tension is reduced to a few millionths of an atmosphere, twenty minutes or half an hour must pass before the pressures in the McLEOD globe and the viscosity bulb are uniform. The normal pressure is always considered to be 760 millims. When the apparatus is full of gas the interior pressure is easily brought to 760 millims., whatever be the height of the barometer, by raising or lowering the mercury reservoir, and so varying the height of the mercury in the tube supplying the fall tubes.

652. A noteworthy point in connexion with the elasticity of glass is observed on the curves in diagram C. They are not continued beyond the 0.02 M exhaustion, but the general form of the curves indicates that, if they were produced beyond the limits of the observations, they would cut the line representing the absolute vacuum. The curves representing the repulsion accompanying radiation evidently go up to the zero point, showing that at an absolute vacuum there would be no repulsion. The curves of viscosity cannot, however, be supposed to end at the zero point

without a sudden change in direction. They evidently meet the top line of zero pressure long before the logarithmic decrement of 0.00 is reached. This means that in an absolute vacuum there would still be a measurable amount of viscosity. This is probably due to the viscosity of the glass torsion fibre, for it has been ascertained that glass is not perfectly elastic, but will take a permanent *set* if kept under constraint for a considerable time. I give an instance which has come under my own notice. In 1862 I purchased a piece of glass lace, and some spun glass from which the lace was made. The spun glass is in long straight threads, about 0.001 inch diameter, and has occasionally been used for torsion fibres. The fibres of which the lace was made were originally straight, but the twists and bends in which they have been kept for eighteen years have permanently altered their direction, and on dissecting a portion of the lace the component fibres remain distorted and bent, even when free to resume their original shape.

Were glass perfectly elastic the logarithmic decrement in an absolute vacuum would probably be equal to *zero*: there would then be no diminution in the arc of vibration, and the torsion fibre once set swinging would go on for ever.

VISCOSITY OF AIR.

653. The mean of a very large number of closely concordant results gives as the logarithmic decrement for air for the special apparatus employed, at a pressure of 760 millims. of mercury and a temperature of 15° C., the number 0.1124. According to MAXWELL the viscosity should remain constant until the rarefaction becomes so great that we are no longer at liberty to consider the mean free path of the molecules as practically insignificant in comparison with the dimensions of the vessel.

My observations show that this theoretical result of MAXWELL'S is sufficiently near the actual fact in air to confirm the accuracy of his reasoning, although there is a variation showing that disturbing influences are at work which make the coefficient of viscosity (taken as proportional to the logarithmic decrement) not quite constant.

The results are embodied in the following table and diagrams.

The first half of Table I. gives the viscosity of air, in so far as it is represented by the log. decs., at pressures intermediate between 760 millims. and 0.76 millim. (1000 millionths of an atmosphere). In order to avoid the inconvenience of frequent reference to small fractions of a millimetre, I now take the millionth of an atmosphere* ($=M$) as the unit instead of the millimetre. The second half of the table is therefore given in millionths, going up to an exhaustion of 0.02 millionth of an atmosphere, the highest point to which I have carried the measurements, although by no means the highest exhaustion of which the pump is capable.

At the high exhaustions, in addition to the observed results, I have given the calculated mean free path of the molecules.

* 1 $M=0.00076$ millim. ; 1315.789 $M=1$ millim.

654. TABLE I.—Log. dec.* of dry air at pressures between 760 millims. and 0·76 millim.
Temp. 15° C.

| Pressure. Millims. | Log. decrement. | Pressure. Millims. | Time of one complete vibration. Seconds. |
|-----------------------|--------------------|-----------------------|---|
| 760 | 0·1124 | 772 | 11·20 |
| 755 | 0·1123 | 633 | 11·10 |
| 750 | 0·1121 | 534 | 11·05 |
| 730 | 0·1117 | 425 | 11·05 |
| 702 | 0·1110 | 336 | 10·96 |
| 685 | 0·1105 | 260 | 10·88 |
| 664 | 0·1100 | 155 | 10·90 |
| 645 | 0·1096 | 106 | 10·80 |
| 627 | 0·1091 | 74 | 10·80 |
| 605 | 0·1086 | 50 | 10·80 |
| 587 | 0·1082 | 23 | 10·72 |
| 572 | 0·1078 | 8 | 10·76 |
| 550 | 0·1073 | 1 | 10·70 |
| 511 | 0·1065 | 0·68 | 10·76 |
| 495 | 0·1062 | | |
| 475 | 0·1057 | M. | |
| 440 | 0·1050 | 235·0 | 10·76 |
| 409 | 0·1043 | 94·0 | 10·72 |
| 395 | 0·1040 | 47·0 | 10·70 |
| 385 | 0·1038 | 13·5 | 10·68 |
| 350 | 0·1032 | 9·0 | 10·72 |
| 324 | 0·1027 | 2·5 | 10·72 |
| 301 | 0·1022 | 1·3 | 10·72 |
| 272 | 0·1019 | | &c. |
| 254 | 0·1016 | | &c. |
| 233 | 0·1013 | | |
| 210 | 0·1010 | | |
| 180 | 0·1008 | | |
| 155 | 0·1006 | | |
| 120 | 0·1004 | | |
| 112 | 0·1003 | | |
| 68 | 0·1002 | | |
| 47 | 0·1001 | | |
| 26 | 0·1001 | | |
| 12 | 0·1000 | | |
| 4 | 0·1000 | | |
| 3 | 0·0994 | | |
| 1 | 0·0988 | | |
| 0·76 | 0·0988 | | |

* In making the experiments described in this paper, and, indeed, in writing the greater part of the paper itself, I have assumed that the logarithmic decrement was a measure of the relative viscosities of the different gases, at least until exhaustions were reached at which the viscosity begins to break down. Professor STOKES has shown that this is not the case except under certain restrictions, and in a note appended to this paper he has deduced the results which follow from my experiments when reduced according to strict dynamical principles.—W. C., August 11, 1881.

TABLE I. (continued).—Log. dec. of dry air at pressures between 1000 M and 0·02 M.
Temp. 15° C.

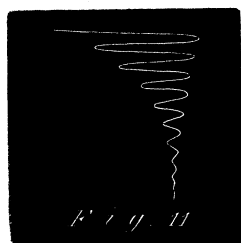
| Pressure. M | Log. decrement. | Repulsive force of radiation. | Mean free path of molecules. Millims. |
|--------------------|--------------------|----------------------------------|--|
| 1000·0(=0·76 m.m.) | 0·0988 | 2·4 | 0·10 |
| 905·0 | 0·0983 | 3·2 | 0·11 |
| 736·0 | 0·0975 | 3·5 | 0·14 |
| 590·0 | 0·0971 | 4·5 | 0·17 |
| 495·0 | 0·0966 | 5·5 | 0·20 |
| 385·0 | 0·0960 | 8·5 | 0·26 |
| 300·0 | 0·0952 | 10·0 | 0·33 |
| 248·0 | 0·0943 | 12·0 | 0·40 |
| 219·0 | 0·0937 | 14·0 | 0·46 |
| 183·0 | 0·0930 | 16·5 | 0·55 |
| 165·0 | 0·0926 | 18·0 | 0·61 |
| 157·0 | 0·0925 | 19·5 | 0·64 |
| 135·0 | 0·0907 | 21·3 | 0·74 |
| 116·0 | 0·0892 | 24·5 | 0·86 |
| 100·0 | 0·0876 | 27·0 | 1·0 |
| 93·0 | 0·0866 | 29·0 | 1·1 |
| 81·0 | 0·0842 | 31·1 | 1·2 |
| 79·0 | 0·0840 | 31·5 | 1·3 |
| 72·0 | 0·0824 | 32·9 | 1·4 |
| 68·0 | 0·0817 | 33·5 | 1·5 |
| 62·0 | 0·0799 | 34·6 | 1·6 |
| 53·0 | 0·0774 | 37·0 | 1·9 |
| 39·0 | 0·0710 | 41·4 | 2·6 |
| 36·0 | 0·0695 | 42·5 | 2·8 |
| 29·0 | 0·0657 | 42·6 | 3·4 |
| 24·0 | 0·0620 | 41·2 | 4·2 |
| 19·0 | 0·0577 | 38·8 | 5·3 |
| 13·0 | 0·0500 | 30·9 | 7·7 |
| 11·0 | 0·0460 | 27·1 | 9·1 |
| 8·0 | 0·0390 | 22·3 | 12·5 |
| 7·2 | 0·0372 | 20·2 | 13·9 |
| 5·9 | 0·0337 | 17·0 | 16·9 |
| 4·1 | 0·0281 | 13·1 | 24·4 |
| 3·4 | 0·0256 | 11·5 | 29·4 |
| 2·6 | 0·0225 | 8·5 | 38·4 |
| 1·9 | 0·0198 | 7·1 | 52·6 |
| 1·3 | 0·0175 | 4·2 | 76·9 |
| 1·0 | 0·0161 | 2·1 | 100·0 |
| 0·55 | 0·0144 | 2·0 | 181·8 |
| 0·46 | 0·0135 | 1·7 | 217·4 |
| 0·22 | 0·0118 | 1·4 | 454·5 |
| 0·14 | 0·0114 | 1·0 | 715·9 |
| 0·06 | 0·0097 | 0·7 | 1666·6 |
| 0·02 | 0·0072 | 0·5 | 5000·0 |
| | 0·00537 | ? | |

655. The pressure and the logarithmic decrement columns are obtained in the following way :—Observations are taken first at frequent intervals during exhaustion, sufficient time being left between the successive experiments to allow the slight heating due to internal friction, and the cooling due to rarefaction to become equalised. Air is then slowly admitted through the drying tubes, and another series is taken. When several hundreds of such determinations are accumulated, they are collected into groups, from which the mean pressure and mean logarithmic decrement for the group have been taken.

In this table I have also given the measurements of the repulsion exerted on the blackened end of the mica plate by a candle-flame placed 500 millims. off. The repulsion due to radiation commences just at about the same degree of exhaustion where the viscosity begins to decline rapidly, and it principally comes in at the exhaustion above 1000 M. The observations are thus conducted :—The torsion fibre and plate being at rest, the shutter obscuring the candle is suddenly removed, and the light allowed to shine on the blackened mica for a series of seven or eight oscillations.

The radiant force deflecting the mica (not including the torsion) is by no means constant, but mounts up during a very appreciable time. The motion of the mica is one of swinging about a point which itself changes more or less slowly with the time. This force begins from nothing, rapidly increases, and attains nearly its full value in a second or two after the candle is let on. The force depends on the heating of the surface of the swinging body by the previous action of the candle.

The path of the index ray is of the following character :—



Starting from zero, the mechanical force drives the index to division 88 ; thence it swings back to 29 ; the next swing brings it to 83, and so on. The problem is, from the varying arcs of oscillation, to find the true zero, or the point at which the index ray would rest supposing the force of repulsion to be constant and inertia absent.

656. Professor STOKES, to whom I am greatly indebted for assistance and advice on the mathematics of this subject, has provided a method for calculating the zero for the swing produced by the candle-flame. Register the stopping-points when the candle is let on in successive swings ; and in an adjacent experiment find the logarithmic decrements, without the candle.

Let l be the logarithmic decrement, N the number whose logarithm is l . Divide the successive arcs by $1+N$, and apply the results to the readings of the second ends of

the arcs, to get the equilibrium readings for the force arising from the candle supposed constant during that swing, and equal to what it was in the middle of the swing.

The following is an example of the observations which I have plotted above, treated in this way :—

Log. dec. 0·066 ; L. $\overline{1+N}$ 0·335.

| Reading. | Arc. | Log. arc. | Less 0·335. | Number. | Zero for swing. |
|----------|------|-----------|-------------|----------------|-----------------|
| I. | II. | III. | IV. | V. | VI. |
| 88 | 88 | 1·944 | 1·609 | 40·6 | <u>47·4</u> |
| 29 | 59 | 1·771 | 1·436 | 27·3 | 56·3 |
| 83 | 54 | 1·732 | 1·397 | 24·8 | 58·2 |
| 32 | 51 | 1·708 | 1·373 | 23·6 | 55·6 |
| 75 | 43 | 1·633 | 1·298 | 19·9 | 55·1 |
| 40 | 35 | 1·544 | 1·209 | 16·2 | 56·2 |
| 68 | 28 | 1·447 | 1·112 | 12·9 | <u>55·1</u> |
| | | | | Mean | 55·9 |

The numbers in column VI. are obtained by applying column V. to column I., by subtraction and addition alternately. The first figures are marked off with a line, because the method gives only a rude approximation for the first swing, as the whole of the force, very nearly, has grown during this swing.

657. With a high logarithmic decrement the process just given should always be used ; but with a low logarithmic decrement, as in the example, it may be simplified by taking the mean of consecutive arcs, then the half means, and then applying these + and - to the successive readings, as in the following example :—

| Reading. | Swing. | Arithmetical mean of II. | Half of III. | Applied + and - to I. = approximate calculated position of equilibrium. |
|----------|--------|--------------------------|----------------|---|
| I. | II. | III. | IV. | V. |
| 0 | | | | |
| 88 | 88 | | | |
| | 59 | 73·5 | 36·7 | <u>52·1</u> |
| 29 | 54 | 56·5 | 28·2 | 57·2 |
| 83 | 51 | 52·5 | 26·2 | 56·8 |
| 32 | 43 | 47·0 | 23·5 | 55·5 |
| 75 | 35 | 39·0 | 19·5 | 55·5 |
| 40 | 28 | 31·5 | 15·7 | <u>55·7</u> |
| | | | Mean | 56·1 |

I have cut off the first swing, which is clearly out of series. The slight diminution of the last three, as compared with the second and third numbers, may not improbably

be real, though the slight uncertainty as to the second makes it doubtful. If it is real, it is probably due to the heating of the hinder face of the mica by conduction from the front face; so that the permanent difference of temperature is a little less than was the difference at a somewhat earlier stage.

658. There is great satisfaction to the mind when it is possible to plot a long series of figures as a curve on paper. Indeed, this is almost the only way in which the meaning of the results can be fully realised. It has been found impracticable to place the curves together in one table, inasmuch as the diagrams necessary to enable the results to be understood, and without which columns of figures are almost valueless, have to be on a scale of increasing magnification. On diagram A (Plate 56) are shown the results recorded in the first part of the table down to a pressure of 0.76 millim. plotted as a curve (marked "air"), the ordinates being the logarithmic decrements, and the abscissæ the pressures in millims. of mercury. The total barometric height, or one atmosphere, is represented by a length of 152 millims. : each millim. on the scale therefore represents 5 millims. pressure of mercury. Gaps in the series have not been filled up by interpolation.

Starting from the logarithmic decrement 0.1124 at 760 millims., it diminishes very regularly, but at a somewhat decreasing rate. Between 50 millims. and 3 millims. the direction is almost vertical, and it will be noticed that a great change in the uniformity of the viscosity curve commences at a pressure of about 3 millims. (shown in the upper part of the curve on diagram A), where the direction suddenly changes and goes off almost horizontally. At this point the previous approximation to MAXWELL'S law begins to fail, and further pumping considerably reduces the logarithmic decrement.

659. To render the gradation of the air curve more uniform, it is now necessary to considerably magnify the scale. Diagram A is on so small a scale that 152 millims. represent the whole barometric column, but the scale to which diagram B is drawn is that of 1 millim. to 5 millionths of an atmosphere, so that the whole atmospheric pressure would be represented by a vertical height of 200 metres. One-thousandth part of this, representing the top 200 millims. of the scale, is all that I give in the compass of this diagram. At the lower part of diagram B (Plate 57) is given a highly condensed scale of the viscosity curve between 760 millims. and 0.76 millim. To bring this condensed scale to the same proportion as that of the rest of the diagram it would have to be 200 metres instead of only 10 millims. long.

Starting from 1000 M the diminution of viscosity is very slight until the exhaustion reaches about 250 M; after that the viscosity gets less with increasing rapidity, and falls away quickly after 35 M is reached.

660. It will be seen, from the almost horizontal character of the upper part of the curve, that the scale is not even now large enough to bring it out properly. I have therefore in diagram C (Plate 58) again lengthened the scale, so that one atmosphere is represented by 5000 metres, and of this I have taken the top 300 millims., giving

the curve for the portion between 60 *M* and 0·02 *M*. On this scale one millionth of an atmosphere is represented by 5 millims. vertical height.*

The "air" curve on diagram C shows the further diminution in the viscosity of air. At the foot of the diagram a straight diagonal line starts from the logarithmic decrement 0·1124 at 1,000,000 *M* (one atmosphere) up to the logarithmic decrement 0·098 at 1000 *M*, and a second line to the logarithmic decrement 0·0794 at 60 *M*. The slope of these lines is that of the condensed curves in diagrams A and B, and is greatly exaggerated, since in order to get the true slope proper to join on to the rest of the curve the lines should be respectively 200 metres and 5000 metres long instead of 30 millims.

661. The dotted curves on the left of diagrams B and C show the variation in the force of repulsion under the influence of radiation; the force gradually increases until it reaches a maximum between 25 and 40 *M*, when it rapidly sinks. This curve agrees very well with similar curves given in former papers, representing the action of light on the radiometer† (334, 382, 481).

The close agreement between the loss of viscosity and the increased action of radiation is very striking up to the 35 millionth, when the repulsion curve turns round and falls away as rapidly as the viscosity.

662. On the right side of diagrams B and C I have given a third curve. The abscissæ represent the mean free paths of the molecules at the various pressures used as ordinates. The mean free paths being very small, to make them comparable with the other dimensions adopted on diagram B, I have multiplied their lengths by 20. Thus at 1000 *M* the mean free path is 0·1 millim., and at 100 *M* it is 1·0 millim. In diagram B, drawn on a scale of 20 to 1, these become respectively 2·0 and 20 millims., but in diagram C, I have given the actual lengths of the free paths of the molecules.

The curves of increasing mean free path and diminishing viscosity closely agree. This agreement is more than a mere coincidence, and is likely to throw much light on the cause of viscosity of gases.

RESISTANCE OF AIR TO THE PASSAGE OF AN INDUCTION SPARK.

663. In describing the apparatus (fig. 1, par. 641) I have mentioned that it is furnished with a resistance tube, *l*. This tube is provided with aluminium poles, so that at any pressure the appearance presented by the induction spark when passed through the tube may be observed. Since the publication of my researches on the phenomena presented by the passage of the induction discharge through high vacua, the present results—which, although never published, precede by a year or two those

* To give some idea of the high exhaustions at which accurate measurements can be taken, I may mention that the highest exhaustion on the table—0·02 *M*—bears the same proportion to the ordinary atmospheric pressure that 1 millim. does to 30 miles, or, converting it into time, that 1 second bears to 20 months.

† Phil. Trans., Part I., 1878: The Bakerian Lecture; Ditto, Part I., 1879. Proc. Roy. Soc., vol. xxv., p. 305.

just mentioned—have lost much of their interest. I will therefore only briefly mention some of the results at a few pressures.

The poles, formed of aluminium, are 4 millims. apart at their ends. The coil when in full work gives a 6-inch spark, but a small battery was used in order to reduce the full striking distance in air to 85 millims.

664. At an exhaustion of 295 M the resistance of 4 millims. of rarefied air in the tube between the poles is equal to 2 millims. outside; that is to say, when the outer terminals of the coil are 2 millims. apart it is a matter of indifference whether the spark passes between them or through the vacuum tube. There is much reddish-violet light round the poles, the appearance being that of ordinary vacuum poles. Traces of green phosphorescence flash out occasionally.

At an exhaustion of 82 M the violet light round the poles has disappeared. The + end of the tube is filled with hazy violet light, and there is a small spark and a brush at the tip of the — pole. Faint green phosphorescence is seen on the glass round the — pole. The resistance of the vacuum is now equal to 24 millims. air space.

Exhaustion 27 M. The violet diffused light is much fainter, and the green phosphorescence is getting stronger. Resistance of the vacuum = 24 millims. of air.

Exhaustion 4 M. No violet light is to be seen. The green light is very strong, and a diffused greenish-yellow light fills the + end of the tube. Resistance of the vacuum = 53 millims. of air.

Exhaustion 1 M. The green phosphorescence is like the last, but somewhat stronger. The spark and brush at the tip of the — pole, first noticed at 82 M, are still there. Resistance of the vacuum = 85 millims. of air space.

Exhaustion 0.5 M. The appearance is similar to the last, but the spark and brush have gone from the — pole. The wires connecting the coil with the tube were now carefully insulated. When the poles are kept apart the striking distance in air (85 millims.), the spark often strikes across rather than pass through the tube, but on separating the poles beyond this distance the discharge flashes intermittently through the tube, sometimes keeping up for one or two seconds.

When thus passing through the tube the flashes of green phosphorescence are very brilliant, particularly at the + end. During the intervals between the flashes a faint band of green light is seen round the inner surface of the tube at the tip of the — pole.

Exhaustion 0.02 M. With the battery and coil as hitherto no discharge whatever passes. On increasing the battery power till the striking distance in air was 100 millims. the spark occasionally passed through as an intermittent flash, bringing out faint green phosphorescence on the glass round the end of the — pole.

665. The terminals of the tube and wires leading to them must be well insulated, and kept away from any part of the apparatus. If this precaution is neglected a spark breaks through from one of the wires to some part of pump or connecting tubes,

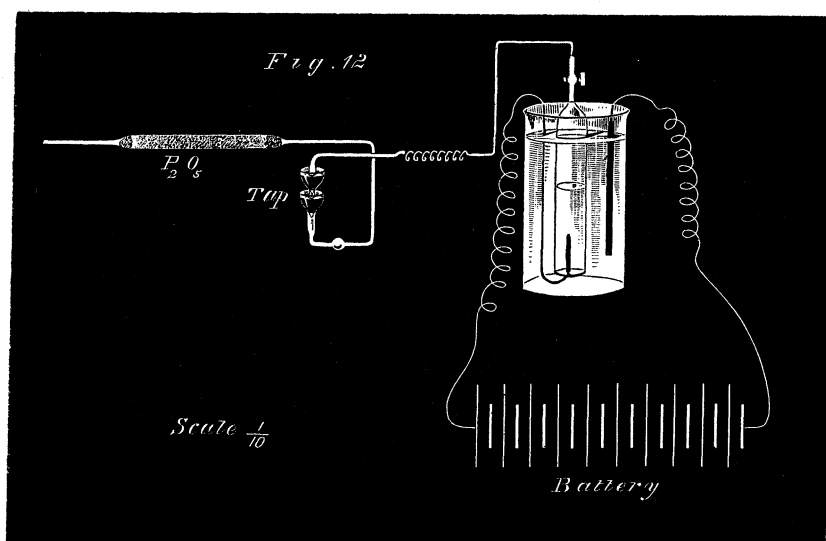
and perforates the glass. The perforation is sometimes so fine as to cause the greatest trouble in finding the leakage, which only shows itself by the inability of the pump to give a good vacuum. Left to itself the logarithmic decrement slowly rises, the repulsive force of the candle increases to its maximum, and then slowly diminishes to zero, the logarithmic decrement continuing to rise till ultimately the internal and external pressures are identical. With a fine perforation it takes several days to go through these phases, and they occur with such slowness and regularity as to afford opportunities for valuable observations.

On one occasion I obtained a much higher exhaustion than 0.02 M. I could not measure it, but from the repulsion by radiation and the low logarithmic decrement (0.00537) I should estimate it at about 0.01 M. The terminals of the vacuum tube and wires leading to them were well insulated, and the full power of a coil giving a 20-inch spark was put on to it. At first nothing was to be seen. Then a brilliant green light flashed through the tube, getting more and more frequent. Suddenly a spark passed from a wire to the glass tube, and broke it, terminating the experiment.

Since these experiments I have frequently got vacua as high, and even higher, but I have never seen one that would long resist the 20-inch spark from my large coil.

VISCOSITY OF OXYGEN.

666. The series of experiments with air show a complete history of its behaviour between very wide limits of pressure. It became interesting to see how the two components of air, oxygen and nitrogen, would behave under similar circumstances.



Experiments were therefore instituted exactly as in the case of dry air, but with the apparatus filled with pure oxygen.

For these experiments the oxygen gas is prepared by the electrolytic decomposition of water containing sulphate of copper dissolved in it, a copper plate being used for

the negative pole and a platinum plate for the positive pole. The apparatus is shown in fig. 12. The reduction of the copper effectually obviates any chance of hydrogen coming off and contaminating the oxygen. The gas is received direct into a bell receiver in the acid liquid, and is thence transferred to the apparatus through a vacuum tap beyond the drying tubes, *w*, Plate 55, fig. 1. The oxygen is always kept under a considerable pressure of water, and is only prepared shortly before it is wanted. The gas is passed into the apparatus very slowly through a considerable length of phosphoric anhydride.

The following table gives the numerical results obtained :—

667. TABLE II.—Log. dec. of oxygen gas at pressures between 760 millims. and 0·76 millim. Temp. 15° C.

| Pressure. Millims. | Log. decrement. | Time of one complete vibration. | |
|-----------------------|--------------------|---------------------------------|----------|
| | | Millims. | Seconds. |
| 760 | 0·1257 | 775 | 11·4 |
| 720 | 0·1247 | 753 | 11·3 |
| 668 | 0·1232 | 623 | 11·2 |
| 632 | 0·1222 | 543 | 11·1 |
| 564 | 0·1205 | 443 | 11·0 |
| 562 | 0·1204 | 343 | 10·9 |
| 496 | 0·1188 | 202 | 10·9 |
| 458 | 0·1178 | 158 | 10·9 |
| 340 | 0·1152 | 93 | 10·8 |
| 318 | 0·1148 | 63 | 10·8 |
| 309 | 0·1146 | 27 | 10·8 |
| 301 | 0·1145 | 7 | 10·76 |
| 249 | 0·1136 | 1 | 10·76 |
| 200 | 0·1130 | | &c. |
| 159 | 0·1126 | | &c. |
| 150 | 0·1125 | | |
| 120 | 0·1123 | | |
| 103 | 0·1122 | | |
| 80 | 0·1120 | | |
| 72 | 0·1120 | | |
| 61 | 0·1119 | | |
| 47 | 0·1119 | | |
| 38 | 0·1118 | | |
| 30 | 0·1118 | | |
| 26 | 0·1119 | | |
| 19 | 0·1119 | | |
| 16 | 0·1121 | | |
| 12 | 0·1122 | | |
| 7·5 | 0·1124 | | |
| 3·8 | 0·1121 | | |
| 1·5 | 0·1115 | | |
| 1·4 | 0·1111 | | |
| 1·1 | 0·1115 | | |
| 1·0 | 0·1115 | | |
| 0·85 | 0·1107 | | |
| 0·76 | 0·1102 | | |

TABLE II. (continued).—Log. dec. of oxygen gas at pressures between 1000 M and 0·3 M. Temp. 15° C.

| Pressure. M | Log. decrement. | Repulsive force of radiation. |
|---------------------|--------------------|----------------------------------|
| 1000·0 (=0·76 m.m.) | 0·1102 | 12· |
| 803·0 | 0·1093 | 12· |
| 658·0 | 0·1088 | 13· |
| 623·0 | 0·1086 | 13· |
| 613·0 | 0·1085 | 13· |
| 360·0 | 0·1070 | 13· |
| 297·0 | 0·1058 | 14· |
| 190·0 | 0·1038 | 20· |
| 171·0 | 0·1033 | 21· |
| 110·0 | 0·0988 | 31· |
| 82·0 | 0·0940 | 35· |
| 70·0 | 0·0912 | 38· |
| 48·0 | 0·0840 | 45· |
| 31·0 | 0·0744 | 44· |
| 28·0 | 0·0724 | 44· |
| 22·0 | 0·0670 | 40· |
| 16·0 | 0·0621 | 35· |
| 12·0 | 0·0585 | 30· |
| 4·0 | 0·0433 | 14· |
| 1·6 | 0·0348 | 7· |
| 0·3 | 0·0302 | 2· |

668. These figures, plotted as curves on diagrams A, B and C, show a great similarity to the air curve. Like it, the viscosity sinks somewhat rapidly between pressures from 760 millims. to about 75 millims. It then remains almost steady, not varying much till a pressure of 16 millims. is reached. Here, however, it turns in the opposite direction, and steadily increases up to 1·5 millim. It then diminishes again, and at higher exhaustions it rapidly sinks. This increase of viscosity at pressures of a few millimetres has been observed in other gases, but only to so small an extent as to be scarcely beyond the limits of experimental error. In the case of oxygen, however, the increase is too great to be entirely attributable to this cause.

669. Oxygen has more viscosity than any gas I have yet examined. The viscosity of air at 760 millims. being 0·1124, the proportion between that of air and oxygen, according to these results, is 1·1185. GRAHAM* makes it 1·1099 (706). I have been unable to find viscosity results of oxygen given by any other observers.

This proportion of 1·1185 holds good (allowing for experimental errors) up to a pressure of about 20 millims. Between that point and 1 millim. variations occur, which I have not been able to trace to any assignable cause: they seem large to be

* *Loc. cit.*, p. 179.

put down to "experimental errors." The discrepancies disappear again at an exhaustion of about 1 millim., and from that point to the highest hitherto reached the proportion of 1.1185 is fairly well maintained.

670. The curves plotted from the observations of the repulsive force of radiation are given in dots at the left side of diagrams B and C. Repulsion commences at a somewhat lower exhaustion, and remains much higher than in air until an exhaustion of 22 M is reached, when the two curves become practically identical.

VISCOSITY OF NITROGEN.

671. Nitrogen is prepared by heating a solution of nitrite of ammonia. If proper precautions are taken to avoid intermixture of air, this process yields it in a very pure state. It is collected in the bell receiver shown in fig. 12 (666). To eliminate aqueous vapour the gas is passed through phosphoric tubes, and then through the tap into the viscosity apparatus, as explained in the case of oxygen. The last traces of aqueous vapour are removed from the nitrogen by allowing it to pass in a very slow stream through a series of tightly-packed phosphoric anhydride tubes, on its way to the viscosity bulb.

Nitrogen was also prepared by burning phosphorus in a confined space of air, and also by the copper turnings and ammonia method; but neither of these processes yielded a gas which gave uniformly such concordant results as did the nitrite of ammonia process.

The following are the tabulated results of observations with nitrogen :--

672. TABLE III.--Log. dec. of nitrogen gas at pressures between 760 millims. and 2·8 M. Temp. 15° C.

| Pressure. Millims. | Log. decrement. |
|-----------------------|--------------------|
| 760 | 0·1092 |
| 717 | 0·1081 |
| 692 | 0·1074 |
| 624 | 0·1059 |
| 582 | 0·1048 |
| 542 | 0·1038 |
| 474 | 0·1023 |
| 403 | 0·1010 |
| 324 | 0·0996 |
| 282 | 0·0990 |
| 245 | 0·0985 |
| 218 | 0·0980 |
| 172 | 0·0976 |
| 165 | 0·0974 |
| 143 | 0·0974 |
| 122 | 0·0973 |
| 117 | 0·0970 |
| 105 | 0·0973 |
| 100 | 0·0971 |
| 87 | 0·0971 |
| 79 | 0·0971 |
| 60 | 0·0972 |
| 50 | 0·0970 |
| 44 | 0·0969 |
| 29 | 0·0970 |
| 21 | 0·0970 |
| 14 | 0·0969 |
| 8 | 0·0969 |
| 6 | 0·0970 |
| 2·1 | 0·0961 |
| 1·4 | 0·0962 |
| 0·85 | 0·0962 |
| 0·76 | 0·0960 |

TABLE III. (continued).—Log. dec. of nitrogen gas at pressures between 1000 M and 2·8 M. Temp. 15° C.

| Pressure. M | Log. decrement. | Repulsive force of radiation. |
|---------------------|--------------------|----------------------------------|
| 1000·0 (=0·76 m.m.) | 0·0960 | 1· |
| 610·0 | 0·0941 | 2· |
| 459·0 | 0·0934 | 4· |
| 345·0 | 0·0930 | 3· |
| 188·0 | 0·0894 | 8· |
| 125·0 | 0·0867 | 15· |
| 84·0 | 0·0820 | 23· |
| 58·0 | 0·0770 | 28· |
| 47·0 | 0·0730 | 30· |
| 26·0 | 0·0600 | 25· |
| 13·0 | 0·0420 | 17· |
| 9·6 | 0·0351 | 14· |
| 8·3 | 0·0318 | 13· |
| 5·8 | 0·0257 | 9· |
| 3·3 | 0·0207 | 3· |
| 2·8 | 0·0178 | 1· |

673. The proportion between the viscosities of nitrogen and air at a pressure of 760 millims. is according to these experiments 0·9715. GRAHAM made it 0·971 (706).

674. A comparison of the air curves with those given by oxygen and nitrogen gives some interesting results. The composition of the atmosphere is, by bulk,

| | |
|--------------------|-------|
| Oxygen | 20·8 |
| Nitrogen | 79·2 |
| | 100·0 |

The viscosity of the mixed gases is almost exactly that which would be inferred from the composition: thus at 760 millims.—

$$\frac{20\cdot8 \text{ vis. O} + 79\cdot2 \text{ vis. N}}{100} = \text{vis. air,}$$

$$\frac{20\cdot8 (0\cdot1257) + 79\cdot2 (0\cdot1092)}{100} = \text{''}$$

$$= \frac{2\cdot61456 + 8\cdot64072}{100} = 0\cdot11255,$$

a result closely coinciding with 0·1124, the experimental result for air. Up to an exhaustion of about 30 M the same proportion between the viscosities of air, oxygen, and nitrogen is preserved with but little variation. From that point great divergence occurs between the individual curves of the three gases. The difficulties of obtaining concordant observations at these high vacua are very great, and the unavoidable errors of experiment are, I think, sufficient to account for any divergence between theory and observation.

OBSERVATIONS ON THE SPECTRUM OF NITROGEN.

675. Spectrum observations during exhaustion give the following results :—

At 55 millims. pressure the band spectrum of nitrogen commences to be visible. The red and yellow bands are easily seen, and the green and blue are exceedingly faint. As the pressure grows less the bands become more distinct, until at 1·14 millim. the band spectrum is at its brightest.

At a little higher exhaustion a change comes over the spectrum, and traces of the line spectrum are observed.

At 812 M both the band and the line spectrum can be seen very brilliantly.

At 450 M the line spectrum is seen in great purity. As the exhaustion becomes higher the lines commence to disappear at the two ends of the spectrum.

At 188 M the lines below λ 610 at the red end, and above λ 400, cease to be visible.

At 94 M a bright greenish-yellow line is visible at about λ 567.

At 55 M this greenish-yellow line is still very prominent. The red lines have disappeared altogether, and the highest blue line visible is one at λ 419. The line λ 567 varies much in visibility; sometimes it cannot be seen, whilst at others it is very visible. Thus—

At 40 M the line λ 567 has quite disappeared.

At 17 M line λ 567 is visible again, being the most prominent line left.

At 12 M line λ 567 is not seen, although several other green and blue lines are left.

At 3 M only three lines are visible in the green, and these are very faint.

At 2·8 M line λ 567 is detected again.

At 2 M only traces of one or two lines can be seen, the faint light of the lines being overpowered by the green phosphorescence of the glass.

Line λ 567 has been seen on several occasions at high exhaustions when the gas under examination has been mixed with a little air. It is probably a nitrogen line, for one of the most brilliant nitrogen lines has a wave length of λ 567·8 (THALÉN), λ 568·0 (HUGGINS), or λ 568·1 (PLÜCKER), and my interpolation curve is not sufficiently accurate to enable me to say that the line I have entered in my notes as being at λ 567

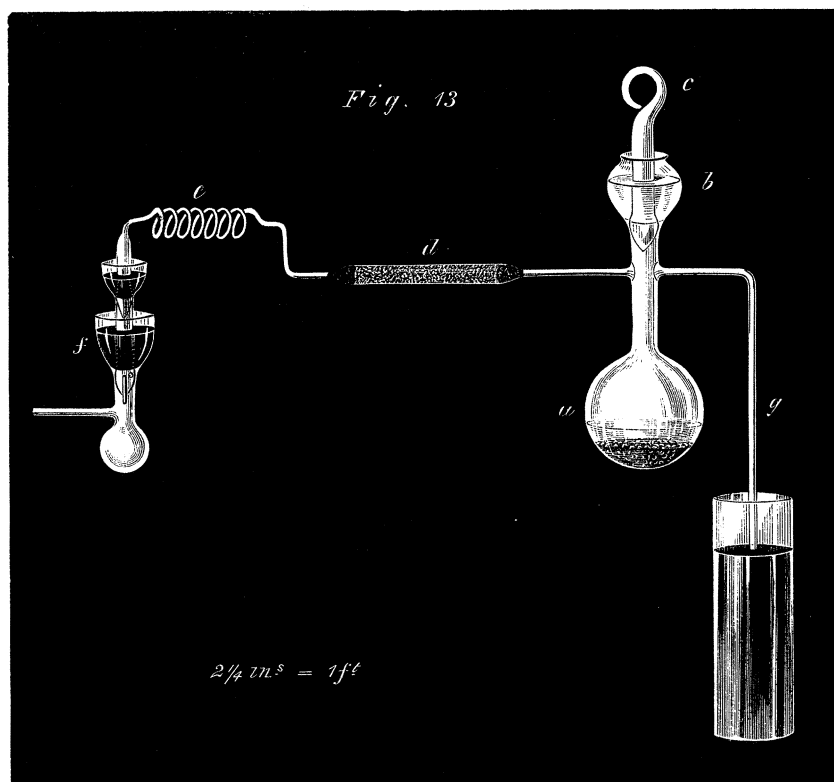
may not in reality be a trifle higher. The reason of its being only sometimes visible may be accounted for by a difference in the sensitiveness of the eye at different times, or by a difference in battery power. This, however, cannot be the whole explanation, for other lines are not found to vary in the same manner.

676. The curve of repulsion exerted by radiation is plotted in dots on diagrams B and C. It is much lower than in oxygen or air, and sinks rapidly after the maximum is passed.

VISCOSITY OF CARBONIC ANHYDRIDE.

677. Several processes have been tried for the preparation of this gas, to avoid the collection over water, and consequent risk of admixture with air. The best methods are the ignition of bicarbonate of soda, and the decomposition of marble by hydrochloric acid. The bicarbonate of soda plan has two great advantages: the generation of gas can be conducted in the sealed-up and exhausted apparatus, and nothing else but carbonic anhydride and water are given off. The amount of water, however, proves a serious inconvenience, as it uses up so much phosphoric anhydride,—therefore the production of the gas from marble and hydrochloric acid was finally employed.

The apparatus is shown in fig. 13.



The marble is contained in the glass flask, *a*, to the upper part of which a thistle-shaped funnel, *b*, with a ground stopper, *c*, is attached. The bulb, *b*, is filled with hydrochloric acid, and by loosening the stopper some of the acid is allowed to run down on the marble. The carbonic anhydride passes along the tube, *d*, which is tightly packed with powdered bicarbonate of soda to stop hydrochloric acid, through the flexible spiral, *e*, to the tap, *f*. On the other side of the flask the tube, *g*, dips into a tall glass containing mercury. The tap is connected with the viscosity apparatus, as shown in the general view in fig. 1.

Before introducing carbonic anhydride into the apparatus the gas is freely generated, and allowed to bubble up for some time through the mercury in the upper reservoir of the tap, the ground tube in it being loosened for this purpose. When it is supposed that all air is driven out of the flask and tubes by the carbonic anhydride, the tube is tightly pressed into the tap so as to close it, and the gas then escapes through the tube, *g*, under considerable pressure of mercury. The viscosity apparatus on the other side of the tap being already well exhausted, the tap is slightly turned to allow a very slow stream of carbonic anhydride to pass into the apparatus, generation of gas being kept up by feeding in hydrochloric acid through the stopper, *c b*. When the apparatus is filled with carbonic anhydride the tap, *f*, is turned off, and exhaustion is proceeded with. These operations are repeated at least three times, several hours being allowed to elapse after filling the apparatus before pumping out the gas, so as to let it soak well into all parts, and displace any other gas which may cling to the surfaces. After the last filling, observations are commenced. Several series are taken, and if, as is sometimes the case, the earlier ones are not uniform with the others, they are rejected.

In the following table I give the results of the observations with this gas :—

678. TABLE IV.—Log. dec. of carbonic anhydride at pressures between 760 millims. and 7·6 M. Temp. 15° C.

| Pressure. Millims. | Log. decrement. | Pressure. Millims. | Time of one complete vibration. Seconds. |
|-----------------------|--------------------|-----------------------|--|
| 760 | 0·1035 | 732 | 11·48 |
| 750 | 0·1033 | 592 | 11·32 |
| 689 | 0·1022 | 512 | 11·28 |
| 665 | 0·1016 | 402 | 11·16 |
| 645 | 0·1012 | 332 | 11·06 |
| 640 | 0·1009 | 222 | 11·02 |
| 620 | 0·1006 | 127 | 10·92 |
| 605 | 0·1001 | 87 | 10·84 |
| 545 | 0·0982 | 37 | 10·80 |
| 540 | 0·0979 | 32 | 10·76 |
| 512 | 0·0970 | 7 | 10·76 |
| 501 | 0·0967 | 3 | 10·76 |
| 460 | 0·0948 | 2 | 10·76 |
| 425 | 0·0937 | 1 | 10·76 |
| 410 | 0·0931 | | &c. |
| 403 | 0·0928 | | &c. |
| 368 | 0·0918 | | |
| 363 | 0·0914 | | |
| 355 | 0·0911 | | |
| 332 | 0·0903 | | |
| 290 | 0·0890 | | |
| 282 | 0·0884 | | |
| 255 | 0·0875 | | |
| 240 | 0·0872 | | |
| 205 | 0·0858 | | |
| 180 | 0·0850 | | |
| 132 | 0·0835 | | |
| 124 | 0·0831 | | |
| 92 | 0·0826 | | |
| 71 | 0·0823 | | |
| 55 | 0·0822 | | |
| 50 | 0·0822 | | |
| 28 | 0·0821 | | |
| 11 | 0·0822 | | |
| 4·5 | 0·0819 | | |
| 2·3 | 0·0817 | | |
| 1·1 | 0·0816 | | |
| 0·76 | 0·0809 | | |

TABLE IV. (continued).—Log. dec. of carbonic anhydride at pressures between 1000 M and 7·6 M. Temp. 15° C.

| Pressure. M | Log. decrement. | Repulsive force of radiation. |
|-------------------|--------------------|----------------------------------|
| 1000 (=0·76 m.m.) | 0·0809 | 1· |
| 588 | 0·0790 | 2· |
| 523 | 0·0785 | 2· |
| 389 | 0·0780 | 2· |
| 345 | 0·0776 | 2· |
| 228 | 0·0770 | 3· |
| 177 | 0·0758 | 5· |
| 158 | 0·0750 | 7· |
| 91 | 0·0717 | 13· |
| 66 | 0·0697 | 15· |
| 58 | 0·0684 | 19· |
| 40 | 0·0630 | 25· |
| 32 | 0·0600 | 25· |
| 15 | 0·0424 | 16· |
| 10 | 0·0347 | 11· |
| 9 | 0·0325 | 10· |
| 7·6 | 0·0298 | 8· |

679. The curves given in diagrams A, B, and C are plotted from the above observations. At first the curve seems to follow the same direction as the air curve. But at a pressure of about 620 millims. it slopes more rapidly till the pressure is reduced to about 50 millims., when the curve again takes the direction of the air curve. The total diminution between 760 millims. and 1 millim. is nearly double that of air.

The proportion between the viscosity of carbonic anhydride and air at 760 millims. is 0·9208. GRAHAM* found it to be 0·807, and KUNDT and WARBURG† 0·806. MAXWELL‡ made it 0·859 (706).

680. The curve showing the variation in the repulsive force of radiation, shown in dots in diagrams B and C, commences late and falls off early, the maximum being very inferior to that obtained in the other gases examined.

OBSERVATIONS ON THE SPECTRUM OF CARBONIC ANHYDRIDE.

681. Observations have also been taken with the spectroscope during the exhaustion of carbonic anhydride. The maximum brilliancy of the spectrum occurs at an exhaustion of about 300 M. After that it gets fainter; at about 75 M the blue band (λ 409 to λ 408) disappears; as the exhaustion gets higher the other bands vanish until, at

* 'Chemical and Physical Researches,' p. 179.

† Phil. Mag., July, 1875.

‡ Phil. Trans., 1866, Part I., p. 257.

a vacuum of about 40 M, nothing is visible but the two lines λ 519 and λ 560. At higher exhaustions these lines disappear, and the phenomena of "radiant matter" commence.

VISCOSITY OF CARBONIC OXIDE.

682. This gas was prepared by heating oxalate of ammonia and strong sulphuric acid, and collecting the mixed carbonic oxide and carbonic anhydride over solution of caustic potash in the bell-jar shown in fig. 12 (666). Previous to entering the apparatus the gases are slowly passed through long tubes containing powdered caustic potash.

Carbonic oxide was also prepared by heating ferrocyanide of potassium with strong sulphuric acid, and passing the resulting gas through potash tubes as before. This is the preferable way to prepare the gas, for it is difficult to remove the last traces of carbonic anhydride when the oxalic acid process is used.

The gas is passed into the well-exhausted apparatus through the tap in the manner already described, and the exhaustion and filling are repeated a sufficient number of times. All usual precautions are taken, as described in the case of gases previously examined.

The following table gives the experimental results obtained:—

683. TABLE V.—Log. dec. of carbonic oxide, between pressures of 760 millims. and 0.76 millim. Temp. 15° C.

| Pressure. Millims. | Log. decrement. |
|-----------------------|--------------------|
| 760 | 0.1092 |
| 687 | 0.1073 |
| 517 | 0.1031 |
| 426 | 0.1012 |
| 353 | 0.1000 |
| 266 | 0.0983 |
| 219 | 0.0979 |
| 125 | 0.0972 |
| 89 | 0.0971 |
| 79 | 0.0970 |
| 32 | 0.0971 |
| 18 | 0.0968 |
| 12 | 0.0968 |
| 10 | 0.0967 |
| 2.6 | 0.0969 |
| 1.4 | 0.0957 |
| 1.2 | 0.0958 |
| 0.76 | 0.0947 |

TABLE V. (continued).—Log. dec. of carbonic oxide between pressures of 1000 M and 6·5 M. Temp. 15° C.

| Pressure. M | Log. decrement. | R pulsive force of radiation. |
|-------------------|--------------------|----------------------------------|
| 1000 (=0·76 m.m.) | 0·0947 | 2· |
| 829 | 0·0945 | 3· |
| 629 | 0·0936 | 4· |
| 474 | 0·0925 | 5· |
| 397 | 0·0921 | 6· |
| 200 | 0·0910 | 13· |
| 188 | 0·0907 | 14· |
| 126 | 0·0877 | 18· |
| 86 | 0·0838 | 20· |
| 55 | 0·0778 | 21· |
| 42 | 0·0716 | 22· |
| 38 | 0·0692 | 22· |
| 31 | 0·0653 | 21· |
| 22 | 0·0580 | 18· |
| 13 | 0·0474 | 14· |
| 12 | 0·0448 | 13· |
| 6·5 | 0·0305 | 7· |

684. These numbers are plotted as curves in the diagrams A, B, and C. They are remarkable as showing an almost complete identity with those of nitrogen on the same diagrams, both in position and shape. The viscosity at 760 millims. is in each case 0·1092. According to GRAHAM the proportion between the viscosities of air and carbonic oxide is 0·971, nitrogen giving the same (706). With my apparatus the proportion is 0·9715.

Like that of nitrogen, the curve of carbonic oxide is seen to be vertical,—*i.e.*, assuming the curve to represent the viscosity, the gas obeys MAXWELL'S law,—at pressures between 90 millims. and 3 millims. The vertical portion in nitrogen is at a little higher pressure: between 100 millims. and 6 millims.

685. The curve of repulsion resulting from radiation, shown in dots in diagrams B and C, is lower in carbonic oxide than in any other gas examined, and, unlike the other gases, there is no sudden rise to a maximum at about 40 M. At lower exhaustions the curve is, however, higher than it is in nitrogen.

OBSERVATIONS ON THE SPECTRUM OF CARBONIC OXIDE.

686. During exhaustion observations were continued on the variations in the spectrum. The ordinary band spectrum is first seen with a few sharp lines terminating the bands.

At 12 millims. pressure a sharp green line is first seen, λ 515. This line rapidly grows brighter as exhaustion continues, and then fades out; it is last seen at a pressure of about 0·9 millim. This line is probably the bright oxygen line, the wave-length of which is given by PLÜCKER at λ 514·4.

At a pressure of 2·8 millims. the spectrum agrees in appearance with the "Carbon No. 2" in WATTS'S 'Index of Spectra.'

At 553 M the bands between the sharp lines appear to be breaking up into masses of fine lines.

At 211 M these fine lines are distinctly visible. The brightness of this spectrum is now near its maximum.

At 100 M the general spectrum is growing faint, but a sharp green line at λ 534 makes its appearance by fits and starts. This is coincident with PLÜCKER'S bright oxygen line λ 534.

After this degree of exhaustion the spectrum rapidly gets fainter. The line λ 534 soon disappears, and the carbon lines also go one after the other, until at an exhaustion of 4 M only two lines are visible, λ 560 and λ 519.

VISCOSITY OF HYDROGEN.

687. Hydrogen gas is prepared in the apparatus shown in fig. 12 (p. 408) by the electrolytic decomposition of well-boiled water acidulated with pure sulphuric acid, a plate of amalgamated zinc being used for the positive pole, and platinum for the negative pole. The gas is collected in a bell receiver and passed into the apparatus when required, exactly as described under *Oxygen* (666). Hydrogen is also introduced into the apparatus in another way. In the tube, I (Plate 55, fig. 1), are pieces of palladium-foil electrolytically saturated with hydrogen; the foil retains the hydrogen even in a vacuum, and when desired gives it out on being heated with a lamp.

Before commencing experiments with hydrogen the apparatus must be exhausted up to the highest point, and then very slowly filled with the gas. Exhaustion is again carried out to a high point, and the slow filling with hydrogen repeated. It is then advisable to allow all to remain undisturbed for at least twenty-four hours, to permit the hydrogen to soak into the apparatus and displace any other gas which may be condensed on the surface of the glass. The whole is again exhausted, and then a third time filled with hydrogen.

Preliminary observations are now taken for viscosity; and the logarithmic decrement at standard pressure and temperature, noted. The pumping out and refilling with hydrogen should now be repeated, observing the logarithmic decrement each time, until it is found that it no longer decreases in value; when this is the case accurate observations are commenced.

688. It has been found that hydrogen has much less viscosity than any other gas; the fact of the logarithmic decrement not decreasing by additional attempts at purification is the test of its being free from admixture. This method of ascertaining the purity of the gas, by the uniformity of its viscosity coefficient at 760 millims., is more accurate than collecting samples and analysing them eudiometrically (706).

Several series of observations in hydrogen have been taken. For a long time it was considered that hydrogen, like other gases, showed the same slight departure from MAXWELL'S law of viscosity being independent of density; for the logarithmic decrement persistently diminished as the exhaustion increased, even at such moderate pressures as could be measured by the barometer gauge. Had it not been that the rate of decrease was not uniform in the different series of observations, I should have con-

sidered that this variation from MAXWELL'S law was due to some inherent property of all gases. After working at the subject for more than a year, it was discovered that the discrepancy arose from a trace of water obstinately held by the hydrogen—an impurity which behaved as I explain farther on (699) in the case of air and water vapour. Since discovering this property, extra precautions (already described at the commencement of this paper (641)) have been taken to dry all gases before entering the apparatus.

The results are given in the following table :—

689. TABLE VI.—Log. dec. of hydrogen gas at pressures between 760 millims. and 0·76 millim. Temp. 15° C.

| Pressure. Millims. | Log. decrement. | Pressure. Millims. | Time of one complete vibration. |
|-----------------------|--------------------|-----------------------|------------------------------------|
| 760 | 0·0499 | 744 | 10·76 |
| 748 | 0·0501 | 614 | 10·76 |
| 582 | 0·0501 | 504 | 10·76 |
| 567 | 0·0498 | 314 | 10·76 |
| 484 | 0·0499 | 134 | 10·76 |
| 428 | 0·0500 | 64 | 10·76 |
| 423 | 0·0500 | 29 | 10·76 |
| 414 | 0·0499 | 8 | 10·76 |
| 399 | 0·0500 | 0·6 | 10·76 |
| 303 | 0·0500 | 7·9 M | 10·76 |
| 301 | 0·0497 | | &c. |
| 283 | 0·0498 | | &c. |
| 268 | 0·0499 | | |
| 212 | 0·0504 | | |
| 209 | 0·0500 | | |
| 201 | 0·0507 | | |
| 193 | 0·0501 | | |
| 174 | 0·0501 | | |
| 148 | 0·0498 | | |
| 128 | 0·0501 | | |
| 108 | 0·0499 | | |
| 103 | 0·0499 | | |
| 101 | 0·0497 | | |
| 96 | 0·0497 | | |
| 76 | 0·0497 | | |
| 72 | 0·0499 | | |
| 61 | 0·0498 | | |
| 33 | 0·0498 | | |
| 22 | 0·0500 | | |
| 17 | 0·0499 | | |
| 14 | 0·0497 | | |
| 11 | 0·0499 | | |
| 9 | 0·0499 | | |
| 7 | 0·0499 | | |
| 6 | 0·0498 | | |
| 2 | 0·0498 | | |
| 1·8 | 0·0500 | | |
| 1·5 | 0·0498 | | |
| 1·0 | 0·0499 | | |
| 0·76 | 0·0498 | | |

TABLE VI. (continued).—Log. dec. of hydrogen gas at pressures between 1000 M and 0·16 M. Temp. 15° C.

| Pressure. M. | Log. decrement. | Repulsive force of radiation. | Mean free path of molecules.* Millims. |
|---------------------|--------------------|----------------------------------|--|
| 1000·0 (=0·76 m.m.) | 0·0498 | 1·0 | 0·10 |
| 921·0 | 0·0498 | 1·0 | 0·11 |
| 526·0 | 0·0497 | 3·0 | 0·19 |
| 421·0 | 0·0496 | 4·0 | 0·24 |
| 330·0 | 0·0495 | 5·0 | 0·30 |
| 314·0 | 0·0493 | 8·0 | 0·32 |
| 234·0 | 0·0488 | 11·0 | 0·43 |
| 205·0 | 0·0486 | 14·0 | 0·49 |
| 179·0 | 0·0486 | 18·0 | 0·56 |
| 168·0 | 0·0485 | 19·0 | 0·59 |
| 155·0 | 0·0484 | 25·0 | 0·65 |
| 147·0 | 0·0482 | 28·0 | 0·68 |
| 135·0 | 0·0479 | 31·0 | 0·74 |
| 122·0 | 0·0475 | 37·0 | 0·82 |
| 110·0 | 0·0472 | 40·0 | 0·91 |
| 95·0 | 0·0466 | 44·0 | 1·1 |
| 79·0 | 0·0457 | 52·0 | 1·3 |
| 65·0 | 0·0446 | 60·0 | 1·5 |
| 59·0 | 0·0441 | 64·0 | 1·7 |
| 54·0 | 0·0435 | 66·0 | 1·8 |
| 48·0 | 0·0430 | 68·0 | 2·1 |
| 45·0 | 0·0422 | 69·0 | 2·2 |
| 41·0 | 0·0417 | 70·0 | 2·4 |
| 37·0 | 0·0408 | 69·0 | 2·7 |
| 33·0 | 0·0394 | 69·0 | 3·0 |
| 29·0 | 0·0384 | 67·0 | 3·4 |
| 26·5 | 0·0373 | 66·0 | 3·8 |
| 22·0 | 0·0358 | 60·0 | 4·5 |
| 20·0 | 0·0351 | 58·0 | 5·0 |
| 16·0 | 0·0333 | 52·0 | 6·3 |
| 14·5 | 0·0324 | 49·0 | 6·9 |
| 12·0 | 0·0304 | 45·0 | 8·0 |
| 8·0 | 0·0270 | 37·0 | 12·5 |
| 6·5 | 0·0253 | 31·0 | 15·4 |
| 5·0 | 0·0232 | 29·0 | 20·0 |
| 4·0 | 0·0214 | 26·0 | 25·0 |
| 2·6 | 0·0191 | 15·0 | 38·5 |
| 1·8 | 0·0172 | 10·0 | 55·5 |
| 1·5 | 0·0169 | 9·0 | 66·7 |
| 1·0 | 0·0157 | 7·0 | 100·0 |
| 0·37 | 0·0130 | 3·0 | 270·0 |
| 0·16 | 0·0118 | 2·0 | 625·0 |

* For convenience I have taken the mean free path of the molecules of hydrogen the same as that of air, viz.: 0·0001 millim., at a pressure of 760 millims, and at 0° C. The actual figures, according to the most recent determinations, are—for air, 0·000095 millim.; and for hydrogen, 0·0000104 millim. The difference between these figures and 0·0001 is too small to show itself on the diagrams.

690. I have plotted the above observations in diagrams A, B, and C. The portion between 760 millims. and 0.32 millim. not varying in logarithmic decrement is represented by a vertical line, shown in diagrams B and C below the principal curve.

The remarkable character of hydrogen is its stiffness. It obey's MAXWELL'S law almost absolutely up to an exhaustion of about 700 M. To this point the line of viscosity is almost perfectly vertical. It then commences to curve over, and when the mean free path begins to assume proportions comparable with the dimensions of the bulb, and approaches infinity, the viscosity curve in like manner draws near the zero line.

691. The repulsive force of radiation is higher in hydrogen than in any other gas. It commences at as low an exhaustion as 14 millims., but does not increase to any great extent till an exhaustion of 200 M is attained; it then rises rapidly to a maximum at between 40 and 60 M, after which it falls away to zero. The maximum repulsion exerted by radiation in hydrogen is to that in air as 70 to 42.6. This fact is now utilised in the construction of radiometers and similar instruments when great sensitiveness is required.

692. Taking the viscosity of air at 760 millims. as 0.1124, and hydrogen as 0.0499, the proportion between them is 0.4439. GRAHAM* gives the transpiration time for hydrogen as 0.4375 taking oxygen as unity, or 0.4855 taking air as unity (706).

693. Professor CLERK MAXWELL† found dry hydrogen to be much less viscous than air, the ratio of its viscosity to that of air being 0.5156. He says, referring to this result: "It appears, from the experiments of Mr. GRAHAM, that the ratio of the transpiration time of hydrogen to that of air is 0.4855, and that of carbonic acid to air 0.807. These numbers are both smaller than those of this paper. I think that the discrepancy arises from the gases being less pure in my experiments than in those of GRAHAM."

694. MM. KUNDT and WARBURG, in the paper already mentioned, assert that according to theory the viscosity should not begin appreciably to diminish as long as the layer of gas is thicker than fourteen times the mean length of path. They also declare that even when the thickness is as much as 300 times the mean length of path a perceptible diminution of the retarding forces commences, becoming greater as the pressure diminishes. They find the ratio between air and hydrogen to be 0.488, and the viscosity to vary according to the following table:—

| Pressure in millims. | Log. decrement. |
|----------------------|-----------------|
| 380.0 | 0.0652 |
| 20.0 | 0.0638 |
| 8.8 | 0.0629 |
| 2.4 | 0.0601 |
| 1.53 | 0.0557 |

Above this exhaustion they found the viscosity rapidly diminished, but no measurements of pressure were taken.

* 'Chemical and Physical Researches,' by THOMAS GRAHAM, p. 179.

† "On the Viscosity or Internal Friction of Air and other Gases," Phil. Trans., 1866, Part I., p. 257.

695. The diminution of logarithmic decrement which MM. KUNDT and WARBURG obtained at moderate exhaustions, and their high ratio between the viscosity of hydrogen and air, is probably due to the presence of a trace of foreign gas, most likely water. They remark that: "On proceeding further to investigate the laws of gas-friction *below* the before-mentioned limit of rarefaction,—

$$\left(\frac{l}{d} > \frac{1}{14}\right),$$

we could not succeed, even with the most careful drying, in removing with sufficient completeness the last traces of aqueous vapour, which, insensible in the above experiments, with the *low* pressures here employed distorted the results. The presence of aqueous vapour was shown, *inter alia*, by this—that the damping moment for a vacuum (so we name a space filled with a gas of $\frac{1}{100}$ th of a millim. pressure mixed with vapour) rose considerably when the apparatus was left to itself. This arose from water separating from the solid parts and evaporating into the vacuum. In consequence of this the theory cannot be quantitatively tested on the results obtained."

It is not unlikely that a trace of foreign gas or aqueous vapour was present in GRAHAM's hydrogen, for he himself remarks that: "The small addition of 5 per cent. of air to hydrogen has a surprising effect in retarding the transpiration of that gas. The effect of 5 per cent. of air in retarding the rate of hydrogen is nearly four times greater than it should be by calculation. The experiment shows the effect which a small amount of impurity must have in deranging the transpiration rate of that gas."*

The same effect is noticed by MAXWELL, who says† that a small proportion of air mixed with hydrogen was found to produce a large increase of viscosity.

696. GRAHAM states that in his experiments the hydrogen "was prepared from zinc which contained no arsenic, and was passed through a wash-bottle containing oxide of lead dissolved in caustic soda, and dried by passing over asbestos moistened with oil of vitriol."‡

In another paper he speaks of drying the gases by means of chloride of calcium tubes, and pumice moistened with oil of vitriol. Guided by the light of recent experience I do not hesitate to affirm that by this means it is not possible to remove the last traces of aqueous vapour from hydrogen gas. It is not even enough to pass the gas through a tube containing phosphoric anhydride lying loose in it. The anhydride must be tightly packed in the tube, so as to offer considerable obstruction to the passage of the gas, which should pass through several feet of such desiccating tube (641, 688). Not until I adopted all these precautions to dry the gas was I able to get perfectly concordant results with different lots of hydrogen gas.

697. With each improvement in purification and drying I have obtained a lower value for hydrogen, and have consequently diminished the number expressing the

* 'Chemical and Physical Researches,' by THOMAS GRAHAM, p. 123.

† "On the Viscosity or Internal Friction of Air and other Gases." Phil. Trans., 1866, Part I., p. 257.

‡ 'Chemical and Physical Researches,' by THOMAS GRAHAM, p. 176.

ratio of the viscosity of hydrogen to that of air. In 1876 I found the ratio to be 0·508. In 1877 I reduced this ratio to 0·462. Last year, with improved apparatus, I obtained the ratio of 0·458, and I have now got it as low as 0·4439. This is much lower than GRAHAM'S number 0·4855 deduced from transpiration. GRAHAM calls this number theoretical, but in discussing the subject it appears that he was quite prepared to find hydrogen depart from the theoretical law which seemed to govern some other of the gases. Thus at page 179 of the collected edition of his works, already quoted, GRAHAM writes: "The times of oxygen, nitrogen, carbonic oxide, and air are directly as their densities, or equal *weights* of these gases pass in equal times. Hydrogen passes in half the time of nitrogen, or twice as rapidly for equal volumes. . . . The circumstance that the transpiration time of hydrogen is one-half of that of nitrogen indicates that the relations of transpirability are even more simple in their expression than the relations of density among gases."

OBSERVATIONS ON THE SPECTRUM OF HYDROGEN.

698. In the description of the viscosity apparatus (641) I mentioned that a spectrum tube with capillary bore was attached to it at *k*. With this apparatus I have taken observations on the spectrum of hydrogen during the exhaustion, using a coil giving a 6-inch spark, and examining the spectrum with a dispersion sufficient to well separate the sodium lines.

No points of special interest were noticed. The red line ($\lambda=656\cdot2$), the green line ($\lambda=486\cdot1$), and the blue line ($\lambda=434$) were seen at their brightest at a pressure of about 3 millims., and after that exhaustion they begin to diminish in intensity. As exhaustion proceeds a variation in visibility of the three lines is observed. Thus at 36 millims. the red line is seen brightly, the green faintly, whilst the blue line cannot be detected. At 15 millims. the blue line is seen and the three keep visible till an exhaustion of 418 M is reached, when the blue line becomes difficult to see. At 38 M only the red and green lines are visible, the red being very faint. It is seen with increasing difficulty up to an exhaustion of 2 M, when it can be seen no longer. The green line now remains visible up to an exhaustion of 0·37 M, beyond which it has not been seen.

It is worthy of remark that, although when working with pure hydrogen the green line is always the last to go, it is not the first to appear when hydrogen is present as an impurity in other gases. Thus when working with carbonic anhydride insufficiently purified, the red hydrogen line is often seen, but I have never seen either the green or the blue line.

INFLUENCE OF AQUEOUS VAPOUR ON THE VISCOSITY OF AIR.

699. In the foregoing experiments many discrepancies were traced to the presence of moisture in the gas (688). The influence of aqueous vapour does not appear to be great when present in moderate amount in gas of normal density, but at high

exhaustions it introduces errors which interfere with the uniformity of the results. A series of experiments were accordingly undertaken to trace the special action of aqueous vapour when mixed with air.

The apparatus as represented in fig. 1 was slightly altered for this purpose, without, however, interfering with the parts affecting the measurements. The drying tubes of phosphoric anhydride were removed, and a small glass bulb filled with pure water was sealed on to the end of the arm *p* (the arm which, working between metal stops, gives motion to the viscosity bulb). The object of attaching the water bulb to this part of the apparatus was to allow the aqueous vapour readily to diffuse into the viscosity bulb, and drive the unsaturated air before it when the pump was worked.

The apparatus, thus arranged and full of air at the normal pressure, was left to itself for twenty-four hours, to allow aqueous vapour to diffuse through it. The temperature was uniformly 15° the whole time.

Observations were simultaneously taken with the candle flame, so as to measure the repulsion due to radiation in the presence of aqueous vapour.

The results are given in the following table :—

700. TABLE VII.—Log. dec. of moist air at pressures from 760 millims. to 0·1 millim, and lower. Temp. 15° C.

| Pressure in millims. | Log. decrement. | Repulsion due to radiation. |
|----------------------|-----------------|-----------------------------|
| 760 | 0·1124 | 0· |
| 700 | 0·1109 | 0· |
| 600 | 0·1084 | 0· |
| 500 | 0·1062 | 0· |
| 400 | 0·1040 | 0· |
| 300 | 0·1014 | 0· |
| 200 | 0·0993 | 0· |
| 100 | 0·0955 | 0· |
| 75 | 0·0937 | 0· |
| 50 | 0·0903 | 0· |
| 40 | 0·0796 | 0· |
| 20 | 0·0589 | 0· |
| 16 | 0·0531 | 0· |
| 15 | 0·0520 | 0· |
| 13 | 0·0516 | 0· |
| 11 | 0·0511 | 0· |
| 8 | 0·0500 | 0· |
| 7 | 0·0498 | 0· |
| 5 | 0·0499 | 0· |
| 3 | 0·0497 | 0· |
| 1* | 0·0497 | 0· |
| 0·1 | 0·0484 | 0· |
| .. | 0·0441 | 1· |
| .. | 0·0432 | 1· |
| .. | 0·0419 | 4· |
| .. | 0·0406 | 5· |
| .. | 0·0390 | 9· |

* At about this degree of exhaustion the last drop of liquid water, which for some time had been rapidly evaporating, disappeared.

701. I was unable to take pressure after 1.0 millim., as the McLEOD measuring apparatus does not give trustworthy indications when aqueous vapour is present. As soon as the pressure in the measuring tube rises above the tension of aqueous vapour, water condenses in it, and measurements can no longer be taken.

These results plotted as a diagram give the curve shown in diagram A, marked "Moist Air."

Up to a pressure of about 350 millims. the presence of aqueous vapour has little or no influence on the viscosity of air. The two curves are in fact superimposed. At this point, however, divergence commences, and the curve rapidly bends over, the log. dec. falling from 0.0903 to 0.0500 between 50 and 7 millims. pressure. Here it joins the hydrogen curve, and between 7 millims. and 1 millim. they appear to be identical.

702. These results are partly to be explained by the peculiar action of water vapour in the apparatus. At the normal pressure the amount of aqueous vapour present in the air, supposing it to be saturated, is only about 13 parts in a million, and the identity of the logarithmic decrement with that of dry air shows that this small quantity of water has no appreciable action on the viscosity. When the pump is set to work the air is gradually removed, whilst the aqueous vapour is kept supplied from the reservoir of liquid. As the exhaustion approaches the tension of aqueous vapour, evaporation goes on at a greater rate, and the vapour displaces the air with increasing rapidity; until, after the pressure of 12.7 millims. is passed, the aqueous vapour acts as a gas, and, being constantly supplied from the reservoir of water (as long as it lasts), washes out all the air from the apparatus, the logarithmic decrement rapidly sinking to that of pure water gas.

This explanation requires that the viscosity of pure aqueous vapour should be the same as that of hydrogen, at all events between 7 millims. and 1 millim. pressure. The facts can, however, be explained in another way. During the action of the SPRENGEL pump sufficient electricity is sometimes generated to render the fall tubes luminous in the dark (52). It is conceivable that under such electrical influence the falling mercury may be able to decompose aqueous vapour at these high exhaustions, with formation of oxide of mercury and liberation of hydrogen. Of these two theories the latter appears to be the more probable, but I have not sufficient data to enable me to decide between them.

703. The presence of water vapour shows itself likewise in the very slight amount of repulsion produced by radiation. Repulsion commences in air at a pressure of 12 millims., whilst at a higher exhaustion the maximum effect rises to over 40 divisions. Here, however, repulsion does not begin till the exhaustion is higher than the barometer gauge will indicate, whilst the maximum action after long-continued pumping is only 9 divisions. This confirms the results frequently met with in my researches on "Repulsion Resulting from Radiation," where the presence of even a trace

of aqueous vapour was found to have strong action in diminishing the sensitiveness of the radiometer and other instruments (130).

704. For a long time concentrated sulphuric acid was used to moisten the interior of the pump, a special stopper being affixed to the pump to admit of the acid being run in without interfering with the exhaustion. For six months observations were taken on air and several other gases, when it was found that the presence of sulphuric acid lowered the logarithmic decrement, and the work had all to be done over again. It is known, from the experiments of Messrs. WANKLYN and ROBINSON, that at a high temperature, and under conditions which admit of diffusion taking place, sulphuric acid dissociates into sulphuric anhydride and water; so it is not improbable that at a high exhaustion a similar decomposition may take place, one constituent being retained in the liquid acid more readily than the other, which escapes into the apparatus and alters the logarithmic decrement.

VISCOSITY OF KEROSOLINE VAPOUR.

705. The rapid diminution of viscosity in the last experiment after reaching the pressure of 400 millims. is probably due to the aqueous vapour in the air being near its liquefying point. It was thought advisable to test this hypothesis by employing a somewhat less easily condensible vapour, which could be introduced into the apparatus without any admixture of air. An experiment was accordingly tried with a very volatile hydrocarbon, commercially known as kerosoline, boiling at a little above the ordinary temperature. The vapour of this body was introduced into the well-exhausted apparatus, when the gauge at once sank 82·5 millims. After the usual precautions to eliminate air a series of observations were taken, with the following results:—

TABLE VIII.—Log. dec. of kerosoline vapour, at pressures between 82·5 millims. and 8 millims. Temp. 15° C.

| Pressure in millims. | Log. decrement. |
|----------------------|-----------------|
| 82·5 | 0·0425 |
| 71·5 | 0·0416 |
| 64·0 | 0·0409 |
| 59·0 | 0·0407 |
| 54·0 | 0·0404 |
| 48·5 | 0·0400 |
| 43·0 | 0·0396 |
| 38·0 | 0·0394 |
| 32·5 | 0·0389 |
| 21·0 | 0·0381 |
| 17·5 | 0·0380 |
| 13·4 | 0·0382 |
| 10·0 | 0·0381 |
| 8·0 | 0·0379 |

These results are plotted on the curve marked "Kerosoline Vapour," on diagram A. The loss of viscosity is more rapid than with any other gas examined except aqueous vapour. Conversely a very great increase of viscosity occurs on increasing the pressure from 8 to 82.5 millims. The explanation of this is that the vapour of kerosoline is very near its liquefying point, and therefore very far from the state of a "perfect" gas (709).

The negative bend in the curve at about 10 millims. pressure, already noticed with other gases (668), is strongly marked with this hydrocarbon vapour.

DISCUSSION OF RESULTS.

706. When discussing the viscosity results obtained with the different gases experimented with, I have given the proportion which I find between the viscosity of each gas and that of air, comparing the ratio with that obtained by GRAHAM, KUNDT and WARBURG, and MAXWELL, as follows:—

| | GRAHAM. | KUNDT and WARBURG. | MAXWELL. | CROOKES. |
|------------------------------|---------|--------------------|----------|----------|
| Air | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| Oxygen | 1.1099 | .. | .. | 1.1185 |
| Nitrogen | 0.971 | .. | .. | 0.9715 |
| Carbonic anhydride | 0.807 | 0.806 | 0.859 | 0.9208 |
| Carbonic oxide | 0.971 | .. | .. | 0.9715 |
| Hydrogen | 0.4855 | 0.488 | 0.5156 | 0.4439 |

I have reason to believe that my results are more accurate than those of other observers. In the case of hydrogen I have not only obtained a much lower viscosity, but the absolute obedience which it pays to MAXWELL'S law is an additional proof of its purity, for any admixture of foreign gas destroys the uniformity of results (688).

707. GRAHAM'S numbers are the theoretical results deduced from his experiments on transpiration of gases. They are, he says,* the numbers to which the transpiration times of the gases approximate and in which they have their limit. GRAHAM concludes that the "times of oxygen, nitrogen, carbonic oxide, and air are directly as their densities, or equal *weights* of these gases pass in equal times. Hydrogen passes in half the time of nitrogen, or twice as rapidly for equal volumes. The result for carbonic acid appears at first anomalous. It is that the transpiration time of this gas is inversely proportional to its density when compared with oxygen." In the Bakerian lecture already quoted, when discussing GRAHAM'S results and their bearings upon his own experiments on the viscosity of gases, MAXWELL says: "It appears to me that for comparative estimates of viscosity the method of transpiration is the best."

708. It must not be forgotten that the pressure of 760 millims. is not one of the constants of Nature, but is a purely arbitrary one, selected for our own convenience

* *Loc. cit.*, pp. 178-9.

when working near the level of the sea. In diagrams A; B, and C I have started from this pressure of 760 millims., and have given the curves through a wide range of exhaustion. But the curves might also be continued, working downwards instead of upwards. Although it is unsafe to indulge in speculation in the absence of data, there are some conclusions which it is quite legitimate to draw from an inspection of the curves. From the shape and direction in which they cut the 760 line it is reasonable to infer their further progress downwards, and we may assume that an easily liquefiable gas will show a more rapid increase in log. decrement than one which is difficult to liquefy by pressure. For instance, hydrogen, the least condensible of all gases, shows no tendency to increase in log. decrement by pressure. Oxygen and nitrogen, which are only a little less difficult to condense than hydrogen, show a slight increase in log. decrement. Carbonic anhydride, which liquefies at a pressure of 56 atmospheres at 15° C., increases so rapidly in viscosity that at this pressure it would have a logarithmic decrement of about 1.3, representing an amount of resistance to motion that it is difficult to conceive anything of the nature of gas being capable of exerting.

Kerosoline vapour is rendered liquid by pressure much more readily than carbonic anhydride. Its curve of viscosity on diagram A shows a great increase in density for a very slight access of pressure (705).

709. MAXWELL'S law was discovered as the consequence of a mathematical theory. It presupposes the existence of gas in a "perfect" state—a state practically unknown to physicists, although hydrogen gas very nearly approaches that state. An ordinary gas may be said to be bounded, as regards its physical state, on the one side by the sub-gaseous or liquid condition, and on the other side by the ultra-gaseous condition. A gas assumes the former state when condensed by pressure or cold, and it changes to the latter state when highly rarefied. Before actually assuming either of these states there is a kind of foreshadowing of change, with partial loss of gaseity. When the molecules, by pressure or cold, are made to approach each other more closely, they begin to enter the sphere of each other's attraction, and therefore the amount of pressure or cold necessary to produce a certain density or viscosity is less than the theoretical amount by the internal attraction exerted on each other by the molecules. The nearer the gas approaches the point of liquefaction the greater is the attraction of one molecule to another, and the amount of pressure required to produce any given density will be proportionally less than that theoretically required by a "perfect" gas. This foreshadowing of the sub-gaseous or liquid state explains how it is that there is such wide divergence from MAXWELL'S law in the case of imperfect gases, such as carbonic anhydride, water gas, and the volatile hydrocarbon kerosoline. At the other end of the scale we find even a more marked divergence from MAXWELL'S law. This is due to the gas commencing to assume ultra-gaseous properties.

THE ULTRA-GASEOUS STATE OF MATTER.

710. A consideration of the curves of viscosity of the gases, especially hydrogen, which are given in the foregoing pages, will, I think, confirm the supposition that a gas, as the exhaustions become extreme, gradually loses its gaseous characteristics, and passes to what I have ventured to call an ultra-gaseous state. Certainly it ceases to possess many of the properties usually held to be the essential attributes of gaseity.

For instance, MAXWELL'S law that the viscosity of a gas is independent of pressure holds good to a certain point, and then it rapidly breaks down. All gases appear to obey MAXWELL'S law between some limits of exhaustion, and diverge from it at others. The change to the ultra-gaseous state commences to be assumed at about an exhaustion of half a millim. In hydrogen the change then proceeds slowly, but in the other gases I have experimented with the change to ultra-gas takes place with greater rapidity.

711. In gases, variation of pressure in different parts of a closed vessel equalises itself with great rapidity, but in the ultra-gaseous state differences of pressure may exist for twenty minutes or more in different parts of the apparatus.

712. In gases, electrically charged bodies do not permanently retain their charge, but gradually discharge themselves. In ultra-gas, however, a pair of electrified gold leaves have remained repelled at absolutely the same angle for thirteen months.*

713. Another property of gases is that of facilitating the cooling of bodies immersed in them, by communicating an increase of motion to the molecules of the gas which carry it to the walls of the containing vessel,—*i.e.*, by *carriage* instead of *convection*.

714. There is little difference in the rate of cooling with increased exhaustion, so long as we work with such ordinary good vacua as can be obtained by air-pumps. For if, on the one hand, there are fewer molecules impinging on the warm body (which is adverse to the carriage of heat), yet on the other hand, the mean length of path between collisions is increased so that the augmented motion is carried farther; the number of steps by which the temperature passes from the warmer to the cooler body is diminished, but the value of each step is correspondingly increased. Hence the difference of velocity before and after impact may make up for the diminution in the number of molecules impinging.

In gases, therefore, the rate of cooling is little affected by rarefaction, the law in this case being analogous to that governing the viscosity.

715. In a paper which I have recently had the honour of reading before the Royal Society,† I show that when the exhaustion is carried to so high a point that the mean free path is comparable with the diameter of the containing vessel, the rate at which heat is conveyed across is much diminished. The molecules are now in the ultra-gaseous state, and further exhaustion produces a notable fall in the rate of

* Proc. Roy. Soc., No. 193, 1879, p. 347.

† *Ibid.*, No. 208, 1880, p. 239.

cooling, an increase of exhaustion from 20 M to 2 M retarding the carriage of heat more than all the previous exhaustion from 760 millims. to 20 M.

716. I have shown elsewhere* that the property of gaseity is pre-eminently a property dependent on collisions. A given space full of air at the ordinary pressure contains millions of millions of molecules rapidly moving in all directions, each molecule momentarily encountering millions of other molecules in a second. In such a case the length of the mean free path of the molecules is exceedingly small compared with the dimensions of the containing vessel, and those properties are observed which constitute the ordinary gaseous state of matter—properties which depend upon constant collisions.

The gaseous state continues so long as the collisions are almost infinite in number and of inconceivable irregularity. But in such high vacua as I now describe the free path of the molecules is made so long that the hits in a given time may be disregarded in comparison to the misses, and the average molecule is allowed to obey its own motions or laws without interference; and when the mean free path is comparable to the dimensions of the containing vessel, the properties which constitute gaseity are reduced to a minimum, and the matter then becomes exalted to an ultra-gaseous state.

In the ultra-gaseous state properties of matter which exist even in the gaseous state are shown *directly*, whereas in the state of gas they are only shown *indirectly*, by viscosity and so forth.

717. The ordinary laws of gases are a simplification of the effects arising from the properties of matter in the ultra-gaseous state; such a simplification is only permissible when the mean length of path is small compared with the dimensions of the vessel. For the sake of simplicity we make abstraction of the individual molecules, and feign to our imagination *continuous* matter of which the fundamental properties—such as pressure varying as the density, and so forth—are ascertained by experiment. A gas is nothing more than an assemblage of molecules contemplated from a simplified point of view. When we deal with phenomena in which we are obliged to individually contemplate molecules, we must not speak of the assemblage as *gas*.

718. An objection has been raised touching the existence of ultra-gaseous matter in highly exhausted electrical tubes, that the special phenomena of radiation and phosphorescence which I have considered characteristic of this form of matter can be made to occur at much lower pressures than that which exhibits the maximum effects. For the sake of argument let us assume that the state of ultra gas with its associated phenomena is at the maximum at a millionth of an atmosphere. Here the mean free path is about 4 inches long, sufficient to strike across the exhausted tube. But it has been shown by many experimentalists that at exhaustions so low that the contents of the tube are certainly not in the ultra gaseous state, the phenomena of phosphorescence can be observed. This circumstance had not escaped my notice. In my first paper on the “Illumination of Lines of Molecular Pressure and the Trajectory of

* Proc. Roy. Soc., No. 205, 1880, p. 469.

Molecules”* I drew attention to the fact that a molecular ray producing green phosphorescence can be projected 102 millims. from the negative pole when the pressure is as high as 0·324 millim. or 427 M. In this case the mean free path of the molecules is 0·23 millim. ; and it is not surprising that with more powerful induction discharges, and with special appliances for exalting the faint action to be detected, the above-named phenomena can be produced at still higher pressures.

719. It must be remembered that we know nothing of the *absolute* length of the free path or the *absolute* velocity of a molecule ; these may vary almost from zero to infinity. We must limit ourselves to the *mean* free path and the *mean* velocity, and all that these experiments show is that a few molecules can travel more than a hundred times the *mean* free path, and with perhaps a corresponding increase over the *mean* velocity, before they are stopped by collisions. With weak electrical power, the special phosphorogenic action of these few molecules is too faint to be noticed ; but by intensifying the discharge the action of the molecules can be so increased as to render their presence visible. It is also probable that the absolute velocity of the molecules is increased so as to make the mean velocity with which they leave the negative pole greater than that of ordinary gaseous molecules. This being the case, they will not easily be stopped or deflected by collisions, but will drive through obstacles, and so travel to a greater distance.

If this view is correct, it does not follow that gas and ultra-gas can co-exist in the same vessel. All that can be legitimately inferred is, that the two states insensibly merge one into the other, so that at an intermediate point we can by appropriate means exalt either the phenomena due to gas or to ultra-gas. The same thing occurs between the states of solid and liquid, and liquid and gas. TRESCA’S experiments on the flow of solids prove that lead and even iron, at the common temperature, possess properties which strictly appertain to liquids, whilst ANDREWS has shown that liquid and gas may be made to merge gradually one into the other, so that at an intermediate point the substance partakes of the properties of both states.

* Phil. Trans., Part I., 1879 : The Bakerian Lecture.

Note on the Reduction of Mr. CROOKES'S Experiments on the Decrement of the Arc of Vibration of a Mica Plate oscillating within a Bulb containing more or less Rarefied Gas.

By Professor G. G. STOKES, Sec. R.S.

Received and Read February 17, 1881.

IN the course of his long series of researches "On Repulsion resulting from Radiation," Mr. CROOKES had frequently occasion to observe the deflections of a light bar or lamina of some substance delicately suspended and oscillating by torsion. When such a bar was set in vibration, the vibrations tended more or less rapidly to subside, in consequence, no doubt, of the viscosity of the gas enclosed in the apparatus. At first it seemed as if the rate of subsidence tended to reach a constant value which remained the same at all higher exhaustions. But as methods of exhaustion were improved, and the gases were so rarefied that the effect of a candle in causing repulsion distinctly fell off, the rate of subsidence of the oscillations was found greatly to fall off too. This falling off at extreme exhaustions seemed to present a very interesting field of study in connexion with the molecular condition of gases. The inquiry would naturally involve the observation of the nearly constant rate obtained at somewhat lower exhaustions; and the same apparatus would serve for experiments on the rate of subsidence at higher densities, up to that corresponding to atmospheric pressure.

A comparison of the rates of subsidence in different gases at great but not extreme exhaustions was further interesting as a new means of determining the ratios of the viscosities of different gases. In fact, at high exhaustions the motion of the gas tends to a condition of ideal simplicity from which a comparison of the viscosities of different gases would immediately result. The effect of the viscosity of a gas on its own motion is regulated by the value of a constant which I have elsewhere* called the index of friction of the gas, namely, the coefficient of viscosity divided by the density. According to MAXWELL'S law, the coefficient of viscosity is independent of the density, and therefore the index of friction varies inversely as the density. Hence as the exhaustion proceeds the motion of the gas tends to become what it would be if the viscosity were infinite, and the bounding surfaces had their actual motion. In the limit, the instantaneous motion of the gas depends only on that of the vibrating plate, to which it is proportional, except in so far as the finiteness of the angle of oscillation entails a

* "On the Effect of the Internal Friction of Fluids on the Motion of Pendulums," Cambridge Philosophical Transactions, vol. ix., p. [8].

difference of position of the plate relatively to the bounding wall of the bulb, a difference however which is trifling on account of the smallness of the angle through which the plate oscillates. The forces therefore arising from the viscosity tend in the limit to vary entirely as the angular velocity, and not, as is the case when the index of friction is comparatively small, partly also on the angular acceleration. The result therefore will be that the oscillations are retarded by a force varying as the angular velocity, and producing therefore a subsidence of the motion such that the proportionate rate of change of the arc is proportional to the coefficient of viscosity.

Mr. CROOKES'S experiments were carefully made from pressures as high as the atmospheric pressure downwards. At first there is a very evident decrease of subsidence as the pressure decreases, except in the case of hydrogen, in which it is very small, we may say insensible. Then it remains very nearly constant for a considerable range of exhaustion, and at last, for extreme exhaustions, it rapidly fades away.

In the second of these three stages the condition of ideal simplicity above mentioned is doubtless approximately attained. If however we confined our attention to this part only of the series, the lower part, although so carefully made, would remain unutilised; and further, we should remain uncertain whether in taking the logarithmic decrement as proportional to the viscosity our approximation was not too rough.

The determination of the motion of the gas corresponding to a given motion of the vibrating solid, and thereby the determination of the forces which the gas exerts on the solid, forms a perfectly definite problem, the solution of which, if it could be effected, would lead to a determination of the coefficient of viscosity from the observed influence of the gas on the motion of the plate. But although in these slow motions the terms in the hydrodynamical equations which involve the squares of the velocities are insensible, so that the equations may be taken as linear, the problem is one of hopeless difficulty except in a few simple cases. In the paper referred to, I have given the solution in the case of a sphere vibrating in a mass of fluid either unlimited or confined by a concentric spherical envelope, and in that of a long cylindrical rod vibrating in an unconfined mass of fluid. In the latter especially of these cases the solution involves functions of a highly complicated form. For a lamina such as that employed by Mr. CROOKES, the problem could not even be solved if the fluid were regarded as perfect, much less when the viscosity is taken into account.

But though we are baffled in the attempt to give an absolute solution of the problem, theory indicates the conditions of similarity of the motion of the gas in two different cases, and enables us thereby to compare the viscosities when those conditions are satisfied.

The bulb, vibrating plate, and torsion thread being always the same, the two things that varied from one experiment to another were the nature and the pressure of the gas, not the temperature, which for the present was kept constant. The moment of inertia of the lamina was sufficiently large to allow the time of vibration to be nearly the same in the different experiments. For the present I will suppose it constant,

reserving to a later stage the consideration of the correction to be made for its variation.

Let ρ be the density of the gas, p the observed pressure, D the density under a standard pressure, μ the coefficient of viscosity, and let accented letters refer to another gas. The dimensions of the terms in the equations of motion show that in comparing two cases in which the nature and pressure of the gases alone differ, the motions will be similar provided

$$\frac{\mu}{\rho} = \frac{\mu'}{\rho'}, \text{ or } \frac{\mu}{pD} = \frac{\mu'}{p'D'} \dots \dots \dots (1)$$

This condition being satisfied, the resultant pressures of the gas on the solid will vary as μ or as ρ ; and as the logarithmic decrements (l) will vary in the same proportion, we shall have

$$\frac{l}{\rho} = \frac{l'}{\rho'}, \text{ or } \frac{l}{pD} = \frac{l'}{p'D'} \dots \dots \dots (2)$$

The equations (1) and (2) are such that when one is satisfied so is the other. It will be convenient to regard (2) as giving the condition of similarity, and then (1) or

$$\frac{\mu}{l} = \frac{\mu'}{l'} \dots \dots \dots (3)$$

gives the ratio of the viscosities at the two corresponding pressures in the two gases.

The times of vibration were practically constant when once the exhaustion was pretty high, at least until the very highest exhaustions were reached, when it fell off a very little; but at atmospheric pressure and at low exhaustions it was somewhat greater, though not much. Its variability will not affect the results obtained by the above method, provided only the times are the same in the two experiments of each pair, which was very approximately the case. Nevertheless it may be well to consider the correction to be made in consequence of the inequality of the times.

Let τ be the time of vibration from rest to rest, then in comparing two similar systems the time-scale must be varied, so as always to be proportional to τ , and the hydrodynamical equations show that for the condition of similarity we have, in place of (1), the equation

$$\frac{\mu\tau}{\rho} = \frac{\mu'\tau'}{\rho'} \dots \dots \dots (4)$$

As the two dynamical systems are not similar as a whole, but only the gaseous parts of them, we must have recourse to the equation of motion of the vibrating lamina. Let θ be the angle of torsion, I the moment of inertia, $n^2 I \theta$ the force of restitution, which will be proportional to the angle of torsion, provided at least the

glass fibre be treated as perfectly elastic, as it doubtless may be in considering the correction to be made for the inequality of the times of vibration, even though its defect of elasticity might not, possibly, be absolutely insensible in its influence on the main motion. Then if there were no fluid the equation of motion of the lamina would be

$$I \frac{d^2\theta}{dt^2} + n^2 I \theta = 0.$$

As in the cases treated of in the paper of mine already referred to, the resultant pressure of the fluid on the lamina (the term "pressure" here including the tangential action), will partly agree in phase with the displacement or force of restitution, partly with the velocity of the lamina. The first part will have the effect of adding to the mass of the lamina an ideal mass depending on the density, viscosity, and time of vibration. From the dimensions of the quantities involved with respect to time and density, this ideal mass must be of the form $\rho f\left(\frac{\mu\tau}{\rho}\right)$. There is no need to express the dependence of the function f on the scale of lengths. In a similar manner the part of the resultant pressure which is multiplied by $\frac{d\theta}{dt}$ must be expressed by ρ multiplied by some other function of $\frac{\mu\tau}{\rho}$ and divided by a time. We may express it therefore by $2\rho n F\left(\frac{\mu\tau}{\rho}\right)$ where n is $\frac{\tau}{\pi}$. Denoting the two functions of $\frac{\mu\tau}{\rho}$ by A and B respectively, we have accordingly for the equation of motion

$$(I + A\rho) \frac{d^2\theta}{dt^2} + 2B\rho n \frac{d\theta}{dt} + n^2 I \theta = 0. \quad \dots \dots \dots (5)$$

The integral of this equation is

$$\theta = e^{-qt}(c \cos mt + c' \sin mt)$$

where

$$q = \frac{B\rho n}{I + A\rho}, \quad m^2 = \frac{n^2 I}{I + A\rho} - \frac{B^2 \rho^2 n^2}{(I + A\rho)^2};$$

and since by definition of n , $m = n$, we have

$$n^2 + q^2 = \frac{n^2 I}{I + A\rho},$$

and then by eliminating A between the last equation and the last but two we have

$$B = \frac{n^2 I q}{\rho n(n^2 + q^2)} \dots \dots \dots (6)$$

Now n is $\pi \div \tau$, and $q\tau$ is the Napierian logarithmic decrement, or $l \div M$, M being the modulus of the common system. Hence (6) becomes

$$B = \frac{a^2 M l \tau^2}{\pi \rho (M^2 \pi^2 + l^2)}$$

and as B is the same in the two systems compared we have

$$\frac{l}{\rho} \cdot \frac{\tau^2}{M^2 \pi^2 + l^2} = \frac{l'}{\rho'} \cdot \frac{\tau'^2}{M^2 \pi^2 + l'^2} \dots \dots \dots (7)$$

an equation which takes the place of (2), and serves to define corresponding densities, and then (4) gives the ratio of the viscosities at those densities, or say, at the corresponding pressures. If we eliminate the ratio of ρ to ρ' between (4) and (7) we get

$$\frac{\mu}{l\tau} (\pi^2 M^2 + l^2) = \frac{\mu'}{l'\tau'} (\pi^2 M^2 + l'^2) \dots \dots \dots (8)$$

which takes the place of (3).

The ratio of the factor $\pi^2 M^2 + l^2$ to $\pi^2 M^2$ alone but little exceeds unity; thus even for oxygen at 760 millims. pressure it is barely 1.0085, and of course the ratio of that factor for one gas to the factor for another gas at the corresponding pressure will differ from unity still less. Hence it is almost a needless refinement to keep in this factor at all. However, even if we retain it in (8) it is quite superfluous in (7), which merely determines what densities are to be deemed to correspond in seeking the logarithmic decrements. For until extreme rarefactions are reached, to which the above investigation no longer applies, the logarithmic decrement changes so slowly that a small error in the density of one gas which is deemed to correspond to a given density in another will make no sensible error in the logarithmic decrement. And not only may the factors above mentioned be omitted, but as the ratio of τ to τ' will differ but little from a ratio of equality, the formula (7) may be dispensed with altogether, and the simpler formula (2) employed. But when the logarithmic decrements have been found, in determining the ratio of the viscosities from (8) it is better not to disregard the quantities by which the ratios of τ to τ' and of $\pi^2 M^2 + l^2$ to $\pi^2 M^2 + l'^2$ differ from ratios of equality. And if we now wish to know more precisely what densities or pressures do correspond, we may obtain them from (4).

In the numerical calculations which follow, the difference in the times of vibration (τ) at *corresponding* pressures in the different gases is neglected, and likewise the difference between the ratios of the factors $M^2 \pi^2 + l^2$ and a ratio of equality. The general effect of this omission, which is very minute, will be considered in the end.

The values of D adopted were, hydrogen, 1; air, 14.42; oxygen, 16; nitrogen, 14; carbonic anhydride, 22; carbonic oxide, 14.

Tables were first formed of the logarithms of $\frac{l}{pD}$ for the different gases for the various pressures given by Mr. CROOKES down to 0.76 millim. The pressures standing against equal numbers in these tables for the different gases would be "corresponding" pressures. The pressures corresponding to a given number may be obtained from the tables by interpolation; and as the experiments were made at close intervals it seemed sufficient to regard only the two adjacent numbers and use proportional parts.

I do not think it worth while to give these tables at length, but I subjoin a small table calculated from them, giving for oxygen, nitrogen, carbonic anhydride, and carbonic oxide the pressures corresponding to air pressures decreasing by 100 millims. from 760 to 160. It will be seen from Mr. CROOKES'S tables that below these pressures there is little variation in l until very high exhaustions are reached. Hydrogen does not enter into the table, as the highest pressure (760 millims.) in the experiments corresponds to a pressure of only about 106 millims. in air. The table contains also the logarithms of the ratios of the pressures in the different gases to the corresponding pressures in air.

| Corresponding pressures. | | | | | Logs. of ratios to corresponding pressures in air. | | | |
|--|-------|-------|-------------------|-------|--|---------|-------------------|---------|
| Air. | O. | N. | CO ₂ . | CO. | O. | N. | CO ₂ . | CO. |
| 760 | 767.3 | 760.8 | 413.3 | 760.8 | + .0042 | + .0005 | - .2645 | + .0005 |
| 660 | 666.6 | 660.9 | 359.2 | 663.0 | + .0044 | + .0006 | - .2642 | + .0020 |
| 560 | 565.5 | 559.6 | 306.2 | 563.8 | + .0042 | - .0003 | - .2622 | + .0029 |
| 460 | 463.7 | 459.0 | 250.0 | 459.8 | + .0034 | - .0010 | - .2649 | - .0002 |
| 360 | 365.9 | 361.6 | 194.7 | 359.5 | + .0071 | + .0019 | - .2669 | - .0006 |
| 260 | 263.2 | 261.8 | 141.9 | 258.3 | + .0053 | + .0030 | - .2630 | - .0029 |
| 160 | 161.2 | 159.5 | 86.4 | 166.7 | + .0033 | - .0013 | - .2676 | - .0022 |
| Mean of log. p'/p | | | | | + .0046 | + .0005 | - .2648 | - .0005 |
| Number, or p'/p | | | | | 1.010 | 1.001 | 0.540 | 0.999 |
| Log. ($p'D' \div pD$), from mean | | | | | .0497 | 1.9876 | 1.9186 | 1.9870 |
| $p'D' \div pD$ | | | | | 1.121 | 0.972 | 0.829 | 0.971 |

An inspection of the numbers in the same vertical column in the right-hand portion of the above table shows that the logarithm in question is constant as nearly as the observations can show. This leads to the following law.

If any pressure be taken in one gas and the pressures found in other gases for which the coefficients of viscosity are as the densities (pressures which have been defined as "corresponding"), then if another system of pressures be taken proportional to the former the pressures in the new system will also correspond; and consequently the ratios of the coefficients of viscosity of the different gases will be the same for the pressures in one such system as in another.

This law is in accordance with MAXWELL'S law, but does not by itself alone prove MAXWELL'S law. It leaves the functional relation between the coefficient of viscosity and the density for any one gas arbitrary, and deduces from thence the relation for all other gases, this relation introducing merely one unknown constant for each. What the law gives may be put in a clear form by a geometrical illustration. I assume BOYLE'S law, so that for any one gas the ratios of the densities in different cases or the ratios of the pressures may be used indifferently.

Let, then, the relation between the viscosity and density be represented graphically by taking abscissæ to represent densities and ordinates to represent coefficients of viscosity. Then the law found above may be enunciated by saying that the curves for all gases are geometrically similar, the origin being the centre of similitude. MAXWELL'S law would give a particular case of such similar curves, namely, a system of straight lines parallel to the axis of abscissæ.

The deviation from uniformity of the logarithmic decrements for any one of these gases at these comparatively speaking high pressures is not therefore in any way inconsistent with MAXWELL'S law, but is fully accounted for by the very natural supposition that the rarefaction is not yet sufficient to render the molar inertia of the gas insensible as regards its influence on the gas's own motion, a supposition which can be shown to be true when we employ the approximately known absolute value of the coefficient of viscosity. The same consideration shows, moreover, that we have only to carry the exhaustion further in order to render the effect of that inertia insensible, and accordingly, *if* MAXWELL'S law be true, to make the logarithmic decrement sensibly independent of the pressure.

That such is actually the case is shown by Mr. CROOKES'S tables or the diagram A, in which they are graphically represented. We observe a manifest tendency for the logarithmic decrement to become constant till the law is interrupted by the breaking down of viscosity attending extreme exhaustions, or by certain deviations which in some cases (as in those of oxygen and kerosoline vapour) show themselves a little earlier: these deviations will be referred to further on; for the present I merely avoid exhaustions high enough to introduce them. This approximate constancy of logarithmic decrement is observed in hydrogen from the first, which is accounted for by the high index of friction of that gas as compared with the others at equal pressure.

This evident constancy or tendency towards constancy in the viscosity as the rarefaction goes on supplies the missing link, and establishes MAXWELL'S law on the basis of Mr. CROOKES'S experiments even taken by themselves. It is not, of course, *directly proved* for the higher pressures in the gases other than hydrogen; its extension to such pressures is a matter of inference, derived from observing, first, that it is found to be true within such limits of density that the condition of ideal simplicity supposed at the commencement of this note is presumably sensibly attained; and, secondly, that above those limits, though we are unable from mathematical difficulties to examine its truth directly, yet we are able to deduce from theory one inference on the

supposition of its truth, which is found to be in accordance with the results of experiment.

Hitherto the ratios of the coefficients of viscosity have been deduced from a part of Mr. CROOKES'S tables, in which the logarithmic decrements changed very evidently with the pressure. We may now deduce those ratios by what may almost be deemed an independent method, namely, by attending only to the part of the tables at which the logarithmic decrement is all but constant. If the condition of ideal simplicity supposed at the outset were quite attained, we might disregard the pressures in the comparison, which would entitle that method to be considered quite distinct from the former; but as that condition is not absolutely reached, it will be proper not wholly to neglect the condition of correspondence of pressure, though a rough determination of correspondence will suffice.

Suppose, then, we take the air pressures from 120 to 26 millims. The ratio of the corresponding pressures in oxygen, &c., is given in the last line but two of the preceding table. The corresponding limits are for oxygen 132 to 29; for nitrogen and carbonic oxide the same (sensibly) as for air; for carbonic anhydride 65 to 14; for hydrogen the limits are not given in the table, but they are 864 and 187 nearly. In strictness each pressure should be considered separately; but as the intervals were not intentionally divided in a different manner for the different gases, and as the logarithmic decrements are very nearly constant between the specified limits, it seems sufficient to take the mean for each gas of those corresponding to pressures that lie between the assigned limits. We thus get for air, $\cdot 1002$; oxygen, $\cdot 1120$; nitrogen, $\cdot 971$; carbonic anhydride, $\cdot 822$; carbonic oxide, $\cdot 971$; hydrogen, $\cdot 500$. Reducing to air = 1, and writing down for comparison the numbers expressing the ratios of the coefficients of viscosity to that of air given in the previous table, we have for the ratios in question—

| | O. | N. | CO ₂ . | CO. | H. |
|----------------------------------|-------|-------|-------------------|-------|-------|
| From air pressures, 760 to 160 . | 1·121 | 0·972 | 0·829 | 0·971 | .. |
| ,, ,, 120 to 26 . | 1·118 | 0·969 | 0·820 | 0·969 | 0·499 |
| Values adopted | 1·120 | 0·970 | 0·822 | 0·970 | 0·499 |

We see that almost identically the same numbers are obtained whether they are deduced from the higher pressures, for which the logarithmic decrements notably diminish with the pressure, or from the part of the tables in which they are nearly independent of the pressure. The greatest difference is in the case of carbonic anhydride, where it is rather more than one per cent. This difference is in part accounted for by the omission of the correction for the time of vibration. If the times of vibration at *corresponding* pressures as determined by Mr. CROOKES be taken, they will be found to be very nearly the same; indeed, the differences are quite comparable with the errors of observation of those times. Perhaps the differences could be got with greater certainty from theory than from observation. According to theory the effect of the

gas on the time of vibration turns mainly on the term $A\rho$. Now, though A is a function which we cannot calculate, yet we know that it is the same at corresponding pressures in two gases. The effect at such pressures varies therefore from one gas to another as the density, and therefore as the coefficient of viscosity. It is here supposed (as is practically true) that the term is so small compared with I , with which it is associated, that its square, &c., may be neglected.

Taking the time of two oscillations (or of one complete oscillation) for air at an exhaustion at which the effect of the molar inertia has ceased to be sensible, but the slight decrease due to the removal of the viscosity has not yet come in, at $10^{\circ}76$, we get for the mean effect at pressures 760,660 . . . 160 about $0^{\circ}20$. The coefficient of viscosity for carbonic anhydride being 18 per cent. less than for air, we get $0^{\circ}036$ for the average difference of times in air and that gas, which is $\frac{1}{300}$ th of the average time; and since according to (8) $\mu \propto \tau$ we must deduct $\cdot 003$ from the $\cdot 829$ given above, leaving $\cdot 826$, the mean of which and $\cdot 820$ gives $\cdot 823$, nearly the number adopted. Similarly the number $1\cdot 121$ for O in the first line should be raised about $\cdot 002$.

There is still a small correction to make depending on the factor $\pi^2 M^2 + l^2$. Since by (8) μ varies as this factor, and l^2 is very small compared with $\pi^2 M^2$, and moreover $\mu \propto l$ nearly, it will suffice to deduct $\frac{l^3}{\pi^2 M^2}$ from l , and use the l 's so corrected. The correction being, however, very small, it will suffice to take an average l and make the deduction for it. The deductions for the six gases came to about $\cdot 005$, $\cdot 009$, $\cdot 005$, $\cdot 003$, $\cdot 005$, $\cdot 001$. Deducting these numbers from the relative viscosities given above, and reducing afresh to the scale air = 1, we get the following final numbers :

| Air. | O | N | CO ₂ | CO | H |
|-------|-------|-------|-----------------|-------|-------|
| 1·000 | 1·117 | 0·970 | 0·823 | 0·970 | 0·500 |

I have left kerosoline vapour to the last on account of the uncertainty as to its vapour density. It is a mixture of different substances, being the more volatile part of petroleum. I am informed by Mr. GREVILLE WILLIAMS that it contains much pentane, the theoretical vapour density of which on the hydrogen scale would be 36. Taking at a venture $D=36$, and choosing suppose the pressure 54 millims., for which $l=\cdot 0404$, and further assuming the limiting logarithmic decrement for air before the breakdown to be $0\cdot 1000$, as it seems to be from Mr. CROOKES'S table, we find $0\cdot 392$ for the relative viscosity of kerosoline vapour. This is pretty certainly too high. If we suppose the true number to be $0\cdot 380$, we get for the air number corresponding to $l'=\cdot 0425$, $l=\cdot 1129$, which from the table of results for air belongs to $p=740$. This would give for the vapour density of kerosoline $D'=\frac{0\cdot 380 \times 740}{1\cdot 000 \times 82\cdot 5}D=3\cdot 408D=49\cdot 16$ if $D=14\cdot 42$.

For the air pressure corresponding to 54 millims. in kerosoline we should have $740 \times 54 \div 82\cdot 5 = 484\cdot 3$. For the corresponding logarithmic decrement we get from

the table of experiments for air $\cdot 1059$. The logarithmic decrement for kerosine at 54 millims. calculated from that for air at 484.3 millims., is $\cdot 1059 \times \cdot 0390 = \cdot 04024$, which comes very near the observed number $\cdot 0404$. It is curious that we should apparently be able to calculate very approximately an unknown vapour density from observations on the decrement of the arc of vibration of a vibrating lamina.

Before considering the falling off of viscosity at high exhaustions, I would point out a result of theory which is of some interest in connexion with the forms of Mr. CROOKES'S curves.

At p. [34] in the paper of mine already referred to I have given in equation (61) an expression (which has to be subsequently multiplied by ρ) for the resistance to a sphere vibrating in a viscous fluid within a concentric spherical envelope. When the index of friction is sufficiently great, as will be the case when the exhaustion is high enough, this expression may be developed according to ascending powers of m , which will be convergent even from the first. It will be found that the successive terms will be multiplied by

$$m^{-2}, m^0, m^2, m^4 \dots$$

where m^2 is a pure imaginary multiplied by $\rho \div \mu$; and from the mode of treatment there adopted it will readily be seen that the terms fall alternately on the arc and on the time.

The same thing may, however, be shown to be true generally, independently of the form of the vibrating body. It is here supposed, as has been all along, that the motion is sufficiently slow to allow us to neglect squares and products of the components of the velocity, or of their differential coefficients. For if $\mu \div \rho$ be very great, we may imagine the hydrodynamical equations solved by successive substitution. First we should neglect the terms in ρ , and solve the equations; then substitute in the terms multiplied by ρ the result of the first approximation and solve again, and so on. And though we cannot actually solve the equations, still this consideration shows that the solution must be of the form

$$a\mu + b\rho + c\frac{\rho^2}{\mu} + d\frac{\rho^3}{\mu^2} + \dots$$

where $a, b, c, d \dots$ involve neither μ nor ρ . And by adopting the artifice for the introduction of the time employed in the paper it readily appears that the terms fall alternately on the arc and on the time. Hence taking the two most important terms only in the expression for the effect on the arc we shall have for l an expression of the form

$$a'\mu + c'\frac{\rho^2}{\mu}, \text{ or } a'\mu + c'\frac{D^2}{\mu} p^2.$$

Hence in a curve plotted with l and p for coordinates, the tangent as p diminishes

would tend to become parallel to the axis of p , and the curvature where the curve cuts the axis of l would vary from one gas to another directly as the square of the density at a standard pressure and inversely as the coefficient of viscosity. For the gases examined the curvatures near the axis of l would therefore vary

| | | | | | |
|-------|------------------------|---------------------|---------------------|---------------------|--------------------|
| for | Air | O | N and CO | CO ₂ | H |
| as | $14.42^2 \div 1.000$, | $16^2 \div 1.117$, | $14^2 \div 0.970$, | $22^2 \div 0.823$, | $1^2 \div 0.500$, |
| or as | 1.000, | 1.102, | 0.971, | 2.828, | 0.010. |

It will be seen in Mr. CROOKES'S diagram A, that if we imagine the curves continued upwards on their old lines, cutting off the changes which take place at very high exhaustions, the tangent tends to become vertical, and, moreover, the rate at which the direction of the tangent changes as we go down agrees well, as far as the eye can judge, with the above figures. We may notice in particular the extreme flatness of the hydrogen curve.

As we proceed upwards to the higher exhaustions, the first thing that strikes us (first in order of occurrence, very far from first in order of magnitude) is the curious increase which is observed in the logarithmic decrement in the case of oxygen and of kerosoline vapour. Small as this is, Mr. CROOKES considers it real. It puzzled me at first, since it occurs while the pressure is still comparatively high, such as 15 millims. or 20 millims., so that the mean free path must still be extremely small, and might, one would naturally suppose, be treated as infinitely small considering the dimensions of the apparatus. It occurred to me afterwards that it is probably referable to the thinness of the vibrating body. As the lamina moves there must in the immediate neighbourhood of the edge be a thin stratum or cushion of gas in which there is a very intense shearing motion. The intensity of the shearing makes up in good measure for the narrowness of the cushion, and renders the effect of the cushion a not insignificant fraction of the whole. The narrowness of the stratum may well be such as to forbid us to treat the mean free path as infinitesimal long before we are prohibited from so regarding it in comparison with the dimensions of the vessel, or the lateral dimensions of the lamina. That among the four unmixed gases examined oxygen should be the one to show this effect, seems to be connected with the fact that at comparatively low exhaustions (such as 0.76 millim.) it shows repulsion effects much the most strongly; and both phenomena seem to indicate that for oxygen the length of path (I do not say *free* path) is comparatively large, "path" here meaning the space throughout which a molecule preserves approximately its original direction of motion.

When we come to those high exhaustions at which the decrement of arc gives way, the law of proportional logarithmic decrements at corresponding (and those proportional) pressures, which we hitherto found to be so accurately obeyed, breaks down altogether. A single example will suffice to show this. Take hydrogen at 330 M,

for which $l=0\cdot0495$. The ratios of corresponding pressures resulting from the numbers for the relative viscosities given on page 443, and the numbers to which they lead, are as follows :—

| Gas. | Air. | O. | N. | CO ₂ . | CO. | H. |
|---|--------|--------|--------|-------------------|--------|--------|
| Ratios of corresponding pressures . . . | 0·1387 | 0·1396 | 0·1386 | 0·0748 | 0·1386 | 1 |
| Pressures corresponding to 330 M in H . | 45·8 | 46·1 | 45·7 | 24·7 | 45·7 | 330·0 |
| l calculated from l in H | ·0990 | ·1106 | ·0961 | ·0815 | ·0961 | |
| l observed | ·0758 | ·0829 | ·0722 | ·0525 | ·0734 | 0·0495 |

It would seem as if when a gas may be treated as a continuous mass with continuously varying conditions of pressure, velocity, &c., as is done in the application of the hydrodynamical equations, a gas is completely defined* as to its mechanical action by two constants, suppose the density at a standard pressure and the coefficient of viscosity; but when the conditions are such as oblige us to take account of the finiteness of path of the molecules, specific differences are manifested which oblige us to introduce at least one constant more in order that the gas may be even mechanically defined; for of course I am not contemplating the chemical properties. It is worthy of note in this connexion that the two gases, oxygen and kerosoline vapour, which showed the phenomenon of a rate of decrease of arc of vibration *increasing* with a decreasing density, are just those which lie at the two extremes as regards viscosity, while as regards density at a given pressure they are separated by carbonic anhydride, which nevertheless does not show the phenomenon in question. It may well be that the mode of encounter of such complex structures as the molecules of a gas varies from one gas to another; and that while some of the laws of gases admit of explanation when the molecules are regarded as elastic spheres, or as particles repelling one another according to some definite law of force, other properties fail to receive an explanation when such a simplification of conception is adopted.

* I here leave out of account such differences as the small deviations from BOYLE'S law which have been observed with different gases.

VISCOSITY OF GASES.

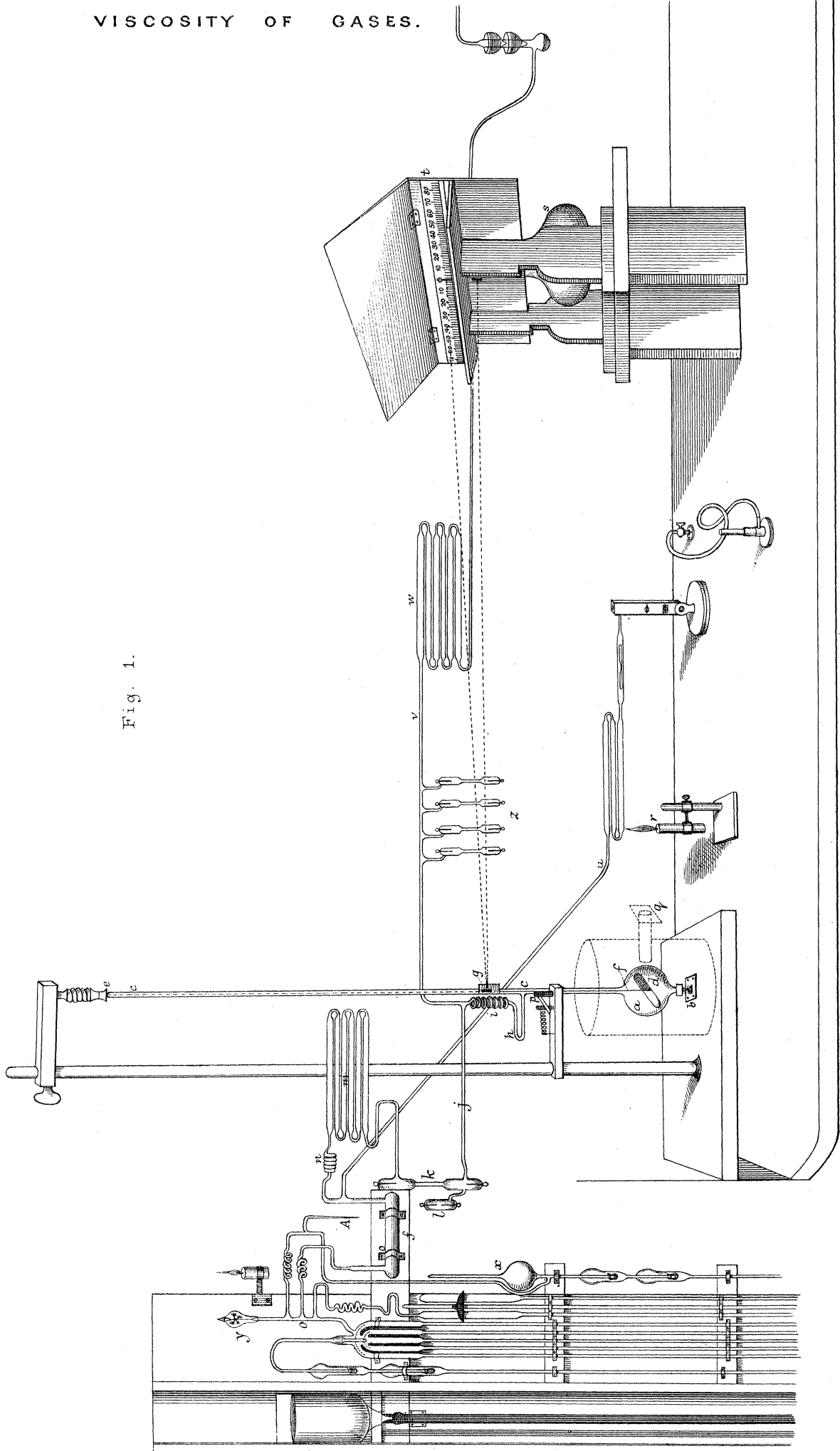
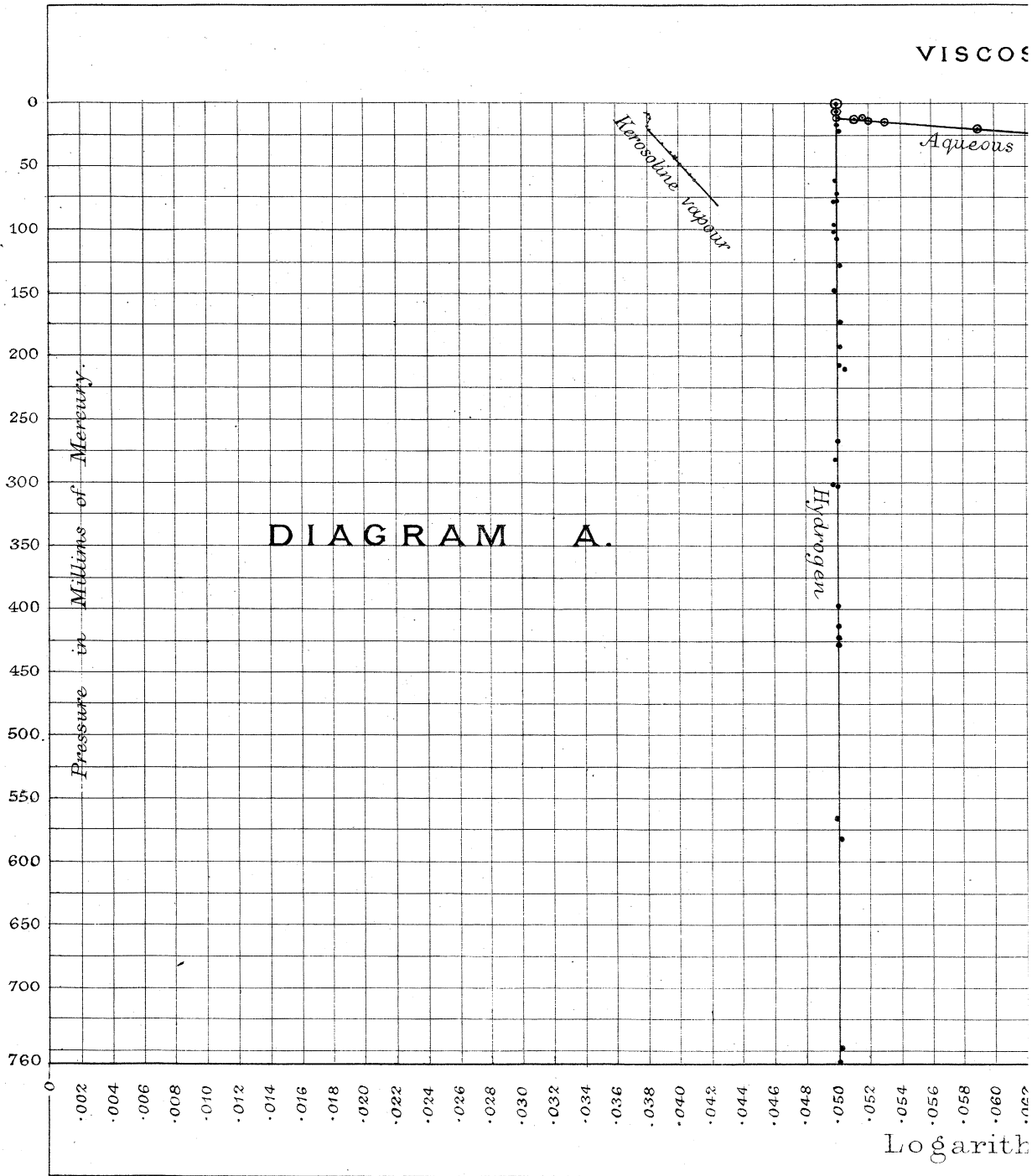
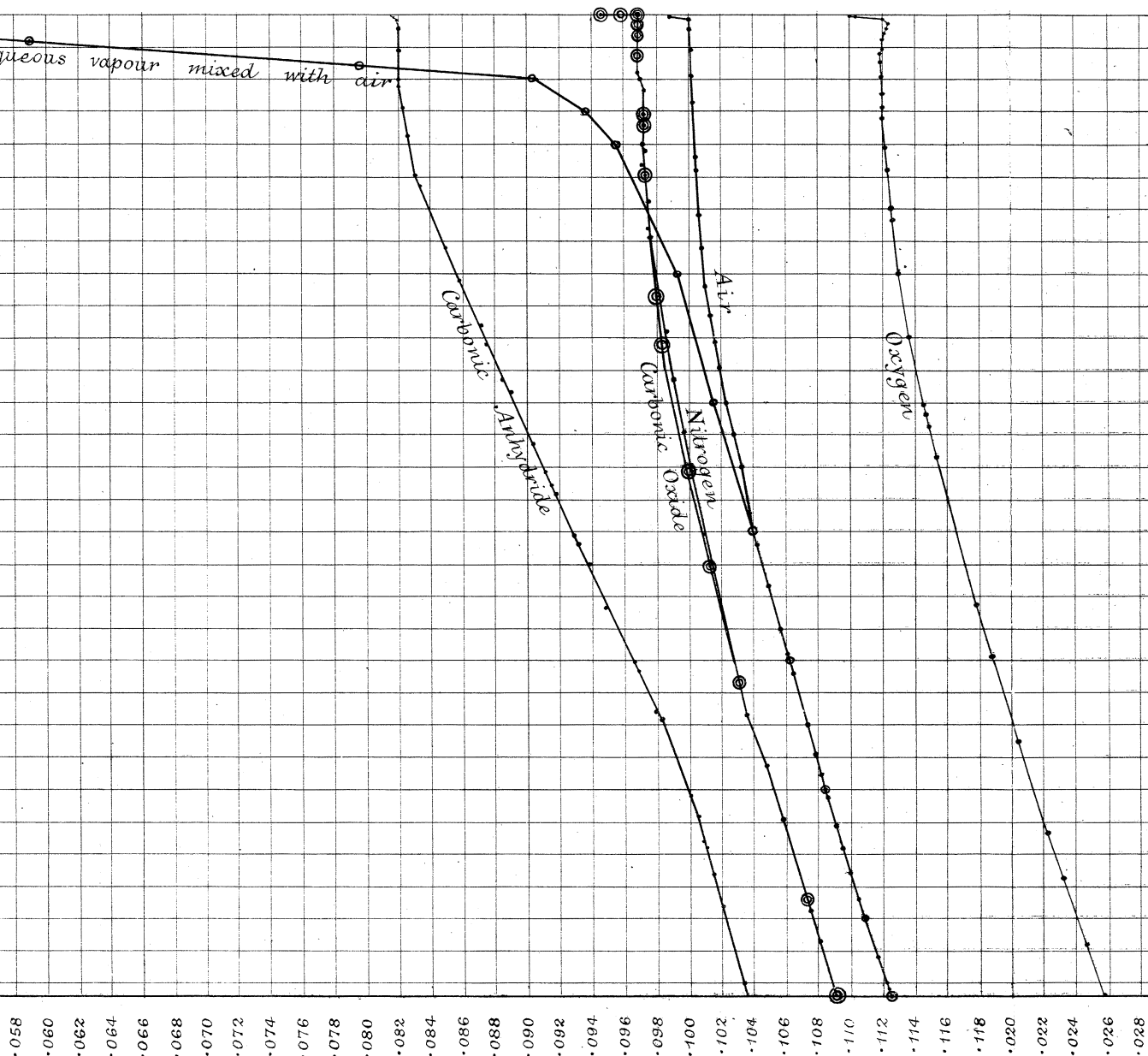


Fig. 1.

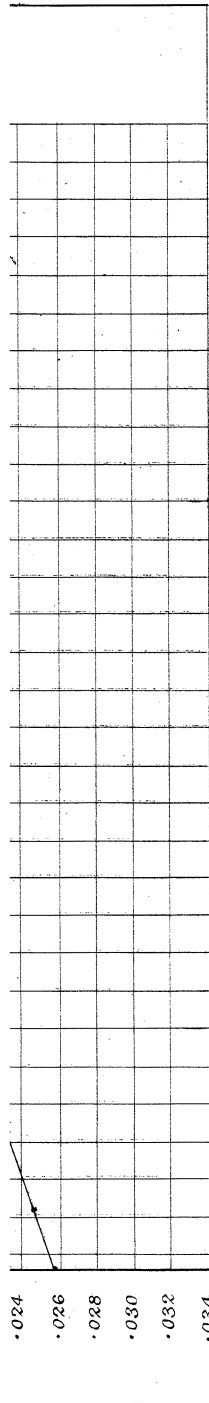


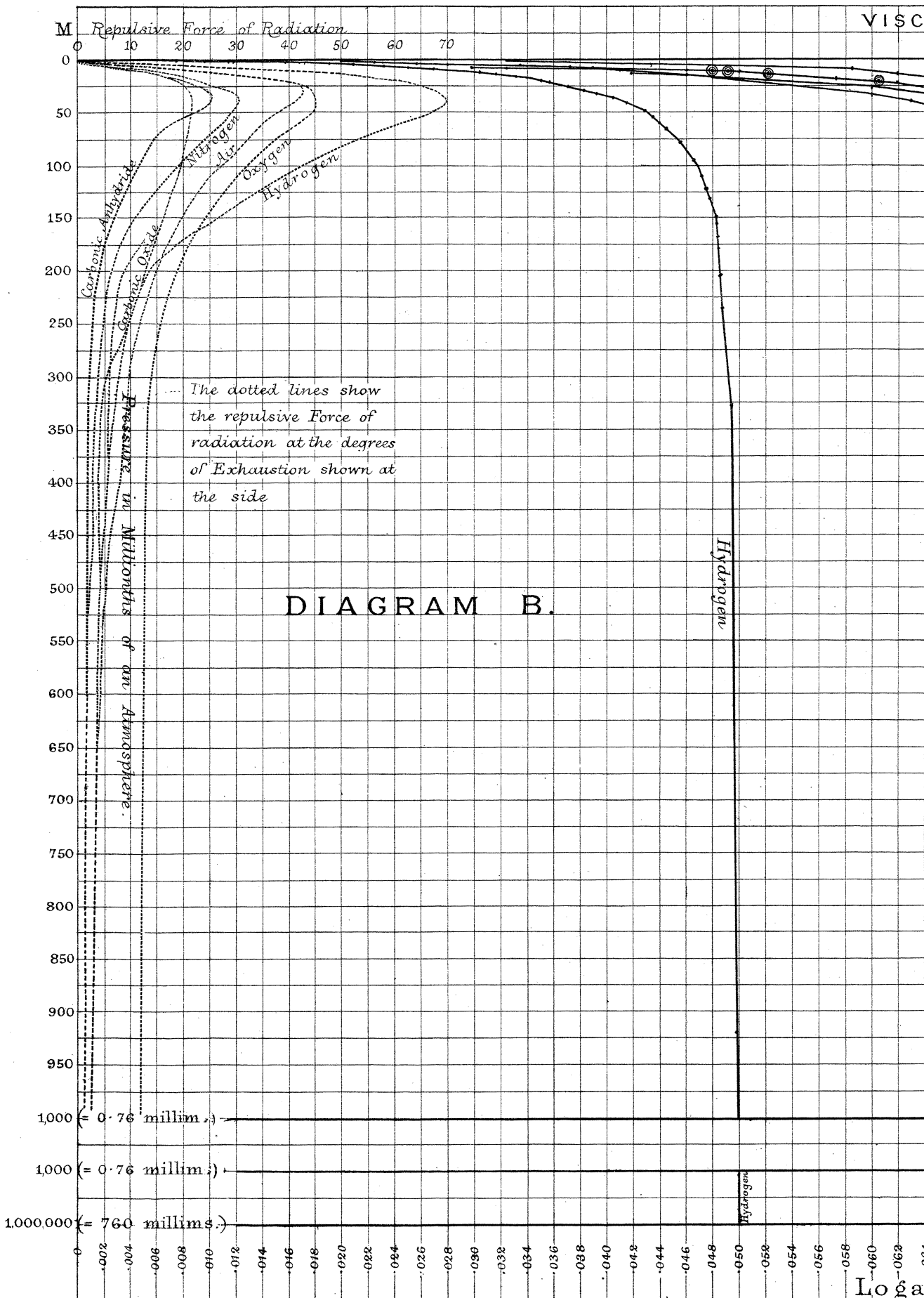
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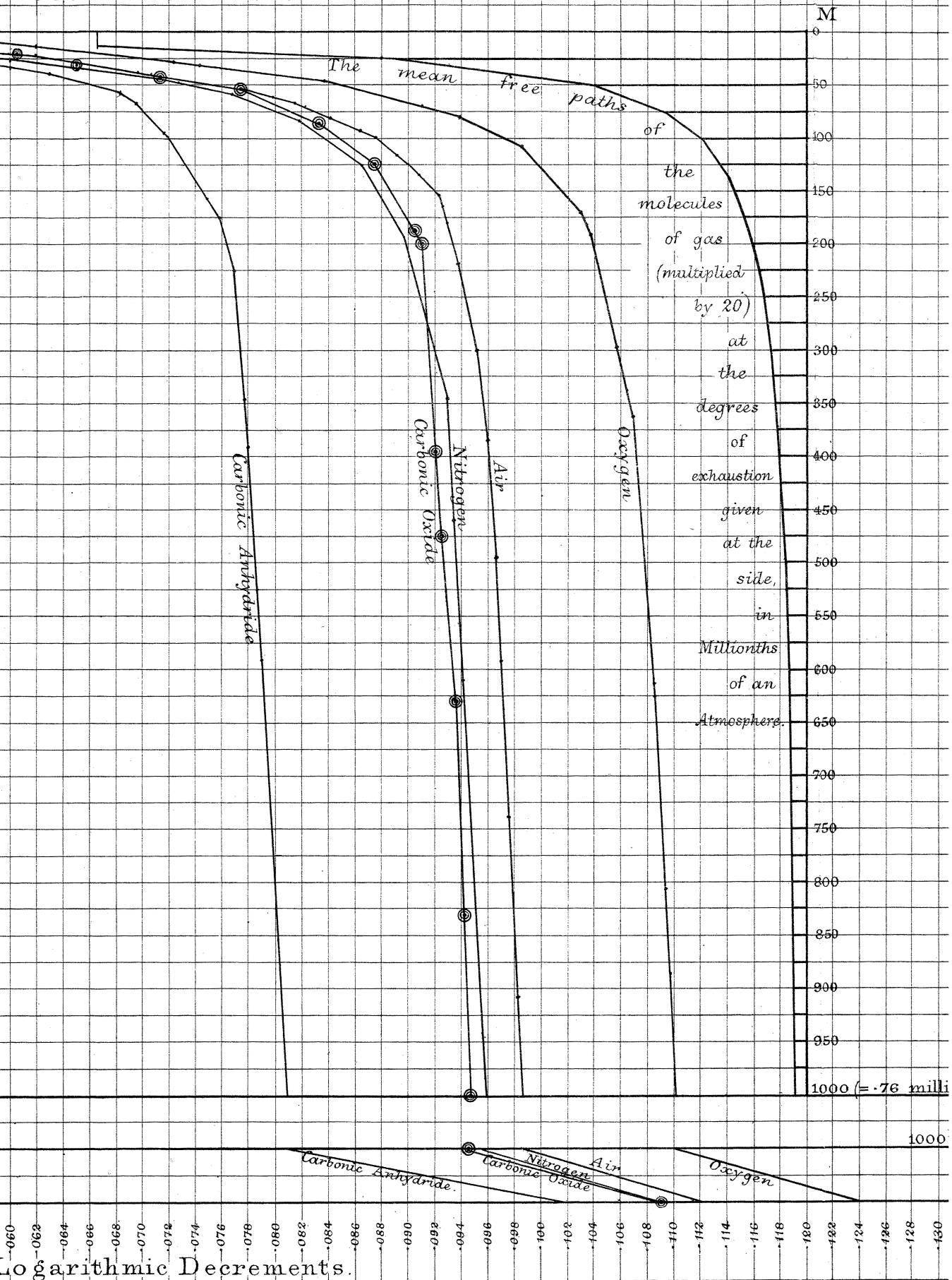
Arithmetic Decrements.

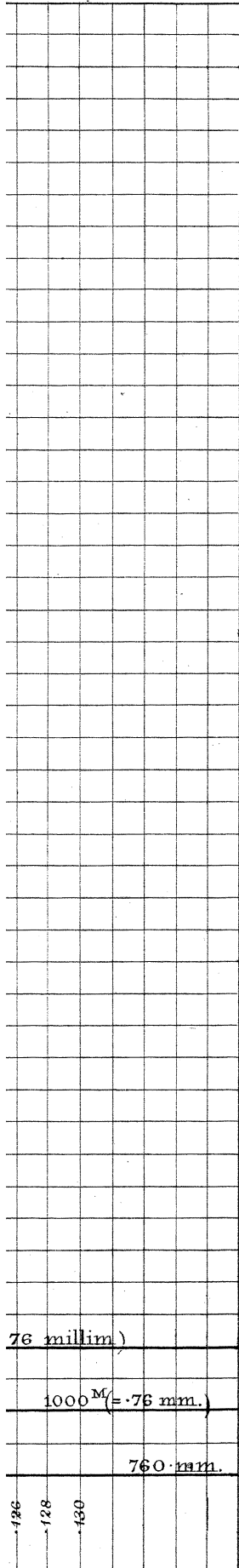
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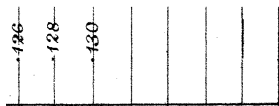


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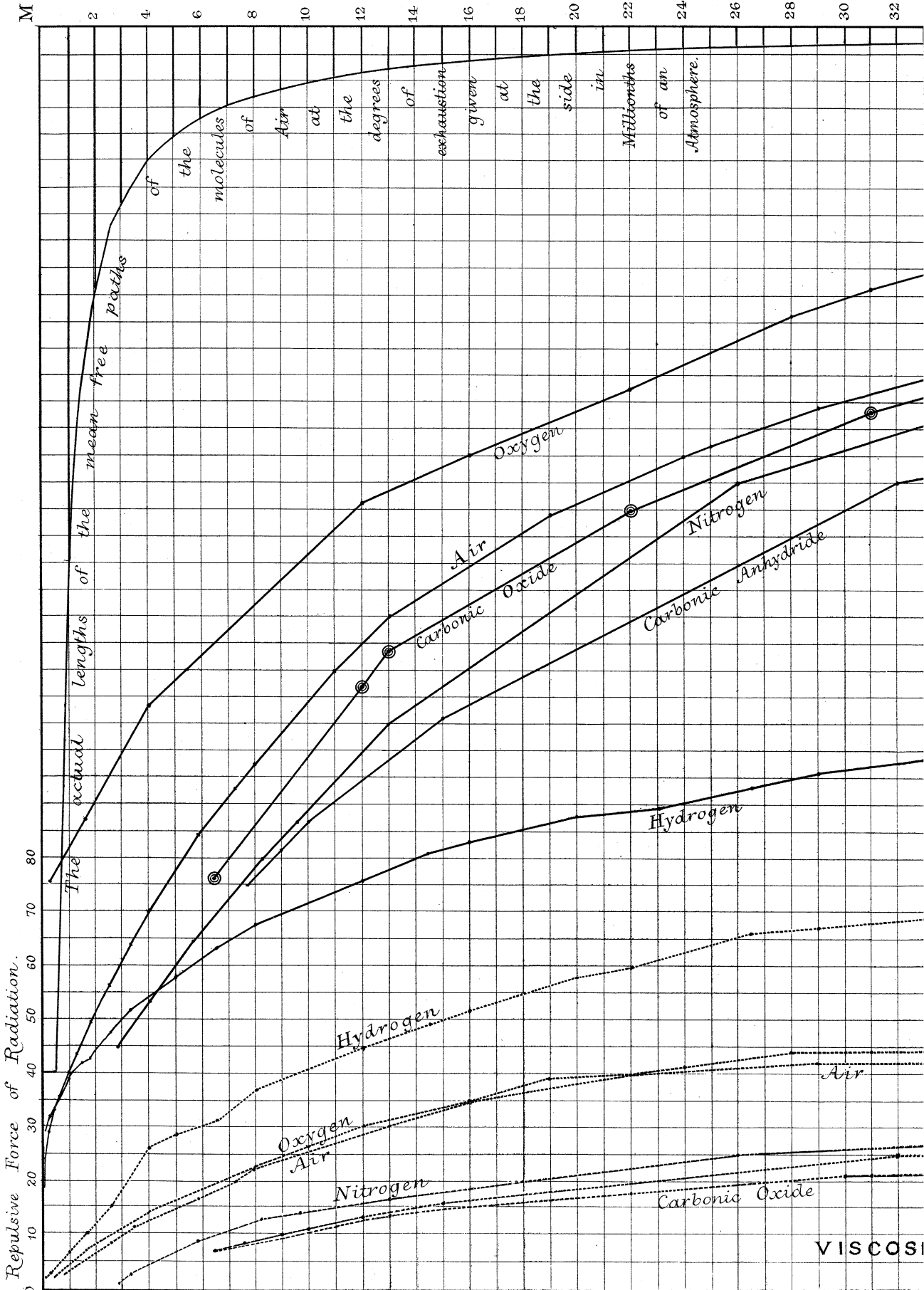
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Logarithmic Decrements.

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| 060 | 062 | 064 | 066 | 068 | 070 | 072 | 074 | 076 | 078 | 080 | 082 | 084 | 086 | 088 | 090 | 092 | 094 | 096 | 098 | 100 | 102 | 104 | 106 | 108 | 110 | 112 | 114 | 116 | 118 | 120 | 122 | 124 | 126 | 128 | 130 |
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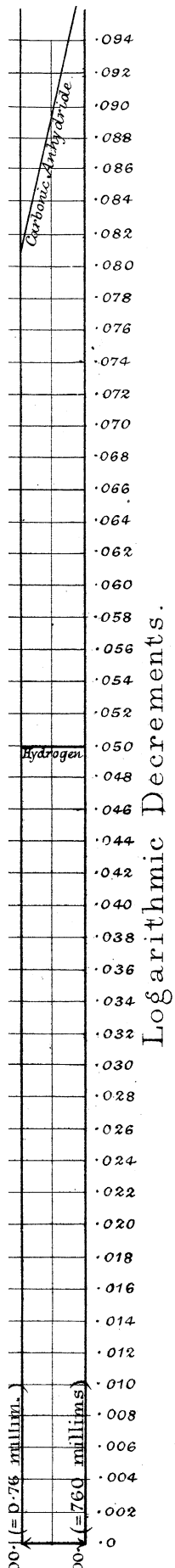


West, Newman & Co. lith.

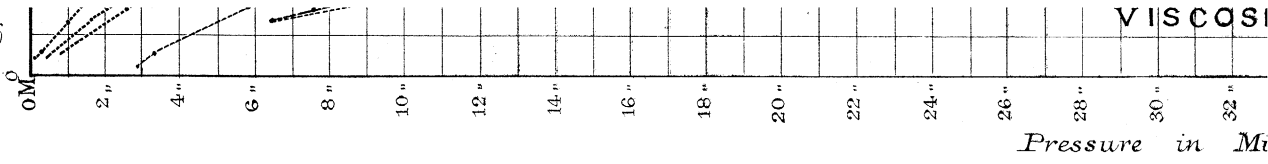


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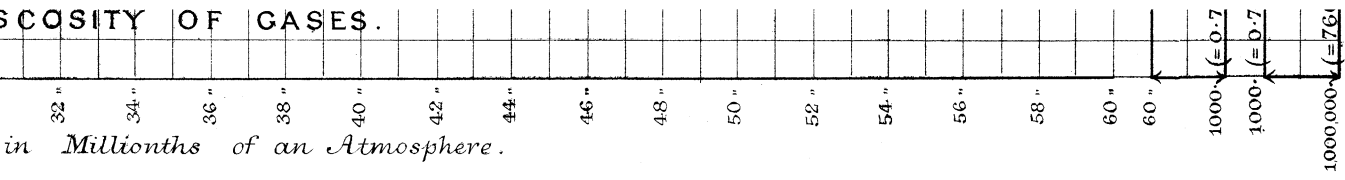
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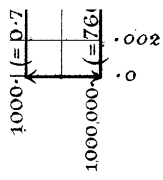
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Pressure in Mi

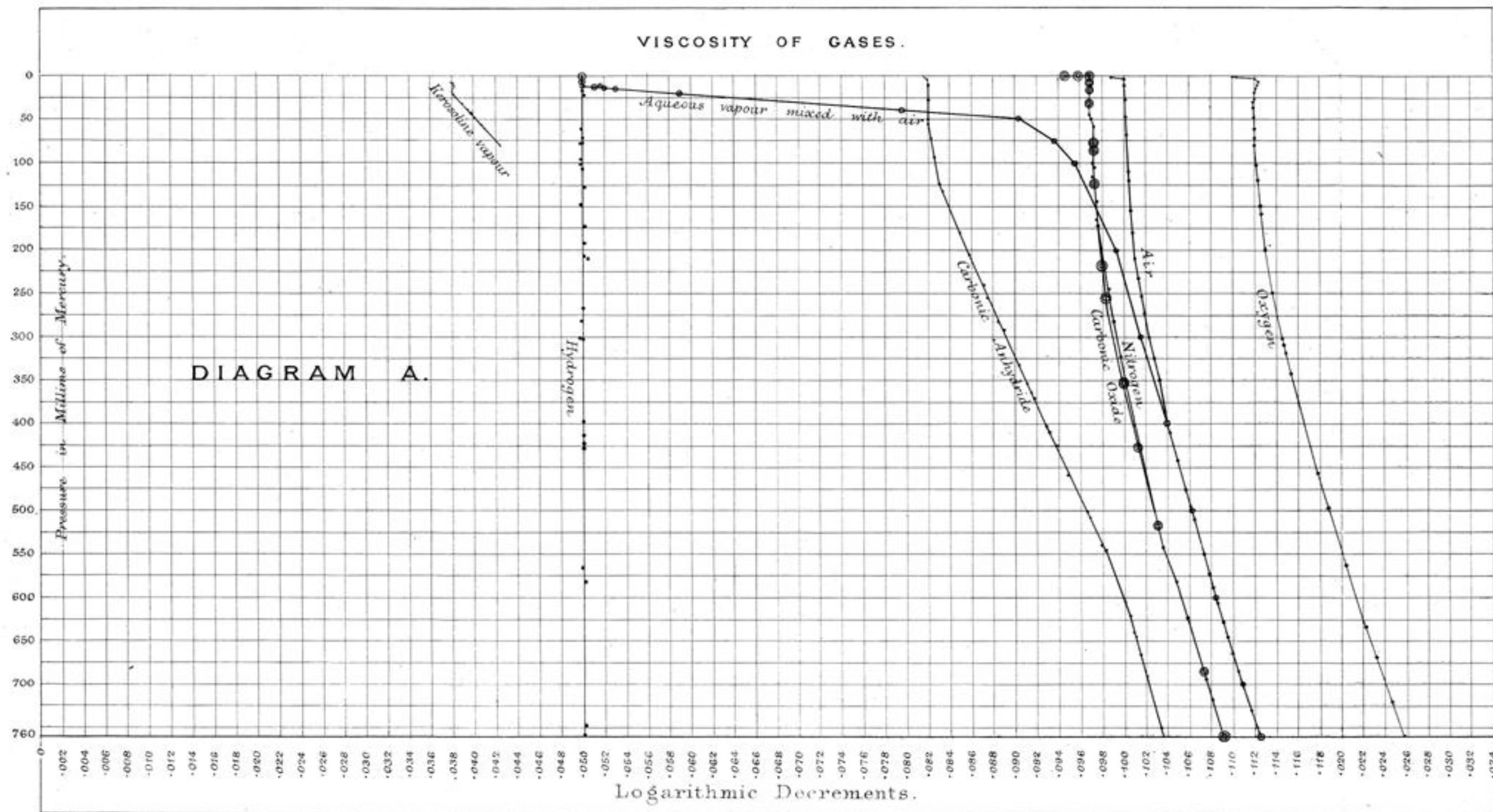
VISCOSITY OF GASES.



in Millionths of an Atmosphere.



West, Newman & Co lith.



VISCOSITY OF GASES

