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New Series.

VOLUME XI.

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ERRATA.

On front of leaf facing Plate IV. (p. 88), for “Explanation of Plate VI.”, read “Explanation of Plate IV.”

In Explanation of Plate VI. (p. 136), under Fig. 2, for “colouration”, read “coloration”.

THE
SCIENTIFIC PROCEEDINGS
OF THE
ROYAL DUBLIN SOCIETY.

Vol. XI. (N. S.), No. 1.

JULY, 1905.

THE EFFECT OF
VERY LOW TEMPERATURE ON MOIST SEEDS.

BY

J. ADAMS, M.A.,

ASSISTANT IN BOTANY, ROYAL COLLEGE OF SCIENCE, DUBLIN.

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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1905.

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THE
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OF
THE ROYAL DUBLIN SOCIETY.

I.

THE EFFECT OF VERY LOW TEMPERATURES ON
MOIST SEEDS.

By J. ADAMS, M.A.,

Assistant in Botany, Royal College of Science, Dublin.

[Read, APRIL 20; Received for Publication, APRIL 22; Published, July 31, 1905.]

SEEDS belonging to seven species—namely, pea, barley, flax, swede, red clover, meadow fescue, and timothy—were chosen for the experiments. The seeds were enclosed in a cloth and buried in moist soil for three days, so that they might absorb water slowly. These moist seeds were then divided into three lots, A, C, D. A fourth lot, B, of dry seeds, was also taken. Lot A, contained in a cloth, was gradually cooled down by evaporating ether to -4° C. and then immersed in liquid air for $23\frac{1}{2}$ hours. Lot B, also rolled in cloth, was immersed in the liquid air for 24 hours without previous cooling. The seeds of lot C were enclosed in a small, corked bottle which was plunged directly into liquid air, where it remained for six hours. Lot D was not subjected to cooling. The three lots of seeds, after being taken out of the liquid air, were enclosed in a vacuum-jacketed vessel to cool slowly. On examining the seeds, the only external change noticeable was that two of the peas in lot A had the seed-coat ruptured. The seeds

were then put in to germinate, with the results shown in the following table:—

TABLE OF GERMINATIONS (per cent.).

Lot.	Time of germination test.	Pea.	Barley.	Flax.	Swede.	Red Clover.	Meadow Fescue.	Timothy.
A.	14 days.	0	0	0	0	0	0	6
B.	14 „	65	96	87	88	90	91	69
C.	14 „	0	0	0	0	0	0	12
D.	15 „	66	95	98	72	72	85	70

The germination of the timothy in lots A and C is to be accounted for by the fact that these seeds had not absorbed water to any appreciable extent when put into the liquid air. To test this point, I put some timothy seeds into water, and found that there was no apparent change in size after six and a half days, while many of the seeds were still hard and dry internally.

So much, then, for the experiments.

When we attempt to draw conclusions from these and previous experiments, we are on more uncertain ground. We may first of all confine our attention to the dry seeds. And we are at once confronted by the question, Did the dry seeds acquire the same temperature as the surrounding medium? On this point there does not seem to be much direct experimental evidence, and the answer is more one of probability than of certainty. Brown and Escombe,¹ in their experiments, kept the seeds for 110 hours at a temperature of -190° C. In the experiments of Prof. Dewar and Sir William Thiselton-Dyer² the seeds were kept for six hours at the temperature of liquid hydrogen (-252° C.). In this last case Prof. Dewar had no doubt but that the seeds were brought to the temperature of the liquid hydrogen. While Sir William Thiselton-Dyer accepts Prof. Dewar's view that the seeds experimented on acquired the temperature of liquid hydrogen, he goes on to say that in the case of seeds which have been heated to 100° C. and still survived "it may be taken as absolutely certain that in this case that temperature never reached the embryo, but

¹ Proc. Roy. Soc., vol. lxii., 1898.

² Ann. of Bot., vol. xiii., 1899.

must have been intercepted by the imperfect conducting power of the seed-coats." Both these statements can scarcely be true. As heat and cold are varying degrees of the same thing, it does not appear evident why the seed-coat should conduct the cold in the one case, and refuse to conduct the heat in the other. However, to test the matter I made the following rough experiment. An ordinary cork, one inch in diameter, and a number of dry bean-seeds were put into a test-tube and kept at a temperature of 100° C. for less than half an hour. They were then taken out and split in two, with the result that the interior of the bean-seeds was hot enough to burn the fingers, while the inside of the cork was also decidedly warm; but the latter was a much less efficient conductor of heat than the beans.

Assuming, then, that the seeds did eventually come to the temperature of the liquid air or liquid hydrogen, were they, therefore, frozen? Air-dried seeds contain about 12 per cent. of moisture, and there is little doubt that freezing, that is, a formation of ice particles, did not take place. It would be as reasonable to think of freezing a dry piece of wood or a handful of hay. Probably the only change that resulted was a slight contraction of volume; but, in the absence of experiments, it is impossible to say how much this contraction amounted to.

It remains to consider the behaviour of the gases in the inter-cellular spaces. These are probably nitrogen, oxygen, and carbon dioxide. As the temperature gradually falls, these gases will doubtless be liquefied—assuming that the seeds have been immersed in liquid hydrogen. A vacuum will result, but the total pressure—allowing 15 lb. to each square inch of surface—would be so small as to have no appreciable effect on the seed. The actual figures for one example may be quoted. The seed of swede turnip is spherical in shape, and has a diameter of $1\frac{1}{2}$ mm. The area of its surface will, therefore, be about $\frac{1}{8}$ of a square inch. If a vacuum is formed inside the seed, the total pressure on the seed will be about $\frac{1}{8}$ of a pound (taking the atmospheric pressure at 15 lb. to the square inch). Now, according to Scott-Elliot's results,¹ the total force required to crush turnip seed is about $1\frac{1}{2}$ lb.; that is, a force nine times as great as that due to the formation of a vacuum.

¹ "Nature Studies—Plant Life," p. 80 (1903).

So that we may say that the total mechanical effect produced in dry seeds by immersing them in liquid hydrogen is very slight.

In the case of moist seeds there is an entirely different series of events. Here the wet seed-coat is an efficient conductor of heat, and the cells of the seed contain a much larger percentage of water. Consequently, freezing of the tissues is only a question of temperature. At what temperature freezing of the above-mentioned seeds begins, I have not attempted to determine. Probably it varies with the species, and with the actual amount of water contained in the seed. That a plant-tissue may be frozen without being killed, seems fairly well established by experiment; and probably this holds good in the case of seeds also. That on still further lowering the temperature, a point is reached at which freezing to death occurs is equally certain from the foregoing experiments. The older theory of freezing was that a formation of ice particles took place within the cell. The more modern theory is that as the temperature falls, contraction of the protoplasm takes place, water passes out from the cell through the cell wall, and freezes outside the cell in the intercellular spaces. The cell-sap left behind in the cell will therefore be more concentrated, and will require a still lower temperature to freeze it. If the temperature falls further, more and more water will pass outside the cell and become frozen. On this theory, if freezing has not gone too far, and if the thawing be gradual, the ice in the intercellular spaces melts, and is absorbed by the cells again, no loss of vitality resulting.

Freezing to death, however, is more difficult to account for. Ewart¹ holds that protoplasm, in order to retain its vitality, requires at least 2-3 per cent. of water. Matruchot and Molliard² believe that, in freezing, exosmosis of water goes on until the protoplasm of the cell, and especially of the nucleus, contains less than the minimum required to maintain vitality. Molisch believes that death by freezing is the same thing as death by desiccation.

If these theories are correct, and we assume that, as continual cooling of the cell goes on, more and more water is withdrawn until the protoplasm contains less than 2-3 per cent., the same argument should apply to the dry seeds which contain about

¹ Trans. Liverpool Biol. Soc., xi., 1897.

² *Comptes Rendus*, cxxxii., 1901.

12 per cent. of moisture. But the dry seeds are not frozen, or, at any rate, are not killed. Consequently we must look for some other explanation.

The intercellular spaces in seeds are small; and after freezing has gone on for some time in moist seeds, the intercellular spaces will become a solid mass of ice. If the temperature is still further lowered, then it seems more likely that complete rupture takes place, causing a separation of the cells from each other, or it is conceivable that ice crystals may be formed inside the cell within the protoplasm itself, and death of the protoplasm may be due to mechanical effects. But whatever the explanation of what takes place, it seems fairly certain that freezing to death can only occur if the seed contains more than 12 per cent. of moisture.

Davenport, in his "Experimental Morphology," summing up the results of experiments on dry seeds, spores, &c., concludes with the generalisation, "That there is no fatal minimum temperature for dry protoplasm." It would, I think, be justifiable to extend this generalisation, and to maintain that there is a fatal minimum temperature for moist protoplasm, and that this fatal minimum lies somewhere above the temperature of liquid air.

But it will be at once obvious that this latter generalisation is apparently contradicted by the experiments of Macfadyen¹ with Bacteria. He kept a number of species in broth cultures immersed in liquid air for seven days, and a second series in liquid hydrogen for ten hours, and found that they still retained their vitality. It must be observed, however, that these experiments were qualitative and not quantitative. In all probability what actually happened was that all the Bacteria in the actively vegetative condition were killed, that some were in the spore condition, and as their protoplasm was in the dry state, these survived and reproduced rapidly when the unfavourable conditions were removed. Klepzo²'s results with Anthrax were entirely different from Macfadyen's.

More recently Smith and Swingle³ carried out more than

¹ Proc. Roy. Soc., vol. lxvi., 1900.

² Centralbl. f. Bakteriol. u. Parasitenk. 1^{te} Abt. xvii., 1895.

³ Science, 31 March, 1905.

100 freezings, with about a dozen different Bacteria—saprophytes, and plant and animal pathogenic forms. Their results are summed up as follows:—"The former idea that Bacteria in general are not harmed by freezing is untenable. It was based on qualitative tests, which are incapable of showing the true state of affairs in the exposed culture. Probably an enormous number of Bacteria are destroyed by every winter, and those which survive come through in the form of endospores or some other resistant shape."

I desire to express my indebtedness to the Royal Dublin Society for the liquid air required for these experiments, and especially to Mr. R. J. Moss, F.I.C., F.C.S., for his assistance in its manipulation.

Royal Dublin Society.

FOUNDED, A.D. 1731. INCORPORATED, 1749.

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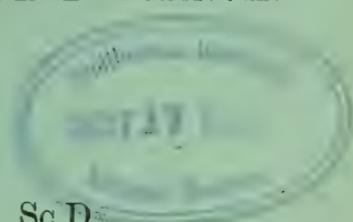
AUGUST, 1905.

NOTE ON THE SUPPLY OF
WATER TO LEAVES ON A DEAD BRANCH.

BY

HENRY H. DIXON, Sc.D.,

PROFESSOR OF BOTANY, DUBLIN UNIVERSITY.



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II.

NOTE ON THE SUPPLY OF WATER TO LEAVES ON
A DEAD BRANCH.

By HENRY H. DIXON, Sc.D.,
Professor of Botany, Dublin University.

[Read, JUNE 20 ; Received for Publication, JUNE 23 ; Published, AUG. 1, 1905.]

URSPRUNG, in a paper appearing in the "Beihefte zum Botanischen Centralblatt,"¹ discusses the possibility of the participation of the living cells of the stem in the elevation of the transpiration current. He considers it *à priori* conceivable that these cells may enter into the process in two different ways—(1) by directly elevating the water, or by partially supporting the hydrostatic head ; and (2) by keeping the vessels and tracheids in a condition suitable for transmitting water.

With regard to the first assumed possibility, it may be observed, as has been pointed out, that no process taking place in the cells adjoining the water-conduits can be effective in raising the water through these conduits as long as water is free to move equally readily up or down in the conduits. Experiments seem to have abundantly proved the absence of valves or other unidirectional structures in the water-tracts of plants. Hence, judging from the known physical properties of the water-conducting tissues and the relation of the living cells of the stem to them, there is no *à priori* reason for supposing that these latter are effective in raising water to levels above themselves during transpiration. Rather all that we know is opposed to such a supposition.

Ursprung, however, seeks to demonstrate this function for the living cells by direct experiment. He quotes, in the first instance, Strasburger's experiments, in which great lengths of stems were killed by immersion in hot water, and, according to him, the result, viz. the withering of the leaves above the killed portions, although

¹ Band xviii., Abt. I., Heft 1, 1904.

these latter were richly supplied with water, shows that the living elements which had been destroyed by the heat were needed to raise sufficient water to keep the leaves turgescient.

Furthermore, he carried out similar experiments himself on a smaller scale, and found that, when very short pieces (only 2-3 cms.) of the supporting branch were killed, practically no harmful effect is noticed on the leaves. If longer pieces are killed, wilting and withering quickly supervene. Ursprung's experiments differed from Strasburger's, and resembled Janse's in the fact that the branches experimented upon were left attached to the plants, and consequently were connected to the root during the experiments.

As the result of his observations he concludes that the living elements of the stem do participate in the elevation of the sap directly by lifting and supporting the water, and also in some cases indirectly by maintaining the water-ways in a condition suitable for conducting water. The latter conclusion he bases on the observation that when loss of water from the surface of the dead stem was prevented by a coating of paraffin, sometimes the harmful effects on the leaves above were less noticeable.

I venture to think, however, that the experimental facts, which Ursprung believes to support his views, could find a more satisfactory explanation in other ways.

For example, if we accept the view that the ascending current is in a tensile state, it is quite conceivable that the high temperature needed for killing the cells would sufficiently lessen the cohesive strength of the water, by increasing its vapour-pressure, and so cause rupture in most or all of the water-columns. When a short region only is killed by heat, the "bleeding" pressure of the remaining living cells would be adequate to restore continuity; while if the discontinuities extend through great lengths of the stem, the ruptures cannot be made good before the diminished supplies cause the leaves to fade.

Another possibility suggests itself. The cells killed by the action of the heat may give up substances in solution to the transpiration current which either may act as poisons to the leaf-cells, or which, by concentrating in the leaves, may act as plasmolysing agents on the cells of the leaves, and cause the fading of the leaves. The fact that a minimum length of the stem must be

killed before the injurious effects are noticed also seems to fit in with this explanation.

Or, again, it is conceivable that substances may be exuded from the dying cells into the conducting tracts, which obstruct the free flow of water upwards, and so prevent an adequate supply being transmitted to the leaves. Such substances might themselves be quite invisible and elude the most careful examination.

In order to obtain a clear view of the matter, I repeated some of the experiments alluded to above. I used *Primula*, *Chrysanthemum*, *Syringa*, *Philadelphus*, and *Cytisus*. My results fully bore out Ursprung's accounts of his experiments. If short lengths only were killed by the application of steam or of water at 95°–100° C., the leaves above scarcely suffered. As the length of the killed portion was increased, more and more of the leaves faded. For example, on a branched specimen of *Chrysanthemum sinense* lengths of 2, 3, and 5 cms. were killed on different branches. Each branch carried 6–8 leaves. The uppermost leaves of all three branches remained fresh and turgescient during the forty days the observation was continued. The lower leaves in the case of the branches of which 3 and 5 cms. were killed wilted on the third day. Two leaves were involved in this injury in the case of the branch where 3 cms. were killed, and three leaves where 5 cms. were killed.

This observation seems to support the view that the withering is due to the presence of a poisonous material, which is supplied in proportion to the length of amount of tissue killed.

If this theory be correct, it should be possible to cause withering by supplying water which has passed through a killed branch to leaves otherwise normally supplied with water. This was found feasible in the following manner:—One branch of a bifurcated shoot of *Syringa vulgaris* was killed by immersion in water at about 90° C. for ten minutes. After this the dead branch was stripped of its leaves, and cold water supplied through it to the leaves supported on the uninjured branch. These leaves then drew supplies of water from two sources, viz. from the roots, and through the dead branch. To facilitate this latter supply a fresh surface was occasionally cut on its distal extremity. The length of the dead branch in my experiments varied from 30–40 cms. Notwithstanding the double supply of water, the leaves on the living

branch in each experiment showed signs of wilting. When the supply through the dead branch was cut off, either by the withdrawal of the water from its end, or by its own clogging, the wilted leaves partially recovered. But in several experiments the edges of the leaves were too far injured to recover, and the injury persisted as a brown margin on the leaf.

The experiment may also be carried on with a straight branch from which the upper leaves and side branches are removed. The stripped upper portion is immersed for a short time in water at about 95° C., and after death so caused, water is supplied through this dead portion to the lower leaves and side branches, which have been left undisturbed. If the supply of water through the upper dead part of the branch is kept up, fading and partial withering of the leaves below will be noticeable in a few days.

Inasmuch as the effect on the leaves depends on the amount of harmful matter carried up from the dead cells, it is evident that immediate or complete withering is not to be expected, for the supply from the dead part is largely diluted with the supply from the roots through the living, and, also, it is difficult to make the supply through the dead part considerable owing to the clogging at the cut surface, and also possibly owing to internal clogging caused by the exudations into the water-capillaries from the dead cells.

Another and simpler method of observing the withering effects of the substances liberated from cells, when killed by heat, may be carried out as follows:—A decoction is made by boiling small pieces of a stem in water for a short time. This decoction, after repeated filtering, is supplied to cut branches of the same tree. It will be found that the leaves of the branches supplied with the decoction fade and wither much more rapidly than those of control-branches supplied with water. For example, three branches of *Syringa vulgaris*, set in a decoction of the stem of the same plant, lost their turgidity within two days, while the leaves of three control-branches were still fresh after five days.

Taken alone, this last observation would not be sufficient to prove that in intact branches the withering of the leaves is due to deleterious substances emerging from the killed cells; for it might be urged that colloid substances in the decoction aggregating on the cut surface obstruct the free transmission of water, and thus

cause the fading by partially cutting off the water-supply. The probability of this explanation is lessened by the fact that the decoction causes the fading even after it has been repeatedly filtered. In any case the observation, taken along with the previous experiments, may be regarded as confirmatory of the view that the fading is largely due to the plasmolysing or poisonous effects of substances extracted from the dead cells.

The contaminated nature of the water supplied through a dead branch may be demonstrated by collecting some of the water transmitted through a branch killed by the application of hot water, as in the previous experiments. If *Syringa vulgaris* is used, the water transmitted is of a dark brown colour, and quite different in appearance from what is transmitted through a living branch under similar circumstances. If this brown fluid is supplied to cut transpiring branches, the latter rapidly fade and wither. When making this experiment, I killed the lower 30 cms. of a straight branch 40 cms. long, by immersion in hot water. The branch was then inverted and water forced through it under a head of 20 cms. The water transmitted was thus filtered through 10 cms. of living wood after its passage through the dead portion. After transmission, it was twice filtered, and supplied to cut branches. These latter faded in two and a half days, while controls did not show signs of fading for several days later.

The foregoing observations seem to me to show that the exudations from the dead cells are sufficient in themselves to cause the fading of the leaves above the killed portions of the stem. However, it also appears evident that if the leaves exerted much tension during the application of the high temperature, this tension might easily cause the rupture of the water-columns, while the tensile strength of the water was diminished owing to its increased vapour-pressure at the higher temperature.

To investigate this possibility I endeavoured to arrange that the water in the conducting tracts should re-establish continuity after the withdrawal of the hot water. In order to do this, I removed an annular piece of the bark in the middle of the heated portion of the branch experimented upon. This annular incision laid bare the wood, and put its tubular elements in communication with the surrounding water. This water, which was applied boiling, was allowed to cool gradually. All this time the

leaves above were wrapped in a damp cloth to reduce evaporation from them to a minimum, and, with it, the tensile stress in the conduits. As the water surrounding the branch cooled, continuity was presumably re-established in most of the ruptured water-columns. The leaves treated in this way did not retain their turgidity appreciably longer than those on branches not ringed, but otherwise similarly treated. Sometimes a small delay in the fading of these ringed branches was noticed; but this might be explained by the dilution, introduced through the ring, of the substances exuded by the dead cells.

The experiment, however, cannot be regarded as satisfactory, as it is by no means proved that continuity is re-established in a sufficient number of capillary tracts in order that an adequate quantity of water may be supplied to the leaves, and consequently we cannot be certain what would happen if continuity were thoroughly re-established. Furthermore, the fading in this experiment cannot be regarded as exclusively caused by rupture, inasmuch as other causes are allowed to act.

CONCLUSIONS.

The considerations mentioned in this note seem to indicate that:—

1. It is unnecessary to attribute to the cells of the stem a special function in the elevation of water, because the leaves above fade when these cells are killed by heat.
2. The fading of the leaves in these cases is probably largely due to the introduction of poisonous or plasmolysing substances into the leaves from the dead cells.
3. Clogging due to the exudation of comparatively impermeable substances into the water-conducting tissues of the plant may also contribute to the fading of the leaves.
4. It is further possible that the application of heat in these experiments may permanently interrupt the water-supply by breaking the water-columns, on the continuity of which the water-supply depends.

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THE INFLUENCE OF
WATER-VAPOUR UPON NOCTURNAL RADIATION.

BY

J. R. SUTTON, M.A., F.R.MET.S.

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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III.

THE INFLUENCE OF WATER-VAPOUR UPON NOCTURNAL RADIATION.

By J. R. SUTTON, M.A., F.R.MET.S.

[COMMUNICATED BY PROF. J. JOLY, F.R.S., HON. SEC. ROYAL DUBLIN SOCIETY.]

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IT has always seemed to me that Tyndall's discovery of the absorption and radiation of heat by the vapour of water has been too hastily applied to meteorological problems. According to his experiments, the absorption of heat from any given source by ordinary atmospheric air containing aqueous vapour is proportional to the quantity of vapour present in a given space. He gave the following table:—

HUMID AIR.		
TENSION.	ABSORPTION.	
Inches.	Observed.	Computed.
5	16	16
10	32	32
15	49	48
20	64	64
25	82	80
30	98	96

“The third column here is calculated on the assumption that the absorption, within the limits of the experiment, is sensibly proportional to the quantity of matter in the tube. The agreement

with observation is almost perfect.”¹ And Tyndall went on to say:—“The power of aqueous vapour being thus established, meteorologists may, I think, accept the result without fear. That 10 per cent. of the entire terrestrial radiation is absorbed by the aqueous vapour which exists within ten feet of the Earth’s surface on a day of average humidity, is a moderate estimate. In warm weather, and air approaching to saturation, the absorption would probably be considerably greater. This single fact at once suggests the importance of the established action as regards meteorology. I am persuaded that by means of it many difficulties will be solved, and many familiar effects which we pass over without sufficient scrutiny because they are familiar, will have a novel interest attached to them by their connexion with the action of aqueous vapour on radiant heat.”²

There seems to be no doubt that Tyndall’s experiments were carefully carried out, and that the observed effects were not vitiated by any extraneous disturbances. But the point which should immediately appeal to a meteorologist, and which Tyndall (not being a meteorologist) seems to have overlooked, is that humid air has always to be considered in two ways, namely, from the point of view of both relative and absolute humidity. By doubling the quantity of vapour in a given space, so long as the temperature is unaltered and no condensation takes place, the humidity is doubled as well as the tension. By doubling the space, the temperature being kept constant, the tension and humidity would both have been halved. If Tyndall had made this latter variation of his experiment, and the absorption had remained the same, then undoubtedly he could have claimed that it was proportional to the quantity of aqueous vapour present. He did not make the variation, however; therefore, so far as his table of absorption is concerned, there is nothing to show that the observed effect might not have been just as much due to the relative as to the absolute humidity.³

¹ J. Tyndall, “On the Relation of Radiant Heat to Aqueous Vapour,” *Phil. Trans.*, vol. cliii., 1863, p. 1.

² *Ibid.*, p. 8.

³ Tyndall did show that a small quantity of ether vapour, under a given pressure, would exert the same absorption upon the radiations from lime-light as when it was

This criticism applies at once to “a representative series of observations made between the 4th and 25th of March, 1850 [by General R. Strachey, R.E.]; during which period the sky remained remarkably clear, while great variations in the quantity of vapour took place. The first column of numbers gives the tension of aqueous vapour; the second the fall of the thermometer from 6.40 p.m. to 5.40 a.m.

Tension of Vapour.			Fall of Thermometer.
·888 inch.	6°·0
·849 „	8°·3
·805 „	8°·3
·749 „	10°·3
·708 „	10°·3
·659 „	12°·6
·605 „	12°·1
·554 „	13°·1
·435 „	16°·5

“The general result is here unmistakable. In clear nights the fall of the thermometer, which expresses the energy of the radiation, is determined by the amount of transparent aqueous vapours in the air. The presence of the vapour checks the loss, while its removal favours radiation and promotes the nocturnal chill.”¹ But it is to be observed that because the period mentioned is only three weeks, the temperature of the air at 6.40 p.m. may not have varied to any great extent during the whole time; and hence the humidity and tension may have varied together. If this is so, then the effect which Tyndall ascribed to the absolute humidity may, as before, have been just as probably due to the relative humidity.

Commenting on the agreement which Tyndall deduces between the observed and computed absorption, Professor Very remarks

compressed to $\frac{2}{3}$ the depth at $3\frac{1}{2}$ times the pressure. But, on the other hand, doubling the actual quantity in a given depth did not double the absorption.

¹ J. Tyndall, “Heat a Mode of Motion,” 1880, p. 383.

that "the air is said to have been humid, and yet, when reduced to a pressure of one-sixth of an atmosphere, to have contained 'less than one-sixth of the vapour necessary to saturate the space.' But if the air was anywhere near saturation at the ordinary pressure, it must have been supersaturated when reduced to a pressure of 5 inches—a fact which was perfectly well known to Tyndall, since he has described it on page 46 of the same work. I can only reconcile these statements by supposing that either Tyndall inadvertently overlooked the increase of relative humidity in air at reduced pressure, when writing this passage, or else that the description of the air as 'humid' is very misleading."¹

The page 46 referred to by Very is in the American edition of "Heat a Mode of Motion," which I have not been able to consult; and I am therefore quite at a loss to imagine what process Tyndall could have described which could justify so amazing a criticism. Pushed to its logical extreme Very's argument implies that water cannot evaporate in a vacuum. Probably the point which Very refers to is the chilling of air by its own rarefaction, which Tyndall thus describes:—"On the plate of the air-pump is placed a large glass receiver filled with the air of this room. This air, and indeed all air, unless it be dried artificially, contains a quantity of aqueous vapour, which, as vapour, is perfectly invisible. *A certain temperature is requisite* to maintain the vapour in the invisible state; and if the air be chilled so as to bring it below this temperature, the vapour will instantly condense and form a visible cloud. . . . A very few strokes of the pump suffice to precipitate the vapour. . . . When the air is allowed to re-enter the vessel, *it is heated*, the cloud melts away, and the perfect transparency of the air within the receiver is restored."² The point of the quotation will be found in the words I have ventured to italicise. Temperature, indeed, is all-important; pressure of no importance at all, excepting that the temperature and pressure will at first, in any such experiment, fall together. Tyndall had very fully described what he called "dynamic radiation and absorption," as resulting from dynamic heating and

¹ F. W. Very, "Atmospheric Radiation," 1900, p. 81.

² J. Tyndall, "Heat a Mode of Motion," 1880, p. 16.

chilling, almost a year before he published the results which Very¹ criticises; and hence it may be taken for granted, I think, that Tyndall intended it to be understood that the temperature of the vapour was the same at each pressure. It is not very likely, judging from Tyndall's record, that any objections to his results can be maintained on the ground of faulty manipulation.

In this connexion one of Boyle's observations is worth quoting here by the way for the sake of its historic interest. After what Tyndall has said with reference to his own experiment with the air-pump, the explanation of the phenomenon (which Boyle does not give) will be obvious :—

“We have observ'd,” says Boyle, “That though we convey'd into the Receiver our Scales, and the *Pendula* [of iron or steel] formerly mention'd, clean and bright; yet after the Receiver had been empty'd, and the Air let in again, the gloss or lustre both of the one, and of the other, appear'd tarnish'd by a beginning rust.”²

Returning again to Tyndall, it seems to me not at all improbable that six times as much vapour in the given space did actually exert about six times as much absorption. But while, with all the respect which is due to Tyndall's great powers as an experimentalist, it may be suggested that such a result is just as likely to be due to the resulting relative humidity as to the actual quantity of vapour present, there is a further objection that the meteorological problem is not necessarily so simple a case as he supposed. The air, according to his own showing, absorbs and radiates heat. It absorbs its own radiations as well as those from the surface of the Earth. Considering a small thickness of the lower air, we may be sure from Tyndall's own results (as indeed he has carefully pointed out) that the drier it is the less heat it will absorb, and therefore, once it is heated, the more slowly it will cool of itself. On the other hand, the surface of the ground should

¹ J. Tyndall, “On the Absorption and Radiation of Heat by Gaseous Matter,” *Phil. Trans.*, 1862, p. 59.

² Robert Boyle, “New Experiments,” 1682, p. 161. Expt. xxxvii. and xxxix. should also be consulted.

cool the faster as the air is drier; and this would cool the lower air by simple conduction. On the other hand, also, a damp air should cool the faster of itself, but check the cooling of the surface of the Earth, or of lower layers of air. The meteorological problem, then, is a composite one; and whatever be the true interpretation of Tyndall's results, it by no means follows that it may be applied immediately, and without hesitation, to such observations as those furnished by General Strachey.

Some years ago I tried to find out whether the cooling of the lower air at Kimberley by night could be regarded as depending upon the amount of moisture present, by comparing the fall of temperature between 8 p.m. and the succeeding minimum upon every clear night in one year with the absolute and relative humidity at 8 p.m. Kimberley has remarkably clear night skies, pretty well or quite one-half of the nights being absolutely free from cloud, so that a single year's observations gave a good series. No certain connexion could be traced between the dew-point at 8 p.m. and the succeeding fall of temperature; but there seemed to be a uniform increase of range of temperature with a decreased relative humidity.¹ The results could, however, only be looked upon as provisional, because, for one thing, the nights are not all of the same length, and, consequently, in the winter there is an interval of quite two hours longer for the temperature to fall in than there is in the summer. To a certain extent this, when allowed for, would show an even greater influence on the part of the relative humidity, since on the whole the percentage of saturation is highest when the nights are longest. However, it seemed worth while to examine the question afresh, using as a standard the fall of temperature in one hour corresponding to the relative and absolute humidity at the beginning of the hour. This I have been doing at spare intervals for some few years; and the more important results are submitted in the present paper. The matter needs ventilation, because if laboratory experiments have given contradictory results, meteorological opinion has been equally indefinite. But first, before calling attention to what I conceive

¹ J. R. Sutton, "Aqueous Vapour and Temperature," *Symons's Met. Mag.*, Aug., 1895.

to be the true interpretation of my results, it may not be amiss if some notice be taken of comparatively recent opinion :—

W. M. Davis remarks that “it has been supposed that the air was a better absorber of terrestrial radiation than of solar radiation; and thus the atmosphere has been compared to a trap which allowed sunshine to enter easily to the Earth’s surface, but prevented the free exit of radiation from the Earth; water-vapour in particular was thought to be very active in this selective process. The general temperature maintained by the atmosphere has been explained largely on these suppositions; but recent observations throw grave doubts upon both of them. Clear air allows the coarse-waved radiation from the Earth an easy outward passage. Water-vapour is, like clear air, a poor absorber of nearly all kinds of waves. It is true that the presence of excessively fine water-particles, sufficient only to make the air faintly hazy, greatly diminishes its power of transmission or diathermanence; but water-vapour—that is, water in the gaseous state—is found by experiment to be as poor an absorber as pure dry air.¹ The temperature of the air is, therefore, now explained as a result of its own absorption and radiation, largely aided by suspended dust and by certain processes. . . .”—such as conduction and convection.² Davis remarks further that “it is only water in the liquid state [*i.e.* in the form of haze or cloud] that exerts a strong control over radiation from the Earth. . . . If the temperature of the air is well above saturation, the range is relatively strong; if near saturation, the range is diminished even though no visible clouding of the sky occurs; if a thin, hazy cloud is formed, the range is greatly reduced.”³

¹ Cf. G. Magnus, “On the Propagation of Heat in Gases”: *Phil. Mag.*, August, 1861, pp. 1, 85 :—“Although it might with certainty be predicted that the small quantity of aqueous vapour which air can take up at the ordinary temperature (not 2 per cent. of its volume at 16° C.) could exercise no influence on the radiation, it appeared desirable to determine experimentally that this supposition was correct. . . . These experiments show that the water present in the atmosphere at 16° C. exercises no perceptible influence on the radiation. That such an influence should be felt as soon as part of the vapour separates as fog, appears very probable” (pp. 105–106).

² W. M. Davis, “Elementary Meteorology,” 1894, p. 32.

³ *Ibid.*, p. 145.

F. W. Very, however, claims that "the chief absorbent of the Earth's atmosphere is water-vapour, but its action is complicated by the relation between vapour and mist. Even considerable changes in atmospheric aqueous vapour in warm weather, if unattended by misty condensation, produce only slight variation in the direct rays of the midday sun—not, however, because water-vapour does not exercise a great absorption, even on solar rays, but because so much moisture is always present in warm weather that nearly all of the rays absorbable by aqueous vapour have been eliminated, and the remaining radiation is comparatively transmissible.¹ Haze, however, of whatever description, . . . acts at all seasons, and independently of the amount of the vapour of water dissolved in the air. Mist and haze have little effect on the emission of radiations of long wave-length from air by virtue of its own temperature, or on the transmission of long ether-waves by the atmosphere; but they have great influence in stopping and scattering those short ether-waves which are especially prominent in sunlight."²

Moreover, "the gradual formation of closed chains as the aqueous vapour approaches saturation must take place most readily if the molecules of vapour are not widely separated by diluting air. Meteorologists have often commented on the peculiarities of nearly saturated air; and some have conjectured that gaseous water exercises no appreciable absorption, and that the absorbent effects attributed to it are really due to a mist of liquid water, relative humidity being more important than vapour-tension as an index of absorptive power. We have seen that gaseous water does produce a very potent influence of its own; but it seems to me to be demonstrated by what precedes that there is a remarkable increase in absorption by water at the critical point of incipient condensation, and as this point is somewhat closely approached. The suffocating sensations experienced in a very hot, muggy atmosphere

¹ My own observations do not at all support this statement. It is an undoubted fact that at Kimberley, under a perfectly clear sky, an increase of aqueous vapour indicates an increase of air-temperature, and a corresponding decrease of the heating effect of the Sun's rays. Such also appears to be the plain interpretation of some recent volumetric work in America.—J. R. S.

² F. W. Very, "Atmospheric Radiation," 1900, p. 79.

are attributable to the partial cessation of the evaporation from skin and lungs; but the thermometric effects, such as the diminution of the daily range of temperature under a clear sky, which becomes very noticeable when the relative humidity is high, can be due only to strong absorption of the long-waved terrestrial radiations; and it is interesting to note that the difference between the absorption of liquid and vaporous water lies chiefly in the greater absorption of longer waves by the former.”¹

Again, “the direct effect of the Sun’s rays upon a normal surface is less in the tropics than in temperate regions, and less at sea-level than upon a mountain-top, owing to the difference in the aqueous component of the air; and the ability of the solar radiation to maintain a high temperature in the torrid zone or at sea-level is due to the accumulation of the thermal energy imparted to the Earth’s surface by reason of the retention of the escaping radiation from that surface by a moist and highly absorbent atmosphere rather than to the direct power of the sunbeam. . . . The penetrative power of the incoming is greater than that of the outgoing rays; and this relative difference, which increases with the amount of moisture in the air, produces an accumulation of thermal energy at the Earth’s surface which would generate a very high temperature were it not that the sign of the function is reversed after sundown. . . . The heat entrapped through the differential transmission of solar and terrestrial radiation by aqueous vapour and carbon dioxide is mainly stored in the lower layers of the atmosphere, and because the absorption of air heavily loaded with moisture is nearly complete for its own radiation.”²

J. H. Poynting and J. J. Thomson take practically the same view as Very:—“One result obtained by Tyndall is that water-vapour has a very considerable absorption for dark radiations—a result which was contradicted by other experimenters. The various methods, however, by which Tyndall obtained evidence of the absorption leave little doubt that his experiments warranted

¹ F. W. Very, “Atmospheric Radiation,” p. 100.

² *Ibid.*, pp. 125, 126. I find a good deal of difficulty in following Very’s argument sometimes, particularly in discerning the dividing line between experimental and speculative results.

his conclusion. It is confirmed by the observations of meteorologists on the greater or slower rate of cooling of the Earth at night, when the air contains less or greater amounts of water-vapour.”¹

In Hann’s “Handbook of Climatology” (Prof. R. de C. Ward’s edition) some previous numerical values of mine are quoted; but the final verdict is not exactly in accordance with them:—“The more water-vapour the air contains, the more readily do light fogs form, although these may be invisible to the eye. It is therefore still uncertain whether the effect of the vapour-pressure here shown is to be attributed altogether to the vapour-contents of the air. Woeikof believes that the connexion between radiation and relative humidity is much more clearly proved. Sutton has recently attempted to show the effect of the water-vapour in the air upon nocturnal cooling by means of some observations at Kimberley, South Africa. For this purpose, he selected the observations made on perfectly clear nights during an entire year. No relation between the dew-point at 8 p.m. and the amount of nocturnal cooling could be established; but that there was a marked relation between the relative humidity and the nocturnal cooling is shown by the following figures:—

RELATIVE HUMIDITY AND NOCTURNAL TEMPERATURES AT
KIMBERLEY.

RELATIVE HUMIDITY AT 8 P.M. (Percentages).				
25-39	40-49	50-59	60-69	70-80 and above.
MEAN DIFFERENCE OF TEMPERATURE BETWEEN 8 P.M. AND THE MINIMUM.				
10°·3 C.	8°·8	7°·6	7°·2	6°·0

¹ J. H. Poynting and J. J. Thomson, “A Text-Book of Physics,” “Heat,” 1904, p. 236.

“In the light of these data, there can no longer be any doubt that an increasing amount of water-vapour in the air diminishes the extremes of temperature.”¹

Unfortunately these authors, with the exception of the last, do not give any references to the results they state; so that we are quite in the dark as to the class of facts and the lines of investigation from which they are derived. It is not unlikely that Poynting and Thomson refer to some such observations as those of General Strachey mentioned above; while Davis and Very may have in mind more general considerations, such as, for example, that while the average amount of moisture in the air at Durban is double what it is at Greenwich, the range of temperature is considerably greater at the former place. At any rate, two main ideas seem to be afloat: one, that the fall of temperature at night is regulated by the quantity of moisture in the air; the other, that moisture has, of itself, no influence, but that nearly saturated air begins to exert a strong absorption, laboratory experiment and meteorological observations being relied upon to support both views. With regard to the second, Very has remarked that “the experiments which have been interpreted in favour of the diathermancy of water-vapour have been refuted long ago; and Professor Davis, since the publication of his book, has given evidence that he no longer adheres to the erroneous doctrine there enunciated. (See his ‘Absorption of Terrestrial Radiation by the Atmosphere,’ *Science*, N.S., vol. ii., p. 485, October 11, 1895).”² Whether this correctly represents Davis’s present attitude is, perhaps, open to question; but it is certainly difficult to read any such renunciation in the article cited. In fact, there is no mention in it, from beginning to end, of the action of aqueous vapour upon solar, lunar, or terrestrial radiations. My own impression is that Davis’s argument is dead against Very’s contention.

In the following Table are given the monthly normals of dew-point, relative humidity, and cloud at 8 p.m., of wind-velocity and

¹ “Handbook of Climatology,” 1903, p. 145. I have not had the good fortune to read Woeikof’s paper.

² F. W. Very, “Atmospheric Radiation,” 1900, p. 84.

of fall of temperature in one hour, from 8 p.m. to 9 p.m., for the four years 1900 to 1903 :—

MONTHLY NORMALS.

MONTH.	Dew-Point at 8 p.m.	Relative Humidity at 8 p.m.	Cloud at 8 p.m.	Wind- Velocity, 8-9 p.m.	Fall of Temperature, 8-9 p.m.
		Per cent.	Per cent.	M. per H.	
Jan., . . .	49°5	45	33	5·5	1·9
Feb., . . .	54·0	53	46	5·3	1·6
March, . . .	52·1	59	34	4·3	1·7
April, . . .	49·1	66	28	4·0	1·5
May, . . .	38·0	56	12	4·0	1·6
June, . . .	34·0	61	17	4·5	1·4
July, . . .	33·3	58	13	4·0	1·8
Aug., . . .	33·8	48	12	4·6	2·0
Sept., . . .	38·6	48	20	5·1	2·4
Oct., . . .	40·9	44	30	6·0	2·2
Nov., . . .	41·4	38	18	6·5	2·5
Dec., . . .	50·1	48	39	5·2	2·2

Such a table as this can, of course, only be expected to indicate in the roughest way the results we are seeking. In fact, it would only be admissible if the clouds remained the same in quantity month by month, and also occupied the same areas of the sky. For clouds may be expected to reflect as well as to absorb heat from the Earth; and while the absorption may be at its lowest when the zenith is clear, both absorption and reflection will exert their maximum effect when the zenith is clouded. It is pretty certain that the disturbing influence of the clouds may at times completely override the effects due to either vapour-tension or humidity; and yet, in spite of so obvious an objection, it is generally the case that averages of this sort are relied upon to demonstrate supposed physical processes in the atmosphere. To avoid being misled, then,

by the introduction of error from this source, monthly averages have been formed for clear nights only, not a single night being included in which any cloud at all could be seen.¹ They are then arranged in two sets, one being a sequence of dew-points, the other a sequence of relative humidity:—

MONTHLY AVERAGES ARRANGED IN ORDER OF DEW-POINT.

MONTH.	Average Number of Clear Nights.	Dew-Point at 8 p.m.	Relative Humidity at 8 p.m.	Wind-Velocity, 8-9 p.m.	Fall of Temperature, 8-9 p.m.
Feb., . .	7	48°·8	Per cent. 43	M. per H. 4·8	2°·0
Mar., . .	10	47·5	50	4·7	2·2
April, . .	12	46·4	61	4·1	1·7
Dec., . .	9	44·1	37	6·1	2·4
Jan., . .	10	42·6	34	6·3	2·5
Nov., . .	15	37·9	34	6·2	2·6
May, . .	20	37·0	56	3·8	1·8
Oct., . .	12	36·9	40	5·6	2·3
Sept., . .	15	36·8	46	4·4	2·3
June, . .	20	32·8	61	4·4	1·6
July, . .	22	32·4	58	3·9	1·9
Aug., . .	20	32·2	47	4·3	2·1

¹ It is important that the sky should be absolutely clear, because the least trace of cloud, even near the horizon, suggests condensation in the vicinity.

[TABLE OF RELATIVE HUMIDITY.]

MONTHLY AVERAGES ARRANGED IN ORDER OF RELATIVE
HUMIDITY.

MONTH.	Relative Humidity at 8 p.m.	Dew-Point at 8 p.m.	Wind- Velocity, 8-9 p.m.	Fall of Temperature, 8-9 p.m.
	Per cent.		M. per H.	
April, . . .	61	46·4	4·1	1·7
June, . . .	61	32·8	4·4	1·6
July, . . .	58	32·4	3·9	1·9
May, . . .	56	37·0	3·8	1·8
March, . . .	50	47·5	4·7	2·2
August, . . .	47	32·2	4·3	2·1
September, . . .	46	36·8	4·4	2·3
February, . . .	43	48·8	4·8	2·0
October, . . .	40	36·9	5·6	2·3
December, . . .	37	44·1	6·1	2·4
January, . . .	34	42·6	6·3	2·5
November, . . .	34	37·9	6·2	2·6

It is evident from these tables that, so far as the present inquiry is concerned, the absolute and relative humidities are quite independent of each other. Nor is there any decided relationship between either and the velocity of the wind, although the latter is certainly highest in the summer, when the relative humidity is lowest. As to a relation between either and the fall of temperature, there cannot be any doubt, I think, that the relative humidity is the only element which shows it. As the air becomes drier the temperature falls faster, and at a rate which, for mnemonical purposes, may be represented by the formula

$$6. H^{\frac{1}{3}}. F^{\frac{1}{2}} = 100,$$

where H is the relative humidity, and F , the fall of temperature in degrees Fahrenheit. A variation in the dew-point from 32° to 49° , corresponding to a variation of vapour-tension of $\cdot 18$ inch to

·35 inch, makes (apart from the accompanying humidity) absolutely no impression upon the rate of fall.

By dividing all the dew-points into sets in order of magnitude, irrespective of the months in which they occur, we have the following results for the four years 1900-1903 :—

Dew-Point at 8 p.m.	Relative Humidity at 8 p.m.	Wind-Velocity, 8-9 p.m.	Fall of Temperature, 8-9 p.m.	Number of Clear Nights.
Under 35°	Per cent. 46	M. per H. 4·7	1·9	273
35°-39°·9	46	4·9	2·2	190
40°-44°·9	45	5·2	2·3	116
45°-49°·9	51	4·0	2·1	56
50°-54°·9	60	3·3	2·0	38
55 and over.	73	2·4	1·5	15

Here again we find absolutely no trace of a fall of temperature depending upon the quantity of moisture present. But we do see plainly that the humidity and the fall of temperature vary together, even though the table has not been arranged with any reference to the saturation percentage. We see it still more plainly by dividing the observations into sets according to the magnitude of the relative humidity :—

Relative Humidity at 8 p.m.	Dew-Point at 8 p.m.	Wind-Velocity, 8-9 p.m.	Fall of Temperature, 8-9 p.m.	Number of Clear Nights.
Under 30 %	37·8	M. per H. 7·3	2·8	68
30 %-39 ,,	37·7	5·8	2·5	123
40 ,, -49 ,,	35·9	4·7	2·2	182
50 ,, -59 ,,	37·1	3·8	1·8	157
60 ,, -69 ,,	38·9	3·6	1·6	96
70 ,, and over.	42·6	3·3	1·5	62

Our previous formula connecting the relative humidity and the fall of temperature applies here also. Since the actual average quantity of water-vapour as indicated by the dew-point is pretty much the same for each item of relative humidity, it follows that the regular decrease in the fall cannot be due to that quantity. We see, however, that the velocity of the wind decreases as the humidity increases; and it might be thought that this is a possible principal cause of the variation in the fall of temperature. Actually it is not so, because an increase in the velocity of the wind after nightfall almost invariably means a temporary elevation of temperature; while the low minima occasionally registered during the winter occur invariably on still nights. But since it is important to determine what the effect of the wind really is, the various velocities have been compared with the other elements:—

Wind-Velocity, 8-9 p.m.	Dew-Point at 8 p.m.	Relative Humidity at 8 p.m.	Fall of Temperature, 8-9 p.m.	Number of Clear Nights.
M. per H. 0—1	39°9	Per cent. 57	2°4	39
1—2	40·6	57	2·4	37
2—3	39·1	55	2·3	100
3—4	39·4	53	2·0	118
4—5	36·1	50	1·9	121
5—6	36·1	46	1·6	108
6—7	36·5	39	2·0	43
7—8	36·6	40	2·1	55
8—9	36·7	33	2·4	24
9—10	38·2	37	2·3	16
10 and over.	37·1	40	2·4	27

It seems from this that as the wind-velocity increases from zero to about six miles per hour, the fall of temperature will gradually diminish; but for further increments of velocity, the fall will gradually increase. A partial explanation of this is to be looked for in the nocturnal temperature gradient. Close to the surface,

and at great altitudes, the air is relatively cold at night; but in the middle reaches, it is relatively warm. We may assume that velocities up to five or six miles per hour can do no more than bring down the air from the middle reaches to mix with the lower air, but that greater velocities may bring down the air from considerable heights. Heating due to adiabatic contraction would doubtless largely neutralize this process.

Some results obtained in 1896 and 1897 gave a somewhat higher wind-velocity corresponding to the slowest fall of temperature, namely, a fall of 3° in two hours, from 8–10 p.m., for a velocity lying somewhere between $6\frac{1}{2}$ and 8 miles per hour; but otherwise the results agree quite well with those of the later period 1900 to 1903. I attempted to use these wind-results for the purpose of applying corrections to the observed fall of temperature so as to obtain better values for the dew-point and humidity factors, but without any particular improvement worth notice. The following are the results:—

Dew-Point at 8 p.m.	Fall of Temperature, 8–10 p.m.	Number of Clear Nights.	Relative Humidity at 8 p.m.	Fall of Temperature, 8–10 p.m.	Number of Clear Nights.
Under 30°	$3\cdot8$	68	Under 35 %	$5\cdot1$	41
30° – $34^{\circ}\cdot9$	$3\cdot6$	98	35 %–39 „	$4\cdot5$	31
35° – $39^{\circ}\cdot9$	$3\cdot8$	68	40 „–44 „	$4\cdot3$	37
40° – $44^{\circ}\cdot9$	$3\cdot8$	33	45 „–49 „	$3\cdot7$	46
45° and over.	$3\cdot3$	29	50 „–54 „	$3\cdot4$	51
			55 „–59 „	$2\cdot8$	36
			60 „–64 „	$2\cdot6$	28
			65 „, & over.	$2\cdot3$	26

Therefore, even after correcting for wind-velocity no essential difference is introduced; and, as before, the dew-points are unimportant.

It is important to determine whether, for a given humidity-percentage, the fall of temperature depends at all upon the temperature itself. The following table shows that it does. It

gives the fall of temperature in four hours for different initial temperatures, according to the relative humidity at 2 a.m., for the two years 1896 and 1897 :—

Initial Temperatures.	RELATIVE HUMIDITY.					
	Under 50 %.	50-59 %.	60-69 %.	70-79 %.	80 % and over.	Average.
	FALL OF TEMPERATURE.					
Under 35°	—	5·1	3·2	3·8	1·9	3·6
35°-39°·9	5·1	4·9	3·7	3·2	3·2	3·7
40°-44°·9	6·7	5·6	4·5	4·4	3·0	4·6
45°-49°·9	8·1	5·6	4·7	3·3	3·5	4·7
50°-54°·9	5·5	5·5	5·2	5·0	3·0	5·1
55°-59°·9	6·4	6·5	5·8	4·0	2·5	5·2
60 and over.	7·7	6·2	5·5	4·2	2·9	6·2

Thus for a given relative humidity the fall will be the more rapid as the initial temperature is higher. As might be expected, there is a good deal of irregularity in the individual items, but the general tendency is evident enough. And the important fact remains that for any assigned initial temperature the fall becomes less as the relative humidity increases. Both facts refute the assertion that the quantity of water-vapour determines the rate of cooling of the air. To particularise the first deduction, it need only be pointed out that the vapour-tension for an initial temperature of 38°, and a relative humidity of sixty per cent., is scarcely one-third of the vapour-tension for an initial temperature of 63° and a relative humidity of sixty per cent. Therefore, if it be true that the cooling will be the more rapid as the quantity of water-vapour decreases, we should expect a greater fall for the lower initial temperature; whereas the table shows very decidedly that the contrary is the case. It is to be observed that, especially for the lower relative humidities of the table, the saturation-point has little, if any, influence upon the falls of temperature shown. For these falls are not more than one-third of the

differences between the initial temperatures and the temperatures of the dew-point; and, moreover, these differences are almost as great for the lower initial temperatures as for the higher. For relative humidities of eighty per cent. and over, the fall of temperature is pretty nearly the same whatever the initial temperature: the reason being, probably, that we are now near the beginning of condensation.

Our observations, then, show a relationship between the nocturnal cooling of the air and the relative humidity, but not any relationship at all to the absolute humidity. But, as we have said, it is a dry air which, of itself, *à priori* because of its feeble radiative power, should cool more slowly than a damp air. We have then to establish a connecting link between these two facts. It is to be found, it seems, in the dependence of the cooling of the ground upon the hygrometric state of the air. During 1899 and 1900 I took a series of observations of the temperatures just under the surface of a bare patch of red sand, comparing the falls of temperature observed on clear nights in the three hours 8–11 p.m. with the absolute and relative humidities. The sand was originally taken from a depth of three or four feet, and contained little or no humus. It was not always in exactly the same condition, being of course damper during the clear nights immediately after rain. I am inclined to think, nevertheless, that this source of uncertainty was insignificant in its effects, and quite lost in the averages. Dew was never visible on the sand during the hours in question. The averages are:—

Dew-Point at 8 p.m.	Fall of Earth Temperature, 8–11 p.m.	Number of Clear Nights.	Relative Humidity at 8 p.m.	Fall of Earth Temperature, 8–11 p.m.	Number of Clear Nights.
Under 35°	5·4	78	Under 30 %	8·3	22
35°–39°·9	5·9	88	30 %–39 „	7·7	51
40°–44°·9	6·1	49	40 „–49 „	6·5	55
45°–49°·9	5·8	38	50 „–59 „	4·7	56
50°–54°·9	5·4	17	60 „–69 „	4·4	39
55° and over	4·3	4	70 „, & over	3·9	51

A previous set of observations made in the same ground, during the winters of 1897 and 1898, gave the following falls of Earth-temperature just under the surface between 8 p.m. and 8 a.m. on clear nights:—

Dew-Point at 8 p.m.	Fall of Earth-Temperature, 8 p.m.—8 a.m.	Number of Clear Nights.	Relative Humidity at 8 p.m.	Fall of Earth-Temperature, 8 p.m.—8 a.m.	Number of Clear Nights.
Under 30°	11·6	57	Under 40 %	14·5	29
30°–34°·9	12·5	70	40 %–44 „	12·8	23
35°–39°·9	13·2	34	45 „–49 „	12·4	31
40°–44°·9	11·9	13	50 „–54 „	11·8	39
45° and over	10·9	5	55 „–59 „	11·3	24
			60 „, & over	11·1	33

Considering the falls of Earth-temperature as compared with the relative humidity, between the hours 8 p.m. and 11 p.m., we see that a simple division by three gives practically the same value as those for the cooling of the air, so long as the air is not more than half saturated. For humid states in excess of this, the air cools faster than the ground.

The falls of Earth-temperature as compared with the dew-point are of exactly the same nature in the two series as those of the cooling of the air, namely, that they increase at first to a dew-point of about 40–45°, after which they decrease again. The explanation is that the humidity of the air chances to have on the whole its minimum values when the dew-point is about 40°–45°.

We see, then, that the lower air takes its temperature chiefly from the ground, but that the great radiative power of its contained water-vapour, when the relative humidity is high, lowers its temperature somewhat faster than it can absorb radiation from the ground. Only in one class of observations have I been able to detect any regulating effect upon the temperature due to the actual quantity of water-vapour present. The observations in question are, however, differential, and the recognised effect probably only indirect. A summary is given below. It shows for clear nights

during 1896 and 1897, the mean differences—(1) between the minimum radiation temperatures at heights of 3 inches and 0 inches; and (2) between the minimum radiation temperatures at heights of 38 feet and 19 feet, compared with the absolute and relative humidities at 2 a.m. In both cases the thermometer nearest the ground reads the lower:—

Dew-Point at 2 a.m.	m_3-m_0 .	$m_{38}-m_{19}$.	Relative Humidity at 2 a.m.	m_3-m_0 .	$m_{38}-m_{19}$.
Under 25°	5°·1	2°·8	Under 40 %	5°·7	1°·5
25°-29°·9	5·3	2·6	40 %-49 ,,	5·6	1·8
30°-34°·9	5·3	2·2	50 ,, -59 ,,	5·1	1·8
35°-39°·9	5·2	2·1	60 ,, -69 ,,	5·1	2·1
40°-44°·9	4·5	1·2	70 ,, -79 ,,	4·7	2·0
45°-49°·9	4·8	1·3	80 ,, & over.	3·9	1·5
50°-54°·9	4·2	0·9			
55 and over.	4·3	1·0			

An explanation of these last results is not likely to be simple, nor indeed does it strictly belong to the subject-matter of this paper.

Probably radiation, convection, and conduction have each an equally important share in producing them; but beyond mentioning this, I venture no further comment.

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THE
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Vol. XI. (N. S.), No. 4.

SEPTEMBER, 1905.

A MODIFIED FORM OF
ELECTRICAL CONTROL FOR DRIVING CLOCKS.

BY

SIR HOWARD GRUBB, F.R.S.,

VICE-PRESIDENT, ROYAL DUBLIN SOCIETY.

[Authors alone are responsible for all opinions expressed in their Communications.]

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1905.

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Dew-Point at 2 a.m.	$m_3-m_0.$	$m_{38}-m_{19}.$	Relative Humidity at 2 a.m.	$m_3-m_0.$	$m_{38}-m_{19}.$
Under 25°	5·1	2·8	Under 40 %	5·7	1·5
25°-29°·9	5·3	2·6	40 %-49 ,,	5·6	1·8
30°-34°·9	5·3	2·2	50 ,, -59 ,,	5·1	1·8
35°-39°·9	5·2	2·1	60 ,, -69 ,,	5·1	2·1
40°-44°·9	4·5	1·2	70 ,, -79 ,,	4·7	2·0
45°-49°·9	4·8	1·3	80 ,, & over.	3·9	1·5
50°-54°·9	4·2	0·9			
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Probably radiation, convection, and conduction have each an equally important share in producing them; but beyond mentioning this, I venture no further comment.

IV.

A MODIFIED FORM OF ELECTRICAL CONTROL FOR
DRIVING CLOCKS.

By SIR HOWARD GRUBB, F.R.S., Vice-President, Royal Dublin
Society.

[Read, JANUARY 17 ; Received for Publication, APRIL 13 ;
Published, SEPTEMBER 9,¹ 1905.]

THE system of electrical control for clocks described in my paper read before the Institution of Mechanical Engineers, Dublin, in July, 1888, and adopted for the various instruments employed in the international photographic survey of the heavens at Greenwich, Capetown, Oxford, Mexico, Melbourne, Perth (W. Australia), &c., has been found to be capable of driving these large equatorial instruments with the necessary accuracy, and to be reliable in its action so long as the electric contacts are in good order.

Within the last few years I have been able to simplify the system, and, by reducing the number of contacts, have eliminated many sources of possible error and failure. This modified form of electrical control has been applied to several instruments with success.

The principle may be thus explained :—On the counter-spindle which works the driving-screw of the equatorial, and which generally revolves once in twenty seconds, is fixed an insulated disc *d*, *d* (see fig., p. 35), shod on its periphery with a discontinuous metallic band *b*, *b*.

By a simple system of rubbing contacts (not shown in the design in order to avoid complication), these bands are connected severally to one end of the magnet-coils which actuate the retarding and accelerating apparatus.

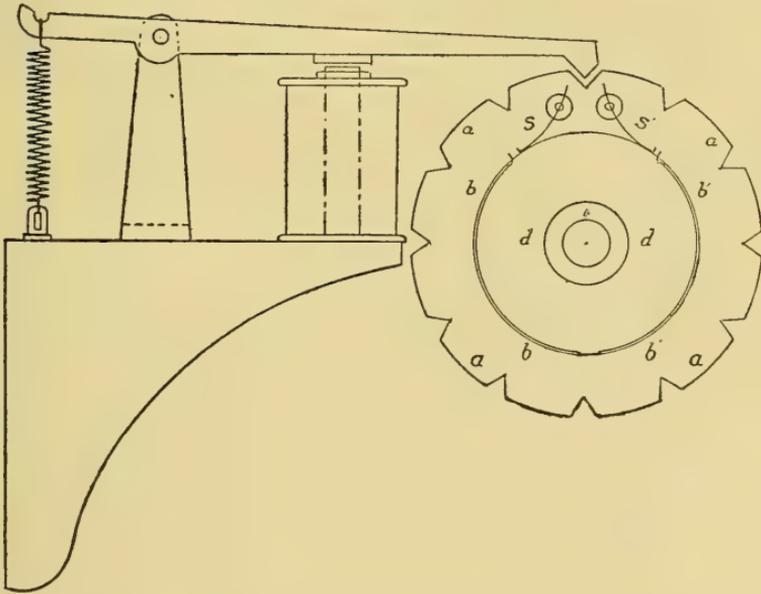
The circuits are so arranged that if “earth” (in this case any

¹ The publication of this paper has been unavoidably delayed.

metallic part of the apparatus) be connected to one of these brass bands, the accelerator is brought into action ; while, if the other be connected to "earth," the retarder is brought into action.

Close beside this insulated disc, and strung loosely on the same spindle, is an un-insulated wheel *a, a*, with twenty V nicks or cuts on its edge.

There is an arrangement by which a small amount of friction can be introduced in the revolution of this wheel on the spindle ; and this can be regulated with great nicety.



Two spring contacts *s, s'*, are so arranged on this toothed wheel that, under ordinary conditions, neither of the springs forms contact with the metal bands on the insulated disc ; but a very slight motion of the toothed wheel on its spindle, in either direction, will cause contact to be made between one or the other of the springs and one or the other of the metal bands, and, in doing so, will bring either the accelerator or retarder into action.

Over this wheel is mounted a lever with a V tooth, which fits into any of the V cuts which happens to be exactly under it.

This lever is actuated by an electric-magnet, through which an instantaneous current passes once a second from the regulating clock, which may be any distance away.

The action is as follows :—

Every second the lever with the V tooth is brought sharply down on the wheel *a, a*. If all be right, this should occur just as the V cut is directly under the tooth, and the spring contacts *s, s*, are in such a position that they do not make contact with either of the brass bands *b, b, b', b'*.

So long as the clock is going correctly, the lever with its V tooth will hit accurately into each V groove; and no connection will take place. If, however, the clock has gained or lost so much as the thirtieth part of a second, the V tooth will not strike accurately into the V cut, but will hit one side before the other, and consequently will slightly displace this wheel on the shaft (it being only carried by friction); and this will immediately bring into action the accelerator or retarder as may be required, and the correction will be repeated at the next stroke, if the error be not completely wiped out.

When the correction is perfectly made, the wheel will be brought back to its normal position by the action of the V tooth.

This arrangement has been found to give as great accuracy as the original form; and it has the advantage of greater simplicity.

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SEPTEMBER, 1905.

A NEW FORM OF RIGHT-ASCENSION
SLOW MOTION FOR EQUATORIAL TELESCOPES,

ILLUSTRATED BY THE DRIVING-GEAR OF THE
CAPE TOWN EQUATORIAL.

BY

SIR HOWARD GRUBB, F.R.S.,

VICE-PRESIDENT, ROYAL DUBLIN SOCIETY.

[PLATE I.]

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1905.

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V.

A NEW FORM OF RIGHT-ASCENSION SLOW MOTION FOR
EQUATORIAL TELESCOPES, ILLUSTRATED BY THE
DRIVING-GEAR OF THE CAPE TOWN EQUATORIAL.By SIR HOWARD GRUBB, F.R.S., Vice-President, Royal Dublin
Society.

[PLATE I.]

[Read, JANUARY 17; Received for Publication, APRIL 13;
Published, SEPTEMBER 9,¹ 1905.]

IN the older forms of equatorials, the slow motion necessary for the accurate setting of the object under observation on the micrometer-webs generally assumed the form of a tangent-screw and nut of some of the various well-known kinds, which, on being turned, moved the telescope itself independently of the driving-arc by a small quantity.

For very fine work it has been found practically impossible to move a large mass, such as a 24-inch telescope, which, with its axes, counterpoises, &c., weighs some tons, through even a very small quantity without giving rise to a slight swinging motion; and this, though of little consequence in visual observations, is apt to leave a trail or wings to the image of the star in photographing.

A slow motion of the form used in my automatic control, consisting of a set of differential wheels, is found to be practically free from this defect.

This arrangement has the effect of increasing or diminishing the rate at which the driving-screw is driven without interfering with the rate of the clock itself.

It is brought into action by stopping temporarily a loose disc which carries a pinion gearing across a pair of differential wheels. So long as this disc is allowed to revolve with the other wheels, it forms a coupling or clutch; but when stopped it produces a slight differential rate between the two unequally-toothed wheels; and

¹ The publication of this paper has been unavoidably delayed.

this accelerates or retards (according to the manner in which the wheels are arranged) the rate of the driving-screw. This slow motion is exceedingly fine, and only used for the most delicate setting.

For a less delicate setting an arrangement has for many years been used by which a motion, backward or forward, can be given to one of the loose discs carrying the pinions, and thus a less delicate slow motion is provided. But even this is very slow when it is desired to move the image of the star any considerable distance across the field of view; and therefore, in the most recent examples, I have found the following arrangement a great convenience.

The edge of one of the loose discs is cut into fine teeth, or preferably, coarsely milled; and a small electric motor is supplied to drive this disc very quickly round in one direction or another.

The electric motor is started, stopped, or reversed by a commutator held in the observer's hand, and connected by a flexible cord to the necessary circuits; and the arrangement is such that, when at rest, the pinion which drives the disc (which is generally made of leather) is completely free from the disc itself, but is brought into gear by a special electric magnet, which is not excited until the motor itself has gained a high speed. Thus the motor starts without load—an important point.

In practice it is not found desirable to pass the compensating heavy current that is used to drive the motor through the long and fine flexible cords which connect the commutator in the observer's hand with the instrument.

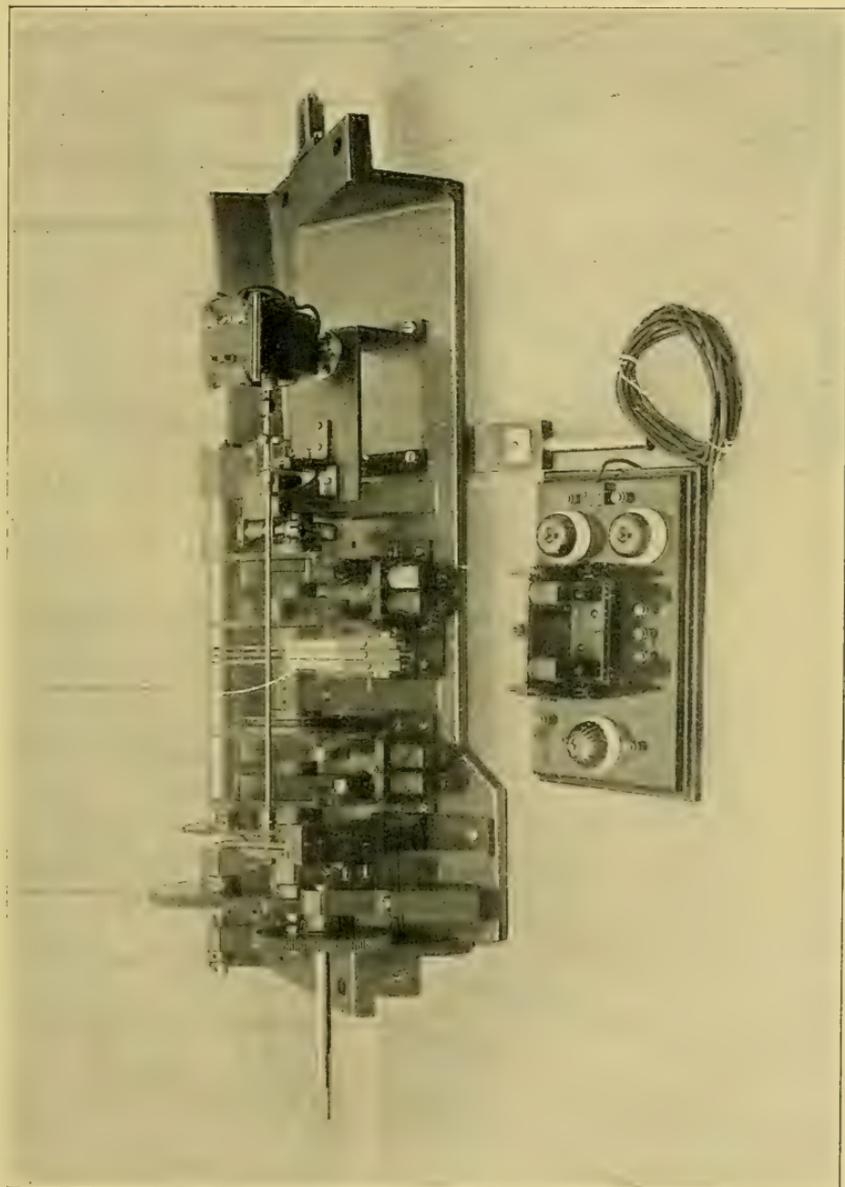
A small current passes from the commutator to a set of relays fixed in any convenient place; and the relays when in action close the proper circuit with the heavy current, and drive the motor forward or backward as desired.

EXPLANATION OF PLATE I.

PLATE I.

Driving-screw, electrical control, and slow motion of the Cape Town 24-inch Refractor.

- a, Driving-screw.
- b, Detector fingers of electrical control.
- c, Electric motor for extra slow motion.
- d, Relays.
- e, Hand commutator, by which either the old or new form of slow motion is controlled.



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FEBRUARY, 1906.

ON TWO NEW IRISH SPECIES OF COLLEMBOLA.

BY

GEORGE H. CARPENTER, B.Sc., M.R.I.A.,

PROF. OF ZOOLOGY IN THE ROYAL COLLEGE OF SCIENCE, DUBLIN.

[PLATE II.]

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VI.

ON TWO NEW IRISH SPECIES OF COLLEMBOLA.

By GEORGE H. CARPENTER, B.Sc., M.R.I.A., Professor of
Zoology in the Royal College of Science, Dublin.

[PLATE II.]

[Read, DECEMBER 19; Received for Publication, DECEMBER 22, 1905;
Published, FEBRUARY 7, 1906.]

FOR the last three years it has been the practice for the agricultural scholars at the Royal College of Science to spend a week or ten days of the summer term on a series of field-expeditions in different parts of Ireland, travelling to a fresh centre each evening. In June, 1905, being one of the staff privileged to join this interesting natural-history tour (during which open-air instruction in Geology, Botany, and Zoology appropriately follows a session's work in the laboratories), I took the opportunity of adding to the material which I have, for several years past, been accumulating towards a study of the Irish apterous insects. The rate of travel, necessarily rapid, limited the time available for collecting. It is all the more satisfactory to find that two Springtails—one from Fair Head, County Antrim; the other from the shores of Lough Melvin, County Leitrim—appear to belong to species hitherto undescribed. It seems advisable, therefore, to publish descriptions and figures of these without further delay. Both insects belong to the family Entomobryidæ. That from Lough Melvin is an *Isotoma*, closely allied to our common *I. viridis* (Bourlet). The Fair Head springtail is an *Entomobrya* of somewhat aberrant structure, forming in many respects a connecting-link between typical members of that genus and *Orchesella*.

Family ENTOMOBRYIDÆ.

Genus ISOTOMA, Bourlet.

Isotoma hibernica, sp. nov. (Plate II., fig. 1-7.)

Length, 3 mm. Feelers, twice as long as the head. Post-antennal organ, oblong-oval; eight ocelli on each side of head (fig. 2). Feet without tenent hairs; large claw with two teeth, small claw with one (fig. 6). Trunk segments with very elongate serrate bristles (fig. 5), especially prominent on the third, fourth, fifth, and sixth abdominal segments. Spring more than half as long as the body, with very elongate dentes (thrice as long as the manubrium); mucro with an apical tooth, and two dorsal teeth close together (fig. 7).

In colour *I. hibernica* is dark violet-brown, with ochreous mottlings on the head and trunk-segments (fig. 1); the feelers and legs are blue-violet, and the spring yellowish-white. The mandible (fig. 4) is of the form usual in the genus and family.

This species is closely allied to *I. viridis*, which it resembles closely in the structure of the feet and the mucrones. It is, however, smaller, and has the feelers, the spring, and the serrate bristles on the hinder abdominal segments relatively longer. The spring in this species, when pointing forwards beneath the body, reaches to the bases of the intermediate legs, recalling the excessively elongate spring of the Arctic genus *Corynothrix* of Tullberg. *I. hibernica* also differs from *I. viridis* in the arrangement of the ocelli, and in the proportional lengths of the antennal segments (as 8 : 12 : 16 : 15). In *I. viridis* the second and third segments are equal in length, and the terminal segment relatively longer. The antennal organ (fig. 3) is represented by a low, broad tubercle.

Genus ENTOMOBRYA, Rondani.

Entomobrya anomala, sp. nov. (Plate II., figs. 8-15.)

Length, 2.5 mm. Feelers thrice as long as the head, six-segmented (figs. 8, 10). Six normal, and two very minute ocelli on

each side of the head (fig. 9). Each foot with a delicately-clubbed tenent hair, a large claw with three minute teeth, and a small simple acuminate claw (figs. 12, 13). Fourth abdominal segment less than twice as long as the third. Spring with dens twice as long as the manubrium; mucro with apical and dorsal teeth and a basal spine (fig. 15).

In colour *E. anomala* is dark bluish-violet, with the hinder edges of the segments, large patches on the mesothorax and metathorax, and streaks and spots on the abdominal segments clear yellow. The head is mostly yellow with violet mottlings, while the feelers and legs are of a paler violet than the body, and the spring yellowish-white. The antennal organ (fig. 11) consists of a small hemispherical papilla, surrounded by a few curved bristles. The catch (of which a rather oblique view is shown in fig. 14) has three somewhat blunt teeth on each limb.

The relatively short fourth abdominal segment, and the six distinct segments of the feeler, are characteristic of the genus *Orchesella*, to which this species—by its facies and general structure undoubtedly an *Entomobrya*—shows, therefore, a decided likeness. In the extreme reduction of the two hinder median ocelli (fig. 9) of the present species we have another approach towards the condition in *Orchesella*, which has six ocelli only on each side of the head. Schäffer¹ described this latter condition in a German species, which he called *E. orcheselloides*; but the fourth abdominal segment was in that case seven to eight times as long as the third. In species of *Entomobrya* the two hinder median ocelli are generally smaller than the others, and a minute ring may be present at the base of the feeler (representing the distinct basal segment of our present species, and of *Orchesella*), as well as an indication of the small third segment. It may be concluded, therefore, that the four-segmented feeler, which characterises so many genera of the Collembola, has been derived by the suppression of segments from a multi-articulate form, probably passing through the six-segmented condition that is preserved in *Orchesella*. The six ocelli of *Orchesella* remain after the loss of

¹ C. Schäffer, "Die Collembola der Umgebung von Hamburg und benachbarter Gebiete." *Jahrb. Hamburg. Wissensch. Anstalt*, xiii., 1896 (p. 193, figs. 114–116).

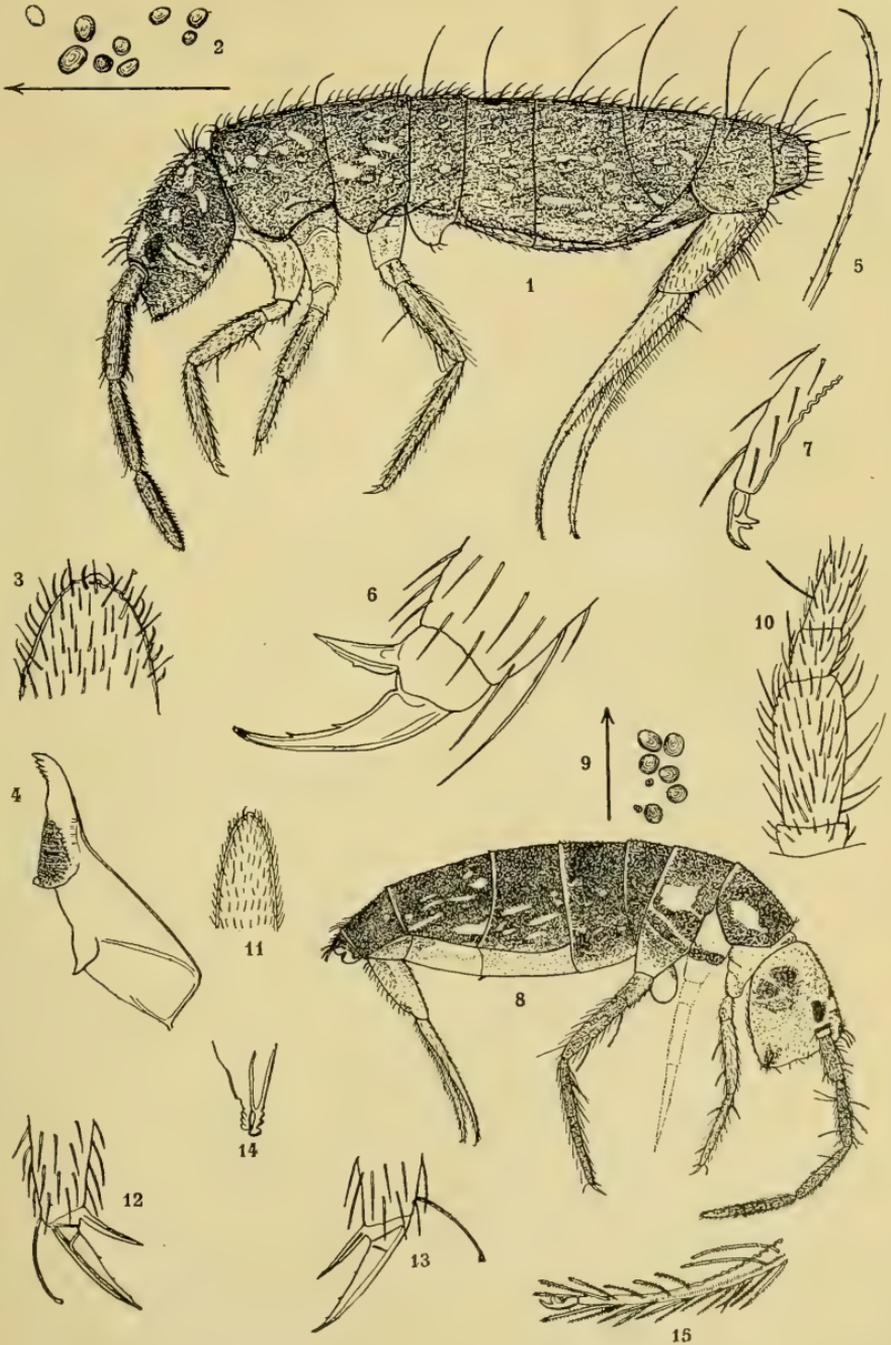
the two which are present in a reduced condition in most species of *Entomobrya*, and in a vestigial condition in the species now under discussion. And as *Entomobrya* is, in most respects, more specialized in its structure than *Orchesella*, we may reasonably suppose that this suppression of ocelli and of antennal segments has taken place independently in many of the genera into which the order has branched off.

EXPLANATION OF PLATE II.

PLATE II.

FIG.

- | | | |
|-----|----------------------------|---|
| 1. | <i>Isotoma hibernica.</i> | Side view. × 30. |
| 2. | „ | Ocelli and post-antennal organ of right side.
× 120. |
| 3. | „ | Tip of terminal antennal segment with
antennal organ. × 240. |
| 4. | „ | Mandible. × 70. |
| 5. | „ | Serrate bristle from abdomen. × 240. |
| 6. | „ | Hind-foot with claws. × 240. |
| 7. | „ | Tip of left dens with mucro. Outer view.
× 240. |
| 8. | <i>Entomobrya anomala.</i> | Side view. × 30. |
| 9. | „ | Ocelli of right side. × 120. |
| 10. | „ | Base of feeler, showing the small basal
and third segments. × 120. |
| 11. | „ | Tip of terminal antennal segment showing
antennal organ. × 240. |
| 12. | „ | Fore-foot with claws. × 240. |
| 13. | „ | Hind-foot with claws. × 240. |
| 14. | „ | Catch. × 240. |
| 15. | „ | End of dens with mucro. × 240. |



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ON ENTOPTIC VISION;
OR,
THE SELF-EXAMINATION OF OBJECTS WITHIN
THE EYE.

BY
PROFESSOR W. F. BARRETT, F.R.S.

[PART I.]

[Authors alone are responsible for all opinions expressed in their Communications.]

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VII.

ON ENTOPTIC VISION ;

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[PART I.]

[Read JUNE 20 ; Received for Publication JUNE 23, 1905 ; Published MARCH 9, 1906.]¹

§ 1.

Most people have observed, and many have been needlessly alarmed at, the semi-transparent objects like notes of interrogation, or pearly strings, which occasionally are to be seen moving across the retina of the eye. These are the so-called *muscæ volitantes*, and are due to shadows thrown on the retina by the minute *débris* of cells and of smaller vessels which are floating in the vitreous humour of the eye, and perceived when they pass close to the retina. They come and go, often with the state of health, and, as a rule, need cause no anxiety.² If instead of a general illumination of the eye a divergent pencil of rays from a point of light near the eye be allowed to enter, the shadows become sharper, owing to the absence of penumbra, and under such conditions these and other small opacities, in the line of vision, at any part of the eyeball, can be seen from their shadows on the retina. A point of light can be readily obtained from any luminous source, by using a

¹ This paper has been unavoidably delayed in publication.

² These shadows are called *muscæ volitantes* ('flies flitting') because the shadow flits away as the gaze is directed to it. From remote times these *muscæ* have been the subject of frequent observation and discussion. The learned Jesuit Deschales wrote an essay on the subject in the sixteenth century. When the eyeball is kept motionless, the *muscæ* appear to be slowly descending ; owing to the fact that the shadow when projected from the retina is inverted, the *muscæ* are therefore *ascending*, and hence are somewhat lighter than the vitreous humour in which they are floating.

short-focus convex lens, or by reflection from either surface of a silver spoon, or, still better, by a pin-hole in a piece of card or metal held close to the eye. With this very simple arrangement anyone can make a self-examination of any small opacities that may exist within the field of vision in either of his eyes.

Looking at a lamp or a bright surface through a pinhole in a card held close to the eye, the circle of light that is seen is not, however, the enlarged image of the pin-hole, but is the shadow cast by the circular aperture of the iris; it is in fact a magnified image of the pupil of the eye, and can be seen to vary in size with the degree of illumination, as the pupil contracts or expands, when a light is brought near to or removed from the eye. It is a sharp shadow, as the source of light from the pin-hole is practically a point, and hence any irregularity in the edge of the iris is clearly seen, as is any obscurity, however small, in the path of the rays.

A pencil of rays emanating from some luminous *point* is called *homocentric* light, as the rays have the same centre of divergence; the smaller the pin-hole aperture, or the point of light, the more perfectly homocentric is the luminous pencil, and the sharper and more detailed becomes the shadow of any small object.¹ By such means not only can minute opacities in the path of the rays be perceived, but objects which only slightly differ in transparency or in refractive power from the medium in which they are suspended, can be detected, if the vision of the observer be not seriously impaired.

§ 2.

This method of self-examination of obscurities which lie in the path of the rays within the eyeball is termed *entoptic* observation (*ἐντός*, within, and *ὀπτικὸς*); a term first given by Prof. Listing of Germany, who published an important paper on the subject sixty years ago.² Two years previously Sir David Brewster had drawn attention to the subject in a valuable investigation, wherein he

¹ The term *Stenopæic*, or *Stenopaic* (Gr. στενός, 'narrow,' ὀπή, 'opening') is usually employed to denote a screen with a small aperture. *Stenöpic* would be a briefer and better term. If the botanists had not already used the word for another purpose, a *micropyle* (Gr. μικρός, 'minute,' πύλη, 'gate'), or micropylic screen, would have been more expressive.

² Listing, *Beitrag zur physiologischen Optik*. Göttingen, 1845.

showed how measurements of the actual size of the obscurities could be made.¹ Brewster, however, only refers to the *muscæ volitantes*. This was followed by a lengthy and excellent paper on Entoptic Phenomena, by Dr. MacKenzie, published in the *Edinburgh Medical and Surgical Journal* for July, 1845 (vol. lxiv., pp. 38, *et seq.*). The subject was then taken up by the famous Dutch physiologist, Donders, who largely added to the value of entoptic observation as a method of diagnosis of the eye. In conjunction with his pupil, Doncan, Donders gave admirable drawings of minor obscurities observed in the different parts of the eyeball, and discusses the whole subject in his well-known treatise on the eye.² A little later, Dr. Jago, of Cornwall, published two papers on the subject in the *Proceedings of the Royal Society*, and another in a *medical Review*, which, however, are more concerned with the medical aspect of the subject.³ The substance of these essays, with many additional observations, was issued by Dr. Jago in 1864 in a small work entitled *Entoptics*.⁴ Finally, Helmholtz devotes a chapter in his classical work, *Handbuch der Physiologische Optik*, to the consideration of the subject, though he does not add any fresh information.⁵ After this the subject appears to have

¹ Brewster, *Trans. Roy. Soc. Edinburgh*, 1843, vol. xv., p. 377. See also an article, presumably by Sir D. Brewster, published in the *North British Review* for November, 1856.

² An English edition of this work was published by the New Sydenham Society in 1864 (vol. xxii.), the excellent translation being made by the late Dr. W. D. Moore, of Dublin. The book is entitled *On the Anomalies of Accommodation and Refraction of the Eye, with a preliminary Essay on Physiological Dioptrics*, by F. C. Donders, M.D. The reference to entoptic observation will be found at pp. 197 *et seq.* See also a paper by Donders, in *Nederlandsch Lancet*, 2nd series, 1847, pp. 365 *et seq.*

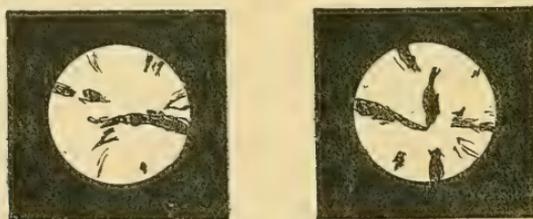
³ Jago, *Proc. Roy. Soc.*, 1855, vol. vii., p. 208; vol. viii., p. 603, also *Medico-Chirurgical Review*, 1859.

⁴ *Entoptics* by J. Jago, M.D., Churchill, 1864. This excellent brochure by Dr. Jago is very little known, and is not referred to by any writer on physiological optics that I have consulted. It had entirely escaped my search in compiling the Bibliography of this subject until quite recently, when the Rev. Dr. Abbott, S.F.R.C.D., found it for me in the Library of Trinity College, Dublin. Curiously enough, Dr. Jago, like other investigators of entoptic vision, misses the important point of the value of this method in the examination of cataract.

⁵ There is unfortunately no English translation of this great work. The French edition is entitled *Optique Physiologique*, and the reference to entoptic vision will be found in sect. 15, p. 204, of that edition.

received but scant attention, owing, doubtless, to the discovery of the ophthalmoscope; and, in recent years, entoptic diagnosis of the eye has been almost completely overlooked, even by ophthalmologists.¹

It is, therefore, not surprising that, in common with many others, I was wholly unaware of the foregoing investigations when my attention was called to entoptic observation by a curious discovery of a defect in my own vision which I noticed some twelve months ago. Looking at a bright sky through a pin-hole in a piece of card held close to the right eye, I was surprised to find the disc of light on the retina obscured by a dark shadow of fixed and definite shape, resembling the letter L reversed (┘). The left eye also presented a shadow when the pin-hole was placed before it, only in this case it was a fainter and straight horizontal bar half way across the disc. Using a very fine needle-hole in a thin sheet of metal, held close to the eye before a good light, the obscurities were seen in great detail, revealing the structure of some partially opaque tissues in the body of each eye. Fig. 1 shows a rough sketch of these obscurities made at an early stage.



LEFT.

FIG. 1.

RIGHT.

Upon consulting the eminent Dublin oculists, Dr. Arthur Benson and Dr. C. Fitzgerald, Surgeon Oculist to the King, the unpleasant fact was revealed that there was incipient cataract in each eye, more developed in the right than the left, and to this cause the shadows which I saw were presumably due. Dr. Fitzgerald carefully drew the shape of the opacity that he had observed, by means of the ophthalmoscope, in each eye. These

¹ Since this paper was read, Dr. Ettles, of London, has drawn my attention to a paper on entoptic vision by Dr. Darier, entitled "De la possibilité de voir son propre cristallin." *Annales d'Oculistique*, vol. cxiv., September, 1895, p. 198.

drawings in rough outline exactly corresponded with what I had previously drawn in much more minute detail from entoptic observation, only the figures I had drawn were taken from inverted images of the opacity in each lens. These drawings, and the reason for this inversion, will be given in Part II.¹

These results led me to make a series of entoptic observations at stated intervals, and ultimately to the construction of a simple instrument for the more convenient drawing and measurement of what is observed. This instrument I propose to call an *Entoptiscope*, and it will be described in Part II., as some improvements I have recently made are now in process of construction. I hope that this instrument may prove a convenient and useful addition to the means already employed for the diagnosis and pathological study of the eye.

§ 3.

It may be asked how entoptic observation can reveal obscurities in the crystalline lens, when, as is well known, if an ordinary lens be partly covered or cut away, or a small opaque object be interposed near it, or a fly walk over the lens, no shadow of the object nor any injury to the image is seen at the focus of the lens. But both theory and experiment show that this is not the case when the image is out of focus; a blurred shadow of any opaque object in or near the lens is now seen, and this shadow becomes distinct and sharp, because free from penumbra, if the lens be illuminated by a light from a point, such as a pin-hole aperture. A simple experiment with a photographic camera will illustrate this. Under ordinary circumstances the diaphragm in front of the lens is not seen on the focussing screen; but throw the screen out of focus and allow a beam of sunlight passing through a small aperture in a piece of card to illuminate the lens, and the image now seen on the focussing screen will be that of the diaphragm and will alter in size with it. The shadow of a fly walking on the lens

¹ I wish to acknowledge my indebtedness to Dr. Charles Fitzgerald for first drawing my attention to the chapter on entoptic observation in Donders' treatise on the eye; and also for the very kind interest which both he and Dr. Benson have taken in this investigation.

will now be clearly depicted on the focussing screen, but will disappear as soon as the image of the pin-hole is once more focussed on the screen. All this is well known and readily explicable, but the exactly similar results that occur in our own eye are not so well known. When the illuminated pin-hole is placed at such a distance from the eye as to be within the power of accommodation of the eye, usually a distance of about 9 inches or a foot, a sharp image of the pin-hole is focussed on the retina, and no shadow of any small object in or near the crystalline lens can be perceived. When, however, the pin-hole is brought close to the eye, accommodation fails to focus its image on the retina, and the shadow of any object in the path of the rays will be clearly seen, and the more sharply the smaller the pin-hole; whilst the circle of light seen on the retina is now not the magnified image of the pin-hole, but the shadow of the iris diaphragm of the eye, as has been already stated.¹

To those who, like myself, suffer from presbyopia, and have lost the power of accommodation for near objects, entoptic observation can be carried on with a large pin-hole, say, 1 mm. in diameter, or any bright spot of light placed at a considerable distance from the naked eye; in my case up to 20 inches. Though the entoptic shadows are now smaller, they are darker and less detailed, and hence their outline can be more easily drawn under such circumstances. To exclude extraneous light, a sliding brass tube, blackened inside, can be made to screw over the pin-hole aperture, so that the observer can adjust the length of this tube, through which he views the aperture.

¹ Entoptic observation was evidently not known in Shakespeare's day. I am indebted to my friend Canon Elliott for drawing my attention to the following apt quotation:—

Cassius. "Tell me, good Brutus, can you see your face?"

Brutus. No, Cassius; for the eye sees not itself,
But by reflection by [from] some other things.

Cassius. 'Tis just;
And it is very much lamented, Brutus,
That you have no such mirrors as will turn
Your hidden worthiness into your eye,
That you might see your shadow."

Julius Cæsar, Act i., sc. 2.

Of course if the presbyopic observer puts on his spectacles, the distant pin-hole is now focussed on the retina, and entoptic observation ceases until the aperture is brought so close to the eye that even with spectacles its image cannot be formed on the retina. *Ceteris paribus* the same thing holds true with myopic vision; hence spectacles of any kind are of no use in entoptic observation, and may entirely destroy the effect sought for.

§ 4.

As the anterior principal focus of the eye may be taken as 14 mm. distant from the cornea, when the pin-hole is placed at this distance, the divergent cone of rays entering the eye will be rendered parallel, and hence the shadow of any object in or between the crystalline lens and the retina will be practically of the same size as the object itself. Obviously, when the illuminated pin-hole is placed nearer to, or further from, the eye than the anterior focus, the shadows will be respectively larger or smaller than the object.¹

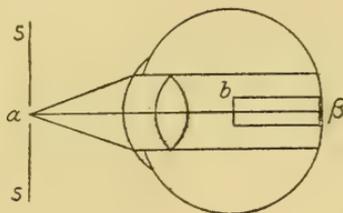


FIG. 2.

This is shown in the accompanying diagrams, where fig. 2 represents the luminous point *a* (or stenopaic screen *s, s*), placed at the anterior focus, the enlarged entoptic object *b* throwing the shadow β ; the rays being parallel within the eyeball, the area of the shadow is the same as that of the object. In fig. 3 the luminous point *a* is placed nearer to, and in fig. 4 further from, the eye than the anterior focus *f*; in the former the rays will diverge as if proceeding from the virtual

¹ The effect of accommodation, it is true, renders the position of the principal focus of the eye slightly variable; and, in the case of looking at a pin-hole near the eye, the principal focus would be somewhat less than that given as accommodation comes into play. The pin-hole, however, should not be looked *at* but looked *through*, and the eye focussed on the distant surface on which the projected image is depicted.

focus f' , and the shadow β will, accordingly, be larger than b ; in the latter the rays will converge, and would meet, if prolonged, in the conjugate focus f' ; accordingly, the shadow β is somewhat smaller than the object b . Hence, in estimating the actual magnitude of any obscurity within the eye it is desirable to place the pin-hole diaphragm at the position of the anterior focus, a little over half an inch (14 mm.) from the surface of the cornea.

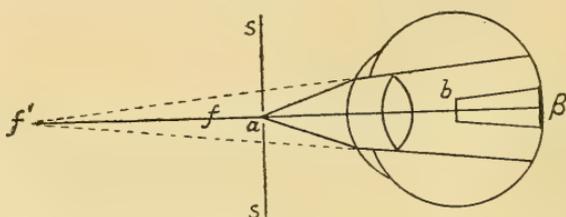


Fig. 3.

Not only the actual size of a microscopic object within the eye can be thus found, but, as will be shown presently, its exact distance from the retina can be determined.

In order to delineate an entoptic object, and estimate its magnitude, the method hitherto employed is one of considerable difficulty to an untrained observer. It is what is known as the method of double vision, and was first suggested by Donders. The procedure is familiar to microscopists; one eye views an object through

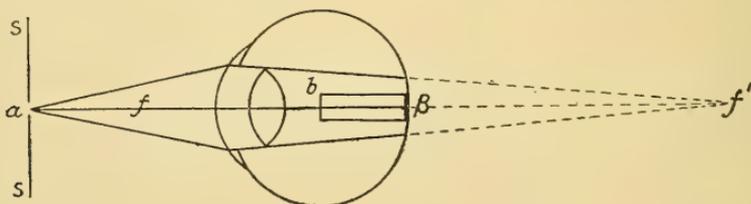


FIG. 4.

a microscope, whilst the other eye looks at a sheet of paper on which the projected image of the microscopic object is seen, and can be sketched with a little practice. Placing an object of known dimensions, such as a finely divided scale, under the microscope, the linear magnifying power of the microscope is found by comparing the actual size of a scale-division with the width apart of the pencil-marks (seen with the other eye), which are placed

at the magnified image of a scale-division. Obviously, if the magnifying power of the microscope is known, the actual size of a microscopic object can be thus found. In like manner an entoptic object can be sketched, and its magnitude estimated, one eye looking through the illuminated pin-hole screen, and the other eye viewing the pencil and sheet of paper on which the enlarged image is drawn; the distance of the paper from the eye being measured, the magnification is the ratio of this distance to the distance of the retina from the optical centre of the eye (16 mm.). But, owing to the difficulty of getting the plane of the image to coincide with the plane of the paper, this method is only feasible to a practised observer. A much simpler and more accurate method of drawing the entoptic image, and one requiring no skill, forms an essential feature of the new Entoptiscope to be described in Part II. Moreover, the actual magnitude of the entoptic object is also found at once by the Entoptiscope without any difficulty.

§ 5.

There are two interesting facts in connexion with entoptic observation which require a brief explanation. On looking through a minute aperture in a card held close to the eye, it will be noticed that an object, such as a pencil-point, can be seen with perfect distinctness, even when brought within an inch or two of the eye, *i.e.*, far within the limit of clear vision; and this notwithstanding that the observer may be hypermetropic or presbyopic. The fact is well known, and is sometimes used for enabling very small print to be read with ease. The accompanying diagram, fig. 5, will help to explain this anomaly. If a small object a, b , be placed near the eye, the screen with pin-hole aperture SS , in the first instance being removed, the pencil of rays from the object reaching the eye at m^1, m^2 , would be refracted and encounter the retina at g, h , and i, f ; the prolongation of these rays would unite at β and a , when a clear inverted image of the object would be formed and perceived, if the retina were at that distance. As it is, however, a blurred and wholly indistinct image is formed on the

actual retina, the cross-section of the cone of rays from the points a and b being shown at g, h , and i, f . These are the circles of diffusion corresponding to those points, and so with every other point of the object. If now a stenopaic screen, SS , be interposed, the luminous cone which enters the eye is restricted to the pencil of rays from the minute area of the pin-hole; and, consequently, all the sections of the cone up to its apex, *i.e.*, the area of the circles of diffusion, are proportionately diminished, so that where the retina intersects the cone of rays, this section has become practically a point; the circles of diffusion (which are areas of confusion of the image) have vanished; and a sharp image of a is formed at f , and of b at g . Moreover, the magnitude of the retinal image is greater than before, coinciding, as will be seen, with the exterior boundary of the rays.

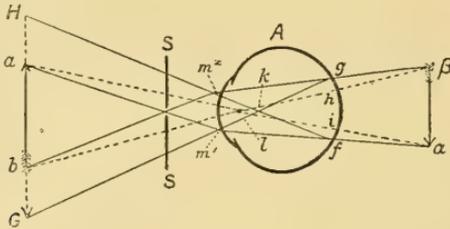


FIG. 5.

If the screen SS were removed, lines drawn from g and f , passing through the nodal point k of the eye, determine the direction in which the retinal image would be seen projected from the eye, and an inverted magnified image of the object a, b , would therefore appear at G, H . Owing to the large visual angle subtended by an object held near the eye, a microscopic object, such as a transparent scale, divided into fifths of millimetres, can be clearly seen when held close to the eye, and viewed through a very minute aperture in an opaque screen. The amount of light reaching the eye through a minute aperture is, of course, very small; but if the light be sufficiently good, this simple method affords an excellent way of seeing minute objects, or of reading well-illuminated small print, when a lens is not at hand, or spectacles are inadequate.

If, instead of holding a small object on the far side of the pin-hole screen SS , it be held between the screen and the eye, a

shadow of the object, and not an inverted, lenticular image, will be thrown upon the retina. This shadow will be erect, corresponding to the position of the object, but will be projected from the retina as an inverted image; thus if a pin, with the head upwards, be held between the screen and the eye, an enlarged image of the pin with the head downwards will be seen. In like manner any obscurity within the eyeball, when revealed by pin-hole vision, is seen completely inverted laterally as well as vertically, though, as with the pin, the shadow of the obscurity on the retina is not inverted.

§ 6.

The fact that in *ordinary* vision we see things erect, though the retinal image is inverted, presents no real difficulty. The mind does not contemplate the retinal image as a photographer views the inverted image of a landscape when focussing his camera. In fact, we are wholly unconscious of the existence of the retina, or of the size or position of the retinal image, except from experiments on eyes other than our own.¹ Visual perceptions are always referred to a position in space external to our eye, and are projected outwardly by our mind along the "line of visible direction," as Brewster termed it. Now, this line is almost exactly coincident with a straight line joining any point in a visible object external to the eye, *if seen by direct vision*, with the corresponding image of that point on the retina. These lines necessarily cross each other at *k*, fig. 5, which is the *centre of visible direction* in the eye. The inverted image, therefore, gives rise to the perception of an erect object and *vice versa*.

The centre of visible direction *k*, fig. 5, may be taken as coinciding with the optical centre of the eye. The optical centre of a thin lens is such that all rays not remote from the axis passing through it are undeviated by the lens; but every lens, or system of lenses, of which the two faces are not in the same medium, as is the case with the eye, has two geometrical points which replace the optical centre of an infinitely thin lens. These two points are termed *nodal points*; and these in the eye lie so close together that

¹ Or by means of a mirror and ophthalmoscope a skilled observer can use his own eyes as if they belonged to some one else.

they do not sensibly differ from a single point. This is situated on the optic axis close to the posterior (the inner) face of the crystalline lens, about 7 mm. from the surface of the cornea, and 16 mm. from the retina.¹ At this point, the object O and its retinal image i subtend the same angle, and their relative magnitudes are in the direct ratio of their relative distances D and d from this point, or,

$$\frac{i}{O} = \frac{d}{D}.$$

Hence, as $i = \frac{d}{D} O$, the retinal image formed of a metre-stick held 1.6 metre from the nodal point (*i.e.*, 1593 mm. from the cornea) will be exactly 1 cm. long.

What determines the lines of visible direction in the case of entoptic phenomena opens up some interesting questions in relation to vision, which I propose to consider in a subsequent note.

§ 7.

Assuming that the perception of entoptic objects near the retina, when no stenopaic screen is used, follows the same law of projection as that of external objects—and experiments indicate that this is the case—an obscurity 1 mm. in diameter near the retina will be perceived as an inverted image 1 cm. in diameter at a distance of 16 cm. from the nodal point, or 15.3 cm. from the cornea. Hence, the linear magnitude x , of an obscurity within the eye, is to the linear magnitude of the projected image S , as the distances d and D of the nodal point from the retina and from the projected image respectively, or

$$x = \frac{d}{D} S.$$

It is, therefore, quite easy for anyone to determine for himself, without using instrumental appliances, the magnitude of any small obscurities within the eye. For example, the *muscae volitantes*, which float near the retina, throw shadows that are

¹ The position of the nodal point is deduced from the curvatures and indices of the refractive media of the eye. Donders and Helmholtz placed the nodal point 15 mm. from the retina of a normal eye; but recent determinations of the refractive index of the lens, &c., give a value more nearly like that obtained by Dr. Young a century ago.

perceptible without using homocentric light. They can, if present, readily be seen upon looking at the sky or any illuminated surface, such as a sheet of white paper placed at a convenient distance from the eye. Keeping the head and eyeball as far as possible motionless, the observer can mark with a pencil on the sheet of paper the length and breadth of the projected image of one of these muscæ. For this purpose the paper can be about one or two feet (30 or 60 cm.) from the eye, so as to be within easy reach of a pencil held by the observer. If the image is too small at this distance, the paper can be placed further off, and the size of the projected image judged by marks previously made on the paper. Knowing the distance of the paper, the length and breadth of the retinal shadow is to that of the projected image as the distance of the nodal point of the eye from the retina (viz. 16 mm.) to the distance of the sheet of paper from the nodal point, or practically from the eye. Thus, in the case of a particularly persistent and large musca I recently noticed in my right eye, the length of the projected image of the filament was about 150 mm., and its breadth 2 mm., the sheet of paper being 60 cm. from the eye. Accordingly the retinal shadow was

$$\frac{16}{600} 150 = 4 \text{ mm. long,}$$

and

$$\frac{16}{600} 2 = 0.053 \text{ mm. broad.}$$

As this musca was very near the retina, its actual size was practically the same as the above.

In making this experiment one eye must be shut, and the eye used should be partly closed so as to give a sharper and darker shadow. Looking through an aperture made in a piece of card with a stout needle, gives a much better result, as already explained: here, however, the magnification of the image follows another law, as will be explained below. In this case the head can be rested on a support—such as the left hand, with elbow on the table—the eye being a foot or so from the sheet of paper, and the perforated card held or fixed close to the eye; excellent drawings and measurements of the reticulated and cellular structure of the muscæ, with the knots and loops of their filaments, can thus be made. Their

mobility is at first very provoking, but they are much steadier when the head is bent over the illuminated sheet of paper lying on a table, than when the head is erect and the paper vertical.¹

We owe to Sir David Brewster the first determination of the magnitude of these muscæ and the first suggestion as to finding their distance from the retina.² He used two lights placed at a distance from the eye: a double shadow of a particular musca was thus thrown on the retina; the lights were then moved closer together till the projected images touched. Measuring the distances of the lights apart and their distance from the eye, and the angle subtended by one of the images of the musca, enabled him to deduce its size and distance from the retina. The nodal point of the eye was taken by Brewster as 0·524 of an inch from the retina, a little less than its true value; the width of the musca he found to be 0·0012, (1/820th) of an inch; this corresponds to 0·03 mm., and its distance from the retina 1/85th of an inch, equal to 0·3 mm.; but their distance varies, and is often further from the retina than this.

§ 8.

When entoptic objects are seen by means of a minute illuminated aperture, or stenopaic screen, and projected on to a surface behind the screen, the magnification of the shadow of the pupil

¹ This is due to the fact that in the former case the muscæ slowly ascend and therefore keep in the line of sight; in the latter they move across and disappear out of the line of sight. The range of their motion is limited owing to the fact that the vitreous humour is divided up by a kind of cellular structure. Many papers and treatises have been written on the subject of the muscæ; occasionally the muscæ appear fixed in position; these are considered symptomatic of the beginning of mischief in the eye, but as a rule they are indicative only of digestive or other slight bodily derangement. In my own case, however, mobile muscæ have certainly increased both in size and persistency since the development of cataract in my eyes, and are worse in the right eye, in which cataract is more advanced. It is curious to note how they begin to appear and float into the line of sight when searched for.

² *On the Optical Phenomena, Nature, and Locality of Muscæ Volitantes, with Observations on the Vision of Objects placed within the Eye*, by Sir David Brewster, D.C.L., F.R.S., Transactions Royal Society of Edinburgh, vol. xv., p. 374, 1843. Brewster unfortunately gives no details of his experiment, nor data upon which he founded his calculation; but in an article on Entoptic phenomena in the *North British Review* for November, 1856, I find these data are supplied. The article is evidently by Brewster himself, and is one of considerable interest.

and of any obscurity within the eyeball *does not follow* the usual law of projected images stated above. Singularly enough, this important fact seems to have escaped observation hitherto, and I must reserve for a subsequent paper the series of measurements I have made that demonstrate the law in this case.¹ This law the Entoptiscope not only determines with precision, but also enables one accurately to investigate other obscure phenomena in the psycho-physiology of vision, such as ocular parallax, &c.

It will be obvious from an inspection of fig. 5 (p. 52) that when entoptic objects are seen through a stenopaic screen, if the lines of visible direction crossed at *k*, the nodal point of the eye, then :— (i) the rays would again cross at the pin-hole aperture, and the image would be re-inverted (that is, it would be seen upright); but this is not the case; and (ii) the enlarged image would be projected on to the surface of the stenopaic screen and its apparent magnitude

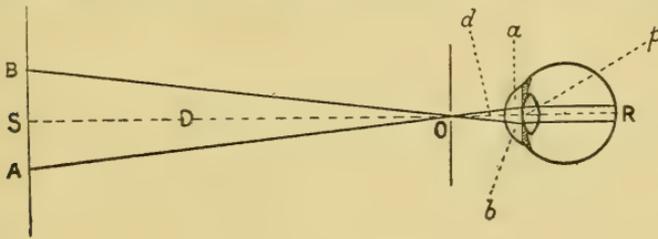


FIG. 6.

would follow the usual law, but neither of these is the case. In fact, the path of the projected shadow corresponds to the path of the incident-rays crossing at the pin-hole aperture only. This is shown at *O* in fig. 6. Hence the magnification is, as might be inferred *a priori*, in the direct ratio of the distance *d* of the pin-hole from the pupil to its distance *D* from the illuminated screen *S* on which the shadow is projected. The pupil *p* forms the base *ab* of the cone of rays on one side, and the projected image of the pupil *A B* forms the base of the cone of rays on the other side. When *O* is at the anterior focus of the eye, the retinal

¹ Even Helmholtz and Donders, and more recent authorities on physiological optics such as Tscherning (*Physiologic Optics*, Eng. Trans., p. 304), appear to have overlooked the obvious considerations stated in the next paragraph, and accordingly have given an incorrect formula for calculating the size of entoptic objects.

shadow R is the same size as the entoptic object, and hence the linear magnitude x of the pupil, or of the obscurity within the eye, is to that of its projected image S , as d is to D , or,

$$x = \frac{d}{D} S.$$

The area of x to that of S is of course as $d^2 : D^2$.

These measurements are easily made with the Entoptiscope, nor does a slight deviation of the pin-hole from the anterior focus make any sensible error.

§ 9.

The distance of entoptic objects from the retina, as Listing has shown, can be ascertained by noting the relative parallactic displacement of the shadow which occurs upon moving the eye.¹

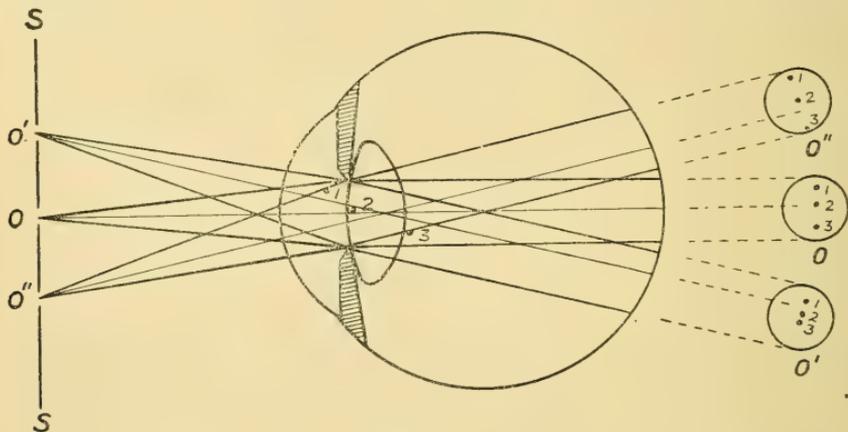


FIG. 7.

This will be readily understood from an inspection of fig. 7, which is accurately drawn to scale. Within the eyeball let us suppose that three entoptic objects exist: No. 1 between the pupil and cornea; No. 2 in the crystalline near the plane of the pupil; No. 3 in the vitreous; therefore nearer the retina than No. 2. The eye is first directed to the central spot of light or opening O in a stenopaic screen. The shadows of the three entoptic objects fall on the retina, and are seen as in the central projection. If now the eye be turned to view first the upper light or opening O' , and

¹ Listing, *Beitrag zur physiologischen Optik*. Göttingen, 1845.

then the lower opening O'' , the shadows are seen on the retina displaced as shown in the upper and lower projections. The entoptic object No. 2 in the plane of the pupil has not changed its position, but No. 1 in front of the pupil, and No. 3 behind, have both been displaced, but *in opposite directions*. Obviously this displacement or parallax is greater as the distance from the pupillary plane is greater, and thus the position of an obscuration within the eye can be found by the observer with a certain degree of accuracy.

This method, however, is not applicable to moving objects like the muscæ, and in any case requires a considerable amount of skill on the part of the observer. Brewster's method is better, and was improved upon by Donders by using two adjacent openings in a

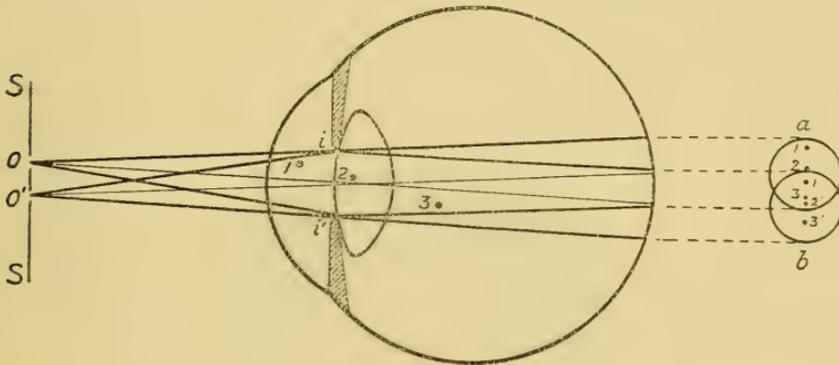


FIG. 8.

stenopaic screen: each aperture about 0.1 mm. in diameter and about 2 mm. apart.¹ Two overlapping images of the pupil are now seen as shown in $a b$ (fig. 8). The closer the pin-holes are together, the more the circles overlap; the distance apart of the centres of the two circles exactly corresponding to that portion of the double image which does *not* overlap: and this distance, when the entoptic rays are parallel, is proportional to the distance between the pupil and the retina. If now an entoptic object, such as No. 2 (fig. 8), lie in the plane of the pupil, its doubled shadow will be as far apart as the images of the pupil, *i.e.* as the centres of the two circles. On the other hand, the doubled

¹ *Nederlandsch Lancet*, 2nd Series, D. 11, 1847. *Archiv. f. physiologische Heilkunde*, viii., 1849. *Accommodation and Refraction of the Eye*, by F. C. Donders, 1864, p. 203.

shadow, if the object lie in front of the pupil, as No. 1, will be further apart than the centres of the two circles, and if between the pupil and the retina, as No. 3, the shadows will be closer together. It is now only necessary to find the breadth of the part of the circles which do not overlap in order to find the relative position of an obscurity in the eyeball. For the distance apart S of the duplicate shadow is in the same ratio to the distance R of the entoptic object from the retina, as the distance apart C of the centres of the two circles is to the distance P of the pupillary plane from the retina; or

$$\frac{S}{R} = \frac{C}{P} \quad \text{hence} \quad R = \frac{S}{C} P.$$

Now the distance P , of the pupil from the retina in a normal eye, may be taken as 19 mm., in a myopic eye about 21 mm., and in a hypermetropic eye about 17 mm. Hence the exact position of the entoptic object in the eyeball can be located.

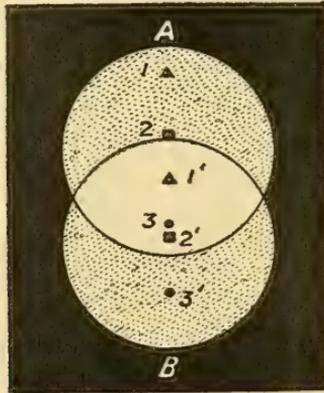


FIG. 9.

This is more clearly seen in fig. 9, where A and B are the overlapping images of the pupil; and the obscurities, in the order of their distance from the cornea, are diagrammatically represented by a triangle, a square, and a circle. As both figs. 8 and 9 are accurately drawn to scale, by using a pair of compasses, the reader can verify the law above stated. In connexion with the Entoptiscope to be described in Part II., I will show how this

measurement can be made in actual practice; and will also describe another and very simple method I have recently devised, which enables an unskilled observer to make an approximate estimate of the position of the obscurities.

§ 10.

By making a large artificial eye, and using a brilliant point of light, it is possible to illustrate in a lecture-room the whole of the principles of entoptic observation and measurement. This was shown at the conclusion of the paper, a small arrow painted on a strip of thin glass or mica being used to represent the obscurity within the eye and placed in different positions in the imaginary eyeball; the shadow of this object being thrown on a ground-glass screen to represent the retina. The source of light was an electric lamp the rays from which passed through an orifice (about a mm. in diameter) in an opaque screen placed before the artificial eye. When the ground-glass screen was moved out of focus, the sharp shadow of the arrow was seen wherever it was placed in the eyeball. The effect of varying the size of the orifice in the opaque screen upon the visibility of the shadow of a small object, held at different parts of the eyeball, can thus be strikingly demonstrated to an audience.

With two closely adjacent pin-holes two partly overlapping circles of light were thrown on the screen; the distance apart of the double shadow of the object thus caused was seen to be exactly the same as the distance apart of the centres of the two circles, when the object was in the plane of the pupil; but this distance diminished in proportion as the object approached the retina. In fact, the exact distance of the object from the artificial retina could thus be readily determined in a lecture experiment.

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ON ENTOPTIC VISION.

[PARTS II. AND III.]

BY

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(PLATES III. & IV.)

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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VIII.

ON ENTOPTIC VISION.

PARTS II. AND III.

PART II.—THE ENTOPTISCOPE AND ITS APPLICATIONS.

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(PLATES III., IV.).

[Read, NOVEMBER 21, 1905; Received for Publication, NOVEMBER 24, 1905;
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§ 1.

IN the present paper the instrument which I have devised for viewing, delineating, and measuring entoptic objects will be described, and some experiments with, and applications of, the Entoptiscope will be given, though its practical use must be left in the hands of the ophthalmic surgeon.

In this instrument, instead of the troublesome method of double vision referred to in Part I., the observer *looks through* the pin-hole orifice on to a brightly illuminated ground-glass screen, placed upon what corresponds to the stage of a microscope. By this means the magnified image of the entoptic object is projected upon the ground-glass below, and the shadow can easily be traced with a pencil. An important feature of this arrangement is that the pencil-point appears to be exactly in the plane of the projected shadow, so that no difficulty is experienced in making a tracing. The observer, especially if presbyopic, will be astonished to find, on looking through the minute orifice, how distinctly he sees the sharp point of the pencil, or of any small object in the field of view, albeit far within the limit of clear vision of his unaided eye. This is due to the homocentric pencil of rays through the pin-hole orifice, and has already been explained in Part I., § 5.

The first form of my Entoptiscope is shown in Plate III., fig. 1, and consists of a pair of vertical brass pillars supporting a head-rest, which can slide from side to side so as to bring either eye vertically over the pin-hole contained in the revolving diaphragm of the eye-piece. This diaphragm has pin-hole apertures varying in diameter from 0.1 to 2.5 of a millimetre, and a pair of pin-holes each 0.1 mm. diameter, and 2 mm. apart, so that by revolving the diaphragm either a single aperture of any given size or a double aperture can be successively brought before the eye. Figs. 1 and 2 show the diaphragm *A* in plan and elevation (the orifices are shown enlarged); the object of the double aperture will be seen later on; an eye-cup screws on to the upper part of the eye-piece (fig. 2).

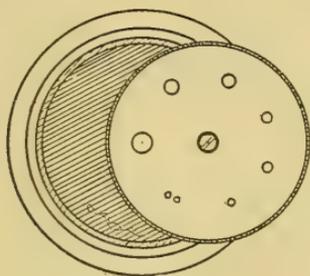


Fig. 1.

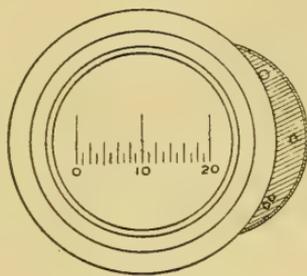


Fig. 3.

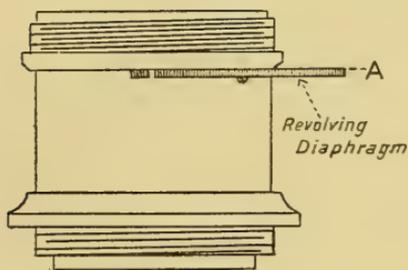


Fig. 2.

Below the pin-hole eye-piece is a transparent scale (fig. 3), divided into fractions of a millimetre; the shadow of this scale falls upon the eye of the observer, and is thence projected much magnified upon the ground-glass stage below, along with the shadows of any opacities seen in the eye. At the base of the instrument (Plate III., fig. 1) is a concave mirror, which can be adjusted so as to illuminate the eye-piece brilliantly, using the light of the sky or that of a lamp. A sharply-pointed and hard pencil

is used by the observer to trace the image seen on the ground-glass stage; and, as stated, pencil-point, scale, the image of the pupillary disc, and the projected shadow of the opacities in the eye are all seen in the same plane with perfect clearness. Hence, if the head and eye are kept steady, the drawing or tracing is made with ease even by an unskilled observer. The only difficulty consists in the contraction and an apparent dilatation of the pupil; the former occurs even in uniform light during accommodation, when the attention is concentrated in the act of drawing. This difficulty, however, is overcome by keeping the eye fixed for a few moments on the pencil-point before the tracing is made, or by dilating the pupil artificially when a careful drawing is required. The latter, a curious elusive dilatation, I will return to presently (see § 8). After the drawing has been made the ground glass can be removed, and a photographic print taken, which is kept for comparison with the tracing made by the observer at a subsequent time. In my own case, so minute and clear are the shadows of the darkened tissues of the crystalline lens, that I can detect the slightest change, noting the gradual extension of the opacity, and could watch week by week the effect of any remedy if such were known.

For convenience of observation, in a later form of the apparatus, shown in fig. 2, Plate III., I have hinged the vertical pillar *P*, so that the observer, when using the instrument, may incline it to suit himself; a single pillar is used in order to leave the hand free to draw on the ground-glass stage *G*, which carries a supporting hand-rest *R*. The eye-pieces *EE* have shaped cups to fit the eye and bring the cornea within a definite distance of the pin-hole. In this way the pin-hole can be placed at the anterior focus of the eye (about half an inch from the cornea), for the reason already explained in Part I.; and the stage is placed at a fixed distance so as to give a definite magnification.

It is important in using the Entoptiscope that the observer should be comfortably seated and completely at ease; he should have his hands free and not be troubled to keep one eye closed; it is much better in fact to keep both eyes open. This is done in using either of the instruments shown on Plate III.; in the smaller one the shaped sliding head-rest keeps all light from

reaching the eyes except through the single revolving diaphragm ; in the larger there are two revolving diaphragms, one (shown at *D*) for each of the eye-pieces *EE* (these are also shown at *DD* in fig. 4, p. 66). The eye that is not under observation is kept in complete darkness by turning *D* until the index marks *O* ; at this position there is no aperture in the diaphragm ; thus either eye can be occluded with ease. The apertures are numbered in order of their size, No. 1 being less than a tenth of a millimetre in diameter, No. 2 larger, No. 3 larger still, and so on. The mirror *M* is plane and not concave, and made sufficiently large to cover the whole of the ground-glass stage *G* with a flood of light reflected from an adjoining incandescent gas lamp or other source of light. As the mirror is carried by the stage and moves with it, the illumination of the field remains unaltered in adjusting the inclination of the pillar to suit the observer. The pillar, stage, and mirror move with stiff friction round the centre *A*, and can be clamped in any position by turning a milled-head screw. In order to prevent any shifting of the observer's head, and to avoid fatigue, a hinged and padded head-rest *H* is fixed in such a position that the forehead rests comfortably upon it. The head-rest is also made to rise or fall, and can be clamped at any elevation to suit the observer.

§ 2.

As the distance between the two eyes varies in different persons, the exact adjustment of the pupil to the pin-hole is accomplished by an ingenious device suggested to me by the remarkably skilful mechanic, Mr. M. Lambert, to whom I am indebted for the admirable construction of the instrument from the rough plans I gave him. This device is shown in fig. 4 (p. 66), and consists in gearing the arms supporting the eye-pieces, so that an automatic adjustment and exact centring occur directly the observer places his eyes in position. Incidentally this arrangement, by means of the scale on the sector *S*, affords a most perfect method of ascertaining the exact pupillary distance of the two eyes, thus replacing the spectacle "trial-frame," or sliding callipers, usually employed for this purpose by the oculist.

As it is obviously an advantage that the oculist should retain a record of the obscurities delineated from time to time by the patient, and photographic printing of the drawing on ground glass involves a little trouble, a direct tracing on paper can be made by the patient.¹ For this purpose the ground glass *G*, Plate III., fig. 2, is lifted out of its clips, and a piece of clear plate-glass of the same size is substituted. On this a piece of tracing-paper cut to the exact size is held by the spring-clips *S*, *S*. The tracing paper is ruled as shown in fig. 5; the object of this is to enable the image of the pupil to be drawn more easily, by making the intersection of the cross-lines the centre of the projected image of the right or left pupil.

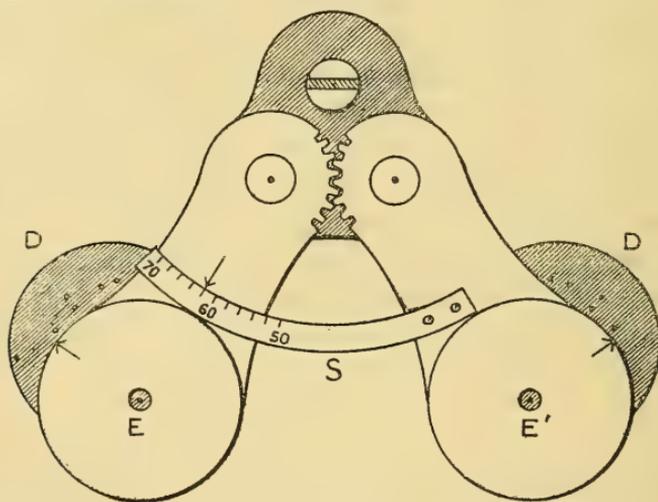


Fig. 4.

It is convenient to know the exact retinal area shadowed by the obscurities at any given time, so that the rate of progress, or amendment, of the defect can be determined. This is accomplished by having the tracing-paper printed in very faintly-ruled 5 mm. squares, such as are shown in part on the right hand of fig. 5. Upon counting the squares covered by the drawing of

¹ There is also a disadvantage in a photographic print of the tracing on ground glass, that it *laterally* inverts the shadows that are drawn, unless the print be taken through the glass, when it is of course less sharp; moreover the tracing-paper can be at once named and dated, and stuck in the practitioner's case-book for future reference.

the shadow which the patient has made, the oculist at once knows (see § 3) the exact area of the entoptic obscurity, or of the pupil, as shown by the dotted circles in fig. 5. A supply of tracing-paper, properly ruled and cut the right size, is provided with the instrument.¹

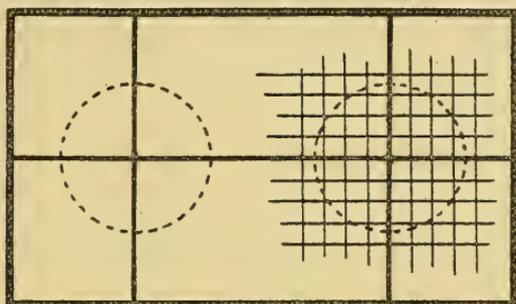


Fig. 5 (reduced one half).

§ 3.

It is certainly astonishing that such an instrument as the foregoing does not appear to have been devised hitherto. Perhaps no instrumental appliance was thought necessary for entoptic observation, which has fallen into disuse since Helmholtz's discovery of the ophthalmoscope. In fact, Donders remarks: "Now that Helmholtz's ophthalmoscope is in our hands, the importance of the entoptic mode of examination for diagnosis is thrown completely into the shade."² With all deference, I venture to think Donders' statement will be found to be inaccurate. It is a remarkable fact that neither Donders nor Helmholtz depicts the entoptic observation of cataract, nor dwells upon the special value of this method in the diagnosis of this defect in vision. Drawings are given of what they and their pupils saw; but these are only of minor defects in the eye. Even in the lengthy article on Ophthalmology in the *Encyclopædia Britannica* and in several text-books on this subject, I can find no reference to entoptic observation. It is obvious that whilst the ophthalmoscope has been of inestimable value to the

¹ The Entoptiscope can be obtained from the well-known opticians, Messrs. Curry and Paxton, 195 Great Portland Street, London, W.

² Donders, *Accommodation and Refraction of the Eye*, p. 204.

profession, it has its limitations, especially when there is any opacity in the anterior parts of the eye; and I imagine that cases may frequently occur when the Entoptiscope can alone enable a correct diagnosis to be made by the ophthalmic surgeon.

In order to save calculation, the distance from the glass stage, on which the image is projected, to the pin-hole aperture, can be made five or ten times the distance of the aperture from the pupil

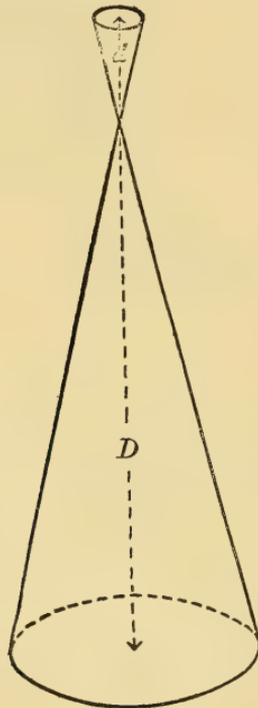


Fig. 6.

of the eye; the linear magnification is thus five or tenfold; and the exact area of the entoptic obscurity is accordingly 25 or 100 times less than the area of the image drawn by the patient.

In ordinary vision, the magnitude of the image of an object on the retina is to the size of the object in the ratio of the distance of the nodal point of the eye from the retina (*viz.*, 16 mm.) to that of the distance of the nodal point from the object. This law also holds true of entoptic vision when the shadows on the retina can be seen by a general illumination of the eye. Helmholtz, Donders, and all recent authorities on physiological optics, so far as I know,

assume the same law holds true when a stenopic screen¹ (*i.e.*, a pin-hole diaphragm) is used, and the entoptic shadow is seen projected through the pin-hole aperture on to a surface beyond. But, as I have explained in Part I., § 8, this is *not* the case, and could not be the case, for the reasons I there adduced. Careful measurements which I have made show, as might be expected, that the magnification is in the ratio of the distance d of the pin-hole from the pupil, to the distance D of the pin-hole from the ground-glass stage or other surface on which the image is projected, as shown in fig. 6. Hence, if the shadow on the retina be the same size as the object (as occurs when the pin-hole is at the anterior focus of the eye), the linear magnitude x , of any obscurity within the eye, is known when that of the projected image S is measured, for

$$x = \frac{d}{D} S.$$

As the pupil is approximately 3 mm. from the cornea, this amount must be added to the distance d of the orifice from the eye.

§ 4.

But the use of the Entoptiscope is not confined to the detection and delineation of opacities in the eyeball. The circular image the observer notices on the stage is not an enlarged view of the orifice through which he is gazing, but, as already mentioned, it is a magnified image of his own pupil. The iris limits the divergent cone of rays entering the eye, and its shadow is sharply depicted on the retina. Hence any irregularities in the iris are at once detected, and can be readily traced by the patient, and the exact size of the pupil accurately determined. *Pupillometry*, as it is called, is one branch of ophthalmology; and the ease, expedition, and accuracy with which it can be accomplished by means of the Entoptiscope will, I hope, render this instrument, in the hands of oculists, a useful means of supplementing the usual external methods of observation of the pupil. Even among the limited number who have so far used the Entoptiscope, I have been

¹ As 'stenopaic' screen (see Part I., p. 44, footnote) may mean either a narrow slit or a small pin-hole in a screen, I shall use the word 'stenopic' to signify the latter only.

struck with the deformation of the pupil occurring and drawn in one or two cases, though the defect was not conspicuous externally to any casual observer.

It is also interesting to note the wide variation in the size of the pupil among different people, under the same degree of illumination and with similar accommodative contraction. The average normal pupil is rather less than 4 mm. in diameter; and a difference in diameter of a fraction of a millimetre is easily registered by the Entoptiscope. For the purpose of measurement it is better not to attempt to trace the whole circle of light seen on the stage, but simply to make a pencil-mark at the extremities of any diameter of the circle, and measure the width apart of the pencil-marks by a pair of compasses. A transparent millimetre-scale can of course be placed on the stage, or the eye-piece micrometer-scale can be used, and the diameter of the circle read off directly; but for an inexperienced observer the pencil-marks I find more satisfactory. The diameter of the pupil being obtained, if it be a normal or fairly circular pupil, it is a great help to draw on the ground glass, or tracing-paper, a circle of this diameter, with the cross-lines of fig. 5 as the centre of each circle, using for this purpose a compass or a coin of the right size. This enables the patient to make his drawing of any entoptic objects with more ease and leisure; still better is it to use as a guide an opaque diaphragm, with a circular aperture of the right size, laid on the stage. Or a movable opaque screen can be used, having two apertures—one corresponding to each eye, and each about 2 cm. diameter. As the magnification of the pupillary image depends on the distance of the screen from the pin-hole, by making this screen with a sliding-tube, to enable it to move up or down the pillar of the instrument whilst it is kept parallel to the stage below, a position will be found by the observer when the diameter of the aperture in the screen exactly corresponds with the area of the image of his pupil; the screen is then kept in this position whilst the drawing is made below.

§ 5.

I have already mentioned in Part I. that it was the discovery of a small permanent obscurity in both of my eyes, before any

opacity was detected by the ophthalmoscope, that led me to devise the Entoptiscope; and I will now give a recent tracing I have made of these obscurities. Fig. 1, Plate IV., is a reproduction of the shadows seen by means of the Entoptiscope, respectively, in my right and my left eye. That these obscurities are due to cataract—that is to say, to partial opacity of the crystalline lens or its capsule—there is no doubt, as will be evident from the careful drawing of the appearance presented in the ophthalmoscope (fig. 3, Plate IV.), which was kindly made for me by the eminent oculist Dr. C. Fitzgerald, of Dublin. As already explained in Part I., § 5, entoptic observation inverts both laterally and vertically the shadows on the retina, whereas the opacity is seen without inversion in the ophthalmoscope. A comparison of the two sets of drawings must therefore be made after the complete inversion of one or the other. This has been done in fig. 2, Plate IV. Dr. Ettles, of London, was good enough to spend some time in making as minute a drawing as was possible of the cataract in my right eye; and a copy of his drawing is given in fig. 4, Plate IV.¹ The much greater detail shown by entoptic observation is obvious; but the entoptic drawing in fig. 1, Plate IV., gives no idea of the wonderful structural detail which the observer sees. The minutest change in the opacity is clearly visible; and, as I have said, the effect of any therapeutic treatment of cataract, if such should ever be found worthy of trial, could be rigorously tested. It is, of course, desirable that the Entoptiscope should be kept in the hands of the profession; otherwise nervous people would be apt to alarm themselves needlessly by its use. In my own case, if a personal reference will be pardoned, I have found the periodic examination of my own eyes a matter of considerable, if not very exhilarating, interest, inasmuch as the slow progress of the cataract, and the curious way in which it spreads, can be watched up to the inevitable end. The only inconvenience so far felt has been due to the increasing astigmatism, which, as I believe is usual, augments with the development of cataract.

¹ I met Dr. Ettles at the Royal Society Conversazione last year, where he was exhibiting that fine instrument the Ettles-Curties Ophthalmometer, and was struck with his scientific enthusiasm and all too rare knowledge of entoptic phenomena.

Another and by no means unimportant use of the Entoptiscope by the oculist will be found in the certainty with which it will enable him to dispel alarm in very many cases where a patient, from perceiving some obscurities such as the *muscæ volitantes* in his field of view, imagines he is about to lose his sight. Looking through the Entoptiscope, if any *muscæ* are present, they will be conspicuously seen slowly moving over the illuminated stage; not only will their characteristic appearance and mobility enable the oculist to make an immediate diagnosis, but their actual size and position in the eyeball can be accurately determined. Fifty years ago, Sir David Brewster pointed out the value of entoptic observation in such cases. He remarks: "Few symptoms appear so alarming to nervous persons as the *muscæ volitantes*; and that these fears can be dispelled by the application of a recondite property of divergent light which has only been developed in our own day is one of the numerous proofs which the progress of knowledge is daily accumulating, that the most abstract and apparently transcendental truths in physical science will, sooner or later, add their tribute to supply human wants and alleviate human sufferings."¹

As the *muscæ* occur nearer the retina than the lens, their shadows can be seen, as is a matter of common experience, without the use of a homocentric pencil of rays. Hence a very simple method, which I referred to, but did not describe, in Part I., § 9, suggests itself for ascertaining approximately the relative position of any obscurities within the eyeball. This consists in gradually increasing the size of the aperture in the eye-piece of the Entoptiscope. Accordingly, a graduated series of orifices is made in the revolving diaphragm of the eye-piece. Upon rotating the diaphragm so that these orifices, from the minutest to the largest, successively come into view, the observer will note a corresponding disappearance of obscurities in the order of their distance from the retina. Finally, with the largest aperture, whilst the definite shadow of even advanced cataract is lost, the far smaller shadows of *muscæ*, or any obscurity very near the retina, still remain. The fears of a patient, if groundless,

¹ *North British Review*, November, 1856.

can be thus set at rest at once. Retinal defects, if existing, are of course still seen, but are easily distinguished from obscurities in the eyeball, and can be examined by retinoscopy.

§ 6.

In order to find the *exact* position within the eyeball of any obscurity, two methods were fully described in Part I. The best method is that of employing two minute and closely-adjacent apertures in the diaphragm; two overlapping images of the pupil are thus produced, together with duplicated shadows of the obscurities. As was fully explained in Part I., § 9, when the path of the rays within the eye is parallel, the distance apart S of the duplicated shadow is in the same ratio to the distance R of the entoptic object from the retina as the distance apart C of the centres of the two overlapping pupillary discs is to the distance P of the pupil from the retina, or

$$R = \frac{S}{C} P.$$

The distance P in a normal eye is 19 mm. As C corresponds to the portion of the circles which do *not* overlap, a comparison of that distance with S can at once be made. If the entoptic object be near, or on the cornea, its duplicate shadow SS is seen further apart than C ; if it be on the anterior face of the crystalline, $SS = C$; if on the posterior face, SS is rather smaller than C ; if near the retina, SS is seen well within the overlapping part of the circles, and much smaller than C ; in this case the duplicated shadows SS are, in fact, quite close together.

Fig. 7, p. 74, is a careful tracing I have made of the obscurities seen in my left eye with a double aperture; the distance C corresponds to the distance apart of the centres of the two circles. If the reader will take the trouble to measure the distance asunder of any of the prominent duplicate obscurities, he will find that distance exactly equal to C ; hence these opacities lie on the anterior face of the lens in the pupillary plane. A small *musca* near the retina is shown, with its double shadow close together at m . Owing to the superposition of the two discs of light, the overlapping part

will be noticed to be brighter than the other portions of the duplicated pupillary disc.¹

The observer will probably notice that on first looking through the Entoptiscope the two circles of light barely overlap; but, as the pupil dilates in the subdued light, the overlapping rapidly increases, soon reaches a maximum, and becomes steady, if the illumination remains unchanged. This is due to the fact that, as the pupil dilates, its projected image enlarges, and the double images or discs of light therefore encroach on each other. Hence, before making any measurements, a moment or two should elapse to allow for the dilatation of the pupil. The duplicating of the image of the pupil is a very delicate method of measuring changes in its magnitude.

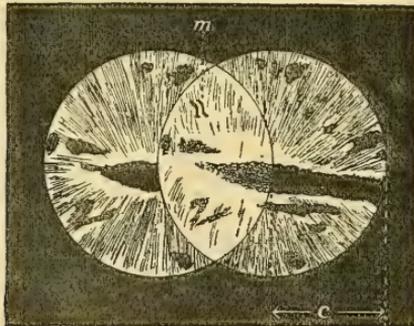


Fig 7.

§ 7.

As the Entoptiscope is designed chiefly for the use of the ophthalmic surgeon, it would be the presumption of ignorance on my part if I entered into its clinical use. But there are several interesting phenomena connected with vision which, I venture to think, will render the instrument of value in physiological and psycho-physical demonstration and research. To some of these I will now briefly allude.

¹ This drawing of the obscurities in my left eye I made nearly six months later than that shown in fig. 1, Plate IV. ; the slow growth of the cataract is thus seen ; the principal addition is the smaller bar parallel to and below the large pen-like horizontal obscurity : the field is darker, and a few additional spots are also scattered about.

The observer, having adjusted the inclination of the instrument to suit his convenience, moves the mirror until a brilliant and uniform light covers the ground-glass stage. A shaded lamp, or incandescent gas-mantle, or a couple of incandescent electric lights, or the bright light of the sky, can be used as the source of light. It is, however, preferable to employ a constant source of light, such as the incandescent mantle placed at a given distance from the mirror. Both eyes should be kept open, and buried up to their sockets in the eye-cups, the head-rest being moved until the forehead is comfortably supported.

(1). When the observer's eyes are adjusted in the eye-cups, and the brightly lighted stage seen through the smallest apertures in each eye-piece, the graduated sector, as already stated, at once indicates the exact distance between the pupils, if this is required.

(2). One of the revolving diaphragms is then turned to *O*, to occlude whichever eye is not under observation. Even without a transparent scale in the eye-piece or on the stage, the observer can readily note the well-known fact that light falling on one eye causes *both* pupils to contract simultaneously. This 'consensual reaction,' as it is termed, and its rate, can be accurately studied with the Entoptiscope. It is only necessary to open suddenly the largest aperture in front of one eye, keeping the smallest aperture before the other, when the contraction of *both* pupils will be seen. Still better, if the stage be dimmed by altering the mirror, an electric lamp brought close under one eye, with the largest aperture open, though not seen by the other eye, nevertheless causes a vigorous contraction of its pupil. The scale, or the ruled squares on the tracing-paper, enables the contraction to be measured, whilst the periodic time of the consensual reaction can be determined by opening and closing the large aperture in front of the electric lamp.

(3). The change of the pupil, during accommodation, has already been mentioned. This 'accommodative contraction,' as well as the direct light reaction in the pupil, is strikingly seen in the Entoptiscope. Turn both diaphragms to *O*; then, after a few moments in darkness, open an aperture in one eye-piece. The contraction of the pupil from light-reaction is first seen. If a

pencil-point be now brought in the field of view on the stage and looked at, accommodation takes place, and the pupillary disc will be seen to contract; the pencil may be suddenly raised near the eye-piece, when a further contraction occurs, owing to the convergence of the eyes that now takes place.

Other causes which give rise to pupillary contraction or dilatation, such as an emotional disturbance, fright, pain, and the action of certain drugs, &c., can be studied more readily, and their effect more accurately measured by the Entoptiscope than in any other way. A magnified view can also be obtained of a slight rhythmic contraction of the pupil (said to be seen by some, though I have not noticed it), which appears to be connected with respiration and the systole of the heart.

§ 8.

(4). One of the most striking phenomena observed with the Entoptiscope is the extraordinary displacement of the projected image of the pupil which takes place when it is seen first by *direct* and then by *oblique* vision. This change in the position of the image, due to a change in the point of view, is not the ordinary parallax displacement; for this does not occur in the Entoptiscope, but is, I find, an *ocular parallax* due to the structure of the eye. The position of an object when seen by direct vision becomes apparently displaced when it is seen by indirect vision, that is when the pencil of rays from the object is oblique to the visual axis. This displacement increases with the obliquity of the rays falling on the pupil, and therefore with the angular magnitude of the cone of rays entering the eye. Hence, if the object were at an infinite distance, it would vanish; hence also the larger the area of the pupil the greater the ocular parallax; if the pupil were a point, it would disappear. I must reserve to a subsequent paper the explanation and discussion of this obscure subject, together with the series of measurements I have made in connexion with it.¹ It will be sufficient here to describe a few experiments on this parallax which can be made with the Entoptiscope.²

¹ In this I have been aided by my assistant, Mr. Warwick, A.R.C.Sc., to whom I am also indebted for several of the drawings in this and the previous paper.

² A paper "On the Law of visible position in single and binocular vision,"

(a). Look through one eye-piece; bring a pencil-point as at b , fig. 8, to the very edge of the projected pupillary disc, looking directly at the pencil. Without moving the pencil or the head, turn the eye to the opposite edge a of the pupillary disc; the pupil will appear to have suddenly expanded to b' , as shown by the dotted lines; and the pencil will, therefore, be now seen well within the disc; but when again the eye turns to b , the disc resumes its first position on that side, and the side a correspondingly expands.

(b). Now shift the pencil outside the disc, between b and b' , as shown by the dot, so that it cannot be seen if directly searched for; when, however, the eye is turned away from it to a , instantly it reappears; this occurs equally well at either side of the disc, with either eye. This paradoxical effect of *seeing an object when you look away from it, and not seeing it when you look directly towards it*, is

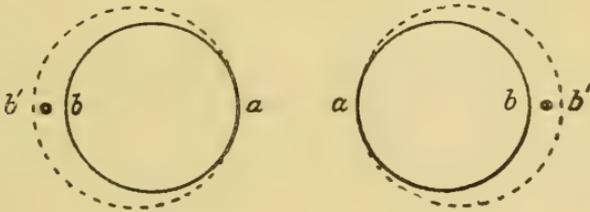


Fig. 8.

not due to the image falling on the blind spot, for it occurs, as I have said, at either side of the disc, or at any portion of the retina oblique to the axis of vision.¹

By making pencil-marks at the limiting points at which the pencil is seen by direct and oblique vision, the magnitude and

published by Sir David Brewster in the Trans. Roy. Soc. Edinb. for 1843, vol. xv., p. 349, contains the first reference I can find to ocular parallax, which Brewster appears to have observed in cases of oblique incidence in ordinary vision. Subsequently Listing investigated the matter, *Beitrag zur Physiologischen Optik*, 1845, pp. 14 *et seq.*, and gave the probable explanation (see next footnote).

¹ The cause of this ocular parallax I will discuss in a subsequent paper. Brewster assigns it to the fact that the eye is not a homogeneous refracting medium; Listing to the fact that the centre of rotation of the eyeball does not correspond to the optical centre or nodal point of the eye. Helmholtz (*Optique Physiologique*, p. 748) agrees with and develops Listing's view, but is unaware of Brewster's earlier discovery and explanation. None of those, nor any later authorities, however, appear to have noticed the remarkable effect of this parallax in entoptic observation with a stenopic screen.

angular value of the parallax can be easily determined. It is this ocular parallax which gives rise to the mysterious and elusive dilatation of the pupillary disc that so puzzles the observer when, in using the Entoptiscope, he begins to trace the outline with a pencil. By keeping the eye always fixed on the pencil-point, and not allowing it to be beguiled by a furtive wandering of the axis of vision, a perfect tracing can be made. Diminishing the angle subtended by the projected image—which can be done by increasing the distance between the pin-hole and the eye—lessens the parallax. For in the Entoptiscope the greater the magnification, the greater the ocular parallax; with distances of the pin-hole from the eye and to the stage respectively of 25 and 125 millimetres, or 1 to 5, an image is given of sufficient magnitude and having very little parallax. For this purpose the eye-cups are made detachable, and a second deeper pair supplied with the instrument.

Another plan of avoiding this troublesome parallax in the Entoptiscope is to use a very small artificial pupil in the eye-piece, close to the eye; a disc with an aperture somewhat less than two millimetres in diameter almost stops the parallax; but this very much restricts the area to be seen either of the pupil or of the crystalline, and hence is not usually advisable.

§ 9.

(5). Upon winking the eyelids, transverse striæ will be perceived on looking through the Entoptiscope, due probably to minute wrinkles in the epithelial layer of the cornea. If one eyelid be winked frequently, as happens in using a telescope or microscope for some time, striæ are formed which remain for some hours, and give rise to a marked defect in vision. The presence of tears also gives rise to long striæ from their prismatic action on the pencil of rays. Rubbing the cornea causes the roughening of the epithelial layer, which gives rise to a peculiar ribbed or mottled appearance in the field of view of the Entoptiscope, but this soon disappears. Dr. Thomas Young was, I find, the first to notice and depict this so long ago as 1801 (see footnote ¹, next page). Helmholtz gives some excellent drawings of these entoptic appearances (*Optique Physiologique*, p. 208).

(6). But more important is the study of the structure of the crystalline lens as seen in the Entoptiscope. The observer will probably notice a star-like figure radiating from the centre of the field of view. This is due to slight differences in refractive power of the fibrous tissue separating the sectors into which the crystalline is known to be divided. This star-figure is sometimes bright, as shown in Plate IV., fig. 5, sometimes dark, the difference being due to the fact that the refraction of the fibres is in some eyes greater, and in some less, than that of the surrounding portion of the crystalline. In his wonderful paper on the "Mechanism of the Eye," published in the Philosophical Transactions upwards of a hundred years ago, Dr. Thomas Young gave a drawing of the radiating structure of the human crystalline, exhibiting ten main radiations, and finer striæ within.¹ These finer radiations are well seen in the crystalline as revealed by the Entoptiscope. Donders and Helmholtz both give several drawings of the lens seen by its entoptic image. Bright spots, due to higher refrangibility, are frequently seen on the crystalline and are shown in Plate IV., fig. 5; these are termed "pearl-spots," and, in some cases, similar dark spherules are seen, due to the lower refrangibility of their structure.²

The eminent oculist, Mr. J. Tweedy, President of the College of Surgeons, London, published in the *Lancet* for December, 1871, p. 776, drawings of the human crystalline, showing its stellate structure, which he was the first to observe in the eyes of several patients by means of intense oblique illumination. Mr. Tweedy was good enough to show me his original drawings which are more detailed than the published reproduction.

¹ *On the Mechanism of the Eye*, by Thomas Young, M.D., F.R.S., Phil. Trans., 1801. This classical research was published when Young was only twenty-eight years old, and contains a number of remarkable discoveries, such as accommodation being due to change in curvature of the crystalline, &c., often attributed to later investigators. No one, however, appears to have noticed that Young was the first to discover entoptic vision. He gives excellent drawings (figs. 32 and 33 in his paper) of the radiating structure of the crystalline and the mottled surface of the cornea when rubbed, as seen when "a minute lucid point such as the image of a candle in a small concave speculum was held very near the eye."

² A magnifying glass is required to see them in Plate IV., fig. 5, which has been reduced from a drawing made by Donders.

Listing and subsequently Donders classified the various entoptic appearances seen in the crystalline and the anterior part of the eye. Excellent drawings of these are given by Donders, and more especially by Helmholtz.¹ But, as already remarked, it is surprising that none of these eminent men noticed the great value of entoptic observation in the case of cataract. I cannot lay claim to the first discovery of this, for, though it was independently observed by myself, Dr. Darier, of Paris, appears to have been the first to draw a cataract thus observed some ten years ago. In a paper he published in a French journal, Dr. Darier says he accidentally noticed an obscurity in one of his own eyes when he viewed a point of light; he was thus led to make an arrangement, consisting of a concave lens and a distant candle, for the better examination of his crystalline.² This arrangement he called an *autophakoscope*; unfortunately, he appears to be quite unaware of the literature or the theory of entoptic observation, and also of the generally accepted terminology; he gives, however, some drawings of what he observed, and is convinced of the value of the method in ophthalmology.

It does not, however, need any instrumental appliances to see one's own crystalline lens. Various simple methods of doing so were mentioned in Part I., § 1. One of the best and simplest is a point of light reflected from some portion of the polished rim of a pair of spectacles worn by the observer, especially when a bright source of light is behind the observer. The homocentric pencil of rays thus obtained enables entoptic phenomena to be well seen, so that if the observer has used the Entoptiscope, and is familiar with what he is to look for, he can readily see his own crystalline, any opacities within his eye, and the changes in the magnitude of his pupillary disc by merely looking at one of the brilliant spots of light reflected from the rim of his own spectacles.

(7). Reference has already been made in § 5 to the ease with which the Entoptiscope enables the *muscæ volitantes* to be seen and their position in the eyeball found. In this case No. 2 or No. 3 pin-

¹ See Donders, *Accommodation and Refraction of the Eye*, p. 200; Helmholtz, *Optique physiologique*, pp. 208 *et seq.*

² "De la possibilité de voir son propre cristallin," par M. le docteur Darier. *Annales d'Oculistique*, September, 1895, vol. cxiv., p. 198. See *Note* on p. 83.

hole aperture and the shortest eye-cups should be used, in order to give a large retinal illumination, and the pillar of the Entoptiscope should be fixed vertically, so that the eye looks directly downwards. The muscæ will now be seen nearly stationary, for being rather lighter than the vitreous humour they will slowly ascend, and thus their motion being in the line of sight their shadows will not be displaced, but become clearer as they approach the retina. Dr. Jago, in his "Entoptics," gives some careful drawings he made of different types of muscæ. Helmholtz, in his "Physiological Optics," also gives some excellent drawings of the muscæ, and divides them into four or five groups according to their appearance. More recent writers have also depicted and investigated the muscæ, so that it is needless to dwell further on this subject. In my own case, as I mentioned in Part I., footnote on p. 56, the muscæ have increased in number, size, and persistency since the development of cataract in my eyes, and are constantly seen when looked for in the right eye, where the cataract is more advanced.

(8). The Entoptiscope also enables the "light-sense" of an observer to be tested, and the threshold of visibility of each eye determined, *i.e.* the degree of illumination which forms the lowest limit of visibility—the *lux-liminal* point, it might be termed. For this purpose the smallest aperture may be used in the case of a normal eye, or larger, in persons suffering from cataract, and a small, steady source of light (such as a night-light) is shifted to different distances from the mirror of the instrument in a well-darkened room. The limiting distance is then measured, and, as the illumination of the ground-glass stage follows the law of inverse squares, the light threshold is at once found, relatively to some standard. The "adaptation-time," or rise of sensibility when in darkness, of the eye of the observer is thus also accurately found; further the visual acuity and colour-sense, under different degrees of illumination, can be conveniently examined in this way.

(9). As was explained in Part I., § 5, a minute object can be clearly seen when held close to the eye and viewed through a stenopic screen. Under such circumstances a highly magnified image of the object is perceived from the large visual angle subtended by the object, whilst the blurring of the image on the retina is prevented owing to the circles of diffusion being reduced

to mere points. The Entoptiscope not only affords a most convenient way of exhibiting this magnification of a microscopic object without the aid of a microscope, but also enables the observer to make an accurate tracing of the magnified image of the object on the ground-glass stage. If the object be placed below the pin-hole, it does not appear inverted; if above, it does; see Part I., § 5, p. 53: the nearer the pin-hole aperture is to the eye, and the nearer the object is to the pin-hole, the greater the magnification. A brilliant source of light, the smallest aperture in the diaphragm, and the shortest eye-cups should be used. More light is obtained by using the clear-glass instead of the ground-glass stage. The microscopic object, liquid or solid, can be placed in the centre of the glass diaphragm of one of the eye-cups referred to in the next experiment (10).

Mr. E. M. Nelson, Past-President of the Royal Microscopical Society, informs me, as this paper is going to press, that some years ago he exhibited to that Society the hexagonal structure of a diatom, "Triceratinum," by means of its shadow on the retina, obtained by pin-hole illumination; the hexagons measured about $\frac{1}{2500}$ th of an inch (0.01 mm.). It was found necessary to use a diminished image of a pin-hole in a card, obtained at the conjugate focus of a wide-angle lens of about half-an-inch focus. The hexagonal structure of the eye of a fly, $\frac{1}{800}$ th inch, Mr. Nelson found quite easy to demonstrate to an observer in this way.

(10). As the refractive index of the cornea is nearly the same, and that of the aqueous humour the same, as water, by immersing the eyes in water, refraction by the crystalline alone becomes effective. This method was employed by Dr. Thomas Young to demonstrate that accommodation was effected by a change in curvature of the crystalline.¹ The experiment can easily be made with the Entoptiscope. The pillar of the instrument is clamped vertically, and an eye-cup, fitted with a glass diaphragm below, is placed in position. The cup is nearly filled with (not quite cold) water, and the eye immersed, so that the cornea is in contact with the water. Open the largest aperture (say 2 or 3 mm. diameter): note (*a*) the focal length of the convex glass lens

¹ *On the Mechanism of the Eye.* Phil. Trans. for 1801, p. 28.

required to be held below the aperture in order to restore clear vision; the refraction by the cornea is thus seen to be far greater than that by the crystalline ($2\frac{1}{2}$ times); this is owing to the latter being immersed in media only slightly differing from itself in refractive power. (b) Keeping the selected convex lens before the aperture, note that accommodation still takes place. (c) Changing the aperture to the smallest size, note that clear vision is now restored without the use of any external glass lens.¹ (d) Note, also, that ocular parallax (§ 8) still remains, though the large corneal refraction is abolished.

Immersion of the cornea in water also enables the observer, if astigmatic, to note whether any residual astigmatism is due to the crystalline lens, or whether any power of astigmatic accommodation by the lens can take place, as some think does occur.

Doubtless other applications of the Entoptiscope will occur to the ophthalmologist. One of the simplest is its use in testing astigmatism by the appearance presented by the luminous point, when the eye of the observer is gradually removed from, say, 3 to 30 inches. (See Part III. (2).) The observer will notice in this experiment how the slightest pressure on the cornea completely alters the appearance of the elliptical diffusion-spot, or other image, which the luminous point assumes in astigmatic eyes. Tscherning goes so far as to say there is no optic defect which is not shown by means of the figures presented by a luminous point.

Note.—I have to thank my friend Dr. C. E. FitzGerald for pointing out to me that Snellen and Landolt, in their classical *Handbuch der Augenheilkunde* published in 1874, vol. 3, p. 178, were the first to speak of the great importance of entoptic examination in observing the development of cataract. They add the proviso "if the patient is sufficiently intelligent." It is true all entoptic examination requires a certain degree of intelligence on the part of the observer; but I have found that a very little instruction enables any one, not hopelessly stupid, to use the Entoptiscope quite successfully.

¹ For my own part I cannot understand why evolutionary processes did not lead to increased sensitiveness of the retina and a pin-hole eye like that of the nautilus, with a projecting cover. Such an eye would have many advantages over our own; no accommodation and no spectacles would be required; no spherical or chromatic aberration would exist, and no cataract would occur. And how did the lens originate? Only in its perfect state would it be of use; and this, we assume, could only have been the result of imperfect stages which would be useless.

PART III.—OTHER ENTOPTIC PHENOMENA.

(1). When the point of light is at a considerable distance—a stenopic screen 4 or 5 feet away, with a bright light behind, or the incandescent gas-mantle of a street lamp over 40 feet away, does very well—beautiful diffraction phenomena will be seen; lines of light, with spectrum tints, are seen radiating in all directions from the common centre. This, sometimes called the ciliary corona, is due to the stellate fibrous structure of the crystalline lens; and the radiations I find become very brilliant and conspicuous when the lens has the numerous small opacities which occur in the growth of cataract. A rainbow-coloured ring is often seen (though I have not noticed it) surrounding these radiations, probably due to the epithelial cells of the cornea or the fibres of the crystalline. A few grains of hycopodium dust, or other powder, scattered on a glass plate, and held between the eye and a distant point of light, give rise to exactly similar diffraction phenomena.

(2). If the stenopic screen, or other brilliant point of light, be placed at different distances from the eye, any astigmatism in the eye can be readily seen, and its meridian accurately determined by the appearances presented. Here, again, Dr. Thomas Young was the first to employ this method of observation; and in his paper of 1801—to which reference has already been made—diagrams are given by Young, showing the various appearances of a luminous point at different distances from the eye. Tscherning, in his “*Physiological Optics*” (English translation, pp. 138-144), gives a series of drawings of the forms presented by a luminous point at varying distances from the eye.

I find that a narrow illuminated slit, capable of rotation through 180° , is far better for judging the amount and the exact meridian of astigmatism. Such a slit when slowly rotated from a vertical to a horizontal axis on either side also forms an extremely delicate method of judging whether spectacles to correct astigmatism have been accurately made or not. If there be any inaccuracy in the meridian or the curvature of the glasses, the slit will, in some position, appear with a faint duplicate image or ghost upon rotation.

(3). There are several other well-known entoptic phenomena which do not require the aid of the Entoptiscope or a stenopic screen for their perception. Such, for example, are the so-called Purkinje's figures: these are the shadows of the capillaries and minute vessels of the retina, which can be seen ramifying in all directions when a candle is moved to and fro on one side of, and a little below, the eye, the observer being in a darkened room, and looking straight in front; or they may be seen by moving a perforated screen to and fro in front of a lamp, or a pin-hole aperture moved to and fro when the eye is directed to a bright sky; still more easily and vividly can they be seen when a very bright spot of light is allowed to fall on the sclerotic coat of the eye, and in this case the minute detail of the arborescent form of the vessels is well seen. In any of these ways oblique illumination is obtained, and retinal sensitiveness increased, by the successive moving of the shadow through the motion of the light or of the head.¹

(4). When the eye is directed to a bright sky or cloud, and a cobalt-blue glass or gelatine film of the right tint suddenly interposed, the *macula lutea*, or yellow spot of the eye, can be seen as a small dark patch in the field of view. The best colour to interpose is a solution of the blue oxalate of chromium and potassium; but I have found a gelatine film, tinted a purplish blue, do very well. The success of the experiment depends on the eye not being focussed on the interposed screen, but kept fixed on the distant cloud. With a stenopic screen kept in to-and-fro motion, and the tinted gelatine interposed, the actual structure of the yellow spot can be seen.

(5). Several observers have noticed that when the opened fingers are moved to and fro in front of the eye, or, still better, the above coloured screen interposed, the eye being directed to a bright cloud, a remarkable movement like the circulation of the blood is perceived in the vessels of the retina. Vierordt, in 1856, first drew attention to this. Prof. Ogden Rood independently noticed it, and published an interesting paper on the

¹ Writers on physiological optics appear to have overlooked the fact that Sir C. Wheatstone gave the first explanation of this phenomenon (*vide* British Association Report, 1832, p. 551).

subject in 1860.¹ Prof. Rood also detected the movement of small bodies which he took for blood-corpuseles, but their size, estimated from their projected shadows, was about double that of blood-corpuseles.

It is quite easy to see this phenomenon if a bright sunlit sky be looked at through a cobalt-blue glass held close to the eye. A rapid succession of bright specks like minute fire-flies are seen darting swiftly onward in numerous broken curved paths of short radius. I hope shortly to publish a note giving further particulars and the actual dimensions of these corpuseles.

Other American observers, Prof. Rogers and Dr. Reuben, in 1861, also drew attention to these streams of particles, and attributed them to moving blood-corpuseles. Helmholtz, who repeated the experiment, states that he could see the phenomenon very well with his right eye, a little to the left of the point of fixation. He came to the conclusion that the circulation of the blood and groups of corpuseles are really thus entoptically seen; but only when small obstacles in the retinal circulation occur, thus a local and temporary stoppage in the circulation takes place. An agglomeration of blood-corpuseles and a variable velocity in the flow of blood through the smaller capillaries are thus produced, which render the phenomenon visible.² The fact has hitherto been overlooked that Dr. Thomas Young noticed this as long ago as 1793. He found that by prolonged pressure on the sclerotic and interrupted pressure on the cornea, temporary stoppage of the circulation in the retinal vessels is produced; and the sudden return of the blood enables the branching capillaries and also the flow of the blood to be perceived.³

(6). It is well known that mechanical and electric stimulation of the retina give rise to luminous appearances to which the name of *phosphenes* has been given. Pressure on any small part of the sclerotic is transmitted to the retina, and causes a bright phosphene to be projected in the opposite direction to the pressure. Young describes and explains this phenomenon; and Helmholtz and

¹ See American Journal of Science (Silliman's Journal), vol. xxx., Sept. 1860; also a second paper on the subject by Prof. Rood in vol. xxxi.

² Helmholtz, *Optique Physiologique*, pp. 221 et seq.

³ Philosophical Transactions, 1793, p. 160.

others have discussed the subject fully.¹ The experiment is best made in a darkened room, and is readily explicable from the law that the stimulation in any way of a nerve-fibre excites only the sensation peculiar to that special group of nerves.

This, however, is to some extent a subjective phenomenon; and into purely subjective optical phenomena, such as the effects resulting from retinal fatigue, after-images, &c., I do not propose to enter.

(7). Microscopists who have worked with high magnifying powers are aware that, with excessive magnification, a peculiar spotty appearance is produced in the field. This is due to the fact that, as the magnification increases, the image of the objective, from which proceeds the light that enters the eye, becomes smaller and smaller until it is practically a luminous point. Thus a homocentric pencil of rays enters the eye; and the shadows of any dust on the eye-piece of the microscope, or of any obscurities on or within the eye, are thrown upon the retina along with the image of the microscopic object. Delicate microscopic details thus become indistinct owing to the fact that the very conditions which create high-power microscopy also create the conditions of entoptic vision. Helmholtz was the first to point this out in his paper on the "Theoretical Limits of resolving Power in the Microscope."² The difficulty appeared to be insurmountable until Mr. J. W. Gordon entirely overcame it by receiving the luminous point of the image of the objective carrying with it the image of the microscopic object on a little ground-glass screen. This, by scattering the light, of course, destroys the homocentric nature of the pencil, and thus gets rid of the entoptic shadows. But the magnified grain of the ground-glass screen now becomes a serious objection; this, however, Mr. Gordon entirely gets rid of by causing the little screen to be kept in rapid eccentric motion by a small electric motor. Under these circumstances eye-observation

¹ *Optique Physiologique*, pp. 266–280. See also *Essai sur les phosphènes*, par Dr. Serre. Paris, 1853, &c.

² *Die theoretische Grenze für die Leistungsfähigkeit der Mikroskope*, von H. Helmholtz, Poggendorff's Annalen, 1874, p. 557. This important paper has been translated by Dr. Fripp, and is published in the Monthly Microscopical Journal, N.S., vol. xvi., p. 15, and in the Bristol Naturalists' Society Proceedings, N.S., vol. i., part 3.

or micro-photographs of objects magnified 7000 diameters exhibit a wonderful clearness and sharpness of definition, as was shown in Mr. Gordon's lecture on the subject at the Royal Institution.¹

(8). The so-called Haidinger's brushes may be mentioned in concluding the summary of these entoptic phenomena. These are seen by some when the sky, or any brightly illuminated white surface, is viewed through a Nicol's prism. A pair of faint yellow tufts or sectors, shaped something like an hour-glass, is seen in the plane of polarization; and, at right angles, the space is filled with a faint blue light. These coloured sectors rotate as the Nicol is turned, showing that the eye can act as an analyser to polarized light. Jamin, Brewster, Helmholtz, and others have suggested various explanations of this phenomenon, which probably depends on a slightly polarizing structure possessed by the cornea or the *fovea centralis* of the eye.²

I cannot conclude this paper without adding my humble tribute of admiration to the amazing genius and almost miraculous range of knowledge possessed by that great Englishman, Dr. Thomas Young, the extent and value of whose discoveries in vision are not even now adequately recognised, though, from the first, Continental physicists and ophthalmologists have done him greater honour than his own countrymen.

¹ *Vide* Journal of the Royal Microscopical Society, 1903, pp. 400 *et seq.*; also Proceedings of the Royal Institution, February 17, 1905.

² *Vide* Brewster's *Optics*, pp. 245 *et seq.*; Helmholtz, *Optique Physiologique*, pp. 552 *et seq.*; G. G. Stokes, Brit. Assoc. Report, 1850, p. 20. Drawings of Haidinger's tufts and the exact measurement of the retinal area they cover, as seen by the author and by one of his senior students, Mr. Ledwidge, will be published shortly, as some light is thus thrown on the seat of this obscure ocular phenomenon.

EXPLANATION OF PLATE III.

PLATE III.

FIG.

1. Experimental form of Entoptiscope. Scale, one-sixth.
2. Entoptiscope for ophthalmic use or research. Scale, one-fourth.
Vide page 64.

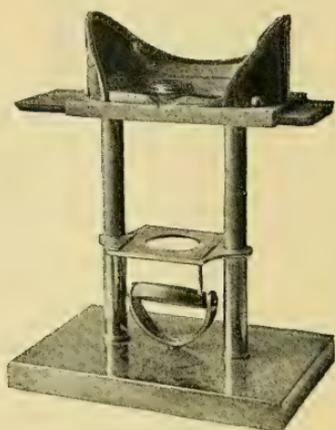


FIG. 1.

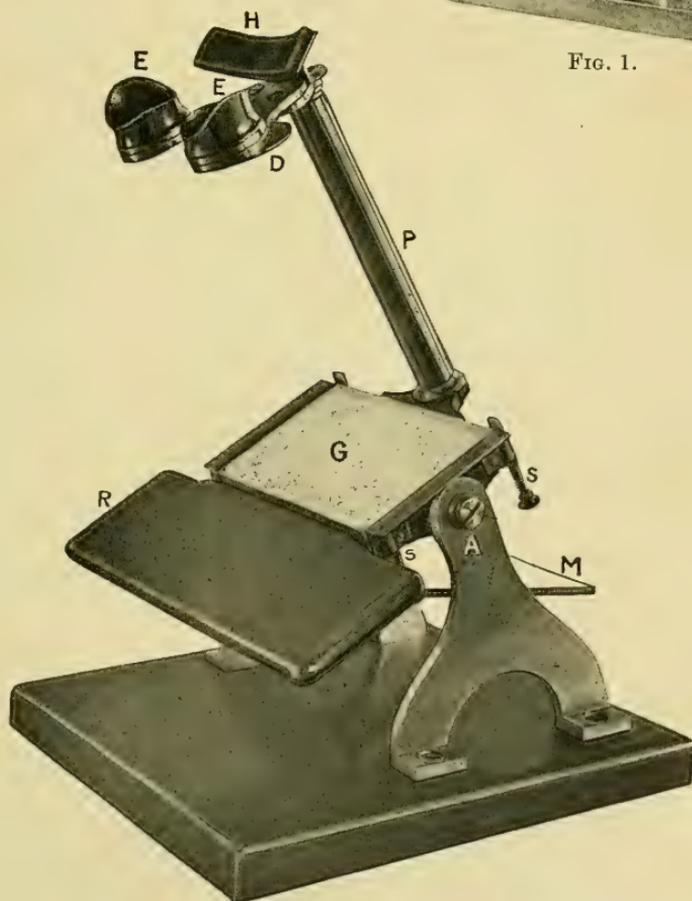


FIG. 2.

ENTOPTISCOPE.

EXPLANATION OF PLATE VI.

PLATE IV.

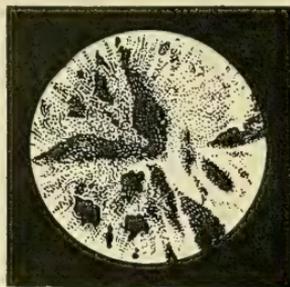
FIG.

1. Pupillary disc and obscurities in crystalline lens of the author's left (L.) and right (R.) eyes, as seen and delineated by the author with the Entoptiscope, showing growth of cataract in both eyes. The pupil and obscurities are magnified 7 diameters.
3. Drawing of the obscurities in the author's eyes as seen by Dr. C. Fitzgerald, of Dublin, by means of the ophthalmoscope, about the same date as the drawing in fig. 1.
2. The same inverted both laterally and vertically to compare with fig. 1.
4. Detailed drawing of the obscurities in the author's right eye, as seen by Dr. Ettles, of London, by means of the ophthalmoscope, for comparison with R., fig. 3.
5. Entoptic view of his right crystalline lens made by Donders, the eye under a mydriatic. The normal stellate structure of the lens is here shown; most persons see in the Entoptiscope the bright star, sometimes with branching lines, indicating the structure of their crystalline.

FIG. 1.



L.

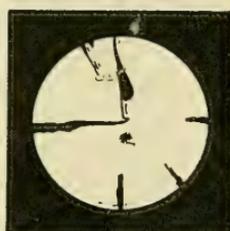


R.

FIG. 2.

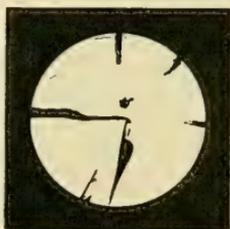


L.

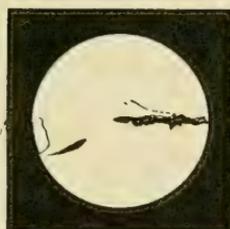


R.

FIG. 3.



R.



L.

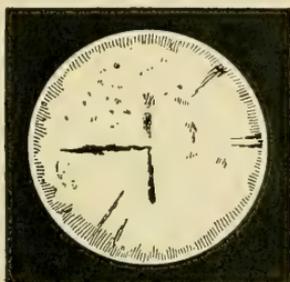


FIG. 4.

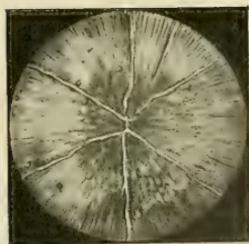


FIG. 5.

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ON THE VAPOUR-PRESSURE OF A PURE LIQUID
AT CONSTANT TEMPERATURE.

BY

SYDNEY YOUNG, D.Sc., F.R.S.,

TRINITY COLLEGE, DUBLIN.

[Authors alone are responsible for all opinions expressed in their Communications.]

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IX.

ON THE VAPOUR-PRESSURE OF A PURE LIQUID AT
CONSTANT TEMPERATURE.

By SYDNEY YOUNG, D.Sc., F.R.S., Trinity College, Dublin.

[Read, FEBRUARY 20; Received for Publication, FEBRUARY 27;

Published, MAY 2, 1906.]

IN a recent number of the *Journal de Chimie Physique* (1905, vol. iii., p. 665), there is a valuable article by Dr. P. Kohnstamm, on "Les travaux récents sur l'équation d'état." Kohnstamm discusses the part played by the Kinetic Theory, by thermo-dynamics and by experiment, respectively, in the development of the subject, and he takes a pessimistic view of the results which have been obtained by experimentalists. Thus, speaking of the three equations of state, $p = c$ for saturated vapours at constant temperature, $p v = RT$ for gases, and $p(v - b) = K$ for liquids, he says (p. 675), "Or, même si l'on veut établir une formule, il est indubitable que les données expérimentales n'y suffisent pas par elles-mêmes. Je passe sur ce qui concerne les liquides, mais où en sommes-nous pour les vapeurs saturées? On connaît un seul exemple (l'isopentane étudié par M. S. Young) où l'on soit parvenu, dans une série d'expériences, à condenser la vapeur saturée à pression constante. Dans tous les autres cas il s'est produit des surélévations de pression et tous les auteurs qui se sont laissés guider exclusivement par leurs expériences (Battelli, Wüllner et Grotrian, etc.) combattent la valeur de la formule indiquée."

It is quite true that in a short paper which I published in 1894 in the *Philosophical Magazine* (vol. xxxviii., p. 569), on the "Influence of the relative Volumes of Liquid and Vapour on the Vapour-pressure of a Liquid at constant Temperature," I referred especially to isopentane, because the data for this substance were more complete than for any other; but I stated that similar results had been obtained with other liquids.

Again, I do not feel that I am justly entitled to the honour of being the sole champion—as an experimentalist—of the discredited formula.

Andrews himself, although he observed a considerable rise of pressure during the condensation of carbon dioxide, attributed this rise to the residual air which he was unable to remove from the gas, and he estimated the amount of air present at $\frac{1}{500}$ to $\frac{1}{1000}$ of the total volume. Andrews clearly stated his belief that if the carbon dioxide had been quite pure, the pressure would have remained constant during condensation; and he discussed the effect which would be produced by a small amount of permanent gas. Amagat (*Mémoires sur l'élasticité et la dilatabilité des fluides, Ann. Chim. Phys.*, 1893), in describing the $PV - P$ diagram, constructed from his observations with carbon dioxide, speaks of that part of the isothermals which corresponds to liquefaction as *straight*; and Kuenen (*Phil. Mag.*, 1897, vol. xlv., 179), who observed a rise of pressure of 0.44 per cent. during the complete process of liquefaction of carbon dioxide at $14^{\circ}95$, and of only 0.21 per cent. at $25^{\circ}85$, attributed the slight deviation of his values from those of Amagat to the presence of a very small amount of residual air.

Again, in the last of a series of papers by Ramsay and myself on the thermal properties of liquids (*Phil. Trans.*, 1892, vol. 183A, p. 107), water is described as differing from the other liquids (ethyl, ether and methyl, ethyl and propyl alcohols), inasmuch as its vapour-pressure was found to depend to some extent on the amount of substance present (in a given volume).¹

From this it is clear that there are other experimenters who consider that for normal substances the evidence is in favour of the formula $p = c$ at constant temperature.

In addition to ether, the three alcohols, and water, I have—either alone, or with the assistance of Miss E. C. Fortey, or Mr. G. L. Thomas—determined the vapour-pressure of twenty-seven carefully purified liquids through a wide range of temperature. From the ordinary boiling-point to the critical point, the vapour-pressures were determined in an apparatus similar in principle to that employed by Andrews, but differing from it in detail. The liquid in the experimental tube was heated by the vapour of a pure liquid boiling under known (usually reduced) pressure, and the vapour-pressure was read on one or other of two air-manometers, which were kept at a nearly constant temperature by a current of

¹ The rise of pressure during the condensation of steam was attributed to the hygroscopic nature of glass.

water. The pressure was corrected (1) for the temperature of the air in the gauges; (2) for the difference in level of the mercury in the experimental tube and the air-gauge; (3) for the pressure of the column of unvaporised liquid; (4) for the expansion of the heated column of mercury; (5) for capillarity; (6) for the deviation of air (in the gauge) from Boyle's law, as determined by Amagat. No correction for the vapour-pressure of mercury was applied, because evaporation through a long column of liquid was found to be exceedingly slow.

In order to obtain trustworthy results, the following sources of error must be taken into account, and guarded against as far as possible:—

1. The presence of impurities, including air dissolved in the liquid, or adhering to the walls of the tube.
2. The vaporisation of mercury.
3. The allowance of insufficient time for equilibrium to be established before taking readings.
4. Variability of temperature of the vapour-jacket (or bath).
5. Too rapid variation in the temperature of the water surrounding the air-gauges.
6. Errors of reading.

1. *Impurities.*—Not only is the actual vapour-pressure of a liquid altered by dissolving some other substance in it, but—except in special cases where a mixture of maximum or minimum vapour-pressure is formed—the composition of the mixture alters as evaporation or condensation proceeds, the vapour being always richer than the liquid in the more volatile component.

The following cases must be considered:—

(a) The dissolved substance (impurity), present, it may be assumed, in very small quantity, is non-volatile. When the volume is increased, so that evaporation takes place at constant temperature, the residual solution becomes more and more concentrated and the vapour-pressure falls. The change of concentration and of vapour-pressure with volume is slow at first, but becomes more and more rapid as the amount of liquid diminishes.

(b) The dissolved substance is gaseous under ordinary conditions, and is not very soluble in the liquid. This case is the

most important, and must occur if air has not been completely expelled from the liquid. Let us consider first what will occur if we start with saturated vapour and slowly condense it. At first the permanent gas will be evenly distributed through the large volume, and its partial pressure will be very small. As condensation proceeds, very little of the permanent gas will be dissolved by the liquid, the greater part remaining diffused through the residual vapour. As the volume diminishes, the pressure of the permanent gas rises, slowly at first, then more and more rapidly, until, when condensation is nearly complete, it may become very considerable, and the final bubble, as pointed out by Andrews, may require to be greatly compressed before the gas in it is dissolved by the liquid.

Suppose, now, that the vapour has been completely condensed, and the liquid left at rest long enough for the dissolved gas to diffuse evenly through it; and that, on increasing the volume again, a bubble of vapour forms at the top of the tube, no ebullition taking place from below. The vapour will then contain very little more permanent gas than that which was originally contained in the liquid which has evaporated, because the diffusion of dissolved gas through a liquid is a slow process. The partial pressure of the gas will, therefore, be little higher than it would be if the whole of the liquid were evaporated and the gas evenly distributed through the vapour. If ebullition from below can be prevented when the volume is again increased, the residual liquid will retain most of its dissolved gas, and the very low partial pressure of the gas in the vapour will remain nearly constant. If, on the other hand, ebullition from below takes place, the dissolved gas will escape into the ascending bubbles, and will quickly be carried up into the vapour. In practice, it is found that ebullition does not readily take place at the lower temperatures, whereas it is quite impossible to prevent it at the highest temperatures.

If, then, a liquid is nearly, but not perfectly, free from dissolved air and if the readings of pressure are taken during evaporation, it may generally be expected that the errors will be very small or negligible at the lower temperatures, but noticeable at the higher ones. It may be remarked also that if the film of gas which adheres so obstinately to glass has not been removed during the filling of the tube, the film may remain on the glass during the

determinations of vapour-pressure at the lower temperatures, but may be expelled when the tube is strongly heated.

When the vapour in the experimental tube has been completely condensed, the more complete the absence of air the greater must be the difficulty in inducing vaporisation again; and it is probable that if the liquid and glass were absolutely free from permanent gas, the difficulty would be insurmountable except at relatively very high temperatures. Great difficulty was actually experienced in most cases in starting vaporisation; and this may be taken as a proof that the removal of air was nearly complete.

Between the extreme cases of (*a*) non-volatile and (*b*) gaseous impurities, we must shortly consider those of impurities, (*c*) less volatile and (*d*) more volatile than the liquid under examination. The influence of such impurities is similar to, but less marked than, that of non-volatile and gaseous substances respectively. The less volatile impurities affect the pressure chiefly at the largest volumes, the more volatile chiefly at the smallest; the greater the difference between the volatility of the impurity and that of the pure substance, the more closely will the effect resemble that produced by the non-volatile and gaseous impurities respectively; the smaller the difference in volatility, the more closely will the form of the curve representing the observed pressures approach that of a gently sloping straight line.

Better results will in all cases be obtained by slow vaporisation, if possible without ebullition, than by condensation.

2. *Vaporisation of Mercury.*—The vapour-pressure of mercury is negligible at low temperatures, but increases more and more rapidly as the temperature rises; it is only 0·27 mm. at 100° and 16·81 at 200°, but at 300° it is 248·6 mm. Any error due to the vaporisation of mercury will, therefore, be of greatest importance at the highest temperatures. That the diffusion of mercury-vapour through a highly compressed gas is an exceedingly slow process is well shown by the results obtained with isopentane (*Proc. Phys. Soc.*, 1895, vol. xiii., p. 621; and *Zeits. Phys. Chem.*, vol. xxix., p. 210). Diffusion through a liquid must be still slower; and, considering the short time required for the determination of the vapour-pressure of a liquid at any one temperature, it is certain that the partial pressure of the mercury-vapour must be a very small fraction of the

maximum vapour-pressure; and, as it is quite impossible to form an estimate, it is safest to assume that no mercury-vapour diffuses through the liquid into the space above.

It must be admitted, however, that a small error is thus introduced, because, after the determinations of vapour-pressure at the highest temperatures, when the condensed liquid was carefully examined with a lens, minute globules of mercury could be seen adhering to the walls of the experimental tube.

It is evident, then, that, during the determination of vapour-pressure, minute quantities of mercury are constantly diffusing through the liquid into the vapour above. When the readings are taken during evaporation, both the total amount of mercury-vapour and the volume occupied by it will be increasing, and the partial pressure will remain small and fairly constant. But if, after the expansion, we again take readings during condensation, additional mercury-vapour will continue to diffuse through the liquid, while that in the space above will become more and more compressed. The partial pressure will, therefore, increase from both causes, and the error will be much greater at the smallest volume than at the largest.

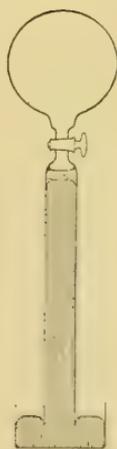
We have thus an additional reason for preferring readings taken during evaporation to those taken during condensation, and also for expecting larger errors at high temperatures than at low.

3. *Insufficient time for equilibrium before taking readings.*—When the volume is increased, evaporation takes place and heat is absorbed. The liquid in the experimental tube is thus cooled, and time must be allowed for heat to be received from the jacketing vapour. But when the experimental tube is cooler than the saturated vapour outside it, condensation of this vapour takes place and the heat thus evolved is rapidly communicated to the tube, and through it to the liquid inside. Experience has shown that a very few minutes suffice to bring about equilibrium even when the experimental tube is at first many degrees cooler than the vapour. On the other hand, when readings are taken during condensation, heat is evolved and the temperature rises slightly. But the fall in temperature of a superheated tube surrounded by the vapour of a boiling liquid is a very slow

process; and, unless much time is allowed before each reading is taken, the temperature and, therefore, the vapour-pressure will be too high, except at the first reading at the largest volume; the error also will tend to accumulate at successive readings. But if much time is allowed, the error due to vaporisation of mercury must increase, and that due to traces of air or other impurity may, and usually will, also increase. On all grounds, then, it is better to commence the readings of vapour-pressure at the smallest and not at the largest volume.

4, 5, and 6. As the errors coming under the last three headings may be in either direction, they do not specially affect the question under discussion, although they are of importance when the actual vapour-pressure of a liquid at a given temperature is being considered.

Battelli and others contend that the vapour-pressure of a pure liquid rises when the volume of vapour, relatively to that of the



liquid, is diminished. If that were really the case, it would, of course, make no difference in what manner the alteration in the relative volumes of vapour and liquid was brought about, whether by condensation, by evaporation, or by removal of part of the vapour or liquid. For example, imagine a barometer tube of the form shown in the figure. Let there be a short column of a pure liquid over the mercury, but below the stopcock, the whole space above the mercury containing nothing but the pure liquid and its

vapour; and let the temperature be kept constant by means of a suitable bath. Let the height of the mercury be first read with the stopcock open, when the volume of vapour is very large relatively to that of the liquid. Then let the stopcock be closed, so as to shut off the bulb. The volume of vapour will now be relatively small, and, according to Battelli, the vapour-pressure should therefore be higher. A depression of the mercury should in that case be observed.

That such a result would actually be obtained seems to me to be inconceivable; at any rate, there must, I think, be ample experimental proof of the variability of vapour-pressure before the formula $p = c$ at constant temperature is rejected.

It is only by the elimination of the errors to which reference has been made that the true relation between vapour-pressure and volume can be ascertained; and if variable pressures are observed, clear proof of the absence of such errors must be afforded. If, on the other hand, it can be shown that the more completely the errors are avoided or eliminated, the smaller is the variability of vapour-pressure with volume; and if, under the most favourable conditions, the variation is found to be negligible, then it may be concluded that satisfactory experimental evidence of the constancy of vapour-pressure has been obtained.

In studying the available experimental data, the following points should specially be noted:—

1. For the various reasons given, better results must have been obtained during evaporation than during condensation.
2. The errors are likely to be greater at high temperatures than at low ones.
3. If any signs of decomposition have been observed, the pressures are likely to be somewhat higher at small volumes than at large.
4. If there are two series of determinations of the vapour-pressures of a stable liquid, and a rise of pressure during condensation (or a fall during evaporation) is observed in the one series (*A*), but not in the other (*B*), and if the mean pressures in series *A* are higher than those in *B*, it may be concluded that air was not completely removed from the liquid in series *A*.

The three substances for which the data are most complete are isopentane, normal pentane, and normal hexane. All three hydrocarbons are perfectly stable, and the critical temperatures of the first two are so low that no appreciable error can have been caused by vaporisation of mercury.

In the opposite Table, details of the experimental results obtained with normal pentane are given, the data including the lowest and highest ratios of the volume of vapour to that of liquid ($V_{vap.}/V_{liq.}$) at each temperature, the corresponding vapour-pressures, the difference in mm., and the percentage difference between the observed pressures.

The mean percentage difference in pressure for the 38 determinations is -0.005 , whereas, according to Battelli, there should have been a marked positive difference.

Three different specimens of isopentane were prepared and examined, and there were altogether 59 determinations of vapour-pressure. Here, again, the mean percentage difference in pressure, -0.007 , was quite negligible, the apparent slight rise of pressure with expansion being, of course, due to experimental error.

With normal hexane the mean percentage difference for 32 determinations (two specimens having been examined) was $+0.074$, a value which, though positive and larger, may be regarded as within the limits of experimental error, an equally large negative value having been observed with di-isopropyl.

A full account of the experimental results, with a detailed discussion of the conclusions to be drawn from them, and of the influence of the various errors to which reference has been made in this paper, will be published in the *Journal de Chimie Physique*. It will be sufficient here to give the mean results obtained with each substance.

In several cases the results were not quite satisfactory, owing either to incomplete removal of air or to partial decomposition of the liquid investigated. The substances (or rather the series, for the same substance may appear in more than one group) are classified as follows:—

- I. Series in which no signs of decomposition were observed, and in which there was no evidence of more than a trace of air being present.

NORMAL PENTANE.

Temperature.	<i>V vap.</i> / <i>V liq.</i>		Vapour-Pressure.			
	<i>A.</i>	<i>B.</i>	<i>A.</i>	<i>B.</i>	Difference.	
SERIES I.					mm.	per cent.
40	0.66	2.42	875	872	+ 3	+ 0.34
50	0.63	2.38	1193	1193	0	0
60	0.60	2.34	1604	1604	0	0
70	0.57	2.27	2119	2121	- 2	- 0.09
80	0.53	2.20	2735	2736	- 1	- 0.04
90	0.50	2.14	3496	3499	- 3	- 0.09
100	0.47	2.08	4409	4410	- 1	- 0.02
110	0.44	2.02	5481	5483	- 2	- 0.04
120	0.40	1.98	6732	6746	- 14	- 0.21
130	0.36	2.06	8186	8187	- 1	- 0.01
140	0.35	2.19	9891	9894	- 3	- 0.03
150	0.30	2.20	11801	11802	- 1	- 0.01
160	0.46	2.50	14058	14061	- 3	- 0.02
170	0.39	2.73	16541	16538	+ 3	+ 0.02
180	0.30	3.09	19346	19351.	- 5	- 0.03
186	0.22	3.66	21191	21188	+ 3	+ 0.01
190	0.14	4.66	22499	22505	- 6	- 0.03
193	0.45	7.29	23535	23538	- 3	- 0.01
195	0.34	31.60	24247	24276	- 29	- 0.12
196	0.23	12.60	24677	24659	+ 18	+ 0.07
196.5	0.15	3.97	24848	24848	0	0
196.8	0.06	6.27	24957	24972	- 15	- 0.06
196.9	0.22	5.48	24992	24996	- 4	- 0.02
197.0	0.16	2.06	25012	25026	- 14	- 0.06
197.1	0.04	2.60	25056	25069	- 13	- 0.05
197.15	0.13	1.51	25088	25094	- 6	- 0.02
130	0.36	1.74	8194	8192	+ 2	+ 0.02
140	0.35	2.19	9912	9903	+ 9	+ 0.09
160	0.46	2.50	14050	14059	- 9	- 0.06
190	0.14	4.66	22473	22484	- 11	- 0.05
SERIES II.						
130	0.91	13.4	8203	8190	+ 13	+ 0.16
140	2.28	69.0	9898	9891	+ 7	+ 0.07
150	1.58	59.9	11833	11817	+ 16	+ 0.14
160	0.96	41.9	14047	14042	+ 5	+ 0.04
180	1.60	83.7	19345	19351	- 6	- 0.03
SERIES III.						
80	6.4	187.0	2734	2740	- 6	- 0.22
100	10.0	609.0	4417	4415	+ 2	+ 0.05
SERIES IV.						
40	35	106,000	873	872	+ 1	+ 0.11

- II. Series in which signs of decomposition were observed at the higher temperatures.
- III. Series in which the removal of air appears not to have been successful.
- IV. Acetic acid, which exhibits molecular association in both the liquid and gaseous states.

For each substance (except acetic acid) the number (N) of vapour-pressure determinations is given, together with the mean percentage difference (Δ) between the pressures corresponding to the lowest and highest volume-ratios ($V_{liq.}/V_{vap.}$). As the errors are likely to be smaller at low temperatures than at high, the data up to 180° and above 180° are given separately.

[GROUP I.

GROUP I.

Stable Substances free from Air.

SUBSTANCE.	Up to 180°.		Above 180°.		At all Temperatures.	
	N.	Δ.	N.	Δ.	N.	Δ.
Isopentane,	55	- 0·007	4	- 0·012	59	- 0·007
Normal pentane,	26	+ 0·005	12	- 0·027	38	- 0·005
Normal hexane,	17	+ 0·07	15	+ 0·08	32	+ 0·074
Normal heptane,	8	+ 0·08	9	+ 0·12	17	+ 0·10
Normal octane,	6	+ 0·07	13	+ 0·11	19	+ 0·10
Di-isopropyl,	13	- 0·16	6	+ 0·12	19	- 0·07
Di-isobutyl,	7	- 0·02	9	- 0·06	16	- 0·04
Hexamethylene,	10	+ 0·03	10	+ 0·05	20	+ 0·04
Benzene,	10	- 0·04	10	+ 0·01	20	- 0·015
Fluorbenzene,	10	+ 0·02	16	+ 0·07	26	+ 0·05
Chlorobenzene,	5	+ 0·11	9	+ 0·05	14	+ 0·07
Carbon tetrachloride, ..	—	—	11	+ 0·06	11	+ 0·06
Stannic chloride,	4	+ 0·03	11	+ 0·03	15	+ 0·03
Methyl formate,	15	- 0·03	10	+ 0·02	25	- 0·014
Methyl acetate,	12	0	20	+ 0·09	32	+ 0·06
Ethyl acetate,	11	- 0·008	11	- 0·005	22	- 0·006
Methyl propionate,	11	+ 0·08	12	+ 0·12	23	+ 0·10
Propyl acetate,	9	- 0·01	12	+ 0·15	21	+ 0·08
Ethyl propionate,	9	+ 0·01	12	+ 0·13	21	+ 0·075
Methyl butyrate,	9	+ 0·09	12	+ 0·20	21	+ 0·15
Methyl isobutyrate, ..	10	+ 0·04	12	+ 0·055	22	+ 0·005
	257	+ 0·009	236	+ 0·069	493	+ 0·037
Hydrocarbons only, ..	152	- 0·001	88	+ 0·047	240	+ 0·016

There can be no question about the stability of the hydrocarbons; and it will be seen that for the 152 determinations of the vapour-pressures of these substances up to 180°, the mean observed alteration of pressure with volume is quite negligible; for the

88 determinations above 180° , the mean observed fall in pressure with expansion is less than 1 in 2,000; and for the whole 240 observations, it is less than 1 in 6,000. Taking all the stable substances together, the mean fall in pressure for the 257 determinations up to 180° is less than 1 in 10,000; above 180° , the fall for 236 observations is 1 in 1,450; and for the whole 493 determinations, it is only 1 in 2,700.

There are 21 substances on the list; frequently more than one specimen was employed; and, as a matter of fact, this part of the investigation involved the preparation and purification of 32 specimens, and the filling of the experimental tube 45 times.¹

Assuming that the vapour-pressure is really independent of the volume, the theoretical value of Δ , 0.000, could only have been obtained if each of the 32 specimens had been absolutely pure and stable, if in each of the 45 fillings air had been completely expelled from the liquid and from the walls of the tube, and if there had been no vaporisation of mercury during any of the 493 determinations (or if the partial pressure of the mercury-vapour had been the same at the largest and smallest volumes in every case).

With a number of substances—the two pentanes, di-isobutyl, benzene, methyl formate, ethyl acetate, and, perhaps, stannic chloride—success seems to have been fully attained, and for several others the differences up to 180° are inappreciable; a complete absence of errors in the whole series of determinations could, however, not be expected.

¹ In this number a few cases are not included in which the liquid was found to contain air, and one in which a trace of non-volatile impurity was accidentally introduced.

GROUP II.

Cases in which Signs of Decomposition were observed.

SUBSTANCE.	Up to 180°.		Above 180°.		At all Temperatures.	
	N.	Δ.	N.	Δ.	N.	Δ.
Ethyl formate,	11	+ 0·02	14	+ 0·09	25	+ 0·06
Propyl formate,	12	+ 0·006	12	+ 0·13	24	+ 0·07
Isopropyl isobutyrate, ..	6	+ 0·14	8	+ 0·32	14	+ 0·24
Bromobenzene,	1	+ 0·30	25	+ 0·29	26	+ 0·29
Iodobenzene,	—	—	14	+ 0·04	14	+ 0·04
Carbon tetrachloride, ..	10	+ 0·19	13	+ 0·21	23	+ 0·20
Stannic chloride,	6	+ 0·26	10	+ 0·26	16	+ 0·26
	46	+ 0·107	96	+ 0·192	142	+ 0·164

It is to be expected that when a substance has undergone partial decomposition, fractionation will take place during evaporation or condensation, and that there will be a fall in pressure in the one process, and a (greater) rise in the other.

It should be noted that the experiments were carried out for the purpose of determining the vapour-pressure of the undecomposed substances, not of studying the effect of decomposition on vapour-pressure. Precautions were, therefore, in many cases taken to protect the substances from decomposition. If all the experiments had been carried out in the same manner as for the stable substances, the decomposition would, in some cases, have been much greater, and the results more striking. On the whole, the values of Δ are decidedly higher than for the stable substances.

GROUP III.

Effect of dissolved Air.

It was occasionally found, after filling and setting up a tube, that the liquid was not quite free from dissolved air. In such cases the tube was usually taken down at once, emptied, cleaned,

and refilled. On two occasions, however, readings were taken at a few temperatures, but were not made use of. The pressures were from 0.1 to 1.0 per cent. higher than were afterwards observed when the tubes were refilled, and the mean value of Δ for the eight determinations was 0.53, which is even higher than for any of the substances which had undergone partial decomposition.

GROUP IV.

The experiments with acetic acid do not throw much light on the question, and need not be discussed.

READINGS TAKEN DURING CONDENSATION.

A few observations were made both during evaporation and during condensation, and a comparison of the results obtained by the two processes is, therefore, possible.

1. *Stable Substances.*

The mean percentage changes in pressure during condensation, Δ_c , and during evaporation, Δ_e , and the differences between them, $\Delta_c - \Delta_e$, are given below, with the number of determinations, N , up to and above 180° .

Temperatures,	N	Δ_c	Δ_e	$\Delta_c - \Delta_e$
up to 180° ,	22	+ 0.206	+ 0.065	+ 0.141
above 180° ,	11	+ 0.269	+ 0.044	+ 0.225

The individual differences, $\Delta_c - \Delta_e$, were positive in every case but one, that of normal hexane at 80° , for which both Δ_c and $\Delta_e = 0$.

If the very slight fall in pressure frequently observed during evaporation were attributable to a real dependence of vapour-pressure on volume, the rise of pressure during condensation should be numerically equal to the fall during evaporation, except for errors in reading and slight differences which might be caused^{3a} by taking readings too quickly. If, on the other hand, the change in pressure is due to the presence of air, mercury-vapour, or other impurity, then, as has been pointed out, the rise in pressure during condensation should be greater than the fall during evaporation.

The fact that the rise was always (with the one exception) greater than the fall, therefore, affords evidence that the small positive values of Δ_e were due to the presence of minute quantities of air or mercury vapour.

2. *Substances which had undergone some Decomposition.*

Temperatures,	N	Δ_c	Δ_e	$\Delta_c - \Delta_e$
up to 180° ,	12	+ 0.57	+ 0.22	+ 0.35
above 180° ,	21	+ 0.96	+ 0.29	+ 0.67

As might be expected, the values of Δ_c , Δ_e , and $\Delta_c - \Delta_e$, are all much higher than for stable substances, and the influence of temperature is very marked.

The formula $p = c$ at constant temperature is not only of great intrinsic importance as an equation of state, but it has indirectly an important bearing on much of the experimental work that has been carried out on substances in the neighbourhood of their critical points. As is well known, many of the results obtained by different observers are contradictory, and are not in agreement with the views expressed by Andrews. Now, if the equation $p = c$ is really true—and in my opinion the experimental evidence brought forward in this paper affords ample proof that it is true—the variability of the vapour-pressure of any liquid during evaporation or condensation at moderate temperatures must be taken as a proof that that liquid contains air or other impurity (assuming, of course, that correct methods of heating, &c., are employed). But if the liquid is not free from such impurity, the phenomena observed near the critical point must, of necessity, be misleading. In my own work—and my results have consistently been in agreement with the views of Andrews—I have always regarded variability of vapour-pressure as a sure indication of the presence of impurity; and when such variability has been observed to any marked extent, I have discontinued the determinations and refilled the experimental tube. The results described in this paper show, I think, that in the case of a stable liquid, constancy of vapour-pressure at moderate temperatures is always attainable.

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JUNE, 1906.

NOTE ON THE SUBLIMATION OF SULPHUR
AT ORDINARY TEMPERATURES.

BY

RICHARD J. MOSS, F.I.C., F.C.S.

(PLATE V.)

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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X.

NOTE ON THE SUBLIMATION OF SULPHUR AT
ORDINARY TEMPERATURES.

BY RICHARD J. MOSS, F.I.C., F.C.S.

[PLATE V.]

[Read, JANUARY 16; Received for Publication, JANUARY 19; Published, JUNE 9, 1906.]

It is well known that sulphur evolves vapour at ordinary temperatures, though nobody has succeeded in measuring the tension of the vapour. In a paper entitled "Chemical Action between Solids,"¹ W. Hallock refers to an experiment of W. Spring, showing that copper sulphide may be produced by simple contact of copper and sulphur; and points out that contact is not necessary, as the vapour of sulphur acts upon the copper. As proof of this he states: "I have made the sulphide at ordinary temperatures with the two an inch apart, and a wad of cotton in the tube between them." Other similar proofs of the formation of vapour at ordinary temperatures might be mentioned; but so far as I can ascertain the actual formation of crystals by sublimation at ordinary temperatures has not been recorded. The following experiment may therefore be of interest.

Twenty-five years ago I placed some fragments of ordinary stick-sulphur in a thin glass tube 14 cm. in length, and $1\frac{1}{2}$ cm. in diameter. The tube was then exhausted by means of a Sprengel pump, sealed, and placed in a drawer in a horizontal position. I examined the tube with a pocket-lens from time to time; but not until nearly twenty years had elapsed did I detect any sublimate. When I first observed a very minute crystal, I hung the tube upon a wall, opposite a window facing due east, taking care to place the side of the tube with the crystal on it furthest from the wall. For the past five years I have examined the tube frequently, and observed the growth of crystals. The whole of one side of the

¹ The American Journal of Science, [3], vol. xxxvii., 1889, p. 405.

tube, the side furthest from the wall, is now studded with minute crystals, which sparkle with the brilliancy of cut diamonds.

The crystals could not be properly examined without removing them from the tube ; and I do not care to interrupt the experiment at this stage. They are apparently rhombic ; but they exhibit greater complexity than crystals deposited from sulphur solutions. The accompanying reproductions from photographs (figs. 1 and 2) give some idea of what the crystals are like. The photographs were taken under a magnification of fifty diameters. Owing to the cylindrical form of the tube, and to the fact that the crystals can only be seen in good definition from the side attached to the glass, it was difficult to photograph them properly.

The largest crystals are not more than 0·2 mm. in length ; and this is the growth of twenty-five years. The temperature has of course varied with the change of seasons ; but the temperature of Dublin is very equable ; and it is improbable that the tube has ever been at a lower temperature than 0° C. or at a higher temperature than 22° C. Had the tube been fixed to the wall throughout the whole period, I expect the crystals would have become visible at an earlier date ; because uniformity in the position of the tube with regard to surrounding objects would tend to localize the differences of temperature which cause the sublimate to settle upon certain parts of the tube. This condition has been observed for the past five years ; and during that time the increase in the number of crystals has been very marked. The increase in the size of some crystals is also very marked ; but the size and form of a crystal are well known to have an important influence upon its rate of growth.

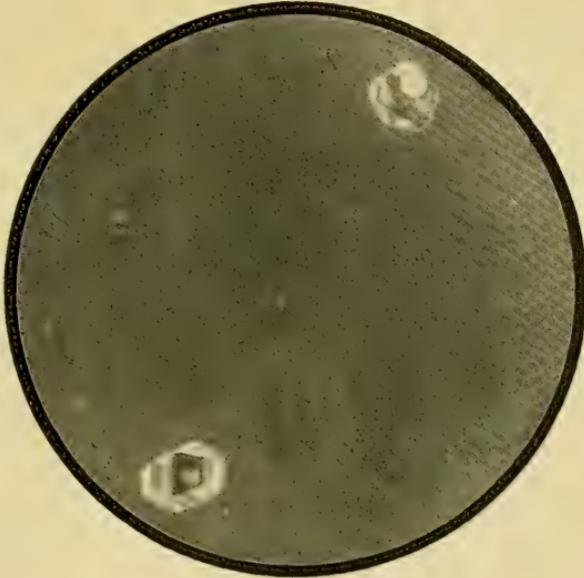


FIG. 1.



FIG. 2.

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ON A POSSIBLE CONNEXION BETWEEN THE ERUPTION
OF VESUVIUS AND THE EARTHQUAKE AT SAN
FRANCISCO IN APRIL, 1906.

BY

THE REV. H. V. GILL, S.J.

[COMMUNICATED BY PROFESSOR A. W. CONWAY, M.A.]

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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XI.

ON A POSSIBLE CONNEXION BETWEEN THE ERUPTION
OF VESUVIUS AND THE EARTHQUAKE AT SAN
FRANCISCO IN APRIL, 1906.

BY THE REV. H. V. GILL, S.J.

[COMMUNICATED BY PROFESSOR A. W. CONWAY, M.A.]

[Read, MAY 15 ; Received for Publication, MAY 18 ; Published, JUNE 15, 1906.]

THE following is a brief account of some simple experiments with rotating bodies, and an application of the principles illustrated by them to explain a possible connexion between seismic disturbances at different localities.

A perfectly balanced teetotum or top will spin about the axis of its spindle with great regularity. If a weight be attached to one side, it will spin with a "wobble." By placing an equal weight exactly opposite the first, regular spinning may be restored. The same result may be obtained by placing several equal weights at equal distances round the circumference.¹

A hollow teetotum was made $\frac{3}{8}$ inch deep, and $1\frac{1}{4}$ inch in diameter. This was made with great care, and could be covered by a plate which screwed on. A number of steel "ball-bearing" balls were also obtained.

1. The teetotum was set spinning, and spun with perfect evenness. While it was spinning, a ball of $\frac{1}{4}$ inch diameter was dropped in. At once the teetotum began to wobble, and the ball could be heard running round the inner edge. A second ball of the same size was then dropped in ; a slight movement of the balls was heard which ceased at once, the wobble disappeared, and once more the teetotum spun perfectly evenly, just as before it had been disturbed. The balls were found to have placed themselves at the opposite ends of a common diameter. The same

¹ *Nature*, April 19th, 1903.

result was obtained when three or more balls of equal size were dropped in. In all cases the balls took up positions equally distant round the circumference.

2. A small weight was attached to the circumference of the teetotum. It spun with a wobble. After several trials with balls of different sizes, one was found which produced even spinning, taking up a position opposite the weight.

3. The teetotum was half filled with water and covered. It spun quite regularly. By carefully arranging the amount of water in the teetotum and the weight of a ball which was also placed inside it, it was possible to obtain perfectly even spinning.

All the above results depend upon well-known principles, and are introduced to illustrate the matter under consideration.

By spinning the teetotum on plates of smoked glass, very interesting curves may be obtained.

Without entering into the discussion concerning the exact shape of the Earth, or the precise state—whether solid or liquid—of its interior, we may consider it as a sphere rotating with great velocity, containing, at least at certain localities, masses of matter which are capable of undergoing displacement. We are, besides, led to believe that volcanic disturbances and earthquakes are merely external indications of much greater disturbances beneath the surface of the Earth.

Suppose at a place near the equator there is, owing to whatever cause, an upward or downward displacement of matter. This would correspond to the addition or subtraction of a weight at a point on the circumference of the teetotum. The Earth would spin with a wobble. The effect of this would be to produce a stress on other points situated on a narrow belt round the Earth's circumference. The places of weakest crust would be the first to yield to this stress. If this resulted in a displacement of matter at a point diametrically opposite to the original disturbance, it would correspond to the addition of a ball to a weighted teetotum. If, however, the first place to yield were some point not diametrically opposite, the presence of these two disturbances, would, as illustrated by the teetotum experiments, produce a displacement at some third point. This would correspond to a teetotum containing three balls. A sudden displacement would be manifested as an earthquake, while a more gradual displacement

would produce a volcanic eruption.¹ In the ideal case the three localities would be expected to be equally distant. It is, however, evident that if the displacements were not of equal intensities, the distances between the places need not be the same, though, in general, we should expect them to be separated by considerable intervals.

That there is a connexion between the frequency of earthquakes and displacements of the poles was called attention to twenty years ago by Professor Milne, and has been studied by him in detail.² It has been calculated that every great earthquake between 1895 and 1902 caused an average displacement of the pole through $-0''\cdot00275$.³ The displacement of matter in connexion with earthquakes is also a fact recognised by writers on this subject.⁴

The theory here suggested is that one such displacement, whether it be gradual as in the case of an eruption, or more sudden as in the case of an earthquake, would be expected to give rise to corresponding displacements at other places more or less symmetrically situated with reference to the Earth's axis of revolution, producing earthquakes or eruptions as the case might be. The following principle on which this view is founded is illustrated by the teetotum experiments:—A rotating body, containing matter capable of shifting its position, tends to keep itself in a state of regular revolution about its axis, owing to the way in which the movable matter automatically disposes itself with reference to the axis of the body.

There were certain circumstances connected with the disturbances which characterised the middle of the month of April, 1906, which seemed strangely to fit in with the views here proposed.

In the first place the three disturbances took place within the space of ten days: Vesuvius very active on April 8th; great earthquake in Formosa, April 14th; earthquake at San Francisco, April 18th.

¹ "The Age of the Earth, and other Essays," by W. J. Sollas, 1905, pp. 84, 85.

² Bakerian Lecture, 1906.

³ Kövesligethy. *Die Erdbebenwarte*, Vol. III., 1904, pp. 196–202.

⁴ British Association, Fifth Report on Seismological Investigation, 1900, p. 109.

Secondly, these three places are all situated on a narrow belt parallel to the equator.¹

Thirdly, the distances between the places are comparable; the differences in longitude are as follows:—

Between Formosa and San Francisco,	116° 34'.
„ Formosa and Vesuvius,	106° 34'.
„ San Francisco and Vesuvius,	136° 52'.

Fourthly, as far as can be judged, the disturbances were of comparable intensities.

All these facts seem to justify the suggestion that these disturbances may have been connected in the way pointed out in this paper. The following sequence of causes and effects might, in view of the theory here suggested, be tentatively proposed: Vesuvius has been more or less active for some considerable time past. A displacement of material in its neighbourhood would have given rise, owing to causes illustrated by the teetotum experiments, to a stress round the Earth's circumference. The places of weaker crust would have given way; Formosa would have been the first to yield: hence the earthquakes there of March 17th and April 14th. The final effect of these two causes—*i.e.*, Formosa and Vesuvius—would have been the earthquake at San Francisco. The latter place is just where we should have expected the connected earthquake to occur according to the views just set forth, especially as that place is located in a region of weaker crust.

It is hardly necessary to add that, in phenomena of so complicated a nature, and depending on many causes, the effect of the forces referred to in this paper would, in many cases, be expected to be partially or totally neutralized by other influences.

¹ Formosa,	Lat. 23° 30' N.	Long. 121° E.
San Francisco,	„ 37° 47' N.	„ 122° 26' W.
Vesuvius,	„ 40° 47' N.	„ 14° 26' E.

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OCTOBER, 1906.

ON ENTOPTIC VISION.

[PART IV.]

BY

PROFESSOR W. F. BARRETT, F.R.S.,

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(PLATES VI.-VIII.)

[Authors alone are responsible for all opinions expressed in their Communications.]

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XII.

ON ENTOPTIC VISION.

PART IV.

BY W. F. BARRETT, F.R.S.,

Professor of Experimental Physics, Royal College of Science for Ireland.

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(PLATES VI.—VIII.)

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THE sense of sight is intended and adapted for the perception of the external world; hence the training of the organ of vision from infancy onwards has rendered it an exquisite instrument for the detection and localization of visible phenomena in the world outside ourselves. But the retina receives impressions from objects within as well as from without the eye; these impressions we have learnt to disregard, and hence do not perceive them unless they are novel and insistent. But even faint, unheeded retinal impressions, from a source within the eye can usually be perceived if they are sought for. The perception of those phenomena the seat of which is within the eye may be called *Entoptic vision*; and the perception of phenomena the seat of which is outside the eye may be termed ordinary or *Exoptic vision*.

In two previous communications which I have recently made to the Society, I have described certain entoptic phenomena, consisting of shadows cast on the retina by minute obscurities within the eye, which are perceived when a luminous point is near the eye.

In high-power microscopy a minute brilliant focal point is formed in such a position that these obscurities, if existing, are well perceived; more conveniently a luminous point is obtained by illuminating a minute aperture in an opaque screen held near the eye. The shadows thrown on the retina can now be projected through the aperture to form an enlarged virtual image on a ground-glass screen at some distance from the eye. This is the principle of the Entoptiscope devised by the author, and described in Part II. In this way not only can incipient cataract be detected, delineated, and its progress observed, but many other entoptic phenomena can be examined with ease.

The present communication deals with a class of entoptic phenomena briefly referred to in Part III., which, though long known, I have recently submitted to careful examination. In this work I have been assisted by one of my senior students, Mr. J. Ledwidge, A.R.C.S.C., who has remarkable facility for perceiving and depicting these phenomena. Mr. Ledwidge has recorded his observations in a Note appended to this paper.

I. HAIDINGER'S TUFTS.

In the year 1844 Professor W. Haidinger, the distinguished geologist and physicist of Vienna, discovered the curious fact that, on looking through a Nicol's prism at a bright sky, there was seen in the direct line of vision a pair of small yellow cones joined apex to apex, like an hour-glass.¹ These the discoverer called *Büschel*, in French *houppes*, or tufts, and they are now universally known as "Haidinger's brushes," though *tufts* would be a more correct translation and designation.² At right angles to these tufts a pale blue or violet colour is usually seen filling the larger space on each side of the apex of the yellow cones (see Plate VI., fig. 1). The major axis of the yellow tufts coincides with the

¹ Poggendorff's *Annalen*, 1844, vol. lxiii., p. 29.

² Brewster speaks of the tufts as "brushes," "tufts," "sectors," and in several places he calls them "bushels"—a term which puzzled me, and doubtless other of his readers, until I found it was meant for the German *Büschel*. I would suggest *fascicula lutea* as a more appropriate name. This would have the advantage of a verbal association with the *macula lutea*, or yellow spot, with which they are closely connected.

plane of polarization of the Nicol's prism, and rotates with the rotation of the Nicol.

If the Nicol prism be kept unmoved, the appearance fades away, and in a few seconds the tufts have vanished from view. When, however, the Nicol is suddenly turned to a different plane, they reappear, only to fade away again in five or six seconds, reappearing on every change in the plane of polarization. This fact, together with the faintness of the light of the tufts, explains why so many persons have failed to see them; for the longer the observer gazes through the Nicol, if the plane of polarization be unchanged, the more hopeless will be the search for "Haidinger's brushes." Brewster states that, in spite of repeated efforts, it was more than twelve months before he saw the yellow tufts, or sectors¹; and Helmholtz remarks that, "malgré les plus grands efforts," he tried in vain for twelve years before he perceived them.²

If the following instructions are attended to, few persons will have any difficulty in seeing what Haidinger discovered. Choose a bright sky, or a white surface brightly illuminated either with the sun, the electric light, or even an incandescent gas-mantle; hold the Nicol close to one eye and shut the other eye; look through the Nicol at the illuminated surface, and there will be seen directly in the line of sight at the extremity of the optic axis, a faint yellow figure very like a little hour-glass, and occupying only a small part of the field of view, subtending an angle of about 3° to 4° in fact. The general appearance and relative magnitude of the yellow tufts compared with the whole field of the Nicol's prism when the open sky is viewed, are shown in Plate VI., fig. 1. The complementary violet tint which fills the space between the yellow tufts is more difficult to see, and has, by Jamin and some others, been attributed to the effect of colour contrast, and, therefore, to a purely subjective effect. This view is, however, rendered improbable from the fact that the blue tint is well seen when a polished black surface is used as the reflecting body. Moreover, one or two friends of mine have found that the blue sectors are seen more distinctly than the yellow, which latter is only faintly visible to one of these observers.³

¹ Brewster's *Optics*, p. 246.

² Helmholtz, *Optique Physiologique*, p. 552.

³ See foot-note, p. 121.

In from three to seven seconds the tufts disappear if the plane of polarization of the Nicol be kept stationary, the period of their duration becoming shorter, and their shape less distinct, as the retina grows fatigued from observation. When a blue glass is held before the Nicol, the tufts appear somewhat smaller, and of a dark-reddish tint, due to the absorption of the yellow rays by the cobalt-blue glass, which transmits the extreme red as well as the blue. Though smaller, the dark tufts seen through a blue glass are somewhat more conspicuous than the yellow when viewed on a bright sky. Hence, if any observer finds a difficulty in seeing the yellow sectors, he should try a blue glass, rotating the Nicol through 90° every two or three seconds.

The fugitive appearance of the tufts when the conditions of observation are unchanged is characteristic of several other entoptic phenomena. Thus the *macula lutea*, or yellow spot, which can easily be seen by the use of proper absorbent media (see p. 120), soon disappears when looked at steadily. It is, however, less fugitive than Haidinger's tufts; on the other hand, the tufts or polarized sectors can be kept continually in view by a very slow rotation of the Nicol's prism: even one revolution in half a minute I find enables them to be kept in sight, their longer axis revolving at the same rate as the Nicol.

Fig. 2, Plate VI., shows the appearance, size, and tint of the yellow tufts, as seen projected on a brightly illuminated sheet of white paper placed 150 to 160 cm. (about 5 feet) from the eye.¹ When the plane of polarization is horizontal, and the Nicol suddenly removed from the eye, the tufts will still be seen faintly, but in a plane at right angles to their previous position. This is, no doubt, due to the feeble polarization of the light reflected from the paper, the Nicol in the first instance localizing their position, for if black glass or a polished surface be substituted for the paper, the effect is much more conspicuous; moreover, under such circumstances, the tufts can be seen in a vertical plane without using the Nicol at all. The light of the sky is polarized at 90° from the sun; hence those who are familiar with the appearance of the yellow tufts can faintly see them without the aid of a Nicol by looking at a bright sky

¹ The plane of polarization in this case is horizontal.

in a position at right angles to that of the sun. By means of Haidinger's tufts the unaided eye can thus not only detect polarized light, but determine its plane of polarization.¹

The tufts, however, cannot be seen, as was first pointed out by Sir G. Stokes,² in light of lower refrangibility than the green. Projecting a brilliant spectrum on to a white screen and looking at the colours through a Nicol's prism, successively from the red to the violet, it will be noticed that the tufts first appear in the green, about the F line, and that they remain visible until the limit of the more refrangible end of the visible spectrum is reached. This explains why Haidinger's tufts cannot be seen in artificial light of low refrangibility, though with ordinary gas-light they may be faintly perceived, not, however, yellow, but of a reddish tint.

Various attempts have been made to explain this curious phenomenon, which for some years after its discovery excited much interest throughout the scientific world. Evidently the cause must be due to some structure in the eye which acts as an analyser to the polarized beam; but what that structure is has excited considerable discussion. We have also to consider the colour and shape of the tufts which suggest that a bi-refracting or depolarizing medium exists in the eye, the light transmitted through which being afterwards analysed by the polarizing structure referred to.

J. T. Silbermann³ pointed out that both the cornea and crystalline lens of the human eye were in each case bi-refracting, but considered the lens to be the origin of the tufts, owing to its structure. This hypothesis was, however, shown to be incorrect by Zokalski,⁴ an eminent Paris oculist, who found that the tufts could be seen when no crystalline lens was present in the eye, four aphakic patients of his seeing Haidinger's tufts clearly.

J. Jamin was of opinion that the cornea was the medium which

¹ Mr. C. T. Whitmell writes to me:—"Haidinger's brushes have always interested me, for I see them every day when I glance at a polished table or at a shining black-board or book, or at the sky 90' from the sun. Thus I can at once find, from the direction of the yellow brushes, the plane of polarization of the reflected light, without the aid of any apparatus but what everyone has in his own eye."

² British Association Reports, 1850, Transactions of the Sections, p. 20.

³ *Comptes Rendus*, 1846, vol. xxiii., p. 629.

⁴ Quoted by Brewster, *Comptes Rendus*, 1859, vol. xlvi., p. 616.

caused the phenomenon.¹ He compared the cornea to a pile of watch-glasses, or layers of lenses centred on a common axis. Jamin states that when such a system is held before the eye and examined with polarized light, an appearance is seen in shape somewhat like Haidinger's tufts. If now a thin bi-refracting crystalline plate, with its axis inclined to the plane of polarization, be placed before this system, when polarized light is transmitted, the appearance of the tufts is fairly well reproduced, as they are now seen coloured with the complementary tints due to the crystal.

Examining the cornea of a pig's eye, which much resembles the human eye, I found it to be strongly bi-refracting; but no appearance resembling Haidinger's tufts was seen when it was placed on the stage of a polariscope.² Moreover, there are many objections to Jamin's theory that the tufts are due to the cornea. The small angular magnitude of the tufts is against this theory; if produced by the whole pencil of rays passing through the cornea and pupil, they should occupy practically the entire field of view instead of the small area actually observed. The Rev. J. Power, of Cambridge, on the other hand, maintains that only a small portion of the cornea is concerned in their production; and he shows by mathematical investigation that under such conditions the curves of equal intensity of light will be equilateral hyperbolas, which, in fact, appear to correspond with the shape of the tufts.³

Sir David Brewster,⁴ however, in an important paper, published in the *Comptes Rendus*, which appears little known in England, pointed out a number of valid objections to the corneal origin of the tufts. It is needless to summarize these. Brewster shows that even when an opaque screen, with a very minute aperture, $\frac{1}{50}$ of an inch (half a millimetre) in diameter, was held before the eye, the tufts were still seen of the same size and shape, though much enfeebled in light; nor was any change in their appearance produced when a very narrow slit replaced the minute aperture, and the slit slowly rotated in front of the cornea.

¹ *Comptes Rendus*, 1848, vol. xxvi., p. 197.

² Either with or without the analyser.

³ *Phil. Mag.*, 1858, vol. xvi., p. 69.

⁴ *Comptes Rendus*, 1859, vol. xlviii., p. 614.

The Entoptiscope, described in my former paper,¹ affords a ready and conclusive means of determining whether the tufts are due to any of the refracting media in the eye. Using a double pin-hole aperture in the diaphragm, each pin-hole being 0.4 mm. in diameter, and the two separated by a space of 1.5 mm., the tufts can be seen when a good light is used and a Nicol's prism placed before the diaphragm. If the tufts are solely caused by any structure in front of the pupil, a double image of the tufts will be seen *more* widely separated than the centres of the duplicated pupillary disc; if due to the crystalline lens or vitreous humour, a double image of the tufts will be seen *less* widely separated than the pupillary discs. Experiment, however, shows that only a *single* image of the tufts is perceived; their origin is, therefore, in the retina itself. This was the view held by Brewster, who maintains that the origin of the tufts must be sought for in a region at the extremity of the optic axis, and suggests that their cause may be due to some peculiar bi-refracting property possessed by the *foramen centrale* (the *fovea centralis*) of the retina.² Haidinger, in a letter to Sir G. Stokes, first published in Stokes's collected papers,³ also takes this view, and (apparently unaware of Brewster's paper) shows that Jamin's theory and experiments do not meet the facts. Helmholtz⁴ strongly supports the retinal origin of the tufts, though he makes no reference to Brewster's paper. Helmholtz points out that many organic fibres and membranes are bi-refracting, and in general act like uniaxial crystals, the axis being parallel to the direction of the fibres, or at right angles to the surface of the membrane. The production of the tufts could thus be explained by assuming that the fibrous layer of the macula lutea (the yellow spot) is bi-refracting, absorbing the extraordinary ray more strongly than the ordinary. The peculiar shape of the tufts, Helmholtz suggests, may be due to the direction of the fibres in the *fovea centralis*, which constitutes the small retinal depression in the centre of the yellow spot. He goes on to remark (quoting from the French edition):—

“Ainsi, d'après l'hypothèse que nous avons faite, un bord de la *fovea*, où les fibres ont en général une direction oblique dirigée vers

¹ See Proc. Roy. Dublin Soc., vol. xi., pp. 60 and 73.

² Brewster, *loc. cit.*, also “Treatise on Optics,” p. 249.

³ “Mathematical and Physical Papers,” by Sir G. Stokes, vol. iv., p. 60.

⁴ *Optique Physiologique*, p. 553.

le centre de la dépression, la lumière devrait subir une absorption plus forte aux endroits où les fibres sont parallèles au plan de polarisation. Si ce plan est vertical, il se formera des parties obscures au-dessus et au-dessous de la *fovea*, des parties claires à droite et à gauche. De même il devrait se présenter des parties plus sombres aux endroits où les fibres ne sont plus obliques à la surface de la rétine, c'est-à-dire au centre même de la *fovea* et vers le bord de la tache jaune. On a vu le phénomène des houppes de polarisation répondre à ces conditions."¹

The coincidence of Haidinger's tufts with the yellow spot was first discovered by Clerk Maxwell, who, in a note communicated to the British Association in 1856, after showing how the yellow spot could be observed, remarks: "By using a Nicol, the brushes of Haidinger are well seen in connexion with the spot; and the fact of the brushes being the spot analysed by polarized light becomes evident."² This, I believe, is the earliest suggestion of the true origin of the tufts.

That Haidinger's tufts are exactly coincident in position with the yellow spot of the retina can easily be proved by means of a coloured screen which transmits light containing no yellow rays, and thus enables anyone to see the yellow spot in their own eyes as a dark patch. The best coloured screen I have tried for this purpose is due to a suggestion made to me by Mr. Whitmell, author of an admirable treatise on colour. This screen consists of a weak solution of the double oxalate of chromium and potassium, which is quite opaque to the yellow and orange rays. Holding such a solution near the eye, before a brightly lighted white surface, the yellow spot is seen most conspicuously as a reddish patch on the general bluish-green ground. If now a Nicol be held before the solution, Haidinger's tufts, or, as I have suggested they should be called, the *fascicula lutea*, can be seen precisely coincident in position with the *macula lutea* or yellow spot.

The retinal area of both the fascicula and the macula varies slightly in different people; it is difficult to fix the exact boundary of the former, but so far as they can be traced, their longer axis is practically coincident with the diameter of the macula or yellow spot. The latter is somewhat elliptical in shape,

¹ Helmholtz, *Optique Physiologique*, p. 554.

² British Association Reports, 1856, vol. ii., p. 12; also Maxwell's Collected Papers, vol. i., p. 242.

the major axis being horizontal, and in like manner the fascicula or tufts appear somewhat longer when seen in a horizontal than in a vertical plane.

Knowing the distance of the nodal point from the retina,¹ the retinal area covered by the tufts can be found by measuring the size of the projected image and its distance from the eye. This does not appear to have been hitherto measured, nor can I find any similar subjective measurements of the yellow spot. I have therefore obtained several determinations of both the macula and the fascicula from different observers. The general result gives the vertical diameter of the yellow spot, and also the vertical axis of Haidinger's tufts on the retina as about 0·8 mm.; the horizontal diameter in both cases is a little greater, going up about one mm. Post-mortem measurements of the yellow spot are found to vary according to the subject. Kölliker found the vertical diameter 0·8 mm., and the horizontal considerably greater; but E. H. Weber made the horizontal diameter 0·8 mm.; so that our subjective measurements may be taken as agreeing with the objective measurements made after death, or on extirpated eyes. The area of the *fovea* is, however, much less than that of the yellow spot; its greatest length does not exceed 0·2 mm. Accordingly, the view taken by Helmholtz and Brewster, and hitherto generally accepted, that Haidinger's tufts are restricted to the *fovea centralis*, is incorrect: their extent is four times greater, and corresponds, as I have said, to the limit of the yellow spot.

Now, throughout the yellow spot the rods of the bacillary layer of the retina are absent; the cones only are present; and it would seem as if some connexion existed between this special structure and the perception of the tufts—that is to say, the detection of polarized light and of the plane of polarization by the unaided retina.

2. THE MACULA LUTEA OR YELLOW SPOT.

It is a singular fact that the region of most distinct vision on the retina should be coloured yellow. One would have thought that this would seriously interfere with colour-perception, especially of blue and green; but we are not conscious of this under ordinary

¹ See Part I., Proc. Roy. Dublin Soc., vol. xi., p. 53.

conditions, albeit, as Sir W. Abney has shown, the selective absorption exercised by the yellow spot does prevent accurate work in matching colours when that part of the retina is used. This occurs when the colours to be matched are held at such a distance from the eye that the retinal image falls on the yellow spot. When the eyes are near to the colours to be matched, say, at the distance of about 2 feet, the retinal image is large, and extends considerably beyond the region of the yellow spot. When, however, the colours are held at a considerable distance from the eye, the retinal image is small, and may be made to fall entirely within the area of the yellow spot. Under such circumstances the blue-green rays are largely absorbed by the spot, and an error in matching those colours then occurs.¹

That there is a definite selective absorption of light by the macula lutea in the living eye was shown by Stokes—quoted by Maxwell²—who employed a weak solution of chromium chloride, through which a white surface was viewed. The solution is of a blue-green colour, transmitting the blue, green, and also the red rays, but opaque to yellow. Accordingly, when a bright cloud or a sheet of white paper, illuminated by the sun or by a beam from the electric light, is viewed through this solution, a dark reddish patch will be seen in the midst of the bluish-green ground, owing to the yellow spot being largely opaque to the blue-green rays of the incident light. As already mentioned, the solution suggested by Mr. Whitmell is even more effective—the double oxalate of chromium and potassium, which is quite opaque to the yellow and orange rays. A bluish gelatine film also serves very well, and is convenient to use. The yellow spot can also be seen if the eye traverses the spectrum.³

Maxwell states that in persons of a dark complexion, the yellow spot is more pronounced than in fair persons. I do not know if examination of extirpated eyes has confirmed this: it would be interesting to know. So far as my own experience

¹ See *Colour Measurement and Mixture*, by Sir W. Abney, D.C.L., &c., p. 117.

² British Association Reports, 1870, page 40; also Maxwell's Collected Papers, vol. ii., page 279.

³ According to Tscherning (*Physiological Optics*, p. 198), there is no trace of a yellow colour seen in the macula when the living eye is examined by the ophthalmoscope! Is this really the case, or is it due to the absence of the yellow spot in certain individuals?

has gone, I have found fair complexions see the yellow spot (by means of the oxalate solution) quite as distinctly as persons with dark complexions. In Plate VII. the shaded, nearly circular patch, marked Y, is the yellow spot as seen by two assistants and myself. Mr. Warwick is dark-complexioned, with black hair. Mr. Ledwidge is fair, with light hair; and I am, or was in youth, more fair than dark. It will be noticed that the area of the yellow spot is nearly the same in all, being slightly larger in the fairest complexion, Mr. L.; the squares represent half millimetres, so that its diameter is about one millim.¹ The horizontal diameter of the macula (as already remarked) is, as a rule, slightly greater than the vertical; its boundary is somewhat irregular and indistinct, but no attempt was made to reproduce this in the drawing.

In determining the area of the macula, the observer was seated about 1 metre from a large sheet of squared paper; and a glass trough, with a weak blue-green solution of oxalate of chromium and potassium, was placed near to one eye, the other eye being closed. The paper was brightly illuminated by the sun, and the horizontal and vertical boundary of the dark reddish patch were noted by the observer and marked on the paper. These intervals were then measured, and also the distance of the paper from the eye. Mr. W. has normal sight; Mr. L. slightly myopic; and I am presbyopic, but had normal sight until recent years. Taking the nodal point as 16 mm. from the retina, except in Mr. L.'s case, when 17 mm. was used, as being more nearly correct, the horizontal diameter of the macula was found to be nearly a millimetre (0.9 mm.); and the vertical slightly less. The angle subtended by the yellow spot is a little over 3°.²

3. THE PUNCTUM CÆCUM OR BLIND SPOT.

It is well known that a lacuna exists in the field of vision corresponding to the region where the optic nerve enters the eye; in this region the sensory filaments of the retina are absent. The

¹ It may only be a chance coincidence, but the two observers who saw the blue sectors in Haidinger's tufts so very clearly were both persons of very fair complexion and light hair.

² Not "6° to 8°," as some authorities state.

blind spot or *punctum cæcum* was discovered by Mariotte upwards of two hundred years ago, and is therefore termed "la tache de Mariotte" in France. As the optic nerve enters the eye on the inner or nasal side of the yellow spot, and a little below the level of the latter, in the visual field the blind spot appears to be slightly *above* the level of the yellow spot, and on the *outer* side of it, owing to the inversion of the projected image. (Expl. Pl. VII.)

The distance which separates the centre of the blind spot from the centre of the yellow spot—the point of fixation of the eye—has been the subject of numerous experiments by Listing, Helmholtz, Dobrowolsky, Mauthner, Snellen and Landolt, and others. The general results of these measurements show that, from the point of fixation to the centre of the blind spot, an angle of 15° is subtended in normal or emmetropic eyes: in the case of myopic eyes the angle may be as small as 11° , and in hypermetropic eyes as large as 19° . This difference obviously arises from the fact that the eyeball is longer in myopic and shorter in hypermetropic than in normal eyes. The *linear* distance, D , between the two points (the centres of the macula and of the papilla) depends upon this angle, a , and on the distance of the nodal point, κ , from the retina, or

$$D = 2\kappa \sin \frac{a}{2} .$$

If κ be taken as 16.6 mm. for emmetropic or normal eyes, as Landolt, Snellen, and Hirschberg have found, then the angle 15° gives D as = 4.3 mm. If κ be taken as 16, then the distance becomes a little less, viz. 4.14 mm. Measurements made upon extirpated eyes correspond to this value.¹

I am indebted to the eminent London oculist, Dr. Lawford, for some measurements of this distance in microscopic slides of the retina (section through the *fovea*). Dr. Lawford finds the mean of three different cases to be 4 mm.; but he hopes to give me some further measurements immediately after removal of the eye.

The dimensions of the blind spot have been found in like

¹ According to Snellen and Landolt, *Traité complète d'Ophthalmologie*, vol. i., p. 621. A full discussion of the blind spot is given in this work.

manner; but there is a considerable difference in the results obtained. The angle subtended by the horizontal diameter has been found by different observers to vary from $3^{\circ} 40'$ to $9^{\circ} 40'$, and the vertical diameter also to vary considerably. The mean of numerous measurements made by Mauthner, on different eyes, gives 6° as the angle subtended by the horizontal diameter of the blind spot;¹ this corresponds to a linear diameter of 1.7 mm., taking the nodal point as 16.6 mm., or 1.67 if the nodal point be taken as 16 mm. This agrees with my own observations (see below), and fairly well with the average obtained by other observers, and also with the actual measurements made after death, or in extracted eyes.

It occurred to me that it would be desirable to repeat these measurements; not only to ascertain the area of the blind spot in a few cases, but also and chiefly for the purpose of finding the value of the important factor κ —the distance of the nodal point from the retina. For this purpose the observer was seated at a definite distance (about a metre) from a sheet of squared paper fixed vertically, and kept one eye (the other being closed) steadily fixed on a mark made on the paper. A blackened drawing-pin, which was fixed to a wire handle, was then moved outwards from the point of fixation until it disappeared from view. This point was marked, and the movement was continued until it re-appeared, when a second mark was made. The vertical diameter was determined in like manner; and the general outline of the blind spot was also found. The same three observers as before (myself, Mr. Warwick, and Mr. Ledwidge) tried the experiment; the result of numerous repetitions closely agreed.

Using the same letters as above, $\frac{D}{k} = \tan a$; hence, if D be taken as 4.2 mm., k can be found by measuring the angle between the centres of the blind spot and of the yellow spot, as seen projected from the eye. On the other hand, taking κ as 16 in my case and Mr. W.'s, and 17 in the case of Mr. L., the distance from the centre of the macula to the centre of the papilla (the blind spot) came out as 4.2 mm. to 4.25 mm. in all three cases. (See B, Plate VII.)

¹ According to Snellen and Landolt, *Traité complète d'Ophthalmologie*, vol. i., p. 621.

The horizontal and vertical diameters of the blind spot, in the three cases, were as follows in mm. :—

Mr. W.,	hor. dia.	1·6,	ver. dia.	1·8	m.m.
Mr. L.,	„	1·5,	„	2·0	„
Prof. B.,	„	1·7,	„	2·6	„

The remarkable vertical length of the blind spot in my own case surprised me; the results are shown on Plate VII. The foregoing results were obtained before I was aware of the measurements made by Continental observers, to which I have already referred. The agreement is remarkable, and establishes the value of κ which we have taken.

4. PURKINJE'S FIGURES.

In 1819 the eminent German physiologist Purkinje noticed that when a candle, held at the side of the head, was moved up and down in an otherwise darkened room, an arborescent figure was seen in the field of vision of the observer, the figure being projected from the eye adjacent to the moving candle. The appearance exactly resembles the branching network of vessels on the retina, and Purkinje rightly concluded that it was caused by the shadow of those vessels thrown on the retina by the glare of the candle. Sir Chas. Wheatstone, in a paper read before the British Association in 1832,¹ showed that, instead of a moving candle, a revolving disc with a circular aperture might be employed, the moving disc being placed between the eye and a source of light.²

Wheatstone also first explained why the appearance was only seen when the candle or the disc was in motion: he showed that to perceive any very small differences of illumination the retina must be extremely sensitive, and that this sensitiveness rapidly decreases when the shadow is stationary owing to the same parts of the retina being stimulated. But when the shadow is

¹ British Association Reports, 1831-32, p. 551. Wheatstone's Collected Papers, p. 223.

² A simple method, which some find successful, is to make a large pin-hole in a piece of card, and, looking at a bright sky or brightly illuminated surface, move the card, which should be close to the eye, from side to side, or up and down; the finer retinal vessels can thus be seen.

made to change its place, by moving the candle or the perforated disc, fresh portions of the retina come into action; and the previously fatigued portions rapidly recover their sensitiveness by a momentary rest. Hence by continually changing the position of the shadow on the retina the figure remains continuously in view.

This experiment shows how quickly the retina becomes fatigued, and how quickly it recovers its sensitiveness for the perception of small differences of stimulation. This, as we have seen, is particularly noticeable in the perception of Entoptic phenomena. A similar result, as is well known, is seen in viewing the image of an extremely faint star; or in detecting the movement of a flame in rapid vibration, such as the so-called singing flame. In the latter case the separate oscillations of the flame, though they may amount to several hundreds per second, can readily be detected by a rapid change in the position of the retinal image, brought about by moving either the eye or the flame, or by rapidly moving a small telescope through which the flame is viewed.

Purkinje's experiments also reveal the fact that visual sensations originate in a part of the retina more deeply seated than the vessels, that is, somewhere between those vessels and the choroid coat.

There are other ways of seeing Purkinje's figures than by a moving candle. It is not generally known that long prior to Purkinje Dr. Thos. Young described a method by which he was able to see the retinal vessels of his own eye. The experiment is described in the first paper published by Young, entitled "Observations on Vision," read before the Royal Society when he was only nineteen years old, and published in the Transactions of the Society for 1793. Young found that by intermittent and forcible pressure on the eyeball he observed "an appearance of luminous lines, branched and somewhat connected with each other, darting from every part of the field of view towards a centre a little exterior and superior to the axis of the eye. This centre corresponds to the insertion of the optic nerve; and the appearance is probably occasioned by that motion of the retina which is produced by the sudden return of the circulating fluid into the veins accompanying the ramifications of the arteria centralis,

after having been detained by the pressure which is now intermittent."¹ I am not aware that anyone has hitherto drawn attention to this early experiment of Young and his remarkably correct explanation of what he observed.

A much better and more convenient method of vividly seeing Purkinje's figures is to allow a brilliant point of light to fall on the sclerotic coat near the cornea. For this purpose it is best to use a pencil of rays from the electric-light or lime-light, though any bright source of light will do if the rays are concentrated by a short focus lens on to the sclerotic. The observer should be seated in a darkened room; and an assistant should manipulate the lens so that the beam of light falls at the right spot where the sclerotic is thin, as it is around the cornea. In this case the shadows of the retinal vessels are thrown directly on the retina by the glare of light from the illuminated point of the sclerotic. The appearance that suddenly starts into view has been admirably depicted by Mr. Ledwidge, and is shown in fig. 1, Plate VIII. In my own case I see the finer capillaries, after branching, again uniting into a single larger vessel. This occurs in all the smaller ramifications seen in the field of view; but Mr. Ledwidge has drawn what he has seen near the *fovea*, where the finer capillaries do not appear to unite again.

The field of view is more extensive than is shown on the plate, a portion only of the original coloured drawing having been reproduced in black and white. The background is of a bright yellow or orange colour; and one portion of the field appears to contain few or no vessels, and has in its centre a peculiar granular or cellular structure. This Mr. Ledwidge will describe in an appended Note, as he saw it more clearly than I did. Helmholtz refers to this particular appearance and compares it to "shagreen leather." If the head be moved slightly in one direction, the magnified projected shadows of the vessels, seen, of course, inverted, will correspondingly be displaced; but the peculiar granular spot will be less displaced than the shadow of the vessels, showing that it is nearer the seat of vision.²

¹ Philosophical Transactions, 1793, vol. lxxxiii., p. 169. Young's Collected Works, vol. i., p. 10.

² Mr. Ledwidge found this smaller displacement to be in the opposite direction to the general network of vessels. (See his Note at end.)

The amount of displacement may be used, and has in fact been used, to estimate the distance between the retinal vessels and that part of the retina where visual impressions originate. This will become clear from the accompanying diagram, fig. 1, which shows how Purkinje's are formed when the illumination is derived from a bright spot of light thrown on the sclerotic. If a be the illuminated point falling on the sclerotic (it should be shown much nearer the cornea), the shadow of a retinal vessel is thrown directly on the retina at the point α , and thence projected, through the nodal point k , to some external position A , where an inverted image is seen. If the point of light be moved to b , the projected image will move to B , or in the same direction as the light.

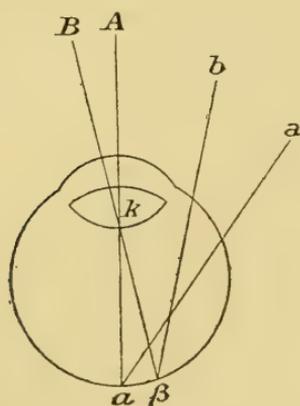


FIG. 1.

If now the distance of the screen on which the image is projected from the eye be known, and the displacement of the image $A B$ be measured, the retinal displacement $a \beta$ can be found as the distance of the nodal point k from the retina is known. If a particular retinal vessel be seen displaced, the rays must intersect it as shown in the diagram; now the distance of the vessel from the sclerotic where a and b impinge can be found, if the position where the rays a and b impinge be known, and accordingly the distance of the retinal vessel from the deeper part of the retina whence the visual impression originates can be calculated. "When this is done, it is found that this distance corresponds fairly well to the distance of the retinal vessels from

the layer of rods and cones."¹ I have been unable to verify this conclusion, as the experiment is one of considerable difficulty, not only because of the elusive character of the observations, but also owing to the uncertainty of determining the distance between the retinal vessels and the points on the sclerotic where the light impinges, for the length of this path will vary in different eyes.

If Purkinje's figures are formed by a candle moved to and fro near the cornea, then fig. 2 illustrates, according to H. Müller, how they are probably produced, a horizontal section of the eye being shown. If the candle be at the point *a*, the illuminated spot on the retina *b* will reflect light, and throw a shadow of some

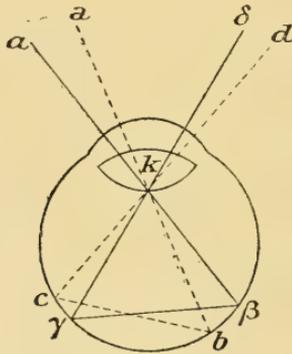


FIG. 2.

intervening vessel upon the retina at the point *c*; this shadow will be seen projected from the eye to some external position *d*. If now the candle be moved from *a* to *a*, the path of the rays will be indicated by β and γ , and the projected image will be seen at δ . That is to say, the projected image moves towards the centre of the field of view as the candle moves from it, both moving in the same direction; but if the candle be raised, the image will be depressed, the image now moving in the opposite direction to that of the candle.²

¹ Sir M. Foster's "Text-book on Physiology," 5th edition, Part iv., p. 1250.

² This will be clear by supposing the candle *a* raised above the plane of the paper; β will then be depressed, whilst γ will be raised, and the projected image δ will be accordingly depressed. In the lateral movement of the candle, when the light passes the pupil of the eye, a change in the direction of the projected image occurs, its motion being now opposite to that of the candle. The projected image, in fact, describes a path somewhat like the letter C turned sideways, thus: C.

In making the experiment, the candle should be held at the side of the head, a little below the level of the pupil, and the gaze directed away from the candle. If now the lighted candle be slowly waved to and fro, either laterally or vertically, whilst the glare of the candle is seen on the one side, the shadows of the vessels will be seen projected on the other side towards which the gaze is directed.

After the eye has been in complete darkness for some time, a curious entoptic phenomenon can be seen when a lighted candle is held near the eye. Numerous streams and patches, of what seems to be a light flocculent matter, will be seen quickly moving on a dark purple background, which covers the field of vision. The appearance somewhat resembles a very brisk agitation and settling of curds in a purple whey. In the course of half a minute or less the moving flocculent streams clear off, and the retina assumes its normal state. The experiment is best made after waking up in the night, and immediately after lighting a bedside candle. It is possible that this phenomenon, which does not appear to be mentioned by any writer on physiological optics, may be connected with the presence of the visual purple on the retina.

5. MOVING CORPUSCLES.

There remains to be described another Entoptic phenomenon to which a brief reference was made in Part III. of these papers.¹ I refer to the rapid succession of bright specks like minute fire-flies which are seen darting across the field of vision when a bright sunlit sky is viewed through a cobalt-blue glass. This phenomenon was first noticed by the eminent physiologist Vierordt, in 1856,² who observed it when looking at a bright sky through the fingers of his hand, which were waved rapidly to and fro in front of the eye; and he connected the appearance with the circulation of the blood in the capillaries of the retina. Intermittent light does not, however, reveal the appearance so well as a blue glass, or a solution of ammonia-sulphate of copper.

¹ Proc. Roy. Dublin Soc., vol. xi., p. 85.

² Archiv für physiol. Heilkunde, 1856, Heft ii.

Professor Ogden Rood, in a paper published in the *American Journal of Science* (Silliman's Journal) for September, 1860, first suggested the use of a cobalt-blue glass for seeing the phenomenon, which he independently discovered. In a second paper, Professor Ogden Rood also gives an approximate measure of the size of the moving corpuscles; assuming them to be close to the retina, he found them to be about $\frac{1}{16000}$ of an inch in diameter, about twice the size of the red corpuscles of the blood.¹ That the appearance was closely associated with the circulation of the blood in the retinal vessels was shown by Dr. Reuben, of America, who noticed that there were periodic jets of these bright particles which synchronised with the beating of his pulse. He considered that the bright appearance was due to the corpuscles acting as microscopic lenses condensing the light on the retina.² In 1870, Dr. Pope, of New Orleans, drew attention to the fact that there appeared to be two classes of these moving corpuscles: one a continuous stream of bright specks, and the other whose path resembled the letter *S*; the latter appeared to have a periodic movement synchronous with that of the pulse.³

Helmholtz states he saw these moving particles, and came to the conclusion that they were an agglomeration of blood-corpuscles arising from some temporary stoppage or variation in the flow of blood through the smaller capillaries in the retina.⁴

In order to see the phenomenon clearly, the observer should look at a bright sky through one or two thicknesses of cobalt-blue glass, the eye being directed to a point some two or three feet beyond the glass, the other eye being closed. There will then be no difficulty whatever in seeing a succession of rapidly moving bright specks, their movement resembling the rapid tossing of balls to and fro by a conjurer. A small streak of light is left behind most of them, doubtless due to the persistence of the impression on the retina, so that some resemble very fine luminous commas. The path of some is like the letter *S*, and there appears to be no cessation in their rapid gyratory and wandering movement.

¹ *American Journ. Sci.*, 1860, vol. xxx., p. 264; and 1861, vol. xxxi., p. 325.

² *American Journ. Sci.*, 1860, vol. xxx., p. 385.

³ *Annales d'Oculistique*, 1870, vol. lxvi., p. 461.

⁴ *Optique Physiologique*, p. 222.

Like other faint Entoptic phenomena, they disappear after gazing at them for a little while, but can be revived at intervals as often as one pleases, a very brief rest being sufficient to renew the sensitiveness of the retina. We have attempted to reproduce what is seen in fig. 1, Plate VIII., though the specks are in many cases mere points, and far more striking and beautiful than can be represented in black and white.¹

In order to estimate their size, a sheet of millimetre ruled paper was fixed vertically in the sunlight at a given distance from the eye; and numerous observations independently made by myself, Mr. Ledwidge, and other assistants. Taking the nodal point as 16 mm. from the retina, the retinal image of the moving corpuscles was found to be from $\cdot 009$ to $\cdot 014$ according to different observers. Assuming the corpuscles to be very close to the sensitive layer of the retina, this would give their approximate diameter, the mean result being about $\cdot 011$ mm., or say the $\frac{1}{2300}$ th of an inch.

A better way of estimating their size I found to be as follows:—Pinholes a millimetre in diameter were made in a small strip of thin metal, which was then fixed to a window-pane facing a bright sun-lit sky. Looking at the pane of glass through two thicknesses of cobalt-blue glass, the moving corpuscles were seen, and the observer moved to and fro until the diameter of the bright specks appeared to be the same as that of the bright apertures in the little opaque screen. This occurred when the eye was from 120 to 160 cm. from the window-pane: the retinal image is therefore $\frac{1}{70}$ to $\frac{1}{100}$ of a millimetre in diameter, and the corpuscles may be taken as about this size, though their diameter varies, and the result can only be regarded as approximate.²

That the phenomenon is associated with the circulation in the retinal vessels appears unquestionable; but that the appearance is due to rolls of red blood-corpuscles seems very unlikely. The enormous number of these corpuscles in the blood is one reason

¹ The drawing gives a better idea of the drift of the corpuscles if it is looked at after turning the page through a right angle.

² Their size may also be estimated by comparing them with the thickness of any definite *musca* seen projected on the same plane: it will be observed that their diameter is far smaller than the width of any of the *musce volitantes*.

against this hypothesis. The dimension of the specks corresponds very well with that of the white corpuscles, the average diameter of which is about $\frac{1}{2500}$ of an inch, whereas the red corpuscles in man are $\frac{1}{3200}$ of an inch, or 0.007 mm. in diameter. The white corpuscles are much fewer in number than the red: the proportion varies, being about 1 to 1000 red after fasting, but after a meal they rise to about 1 to 400 red; they are distinguished also by their solitariness, their higher refractive power, their spherical shape, and their transparency. They also exhibit amœboid movements, and the protoplasm of which they consist "presents a network of very fine contractile fibrils" (Carpenter).

The function of the blue glass in enabling the phenomenon to be perceived now becomes apparent. Viewed through such a glass the red corpuscles either would not be seen at all or would appear as faint dark specks, whereas the transparency of the white corpuscles would cause them to be seen as bright specks. A simple experiment illustrates this. Scattering on a black surface a number of small fragments of bright-red paper, interspersed with some minute scraps of white paper, the latter are hardly discernible amid the red until a blue glass is interposed; now the white particles are vividly seen, whilst the red disappear, and are indistinguishable from the black surface. Hence the more perfectly monochromatic the blue medium—e.g., a solution of the ammonia-sulphate of copper,—the more conspicuous will become the moving corpuscles in the eye, as I found to be the case.

I am therefore of opinion that the appearance is due to the white blood-corpuscles, either in the retinal vessels or migrating from the capillaries. The rapidly moving points of light which are seen may be due to those corpuscles which are near the walls of the capillary vessels acting as minute spherical lenses; and the larger specks, with a slower and more wandering movement, may be the amœboid movements of the white corpuscles which have escaped through the walls of the vessels.

But these questions must be left to the consideration of physiologists, who will, I hope, be led to repeat these and other experiments on Entoptic vision, more especially in view of the great importance attached to the white corpuscles, or phagocytes, since Metchnikoff propounded his doctrine of phagocytosis. It becomes, therefore, of the utmost interest to watch the behaviour

of these moving corpuscles in the eye in various states of health and under the influence of alcohol and other drugs which hinder and destroy their activity.

The subject of *phosphenes*, or the luminous impression produced by pressure on the eyeball, or other stimulation of the retina, and of *after-images* and of *ocular spectra*, are subjective Entoptic phenomena, which have been fully dealt with by writers on physiological optics, and into these I do not propose to enter. I have not, however, met with any reference by these authorities to some curious subjective entoptic phenomena, described by Sir John Herschel in a lecture, on "Sensorial Vision," delivered in 1858, and published in his "Familiar Lectures on Scientific Subjects." Sir John states that, when the eyes were in complete darkness, he frequently saw covering the field of vision patterns of perfect symmetry and geometrical regularity, sometimes lozenge-shaped, but often passing into more complex forms of equal symmetry. He discusses how these geometrical spectra can originate, for they do not appear to be retinal impressions, or mental reminiscences; they do not arise from any conscious effort of the mind; they recurred, in different shapes, just before lapsing into unconsciousness on two occasions when he was under chloroform; and he suggests that they afford some evidence "of a thought, an intelligence working within our own organization distinct from that of our own personality,"¹ or, as psychologists would now say, they afford some evidence of a "sub-conscious self."

¹ "Familiar Lectures on Scientific Subjects," by Sir J. F. W. Herschel, Bart., K.H., D.C.L., F.R.S., &c., p. 412.

NOTE BY J. LEDWIDGE, A.R.C.S.C.

As suggested by Professor Barrett, I add a brief statement of the appearances presented to me by the phenomena which the Professor has described.

1. *Haidinger's tufts*.—The yellow sectors appear to me also very like an hour-glass in shape; the blue or violet areas at right angles to the yellow I see clearly; they much resemble the shape of the moon in her third quarter (see fig. 1, Plate VI.), and sometimes seem to unite across the narrow part of the hour-glass-shaped area. In general the tufts vanish with me in rather less than three seconds, so that the Nicol must be kept moving to see them continuously. When a blue glass or a blue solution of the oxalate of chromium and potassium is held before the Nicol, the tufts occupy a slightly smaller area than the claret-coloured area due to the *macula lutea* or yellow spot, as I have noticed a fringe of the claret colour on the outside of the three-quarter-moon-shaped area of the tufts. This agrees with my measurement of the *macula* and the tufts; the former appears to be approximately 1 mm. and the latter 0·8 mm. in their longest diameter. In repeating the double pinhole experiment described by Prof. Barrett, I could only see a single image of the tufts, no matter what part of the duplicated image of the pupil the gaze was directed to, thus verifying the Professor's observation. I tried whether the tufts could be seen by focusing a polarized pencil of rays from the electric arc on the *sclerotic*, but could not see them; the non-appearance of the tufts may, of course, be due to their extreme faintness under these conditions, or to the fact that the rays did not fall on the yellow spot. The existence of Haidinger's tufts show that the light of direct vision is always polarized. This fact seems to me one of considerable interest in the theory of vision.

2. *Purkinje's figures*.—Plate VIII., fig. 1, is a careful drawing of Purkinje's figures as I see them when a brilliant point of light falls on the *sclerotic*. In the central part there appears to be

an area where no shadows of the vessels are seen, and around this area the finer branching capillaries appear to me to end abruptly. This area is at the retinal extremity of the line of sight, and surrounds the point of fixation. Some of the retinal vessels I observe cross each other. In certain positions of the eye I have occasionally noticed that the shadows of the vessels where they spread from the optic nerve can be seen. In this case the light must fall obliquely on the retina in order to cast the shadows outside the area of the blind spot.

One part of the area where there are no vessels presents a peculiar appearance, being covered with what appears to be the shadow of small round cells, closely grouped together. Except for these shadows the intensity of the light over this area seems to be greater than in the remaining part of the field. On moving my head upwards the shadows of the vessels move downwards; but the granular area, or shadow of the cells, moves in an opposite sense, but at a much slower rate. The point of light illuminating the sclerotic being fixed, the upward movement of the head will cause the point of light to descend, and the projected image of the vessels must therefore be formed, as shown in fig. 1, p. 127. The cells of the granular area are probably in the fovea; and, owing to the fact that there is a depression in the retinal surface at this point, the light must fall almost perpendicularly to enable the appearance to be seen. I have noticed that there appear to be two layers of these cells, for they do not all move at the same rate when the head or eyeball is moved; one layer appears nearer the sensory filaments than the other.

When pressure is exerted on the side of the closed eye, the vessels immediately appear, but they now appear as a bright arborescent figure on a dark field; the impression is not, however, sufficiently enduring or strong enough to enable me to draw the figure seen.

3. *Moving corpuscles*.—Pressure on the side of the closed eye also sometimes reveals streams of luminous spots having a pulsatory motion, which appears to synchronize with the beats of the pulse. These moving corpuscles can, however, be seen more clearly by looking at a bright sky through cobalt-blue glass. I have attempted to depict them in fig. 2, Plate VIII. There appear to be two classes

of these specks or corpuscles; one set very numerous, moving rapidly in small arcs of circles, and at the same time having a brisk translatory movement across the field of view, the path being indefinite and sinuous. The specks of the second class enter the field in jets at each beat of the pulse, and describe a path somewhat like the letter S, disappearing after having traversed a small portion of the field of view. Even *without* a blue glass, I can see these shining specks when a bright sky is looked at. Others have also observed the same thing.

At Professor Barrett's suggestion I have attempted to measure the retinal diameter of these specks, when seen projected on to a white surface at a known distance from the eye. But the results vary a good deal; the retinal image, and therefore the diameter of the corpuscles if they are near the retina, seem to lie between the $\frac{1}{2000}$ to $\frac{1}{5000}$ of an inch, the latter being minute points of light and really not measurable, but the larger measurement may be taken as fairly correct.

EXPLANATION OF PLATE VI.

PLATE VI.

Fig. 1.—Haidinger's tufts, as seen through a Nicol's prism on a clear sky ; plane of polarisation vertical.

Fig. 2.—Haidinger's tufts, as seen projected on a brightly-lighted sheet of paper placed 160 cm. (about 5 feet) from the eye. The plane of polarisation is here horizontal, and the diffuse transverse violet colouration is omitted.



Fig. 1.

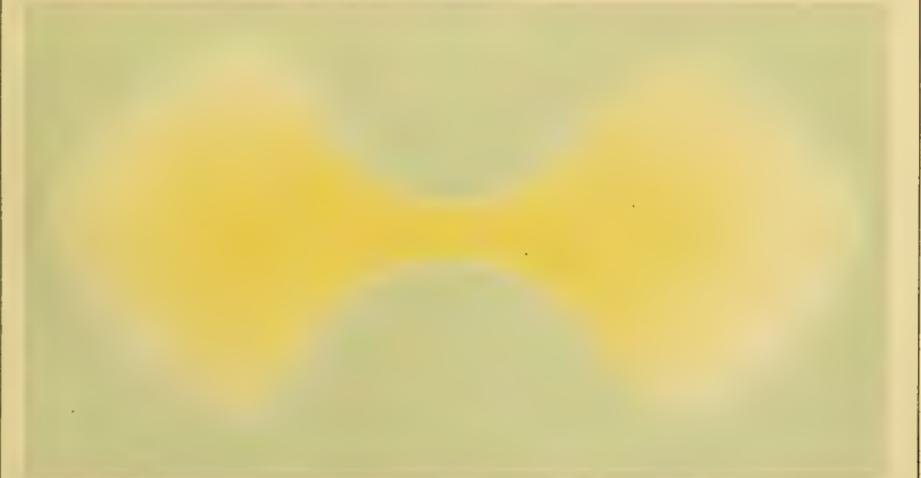


Fig. 2.

EXPLANATION OF PLATE VII.

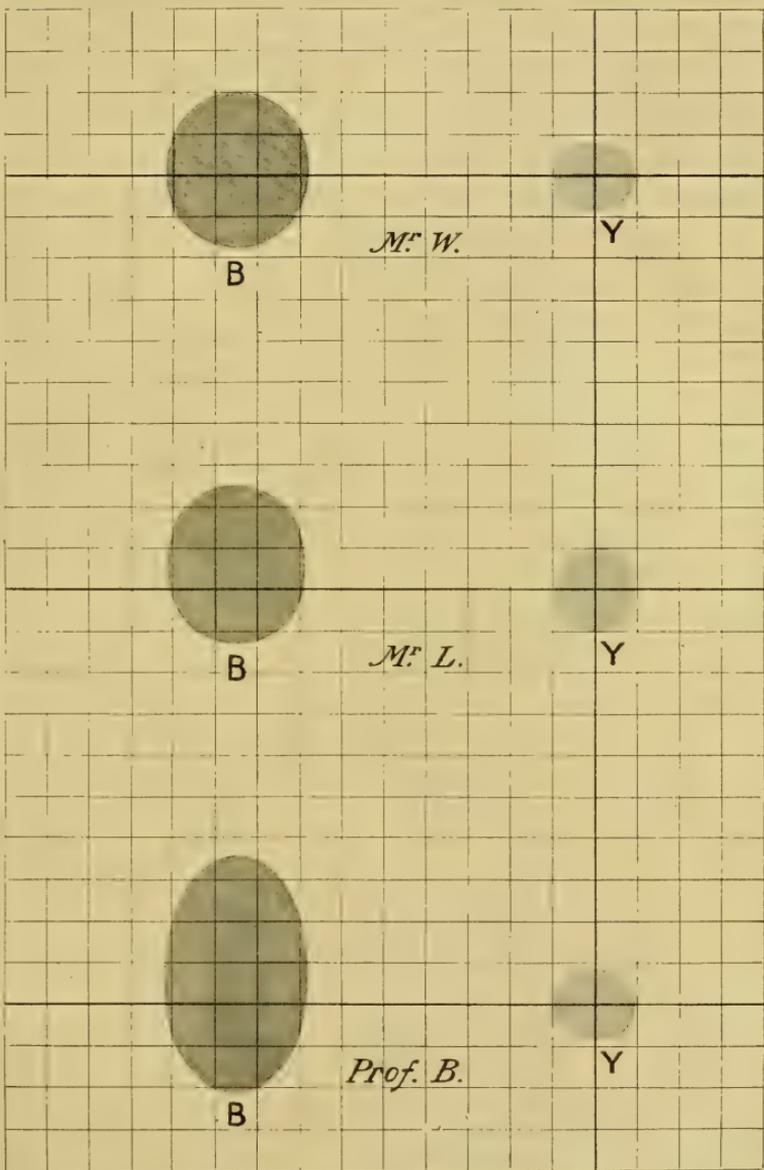
PLATE VII.

Projected images of the blind spot, B, and of the yellow spot, Y, as seen by three observers. The fine lines correspond to actual retinal distances of half a millimetre; hence the squares represent retinal areas of half-millimetres squared.

Nothing is easier than an ocular proof of the blind spot. Close the right eye, and look *steadily* at the cross on this page with the left eye. When the eye is about 12 or 13 inches from the paper, the letter B will fall on the blind spot, and disappear. Resting the head on the right hand, with elbow on the table, gives about the right distance; if the B is still visible, move the head a little further from or nearer to the paper.



In the above, the distance of the blind spot from the yellow spot, or point of regard, is twenty times the retinal distance; and the distance from the paper at which the B disappears is twenty times the value of k (distance of nodal point from retina) for the particular observer.



EXPLANATION OF PLATE VIII.

PLATE VIII.

Fig. 1.—Purkinje's figures, or shadows of the retinal vessels seen entoptically. The appearance shown is that exhibited near the *fovea*, which latter probably gives rise to the granular appearance seen near the centre.

Fig. 2.—Moving corpuscles near the retina, seen entoptically. They are probably due to the white corpuscles of the blood, and are seen as actively moving points of light, smaller than are actually depicted in the figure.

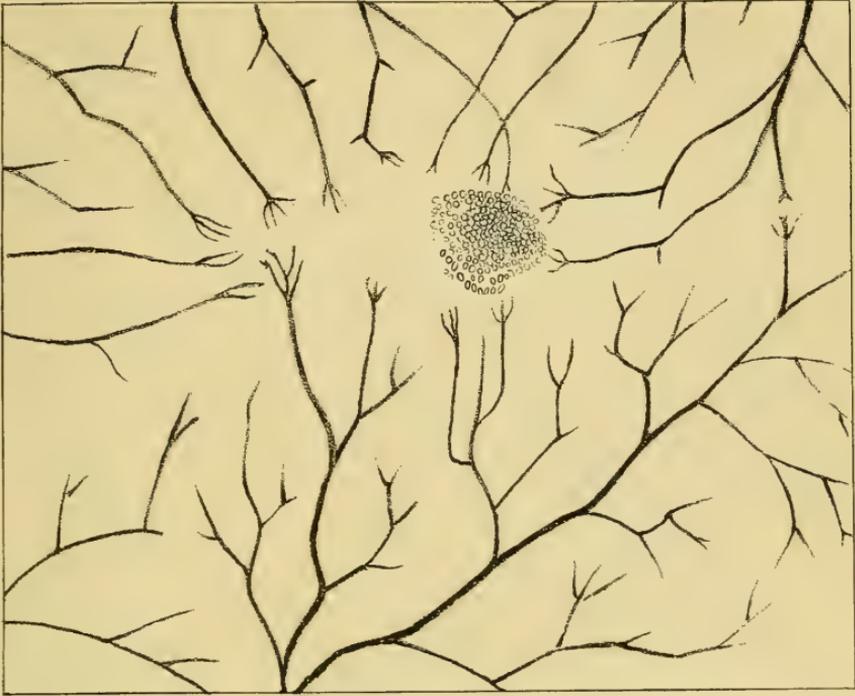


Fig. 1.



Fig. 2.

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Vol. XI. (N. S.), No. 13.

FEBRUARY, 1907.

A CONTRIBUTION TO THE STUDY OF
EVAPORATION FROM WATER-SURFACES.

BY

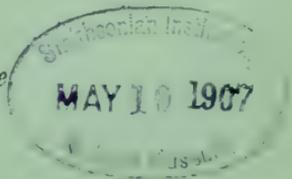
J. R. SUTTON, M.A.

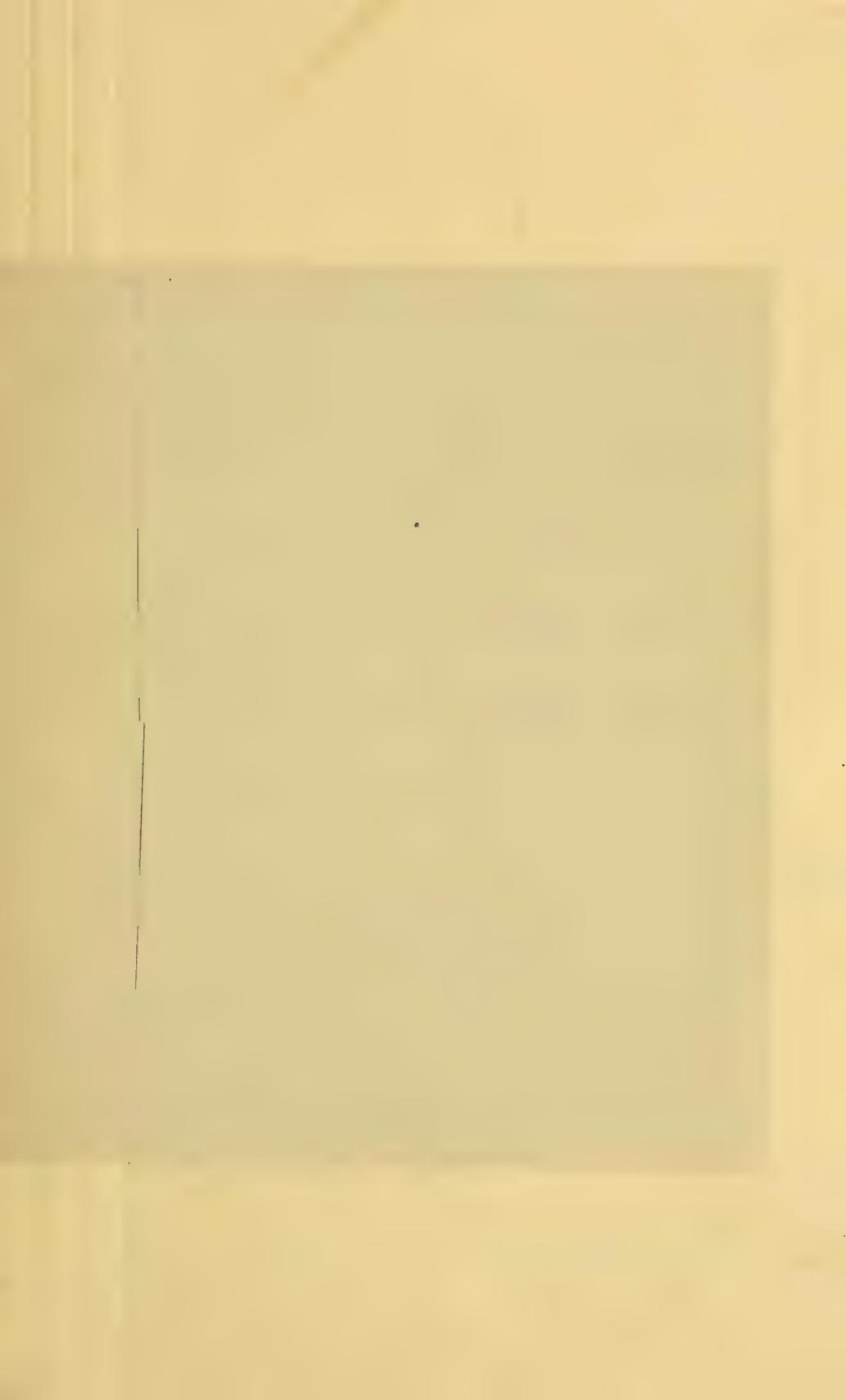
(PLATE IX.)

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XIII.

A CONTRIBUTION TO THE STUDY OF EVAPORATION
FROM WATER-SURFACES.

By J. R. SUTTON, M.A.

(PLATE IX.)

[COMMUNICATED BY PROF. J. JOLY, F.R.S., HON. SEC. ROYAL DUBLIN SOCIETY.]

[Read, NOVEMBER 21; Received for Publication, NOVEMBER 23, 1906;
Published, FEBRUARY 21, 1907.]

MOST of the observations and experiments described in this paper were commenced with the idea of testing a number of previous results made by others, which have been published with some confidence and apparently favourably received. They are also, to a certain extent, a development of some previous work of my own.¹ The climate of the table-land of South Africa is very favourable to work of this sort, on account both of the great average rate at which water evaporates in the open air, and also of the much wider range of moisture conditions than is to be usually met with elsewhere. The whole of this paper refers to experiments made under meteorological conditions, that is to say, under the open sky, or in louvered screens, the water-surfaces being warmed or cooled by contact with the air alone. In this respect the circumstances of the investigation differ entirely from the usual product of the laboratory, in which the usual (and fatally defective) way of increasing the "evaporation" from a water-surface is to heat it from below over a stove or lamp.

The principal instruments employed here have been :—

1. A Piche atmometer of the usual form, in which water is evaporated from a moistened surface of porous paper. It is assumed that the evaporation is equal from equal areas all over the exposed part of the paper disc above and below. The tube is graduated on the glass to equal volumes, and the factor required

¹ See, e.g., J. R. Sutton, "Results of some Experiments upon the Rate of Evaporation," *Trans. South African Phil. Soc.*, 1903, xiv., Part 1: "Results of some further Observations upon the Rate of Evaporation," *Report of the South African Association for the Advancement of Science*. 1904.

to reduce the scale-readings to depths in inches has been computed equal to $\cdot 00415$. This reduction, however, has not been performed in every case for the purposes of this paper. The instrument is suspended in a large louvered screen of $8 \times 8 \times 8$ feet dimensions.

2. A galvanised-iron tub of 14 inches diameter and 18 inches deep, having a tap at the bottom for the purpose of adjusting the water-surface quickly and accurately to zero. It stands alone in a single-louvered screen whose dimensions are 46 inches long, by 34 wide, by 6 feet high over all. The amount of evaporation is read from a lever which, actuated by a float, travels over a graduated dial, and magnifies the fall in level ten times. A thermometer is attached in such a way that its bulb dips just beneath the surface of the water.

3. A circular steel tank, rather over 46 inches diameter, and 29 inches deep, placed in the centre of a cemented brick cistern of about 7 feet square. The walls of the cistern rise some 8 inches higher than the rim of the tank. The outer cistern is kept supplied with water up to a level about equal to that of the evaporating surface of the tank, but there is not any communication from one to the other. An iron pipe opens under the centre of the tank, passes through the side of the tank—to which it is secured by water-tight check-nuts—outwards through the wall of the cistern, and thence underground to a vertical cylindrical vessel set under the floor of the barometer room. A large, hollow copper ball floating in the cylinder carries a vertical wooden rod which is attached to the short end of a light brass lever balanced upon knife-edges. A pen at the other end of the lever writes a magnified record of the fluctuations in the level of the water upon a long drum rotated by clockwork. Thus the records obtained are of both evaporation and rainfall, the pen rising for the one and falling for the other.

4. A piece of apparatus intended to give the evaporation from the surface of water in vessels placed at the bottom of heavy metal tubes of 3.13 inches diameter, and 1, 2, and 3 feet long, respectively. The tubes are furnished with broad flanges for feet, and stand when in action upon a sheet of thick rubber insertion nailed to a block of wood. They are also furnished with swing-handles by means of which they may be expeditiously raised and hung on hooks when it is necessary to attend to the water-vessels. The weight of the tubes is sufficiently great to

press firmly into the rubber and so prevent any access of air below. The water-vessels are silver-plated cups set into holes bored into the block of wood. These cups are $2\frac{1}{2}$ inches deep inside, about $2\frac{3}{8}$ inches diameter near the bottom, and about $2\frac{1}{2}$ inches diameter near the top; their rims are turned out to a diameter of $2\frac{3}{4}$ inches. The holes are about $2\frac{1}{2}$ inches diameter, and $2\frac{1}{4}$ inches deep. Thus the rims of the cups project about $\frac{1}{4}$ inch above the base; the water-surface being therefore nearly level with the base. For comparison, a similar cup (called here the "open cup") is hung by a thin wire from the top of the apparatus. The loss by evaporation was determined by weighing. At 8 a.m. each day the cups were nearly filled with clear rain-water, the weight of the cup and water together being nicely adjusted in a sufficiently delicate balance to 3750 grains, of which the cups themselves averaged about 1500 grains. The temperature of the water in the cups was carefully observed with a delicate thermometer at 5, 8, and 11 p.m., and 8 a.m., and occasionally also at 11 a.m. and 2 p.m.; and at the same times the loss by evaporation was determined. The open cup was retained in the same position throughout the experiment, but the other cups were permuted from day to day from one pipe to another, so that individual differences in the cups might be smoothed out in the averages.¹

Since it is likely that the evaporation between 8 a.m. and 5 p.m. would not be quite the same when the temperature and evaporation were only read at 5 p.m. as it would be if these quantities were read also at 11 a.m. and 2 p.m. (on account of the disturbance possibly caused by taking the temperature of the water and removing the cups from the stand to weigh them), a separate series was formed for the more frequent readings. We thus have one series of observations made upon 15 days, with readings at 11 a.m., 2 p.m., 5 p.m., 8 p.m., 11 p.m., and 8 a.m.; five series, averaging 23 days each, with readings at 5 p.m., 8 p.m., 11 p.m., and 8 a.m.; and there is also a series of observations made upon 5 days in which the readings were only taken at the end of the 24 hours, namely, at 8 a.m.

We have also nearly simultaneous observations made with the Piche atmometer; with the tub at 11 a.m., 2 p.m., 5 p.m., 8 p.m.,

¹ It has not been thought necessary to reduce grains to grams, nor degrees F. to C.

11 p.m., and 8 a.m. each day; and hourly observations from the tank. The temperature of the water in the tub was observed, but I have not been able to devise trustworthy observations of the temperature in either the tank or the Piche atmometer. Moreover, hourly values of the temperature of the dry bulb, wet bulb, and dew-point are available, as well as those of the velocity of the wind, and the relative humidity. I have assumed that the mean temperatures of the various water-surfaces between 5 and 8 p.m., and between 8 and 11 p.m., is the arithmetic mean of the temperatures at 5 and 8 p.m., and at 8 and 11 p.m., respectively. A similar assumption would not be safe for the longer time intervals.

The following are the means of the various temperatures:—

TABLE 1.—(114 days.)

	5 p.m.	8 p.m.	11 p.m.	8 a.m.
Open Cup,	70°5	63°6	59°2	58°0
One-foot Pipe,	73·6	68·8	63·7	56·9
Two-foot ,,	73·7	69·2	64·5	57·4
Three-foot ,,	74·0	69·8	64·8	57·5
Tub,	67·5	66·1	64·0	58·8
Air,	75·0	64·8	60·2	62·3

TABLE 2.—(15 days.)

	11 a.m.	2 p.m.	5 p.m.	8 p.m.	11 p.m.	8 a.m.
Open Cup,	68°4	72°4	70°9	63°3	58°8	56·2
One-foot Pipe,	64·4	72·8	74·9	68·8	63·7	55·1
Two-foot ,,	64·6	72·7	74·7	69·4	64·5	55·8
Three-foot ,,	64·5	72·8	75·1	70·0	64·9	55·8
Tub,	60·7	66·6	67·6	66·0	63·8	57·9
Air,	75·4	79·9	75·8	64·7	59·5	60·3

We see from this that the temperature of the air is at all times greater than that of the open cup; while it is greater than that of the three pipes and of the tub during the day, but less during the night. On the other hand, the temperature of the surface of the water in the tub is less than that of the three pipes during the day, but greater at night.

The following are mean values:—

TABLE 3.—(114 days.)

	8 a.-5 p.	5 p.-8 p.	8 p.-11 p.	11 p.-8 a.	
Dry Bulb, Maximum Vapour-Tension,	73.4	69.5	62.5	57.2	degrees F.
" Dew-Point, "	.856	.761	.591	.493	inch.
" Maximum Vapour-Tension,	46.8	46.0	45.4	45.3	deg.
Relative Humidity,	.334	.326	.324	.325	inch.
Wind-Velocity at 45 feet,	42	46	56	66	per cent.
Open Cup, "	5.7	3.7	3.7	3.5	miles per hour.
One-foot Pipe, "	—	67.1	61.4	—	deg.
Two-foot " "	—	71.2	66.2	—	"
Three-foot " "	—	71.4	66.8	—	"
Tub, "	—	71.9	67.3	—	"
		66.8	65.0	—	"

TABLE 4.—(15 days.)

	8-11 a.	11 a.-2 p.	2-5 p.	5-8 p.	8-11 p.	11 p.-8 a.	
Dry Bulb, Maximum Vapour-Tension,	68.7	78.3	78.9	69.6	62.2	55.5	deg. F.
" Dew-Point, "	.725	.997	1.016	.751	.584	.459	inch.
" Maximum Vapour-Tension,	44.1	43.4	43.3	44.4	44.1	44.1	deg.
Relative Humidity,	.298	.288	.286	.300	.300	.303	inch.
Wind-Velocity at 45 feet,	43	30	30	42	53	67	per cent.
Open Cup, "	5.3	7.4	6.0	2.9	3.0	2.7	miles per hour.
One-foot Pipe, "	62.4	70.4	71.6	67.1	61.0	—	deg.
Two-foot " "	59.4	68.6	73.8	71.8	66.2	—	"
Three-foot " "	59.9	68.6	73.7	72.0	67.0	—	"
Tub, "	60.0	68.7	74.0	72.5	67.4	—	"
	59.0	63.7	67.1	66.8	64.9	—	"

Now, according to the most popular current theories of evaporation, the numbers in these four Tables would indicate that the loss by evaporation from each type of gauge must be greatest in the afternoon, say from 2 to 5 p.m. Stefan's formula, for example, makes the loss by evaporation proportional to $(P - p'') / (P - p')$ where P is the barometric pressure, p' the vapour-tension at the surface of the water, and p'' the vapour-tension at the temperature of the dew-point.¹ Fitzgerald's formula makes it proportional to $\frac{1}{2}(p' - p'')(1 + W/2)$, where W is the velocity of the wind at the surface of the water.² None of my results, however, agree with either formula. Let us consider first of all a set of observations of the evaporation from the tub made upon every day during the six months, October, 1905, to March, 1906. The following are daily averages for each month:—

TABLE 5.—(1). *Evaporation from the Tub.*

	11 p.-8 a.	8 a.-11 a.	11 a.-2 p.	2 p.-5 p.	5 p.-8 p.	8 p.-11 p.	
Oct.,	·088	·051	·058	·059	·047	·043	} inches.
Nov.,	·082	·050	·057	·058	·036	·037	
Dec.,	·092	·050	·056	·055	·046	·039	
Jan.,	·075	·044	·056	·049	·038	·027	
Feb.,	·058	·039	·045	·038	·029	·021	
Mar.,	·050	·033	·045	·041	·031	·018	
Mean,	·074	·045	·053	·050	·038	·031	

¹ See T. Preston, *Theory of Heat*, p. 291. I have not been able to consult Stefan's memoir at first hand. Hann's *Handbook of Climatology* (Prof. R. de C. Ward's Ed.), 1903, p. 71, quotes it differently, *i.e.* "According to Stefan, the rate of evaporation is proportional to the log. of a fraction whose numerator is the air-pressure, and whose denominator is the air-pressure diminished by the maximum vapour-tension."

² See C. Abbe, *Meteorological Apparatus and Methods*, 1888, p. 376. Stelling's formula seems to be similar to Fitzgerald's, but the coefficients vary with the season—which is fatal to it. See H. H. Kimball, "Evaporation Observations in the United States," *Monthly Weather Review*, Dec., 1904.

(2). *Temperature of Water.*

	11 p.	8 a.	11 a.	2 p.	5 p.	8 p.	11 p.	
Oct.,	65·8	59·2	63·9	68·3	69·6	68·1	66·0	} degrees.
Nov.,	68·4	63·7	68·3	71·6	72·4	71·1	68·7	
Dec.,	72·8	67·7	71·5	74·8	76·3	75·1	72·6	
Jan.,	74·6	69·5	73·2	76·5	77·5	76·4	74·7	
Feb.,	71·0	65·7	69·2	72·9	74·0	72·8	70·9	
Mar.,	67·2	61·8	65·3	69·2	70·2	69·0	67·0	
Mean,	70·0	64·6	68·6	72·2	73·3	72·1	70·0	

(3). *Temperature of Dew-Point.*

	11 p.—8 a.	8 a.—11 a.	11 a.—2 p.	2 p.—5 p.	5 p.—8 p.	8 p.—11 p.	
Oct.,	36·0	39·3	39·5	39·1	38·7	37·3	} degrees.
Nov.,	47·0	47·6	46·1	45·5	46·1	46·2	
Dec.,	49·7	50·2	48·7	48·1	48·5	49·1	
Jan.,	55·1	54·5	52·3	51·5	52·6	54·3	
Feb.,	53·0	54·3	52·9	51·2	52·2	52·8	
Mar.,	50·2	52·0	50·4	49·1	49·6	50·0	
Mean,	48·5	49·6	48·3	47·4	48·0	48·3	

(4). *Barometric Pressure.*

	11 p.—8 a.	8 a.—11 a.	11 a.—2 p.	2 p.—5 p.	5 p.—8 p.	8 p.—11 p.	
Oct.,	26·115	26·140	26·094	26·052	26·071	26·109	} inches.
Nov.,	·097	·119	·074	·034	·052	·082	
Dec.,	·046	·071	·033	25·981	25·987	·028	
Jan.,	·058	·081	·049	26·002	26·006	·044	
Feb.,	·080	·110	·080	·041	·047	·075	
Mar.,	·117	·144	·109	·066	·072	·102	
Mean,	26·085	26·111	26·073	26·029	26·039	26·073	

(5). Wind-Velocity.

	11 p.-8 a.	8 a.-11 a.	11 a.-2 p.	2 p.-5 p.	5 p.-8 p.	8 p.-11 p.	
Oct.,	2·8	6·2	7·3	8·1	5·6	4·3	} miles per hour.
Nov.,	4·0	7·1	7·8	7·5	5·0	4·3	
Dec.,	4·5	6·6	6·3	6·3	5·8	5·1	
Jan.,	3·1	5·8	6·7	6·8	3·7	3·1	
Feb.,	3·4	5·9	5·6	5·1	3·2	3·0	
Mar.,	4·5	6·5	7·0	6·5	4·7	4·1	
Mean,	3·7	6·3	6·8	6·7	4·7	4·0	

The mean vapour-tensions at the temperature of the water and the temperature of the dew-point, proper to Table 5 (2) and (3), are—

	11 p.-8 a.	8 a.-11 a.	11 a.-2 p.	2 p.-5 p.	5 p.-8 p.	8 p.-11 p.	
Water,	—	·652	·744	·805	·804	·760	} inch.
Dew-Point, }	·342	·356	·339	·328	·335	·339	

If now we substitute in Stefan's formula values of P , p' , p'' from Table 5 (4), (2), (3), we deduce a practically constant rate of evaporation, at all events between sunrise and midnight, contrary to all experience. Again, assuming that the air-movement inside the screen containing the tub is one-third (a liberal estimate) of that at 45 feet, we get the following relative numbers by Fitzgerald's formula :—

TABLE 6.

	8 a.-11 a.	11 a.-2 p.	2 p.-5 p.	5 p.-8 p.	8 p.-11 p.	
Calculated	·030	·043	·050	·042	·036	inch.
Observed } minus	+ ·015	+ ·010	·000	- ·004	- ·005	inch.
Calculated }	50	23	0	10	14	per cent.

These are large differences, and it may, I think, be reasonably claimed that they throw a considerable element of doubt upon the physical reality of Fitzgerald's formula. Nor are the averages

for each month very much more exact. The following are daily averages for each month for the whole intervals between 8 a.m. and 11 p.m.:—

TABLE 7.

	<i>P</i>	<i>p'</i>	<i>p''</i>	Wind	Evaporation		
					Observed	Computed	O - C
	inch	inch	inch	M. per H.	inch	inch	inch
Oct.,	26·093	·637	·236	6·3	·258	·229	+ ·029
Nov.,	·072	·716	·315	6·3	·238	·229	+ ·009
Dec.,	·020	·812	·346	6·0	·246	·260	- ·014
Jan.,	·036	·857	·403	5·2	·214	·240	- ·026
Feb.,	·071	·756	·399	4·6	·172	·179	- ·007
Mar.,	·099	·664	·364	5·8	·169	·167	+ ·002
Mean,	26·065	·736	·339	5·7	·216	·216	

Using these numbers, Stefan's formula, as before, gives a practically constant result month after month, mainly because $(P - p'') / (P - p')$ is very nearly constant under prevailing summer conditions at Kimberley.

The quantities of evaporation from the tub, the Piche atmometer, and the open cup, for the periods dealt with in Tables 3 and 4, give pretty much the same sort of result as Table 5.

TABLE 8.—(114 days.)

	8 a.-5 p.	5 p.-8 p.	8 p.-11 p.	11 p.-8 a.	
Tub, .	·012	·008	·006	·005	inch per hour.
Piche, .	4·2	2·4	1·8	1·2	units per hour.
Open Cup,	18·7	9·7	5·7	3·6	grains per hour.

TABLE 9.—(15 days.)

	8 a.-11 a.	11 a.-2 p.	2 p.-5 p.	5 p.-8 p.	8 p.-11 p.	11 p.-8 a.	
Tub, .	·013	·014	·012	·005	·007	·004	inch per hour.
Piche, .	3·7	5·1	5·2	2·4	1·7	1·1	units per hour.
Open Cup,	14·4	29·6	24·5	9·5	5·8	3·0	grains per hour.

Here again we see that both the tub and the open cup show the maximum evaporation between 11 a.m. and 2 p.m. The Piche atmometer does indeed evaporate, if anything, a little faster after 2 p.m. than before; but that is probably due to the fact that its small mass is much more readily influenced by the temperature of the air and by the wind, and no doubt chiefly by the latter, as appears from a comparison between Tables 4 and 9. The rapid rate of evaporation between 8 and 11 a.m., as compared with the much slower rate between 5 and 8 p.m., in spite of the much lower temperature of the earlier hours, is remarkable, and receives no manner of explanation from the formulæ we have quoted.

Still more remarkable is the exactly opposite state of things in the iron tubes, where the evaporation goes on increasing after sunset for some hours after the temperature of the water has begun to fall, and is indeed four times as great from 8 to 11 p.m., and nearly twice as great from 11 p.m. to 8 a.m. as it is from 8 to 11 a.m. The following are hourly averages:—

TABLE 10.—(114 days.)

	8 a.—5 p.	5 p.—8 p.	8 p.—11 p.	11 p.—8 a.	
One-foot Pipe. .	2·3	5·6	3·8	1·7	} grains per hour.
Two-foot Pipe, .	1·9	4·6	3·0	1·4	
Three-foot Pipe, .	1·7	3·8	2·4	1·1	

TABLE 11.—(15 days.)

	8 a.—11 a.	11 a.—2 p.	2 p.—5 p.	5 p.—8 p.	8 p.—11 p.	11 p.—8 a.	
One-foot Pipe, .	1·0	2·5	4·9	6·2	4·1	1·8	} grains per hour.
Two-foot Pipe, .	0·8	1·9	4·1	5·1	3·3	1·5	
Three-foot Pipe, .	0·8	2·0	3·6	4·0	2·7	1·2	

It is curious how the relative ratios of the quantities evaporated in the three pipes vary. Before noon the water lost in the three-foot pipe is as great as, or greater than, that lost in the two-foot pipe; but afterwards, for the rest of the day, the loss in the two-foot pipe is very nearly the arithmetic mean of the losses in the

other two. The ratio of the evaporation in the one-foot pipe to that in the three-foot is about $5/4$ before noon; $4/3$ during the afternoon, and $3/2$ after sunset. Evidently, then, the evaporation observed here is not inversely proportional to the length of the tube, nor anything like it. Two points are in fact doubtful according to these observations—one, that the air in immediate contact with the water is even *nearly* saturated with water-vapour; the other, that the vapour-tension gradient in the tube is uniform. With regard to the second point, it is to be noted that the diffusion formula

$$E = Kp'/l$$

[where E is the quantity of water evaporated,

K the coefficient of diffusion,

p' the vapour-tension at the temperature of the water, and

l the length of the tube]

necessarily breaks down for very short tubes in air, because an indefinitely short tube would premise an infinitely rapid evaporation. It is, moreover, to be noted that in my experiments the temperature of the water is not in general the same as that of the surrounding air, as it perhaps mostly is in laboratory researches. My tentative suggestion is that the diffusion formula under meteorological (not laboratory) conditions only holds good in tubes whose length is great, measured in terms of their diameter, but that in other cases, provided the tubes are not too short, it approximates more nearly to the form

$$E = Kp_i/l$$

where p_i is the true vapour-tension immediately above the surface of the water. If this is so, then Tables 10 and 11 indicate a vapour-tension at the bottom of the three-foot tube twice as great as that at the bottom of the one-foot tube. Failing this compromise, the results are better expressed by

$$E^3 = Kp'/l,$$

although this is far from exact for the three given lengths.

The ratios between the total quantities of evaporation from the four cups, *i.e.* the open cup and the three in the pipes, are

$$385 : 100 : 82 : 68.$$

A pretty good working formula for these ratios is

$$E = a + bl + cl^{\frac{1}{2}} + dl^{\frac{1}{3}} \dots$$

four terms of which give

$$\begin{aligned} a &= + 385 \\ b &= - 71 \\ c &= + 706 \\ d &= - 920 \end{aligned}$$

This would give a relative evaporation in a five-foot pipe of 36, which is perhaps not far wrong. For longer tubes, however, say of upwards of 10 feet, more terms would be necessary. Of course such a formula is not in any sense the expression of a "law." Nor is it applicable from hour to hour, although it answers very well for the whole-day totals.

An important point arises in connexion with the quantities of water evaporated in the iron pipes at different hours of the day: suppose the water and the air above it to be at the same temperature, and evaporation to be proceeding at a certain uniform rate; if the overlying air have its temperature raised without raising the temperature of the water, will the rate of evaporation be increased? If Fitzgerald's formula be true, it will not; for, according to that, the rate depends only upon the differences of vapour-tension. A moment's consideration, however, will show that *a priori* the evaporation should probably increase. For if the air were cooled sufficiently, it would become saturated at its temperature, and any more vapour than would be required to saturate the space must obviously be condensed, and evaporation would cease. Wherefore, since again raising the temperature of the air to its original degree would restore the evaporation to its original rate, it follows that a raising of the temperature of the air from the dew-point must increase the rate of evaporation. That is to say, there should be a factor in any evaporation formula dependent on the relative humidity of the air over and above the factor dependent on the difference $p' - p''$.

Clerk Maxwell gave expression to an idea¹ which in essentials is much the same as Fitzgerald's:—"Consider two gases in the same vessel, the proportion of the gases being different in different parts of the vessel, but the pressure being everywhere the same. The agitation of the molecules will still cause more molecules of the first gas to pass from places where that gas is dense to places where it is rare than in the opposite direction." Such a statement

¹ *Encyclopædia Britannica*, 9th. ed., 1877, vol. vii., p. 216.

is probably only exact in the case of a permanent gas. For consider an extended volume of air containing aqueous vapour, whose temperature at the one end *A* is say 60° , and at the other end *B* 100° . Let the vapour-tension at *A* be $\cdot 52$ inch, and at *B* $1\cdot 00$ inch. At *A* the air is saturated at its temperature; at *B* it is much drier. According to Clerk Maxwell's statement, the aqueous vapour would diffuse from *B* to *A*, because there is a less quantity of it at *A*. Now one of the purposes of this paper is to inquire whether the unbalanced flow of vapour may be not along the absolute humidity gradient, but along what might be called the potential humidity gradient, which is probably a sort of compromise between the absolute and relative humidities. We do indeed often meet with the assertion, made in a loose, descriptive sort of way, that the rate of evaporation depends upon the dryness of the air. But most often the author is not quite clear as to what he means by "dryness." If, however, for "dryness" we substitute "relative humidity," then it seems highly probable that the statement contains a large element of truth.

If this be so, then the air must be in a certain sense hygroscopic, and in part analogous to a hair hygroscope. Abbe has remarked that the rate at which vapour diffuses through a porous diaphragm depends on the difference of vapour-tension between one side and the other of the diaphragm, and claims that, "undoubtedly, a similar diffusion into animal and vegetable cells through their thin walls is the basis of the hygrometric action that is utilized in the hair hygrometer of Saussure." This, however, is hardly likely to be quite the case. For it is a matter of ordinary observation that if a wisp of human hair, which has been thoroughly cleansed in a soda solution and dried, be placed in a delicate balance in unsaturated air containing a given constant quantity of aqueous vapour, any decrease of temperature (which of course increases the relative humidity) will cause the wisp of hair to become heavier, and any increase of temperature (decrease of relative humidity) will cause it to become lighter—*i.e.*, to absorb or give out moisture without any regard to the actual vapour-tensions inside or outside the hair.¹ Is it not a more likely explanation

¹ My own observations, however, only show this in a rough way: I have so far failed in obtaining a definite relation between the increase of relative humidity and the increase of weight of the hair.

that the increased kinetic energy of the outside aqueous molecules at a higher temperature (and lower humidity) tends by increased bombardment to break up the more readily the cohesion of the groups of molecules within the substance of the hair?

Here we may remark upon an exceedingly interesting discussion raised by an anonymous correspondent in the *Monthly Weather Review* some years ago.¹ Among other questions he submitted the following:—"Is there any clear explanation why increasing the temperature of a space increases the capacity of that space for vapor? If I understand correctly, a space becomes saturated when the vapor-pressure becomes such that for every molecule of water forced into it from the evaporating surface one is forced out. When this equilibrium is attained, would it not seem that raising the temperature of the vapor in the space would, by causing an increase in the vibration of the vapor molecules, cause a greater expansive force, and thus prevent rather than allow more vapor to pass in? Of course experiment proves that more will pass in and can exist in the vapor state when the temperature is raised, but is there any explanation for it?"

In his answer to this question the editor of the *Monthly Weather Review* wrote as follows:—

"Any satisfactory explanation of the fact that the capacity of space for vapor increases with the temperature of the space, or, what is the same thing, the temperature of the vapor, must depend upon our knowledge of the nature of heat and molecules. According to the commonly accepted mechanical theory of heat and the kinetic theory of gases, the heat contained within a mass of vapor is simply the sum-total of the kinetic energy of the rapidly moving molecules of vapour. The molecules of a gas are supposed to be far apart, relative to their own size; but by moving rapidly, by rebounding against each other and against the boundary of the enclosure, they occupy or dominate a large volume. To increase the temperature of this enclosure is to increase the velocity of these molecules, and therefore the number of impacts and reflections that occur per second.

"By increasing the velocity and therefore the kinetic energy of the molecules, we also increase the momentum with which they

¹ For September, 1902.

strike each other and the boundary surface, that is to say, we increase the general expansive pressure of the vapor. If no liquid is present, and therefore if no evaporation throws more vapor into the space, then this increase of pressure corresponds to that due to the ordinary coefficient of expansion of the gas; but if we allow heat to break up liquid molecules into gaseous ones, and evaporation to increase the number of molecules in the gaseous space until it is saturated at the new higher temperature, then the increase of pressure is the sum of two causes, namely, the increased momentum of the old molecules, and the added momentum of the new ones. . . .

“In order that our correspondent and readers may have the choice of several methods of looking at this question, we give the following extracts from recent correspondence:

“Under date of April 4, 1902, Professor J. S. Ames, of Johns Hopkins University, Baltimore, Md., writes as follows:—

“‘My understanding of the reason why an increase in temperature increases the evaporation of a liquid has always been along the lines that the effect of temperature upon the liquid is such as to so increase the velocity of the particles that more of them are able to escape from the surface, and that therefore the evaporation is increased. At the same time, of course, there is an increase in the velocity of the particles of vapor. But the question as to these particles reaching the liquid surface is more one of the mean free path than of anything else, and this is not affected to any such extent as to increase the rate of condensation to so great an extent as the evaporation.’

“Under date of April 15, Professor J. Willard Gibbs, of Yale University, writes as follows:—

“‘In regard to your correspondent’s question, we must remember that the average velocity of molecules in the liquid is increased as much as the average velocity in the vapor (when the temperature is increased). The restraining power of the attractions in the liquid will evidently have less effect in these greater velocities.’

“Dr. Edgar Buckingham, now physicist in the Department of Agriculture, under date of May 10, 1902, writes as follows:—

“‘Heating a gas or vapor in an enclosed space of fixed volume increases its pressure. If we accept the hypothesis that matter is made up of molecules, or separate particles, we account

for this increase of pressure by saying that the energy put into the vapor in the form of heat to raise its temperature, has gone, at least in part, to increasing the kinetic energy of translation of the molecules, so that when the vapor is hotter its molecules fly about more violently, strike harder and oftener on the walls of the enclosing vessel, and so exert a greater pressure.

“ ‘ Now suppose that a part of the enclosing wall consists of the surface of the liquid from which the vapor has been sent off. If we raise the temperature of the vapor without raising that of the liquid, we cannot have a state of equilibrium, and we cannot speak of a definite pressure of the vapor, or of a definite vapor density ; we must always keep the liquid and the vapor at the same temperature, and imagine them heated or cooled simultaneously.

“ ‘ Suppose then that we heat a liquid in contact with its vapor, the two being enclosed in an envelope of invariable volume. According to the kinetic hypothesis, the vapor molecules fly about more violently ; they strike the surface of the liquid harder and oftener ; and we should naturally expect more of them to get caught among the molecules of the liquid, so that the vapor density would decrease, and we should have, in effect, a condensation of vapor, and a decrease in the vapor density.

“ ‘ But we have been considering only the vapor without paying any attention to the liquid, and this upsets our former conclusion. It is true that more molecules of vapor may get caught in the liquid, and so be condensed or become a part of it. But, on the other hand, the kinetic hypothesis assumes that the molecules of a liquid also are in a state of motion, although they move through shorter distances, and with less freedom than the molecules in the vapor. Heat applied to raising the temperature of the liquid increases the violence of motion of the molecules of the liquid too. Hence more particles are likely to arrive at the surface of the liquid, from within it, with sufficient velocity to tear themselves away from the attraction of their fellow-molecules and fly away freely into the space filled with the vapor.

“ ‘ There are thus two opposing tendencies : one for the molecules of the liquid to fly off into the vapor space, and the other for the molecules of vapor to get entangled in the liquid. . . . But there is no way of seeing *à priori* why the one tendency should increase faster than the other, because we do not

know enough about the internal structure of liquids, or the way in which the mutual attraction of their molecules is influenced by temperature. We may, to be sure, say that we know that the cohesion of liquids decreases as the temperature rises, because we know experimentally that the surface-tension (which is an expression of the cohesion) does decrease with rising temperature.¹ Hence we may say that, with rising temperature, the violence of motion of the molecules in both liquid and vapor increases, but the restraining attractions in the liquid decrease, and there is nothing on the side of the vapor to offset this. And so, on the whole, we might expect just what actually happens.'

“Under date of May 27, 1902, Prof. Ernest Merritt, of Cornell University, Ithaca, N.Y., writes as follows:—

“‘To make the point raised by your correspondent perfectly definite, let us suppose that a certain quantity of water is placed in a closed vessel, the space above the water containing saturated vapor. The presence of air would, of course, not modify the conditions essentially. If the temperature of the whole mass is raised, it is a matter of observation that some of the water evaporates and the vapor becomes more dense, yet the pressure of the vapor is increased, and therefore the tendency of vapor molecules to go back into the liquid is greater than at the lower temperature. From the standpoint of the kinetic theory, I think the explanation is somewhat as follows:—

“‘Owing to the rapid motion of the molecules, some of the more rapidly-moving water molecules are continually escaping from the attraction of their neighbors and passing out into the vapor, while some of the vapor molecules are at the same time continually returning again to the liquid. When these two processes just balance one another, the vapor is said to be saturated. Now if the temperature is raised, the motions of the molecules become more rapid. This is true not merely in the vapor, where their increased speed leads to greater pressure, but also in the liquid, where the result is an increased tendency for molecules to escape into the vapor. More molecules return to the liquid each second than before, but more molecules also leave the liquid each second. At first glance it is impossible to tell which of these

¹ [That is, increase of evaporation is, in a sense, synonymous with decrease of surface-tension. At the same time, other things being equal, drops will evaporate faster than plane-surfaces, because of surface-tension.—J. R. S.]

two opposing tendencies will prevail: whether the water will evaporate or the vapor condense. A closer consideration shows, however, that the former is what should be expected.'”

It will be observed that in each of these replies the question as to what will happen, supposing the temperature of the space to be raised, and not that of the water, is ignored, and the phenomenon treated as if the water and the space above are always at the same temperature. Dr. Buckingham does, indeed, notice it, but passes it over as an impossible state of things. Now, in nature it is seldom that an evaporating surface of water, and the space a little above it, are at the same temperature; in fact (as appears from Tables 1 and 2), a small body of water in a screen is almost always cooler than air round about. In Kimberley it often happens that a warm north wind springs up early in the morning, and blows over the surface of the water that has cooled considerably during the preceding night; and, therefore, the question is a perfectly legitimate one, and not to be passed over as unworthy of consideration.

Returning again to Tables 1 and 2 we see that shortly after 5 p.m. the temperature of the air and that of the water in the metal tubes are about the same; before that time the air is the warmer, afterwards it is the cooler. If then there be also a humidity factor, we should expect, other things being the same, that the rate of evaporation would be greater during the day, before 5 p.m., and less afterwards. But, as we have seen in Tables 10 and 11, the exact reverse is the case. And we might jump to the conclusion that by raising the temperature of the space to something higher than that of the water, we should indeed cause more of its aqueous molecules to strike the water, and become entangled therewith, than before;¹ while, since the water would retain for a time its original temperature, the number of molecules passing from the liquid to the air would be unaltered. We shall see presently that this is not a likely explanation of the fact.

Assuming, for the sake of argument, that the stratum of air immediately in contact with a water-surface is completely saturated, we have the following quantities of evaporation, &c., corresponding to assigned relative humidities of the open air:—

¹ In the open air the aqueous molecules would also fly off in the opposite direction; in a confined space they would not.

TABLE 12.—Open Cup.

Relative Humidity.	5 p.m. to 8 p.m.					8 p.m. to 11 p.m.				
	T	δ	W	E	No.	T	δ	W	E	No.
24 % and less .	76.3	inch .668	M. per H. 8.5	grains 69	5	° —	inch —	M. per H. —	grains —	—
25-29 % .	75.6	.602	7.3	64	7	69.2	.438	6.9	40	4
30-34 % .	72.9	.508	4.0	45	16	73.6	.531	3.3	30	3
35-39 % .	69.5	.434	3.1	34	21	66.1	.386	4.7	27	9
40-44 % .	65.0	.352	2.7	25	17	63.0	.324	4.3	24	14*
45-49 % .	64.5	.319	3.2	23	17	59.9	.274	3.8	21	16
50-54 % .	65.9	.307	2.7	21	23	55.7	.219	3.4	13	17
55-59 % .	59.6	.235	2.0	13	4	59.6	.219	3.5	14	15
60-64 % .	69.1	.253	3.1	19	4	61.9	.221	2.3	13	15
65-69 % .	66.8	.209	3.9	14	4	62.4	.186	3.3	13	9
70-74 % .	66.5	.185	3.0	15	1	63.8	.175	3.2	12	6
75-79 % .	67.8	.146	2.8	12	4	68.0	.153	2.9	8	3
80 % and over .	62.3	.076	4.9	7	6	62.7	.080	3.5	6	15

* There were 16 observations in this group, but two were rejected.

In Table 12 the water-temperatures T of the open cup, the differences δ between the vapour-tensions at the temperatures of the water and dew-point,¹ the velocity W of the wind at a height of 45 feet, the evaporation E in grains from the open cup, and the number of observations, have been arranged in groups corresponding to each 5 per cent. of relative humidity in the free air for the two periods 5 to 8 p.m. and 8 to 11 p.m. According to this we see that, saving a few minor irregularities introduced when the number of observations in any group is too few—(1), the temperature of the water is at a minimum when the air is about one-half saturated, but increases pretty uniformly on either side, as the air becomes drier or damper, to at least 25 per cent. on one side, and to about 80 per cent. on the other. Relative humidities, exceeding 80 per cent., are generally associated with rain, and hence the low temperature conditions.

(2.) The velocity of the wind is apparently non-effective.

(3.) The differences of vapour-tension decrease as the relative humidity increases; and (4), so does the rate of evaporation.

So far as (3) and (4) are concerned, therefore, there is nothing to show whether the decrease of evaporation is dependent upon the increase of relative humidity, or the decrease in the differences of vapour-tension.

¹ The wind is known to be most influential in promoting evaporation. The Kimberley observations, however, have not hitherto yielded sufficient information upon which to base a numerical estimate of its effect. The reason seems to be that a strong wind often brings an increase of moisture, and therefore its effect is almost entirely neutralized.

If now we arrange the details from which Table 12 was made into subordinate groups in which, for each 5 per cent. of relative humidity, δ is greater or less than its median value, we get the following averages:—

 TABLE 13.—*Open Cup.* (1.) 5 to 8 p.m.

Relative Humidity	$\delta < \text{Median}$				$\delta > \text{Median}$			
	No.	<i>T</i>	<i>W</i>	<i>E</i>	No.	<i>T</i>	<i>W</i>	<i>E</i>
30–34 %	8	68°6	5·8	45gr.	8	77°1	2·3	45gr.
35–39 %	11	63·9	3·3	27	10	75·5	2·7	42
40–44 %	8	57·3	3·5	20	9	71·8	2·1	31
45–49 %	13	58·9	3·4	18	14	69·7	3·1	27
Total,	40	61·9	3·9	26	41	73·0	2·6	35

(2.) 8 to 11 p.m.

40–44 %	7	55·7	5·2	20	7	70·4	3·4	27
45–49 %	8	50·0	3·1	13	8	69·7	4·6	28
50–54 %	9	50·1	3·3	12	8	61·9	3·4	15
55–59 %	8	54·7	3·6	11	7	65·2	3·5	18
Total,	32	52·5	3·8	14	30	66·7	3·7	22

Table 13 gives us the following further particulars:—For each given humidity group the evaporation is greater or less according as the difference of vapour-tensions is greater or less. But it also happens that the temperature of the water is greater or less under the same circumstances. Wherefore, so far as Table 13 can help us, the rate of evaporation might depend upon either the differences δ or the temperatures *T*, or both.

Tables 14 and 15 give corresponding information to that of Tables 12 and 13; but for the one-foot pipe.

TABLE 14.—*One-foot Pipe.*

Relative Humidity.	5 p.m. to 8 p.m.						8 p.m. to 11 p.m.					
	<i>T</i>	δ	<i>W</i>	<i>E</i>	No.	<i>T</i>	δ	<i>W</i>	<i>E</i>	No.		
	°	inch	M. per H.	grains		°	inch	μ M. per H.	grains			
24 % and less	81.5	.830	8.5	33	5	—	—	—	—	—		
25-29 %	80.5	.760	7.3	29	7	75.5	.650	6.9	24	4		
30-34 %	77.7	.653	4.0	24	16	78.7	.684	3.3	25	3		
35-39 %	73.9	.549	3.1	20	21	72.0	.525	4.7	19	9		
40-44 %	69.2	.453	2.7	17	17	69.1	.451	4.5	15	16		
45-49 %	68.5	.411	3.2	15	27	65.2	.390	3.8	14	16		
50-54 %	69.7	.391	2.7	13	13	60.7	.308	3.4	10	17		
55-59 %	63.1	.301	2.0	11	4	64.3	.311	3.5	9	15		
60-64 %	73.1	.364	3.1	11	4	67.0	.338	2.3	10	15		
65-69 %	70.3	.299	3.9	9	4	67.4	.299	3.3	9	9		
70-74 %	72.0	.320	3.0	10	1	68.4	.279	3.2	8	6		
75-79 %	71.0	.229	2.8	5	4	72.4	.264	2.9	8	3		
80 % and over	65.8	.157	4.9	4	6	65.9	.149	3.5	4	15		

TABLE 15.—*One-foot Pipe.* (1.) 5 to 8 p.m.

Relative Humidity.	$\delta < \text{Median}$				$\delta > \text{Median}$			
	No.	<i>T</i>	<i>W</i>	<i>E</i>	No.	<i>T</i>	<i>W</i>	<i>E</i>
30-34	8	73 ^o .8	5.2	22gr.	8	81 ^o .5	2.8	26gr.
35-39 %	10	67.9	3.6	18	11	79.4	2.7	22
40-44 %	8	61.4	2.6	14	9	76.2	2.9	18
45-49 %	14	63.3	2.9	13	13	74.1	3.6	17
50-54 %	6	64.3	3.3	12	7	74.3	2.2	15
Total,	46	65.9	3.5	16	48	77.0	2.9	20

(2.) 8 to 11 p.m.

35-39 %	4	68.1	5.4	17gr.	5	75.1	4.2	22
40-44 %	8	61.9	5.2	12	8	76.4	3.8	17
45-49	8	55.5	3.1	11	8	74.9	4.6	17
50-54 %	9	55.2	2.2	9	8	66.9	3.4	11
55-64	15	60.3	3.2	9	15	71.0	2.6	11
Total,	44	59.4	3.8	10	44	72.4	3.5	14

Tables 14 and 15 give substantially the same result as Tables 12 and 13, the only difference being in degree rather than in kind. The temperatures of the water in the pipe for the hours considered are higher than those of the open cup, and therefore the differences of vapour-tension are greater, while the quantities of evaporation are less. As with the open cup, when δ is less than the median the minimum temperature of the water comes with a lower relative humidity than when δ is greater. It is worth while noticing such points as these, because they illustrate the complexity of the processes in which evaporation is wrapped up, and the difficulty of separating the important agencies from the uninfluential.

In Table 16 we have the following quantities of evaporation corresponding to assigned differences of vapour-tension between the temperature of the water and that of the dew-point.

TABLE 16.—Open Cup.

δ	5 p.m. to 8 p.m.						8 p.m. to 11 p.m.					
	T	H	W	E	No.	No.	T	H	W	E	No.	
inch < .100	59.8	93	M. per H. 5.2	grains. 4	4	61.5	% 88	M. per H. 3.9	grains 5	10		
.100-.149	67.3	78	3.8	13	5	55.2	70	2.6	8	14		
.150-.199	57.7	62	3.2	13	9	55.4	58	3.6	12	25		
.200-.249	60.3	55	3.4	18	9	60.1	57	3.2	14	30		
.250-.299	60.8	48	2.6	18	17	65.5	52	4.3	22	16		
.300-.349	64.7	45	3.3	23	22	67.4	50	2.7	20	4		
.350-.399	70.3	45	3.9	30	15	68.0	42	3.9	26	12		
.400-.449	71.2	40	3.7	35	12	71.1	42	4.5	28	7		
.450-.499	73.2	36	4.2	45	7	73.0	84	3.8	36	3		
.500-.549	74.2	34	3.7	45	12	72.8	30	5.1	34	5		
.550-.599	76.7	33	3.0	45	7	—	—	—	—	—		
.600 and over	78.7	25	5.9	64	10	—	—	—	—	—		

Here we see that as δ increases the temperature T of the water increases, the relative humidity H of the air decreases, and the evaporation E increases, while the velocity W of the wind is of uncertain influence, as before. Thus, so far as Table 16 goes, the rate of evaporation may depend either upon δ , or T , or H , either or all. Now it is known that an increased water-temperature will increase the rate of evaporation, although it is possible that the effect has been somewhat overestimated. In any case it will not be necessary to discuss this particular point at present.

If we arrange the details from which Table 16 is derived into groups of given vapour-tension differences, in which the relative humidity is greater or less than its median value, we get the following averages:—

TABLE 17.—*Open Cup.* (1.) 5 to 8 p.m.

Difference of Vapour-Tension	H > Median				H < Median			
	No.	T	W	E	No.	T	W	E
inch		°				°		
·150--·249	9	65·3	3·4	15gr.	9	52·7	3·2	16gr.
·250--·299	8	65·5	2·9	17	9	56·6	2·4	18
·300--·349	10	67·0	2·6	20	12	62·7	3·8	25
·350--·399	9	72·9	4·4	31	6	66·3	3·2	27
·400--·449	6	73·3	2·1	35	6	69·0	5·4	35
·450--·549	10	75·1	2·4	39	9	72·4	5·0	51
·550--·599	3	76·9	2·0	38	4	76·5	3·7	50
Total, .	55	70·2	3·0	27	55	63·7	3·9	30

(2.) 8 to 11 p.m.

·100--·149	7	65·1	3·0	8	7	45·4	2·2	9
·150--·199	12	61·1	3·5	11	13	50·0	3·8	13
·200--·249	15	64·1	3·1	14	15	55·6	3·3	14
·250--·299	7	68·4	1·9	17	9	63·2	6·1	26
·300--·399	8	70·0	3·0	23	8	65·6	4·1	27
Total, .	49	65·1	3·0	13	52	55·7	3·9	17

Here we have the following results:—As δ increases the evaporation increases; T , on the whole, increases, but shows no particular influence over the rate of evaporation; W is again apparently almost non-effective. But the important fact is this, that the rate of evaporation is greater when the relative humidity is less, in spite of the fact that a low percentage of relative humidity evidently implies a low water-temperature. It is therefore to be inferred that the relative humidity of the air is a much more influential agent than the temperature of the water in promoting evaporation. At the same time, it must not be forgotten that a more rapid evaporation necessarily produces some cooling of the water-surface.

In Tables 18 and 19 will be found corresponding information to that of Tables 16 and 17, but for the one-foot pipe.

TABLE 18.—One-foot Pipe.

δ	5 p.m. to 8 p.m.						8 p.m. to 11 p.m.					
	<i>T</i>	<i>H</i>	<i>W</i>	<i>E</i>	No.		<i>T</i>	<i>H</i>	<i>W</i>	<i>E</i>	No.	
inch <.100	59.5	94	M. per H. 5.6	grains 1	3		59.1	94	M. per H. 3.7	grains 1	3	
.100-.149	—	—	—	—	—		68.4	86	1.9	4	2	
.150-.199	68.0	78	3.0	4	1		60.6	76	3.5	5	13	
.200-.249	62.4	65	3.5	7	10		58.8	61	2.9	7	16	
.250-.299	66.2	64	2.1	10	7		60.7	55	3.6	10	16	
.300-.349	63.2	50	2.5	13	14		65.7	58	3.2	10	25	
.350-.399	68.3	51	3.7	14	11		70.4	56	4.7	11	11	
.400-.449	69.9	46	2.5	15	18		71.2	52	3.5	14	12	
.450-.499	73.0	45	4.4	17	14		73.6	44	3.6	16	5	
.500-.549	74.4	40	3.4	18	8		74.3	41	4.3	18	12	
.550-.599	76.7	39	5.1	20	8		75.8	43	2.8	20	3	
.600-.699	78.5	35	3.7	23	18		78.7	34	5.2	23	10	
.700 and over	83.0	28	5.0	30	17		—	—	—	—	—	

TABLE 19.—*One-foot Pipe.* (1.) 5 to 8 p.m.

δ	H > Median				H < Median			
	No.	<i>T</i>	<i>W</i>	<i>E</i>	No.	<i>T</i>	<i>W</i>	<i>E</i>
inch		°				°		
·200-·249	5	70·1	3·2	6gr.	5	54·5	3·9	9gr.
·250-·299	4	72·3	2·8	8	3	58·2	1·0	12
·300-·399	11	70·6	3·5	12	14	61·4	2·8	14
·400-·499	15	74·3	3·2	15	17	68·6	3·5	17
·500-·599	7	77·1	2·9	17	9	74·3	5·4	21
·600-·699	10	79·5	2·2	22	8	77·1	5·7	24
·700 & over	8	82·3	2·2	27	9	82·6	7·5	32
Total, .	60	75·4	2·9	16	65	69·3	4·3	19

(2.) 8 to 11 p.m.

·150-·199	7	67·0	4·0	5gr.	6	53·2	2·9	6gr.
·200-·249	8	65·1	2·9	6	8	52·5	2·9	9
·250-·299	8	64·0	3·2	9	8	57·3	4·1	10
·300-·349	12	69·8	3·6	10	13	62·0	2·8	11
·350-·399	5	71·4	3·5	11	6	69·5	5·7	12
·400-·449	6	74·5	2·2	12	6	67·9	4·7	15
·450-·549	9	75·4	3·7	17	8	72·6	4·6	18
Total, .	55	69·5	3·3	10	55	62·0	3·8	12

The results of Table 18 differ from those of Table 16 in one important respect: that when the differences of vapour-tension, the relative humidity, and the water-temperatures are about the same from 5 to 8 p.m. as they are from 8 to 11 p.m., the evaporation in the pipe will be about the same in the two intervals; whereas under the same equalities the open cup will lose considerably more from 5 to 8 p.m. than from 8 to 11 p.m. Table 19 is in effect much the same as Table 17, excepting of course that the observed evaporation is less. In both cases when δ is small the temperature of the water is much less for low relative humidities than for high; but as δ increases the temperature of the water for a low relative humidity more and more approximates to the temperature for a

high relative humidity, and, evidently, it is just when δ is large that the effects of a decreased relative humidity are most strongly felt. The essential fact that an accelerated evaporation corresponds to a diminished humidity holds good for the pipe just as it does for the open cup. Before leaving this part of the subject it is perhaps worth while suggesting that in this case also as in that of the hair hygrometer the reason why there is probably a humidity factor in the process of evaporation from a water-surface is that the greater average kinetic energy of the aqueous molecules at the higher temperature of the space is the more competent to break up the closed chains of molecules in the surface of the water. Thermal effusion is probably not concerned in the process excepting to a very small extent.

In Tables 24 and 25 at the end of this paper will be found a summary of the results for different intervals and periods. A comparison between these and the smaller tables in the text suggests the following provisional conclusions: that while differences between the vapour-tensions at the water-surface and in the open air are competent to influence the rate of evaporation to a large extent, the intensity of the effect of vapour-tension differences is profoundly modified by the relation the temperature of the dew-point bears to the temperature of the air—or, in other words, is profoundly modified by the relative humidity. The water-temperatures are, as such, probably of no great importance, initially at any rate; but when considered in conjunction with the temperature and relative humidity of the air, an influence becomes apparent which, so far as I know, has not hitherto received due recognition. It seems to me to be extremely probable that after the relative humidity of the open air and the differences of vapour-tension (*i.e.* $\delta = p' - p''$) have been allowed for, much of the observed evaporation, from whatsoever form of water-surface or type of gauge, is due to convection currents. Thus, for example, in the case of the three metal pipes we see that the evaporation is not most rapid when the temperature of the water, or of the air, is highest, or when the relative humidity is least, or when the differences of vapour-tension are greatest, either, or all, but when, in addition to favourable values of these, the temperature of the air falls below that of the water-surfaces. According to the observations we get the maximum effect in the pipes between

5 p.m. and 8 p.m. During the hot and dry hours about mid-day, whatever evaporation due to the absolute or relative humidity there may be, the columns of air in the pipes are in stable equilibrium, with warm air above and colder (though moister) air below, so that whatever is evaporated from the water-surfaces can only be carried off by the comparatively slow process of diffusion. After sunset, however, although the evaporation actually due to the relative and absolute humidities alone is less, a condition of unstable equilibrium is set up inside the pipes, and hence the aqueous vapour is the more readily removed to a distance, as it is formed by convective action. In the case of the open cup, which is practically always cooler than the surrounding air, the maximum convection effect will necessarily be the opposite to that in the pipes, namely, when the temperature of the air *exceeds* that of the water by the greatest amount—say about noon—for at that time the cooler vapour-laden air overlying the water will the more readily flow off and be displaced by the warmer air surrounding it. In the case of the tub, which is warmer than the air for a great part of the night, but colder at other times, we should expect a maximum about noon on account of the overflow of cool vapour-laden air, and a tendency to a second maximum between sunset and midnight on account of a mild upcast of relatively warm, moist air. With the object of testing this point, I have made a short series of observations upon the rate of evaporation in the metal pipes when these have been slightly raised to permit some communication between the air at the bottom of the pipes and that outside. With the pipes raised $\frac{3}{16}$ and $\frac{9}{16}$ inch by means of pieces of wooden lath placed under the base flanges, the following were the average results:—

TABLE 20. 13 days.

Time Intervals	One-foot Pipe		Two-foot Pipe	
	$\frac{3}{16}$ inch	$\frac{9}{16}$ inch	$\frac{3}{16}$ inch	$\frac{9}{16}$ inch
8 a.m. to 5 p.m. .	35	53	33	27
5 p.m. to 8 p.m. .	20	27	21	31
8 p.m. to 11 p.m. .	14	17	15	21
11 p.m. to 8 a.m. .	22	27	24	32

Only ratios must be considered in this Table, for the observations with the two pipes were not made simultaneously. It will be understood, of course, that the air near the ground inside the screen containing the pipes is colder than it is at one and two feet higher, *i.e.*, at the levels of the mouths of the pipes, especially at night, and consequently that the interchange of air below may not be very vigorous. Moreover, the air-channels below the flanges are very small. In spite of this we see from Table 20 that our modification of the experiment has considerably altered the diurnal variation of the rate of evaporation in the pipes, transforming it into something more nearly like that of the open cup than it was before. We see, in fact, that the hourly rate of evaporation between 5 and 8 p.m., instead of being (Table 10) two and a half times as great as that between 8 a.m. and 5 p.m., is now only about half as great again.

If the curious, dissimilar, diurnal curves of evaporation in the metal pipes, from the tub and from the open cup, be really due in great part to convection currents, the same cause may be responsible for the want of symmetry in the diurnal curve of evaporation from the large tank.

In Table 21 (page 168) are given the hourly average quantities of water evaporated from the tank for each month, derived from observations made between August, 1899, and July, 1906—seven years. Generally speaking, in the winter there are three maximum points on the curve. The first is about the time of sunrise,¹ and is sometimes very pronounced; the second is the normal maximum in the afternoon; the third comes somewhere between 9 and 11 p.m. In the summer the first and third maxima become faint or abortive. The first minimum points are very curiously arranged. In the summer they group themselves about the hour before sunrise; but in the winter-half of the year they plainly work back almost to midnight. The consequence is that the average time of the first minimum for the year falls about 4 a.m., *i.e.*, nearly two hours earlier than the minimum of either air-temperature or wind-velocity, or the maximum of relative

¹ There are trees to the east of the tank, and in consequence the rays of the sun do not reach the water for some considerable time after sunrise, more especially in the winter. The average evaporation at sunrise in July is sometimes greater than the normal maximum in the early afternoon.

TABLE 21. — Hourly Average Quantities of Evaporation from the Tank.

Hour ending	Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Year
I.	inch .222	inch .177	inch .135	inch .083	inch .058	inch .032	inch .029	inch .056	inch .095	inch .156	inch .212	inch .238	inch 1.493
II.	.226	.168	.135	.082	.061	.032	.033	.062	.104	.146	.208	.235	1.492
III.	.211	.169	.129	.092	.061	.032	.033	.062	.099	.152	.197	.230	1.467
IV.	.203	.165	.122	.089	.062	.032	.038	.064	.095	.151	.195	.214	1.430
V.	.199	.153	.123	.091	.065	.043	.039	.064	.103	.143	.183	.205	1.411
VI.	.206	.156	.124	.087	.065	.037	.037	.056	.109	.171	.219	.230	1.497
VII.	.236	.168	.150	.101	.072	.062	.071	.106	.154	.195	.242	.259	1.816
VIII.	.246	.187	.154	.106	.092	.110	.141	.148	.162	.203	.235	.245	2.029
IX.	.263	.197	.160	.127	.110	.114	.129	.139	.183	.240	.273	.290	2.225
X.	.319	.208	.187	.135	.123	.116	.133	.145	.196	.282	.336	.365	2.545
XI.	.396	.265	.234	.162	.134	.118	.144	.190	.252	.336	.421	.430	3.082
Noon	.478	.319	.293	.215	.174	.139	.160	.216	.295	.411	.488	.508	3.696
XIII.	.568	.391	.374	.268	.222	.156	.187	.264	.356	.464	.548	.585	4.383
XIV.	.611	.441	.395	.295	.235	.174	.201	.278	.364	.494	.581	.633	4.702
XV.	.619	.452	.427	.287	.214	.145	.178	.279	.371	.504	.590	.635	4.701
XVI.	.597	.445	.393	.257	.162	.117	.148	.214	.332	.464	.576	.628	4.333
XVII.	.553	.398	.339	.183	.098	.062	.076	.168	.266	.405	.537	.583	3.661
XVIII.	.473	.320	.258	.123	.066	.035	.041	.088	.173	.305	.439	.506	2.827
XIX.	.382	.256	.184	.103	.058	.039	.033	.069	.123	.230	.336	.399	2.212
XX.	.303	.212	.167	.109	.070	.034	.037	.071	.124	.208	.297	.330	1.962
XXI.	.287	.205	.150	.098	.065	.035	.041	.074	.112	.195	.272	.289	1.823
XXII.	.267	.195	.140	.100	.061	.036	.040	.075	.108	.190	.256	.276	1.744
XXIII.	.246	.194	.149	.097	.069	.047	.045	.070	.116	.178	.251	.255	1.717
Midnight	.233	.176	.132	.087	.063	.035	.036	.063	.103	.163	.230	.248	1.569
Total, .	8.344	6.012	5.054	3.377	2.460	1.782	2.050	3.021	4.395	6.384	8.122	8.816	59.817

humidity. Some supplementary process, in addition to those of difference of vapour-tensions, relative humidity, and wind-velocity is evidently required; and if convection currents are not to be postulated, it is difficult to see what is. My observations made with the metal pipes do certainly seem to show that the rate of evaporation may go on increasing even though the temperature of the water-surface be falling, provided that the temperature of the air fall faster still; and that the rate may decrease under a rising temperature, provided that the air is warmed much more rapidly than the water; subject in both cases, however, to the governing elements of relative humidity. If future observation should confirm this conjecture, the possibility follows that the evaporation from the surface of the sea at night may actually be as great as or greater than it is by day. It has been stated before more than once that the evaporation from a large water area may be nearly as great at night as it is by day, because the temperature of the water does not vary much in the course of twenty-four hours under insolation and radiation. My contention is that the evaporation may actually be greater at night, not so much because the water is warm as because the air is colder. It would not be easy to prove this by direct observation with the evaporimeter and hygrometer; but certainly indirect observation, so far as it goes, is not antagonistic to the idea. To begin with, the sea is somewhat warmer at night and colder by day than the air. Then, according to the *Challenger Report*, the relative humidity over the open sea has its maximum value about 2 a.m., and not just before sunrise, when the air is coldest; while the sky is most clouded at sunrise. This is just what ought to happen supposing filaments of moist air from the surface to ascend more and more vigorously as the difference of temperature between air and sea became more marked, and to be replaced by descending filaments of drier air. Naturally, the hygrometer would not show that more water was being evaporated because the accumulation of vapour would occur in the higher levels.

Davis's *Elementary Meteorology* contains the following interesting statement:—"It is supposed that the energy needed in evaporation of water is expended in overcoming the attraction that exists between the molecules while the water is in the liquid state. The supply of energy to do this hidden work often

comes from the sensible heat of some adjacent substance. When water evaporates from the sea or from a lake or river, or from the wet surface of the land, the energy needed to change its state may be derived, in part, from the heat of the adjacent water or land; but in the usual case of evaporation proceeding under sunshine, it is supposed that the energy of insolation may pass directly to the work of overcoming the inter-molecular attractions of the water, and thus changing it to the gaseous state, without taking the intermediate form of heat. This is illustrated in the ordinary experience of a drying day after a rainstorm. The surface of the land, everywhere wet from the rain that fell from the clouds the day before, is then shone upon by the sun's direct and indirect rays from the clear sky. Instead, however, of there being a rapid rise of temperature, there is a rapid drying of the ground; the energy of insolation received upon the surface of the ground is expended in changing the state of the water more than in increasing the molecular activity of the ground or of the water. In the same way the strong insolation absorbed at the surface of the torrid oceans is devoted more to causing evaporation than to raising the temperature of the water; hence in good part for this reason the oceans around the equator are relatively cool."¹

It must be granted that this statement which Davis puts so well embodies a most important idea, and is worth careful attention. Nevertheless, my own experiments up to the present time do not conform very well with the suppositions. I have not been able to find that the energy of insolation, *as such*, and acting alone, is capable of evaporating water from either a water- or a land-surface. On the contrary, let the sun shine ever so brightly, there will not be a great evaporation unless the air be dry. But if the air be dry, the evaporation will be comparatively rapid, and this will prevent any great rise of temperature. It is well known that a porous surface, if kept saturated, will evaporate as fast as (perhaps faster than) a water-surface of the same area. In the five years, 1900-1904, for example, my observations gave the following average comparative quantities of evaporation from the tub, and from the Piche atmometer, using the factor .00415 for reducing the scale readings of the latter to inches:—

¹ W. M. Davis, *Elementary Meteorology*, 1894, p. 140.

TABLE 22.—*Comparative Quantities of Evaporation.*

	Piche Atmometer	Screened Tub
	inches	inches
January,	9·17	7·92
February,	7·11	5·77
March,	5·71	4·54
April,	4·71	3·45
May,	5·21	3·48
June,	4·08	2·68
July,	4·75	3·03
August,	6·54	4·41
September,	7·88	5·56
October,	9·21	7·21
November,	10·55	9·26
December,	9·56	8·63
Year,	84·48	65·94

According to these results, the annual average evaporation from the tub is only 78 per cent. of that from the Piche atmometer, the winter average being only 65 per cent. Probably a smaller tub would evaporate more than a larger one; but the further amount cannot be great, since a copper pan 8 inches in diameter and 5 inches deep, exposed to the open sky at Kimberley, only loses about 90 inches in a year. Such a gauge becomes very hot during the day, and its high temperature and free exposure naturally contribute largely to increasing the loss by evaporation. Exposed in a louvered screen, it would, of course, lose much less than in the open air.¹

It is to be remembered that the evaporating surface of the Piche atmometer is kept completely saturated by the superimposed column of water, and therefore the loss is maintained at its maximum rate under the given conditions of exposure. But the loss will evidently be curtailed if the porous surface become drier. What is called a "drying day after rain" only really attracts so

¹ "Gauges" of this pattern are usually supplied with a wire mesh, a sort of *cheval de frise*, to keep birds and animals from the water. This, perhaps because it breaks up the wind-currents, hinders the ordinary process of evaporation.

much attention, because the saturated earth evaporates rapidly. What the unobservant observer seems not to notice is that irrigated land dries up even more quickly in dry weather than land wetted by rain. In any case, the rate of drying depends to a great extent upon the nature of the soil: sand, *e.g.*, drying much more quickly than clay. The following is a case in point:—Some months ago I made a series of comparative observations upon the ordinary poor red sand of the South African veldt and the blue clay of the Kimberley diamond mines, noting the behaviour of each with respect to the absorption and radiation of heat, and the absorption and evaporation of water. A rough measurement gave the relative specific gravity of the sand to the clay as about 13: 14, and the latter showed a much smaller range of temperature than the former, when the two were exposed side by side in the open air. Also water percolated much more freely into the sand than into the clay. In the experiment that bears directly upon this discussion I took equal weights of sand and clay, dried them, crushed them up as fine as possible, packed them tightly into nearly identical silver-plated cups, and then saturated them as nearly as possible with equal weights of water, the total weight of earth and water being finally 4728 grains. They were then placed side by side in the shade,¹ with the object of keeping them at nearly the same temperature. The following were the synchronous losses by evaporation until they attained a sort of hygroscopic balance with the air.

TABLE 23.—*Comparative Losses by Evaporation.*

		Blue Clay	Red Sand
First	to Third day, . . .	90 grains	109 grains
Third	„ Fifth day, . . .	75 „	114 „
Fifth	„ Seventh day, . . .	58 „	66 „
Seventh	„ Tenth day, . . .	30 „	24 „
Tenth	„ Twelfth day, . . .	29 „	19 „
Twelfth	„ Fifteenth day, . . .	21 „	8 „
Fifteenth	„ Twenty-second day, .	17 „	0 „
Twenty-second	„ Twenty-eighth day, .	— 3 „	— 8 „

¹ In the shade of a louvered screen.

This particular experiment was made in April—one of our most humid months. It appears that the sand evaporated much more rapidly than the clay for the first week, but afterwards, when of course it had less to lose, it lost less. By the twenty-eighth day both earths were gaining or losing according to the humid state of the air. The *minus* signs on the last line stand for gains.

Before closing this already lengthy paper there is one point which, although somewhat foreign to its main purpose, may not be without interest: will an electrified water-surface evaporate more or less than an unelectrified one? About the middle of the eighteenth century the Abbé Nollet, experimenting with capillary tubes, came to the conclusion that all organized bodies (which according to his view were to be considered as assemblages of capillary tubes) evaporated or perspired more when electrified than usually. He also “electrified liquors of all sorts in open vessels, and remarked that the electrification augmented their evaporation, in some more, in others less, according to their different natures.” He justly observed, however, that it is not so easy a task to draw a safe conclusion from the experiments as might at first be imagined.¹ In commenting upon and criticising Nollet’s results, Ellicot quoted some experimental work of his own from which he concluded that an increased flow through capillary tubes did not depend upon a mere electrification of the water, but upon the passage of an electric current.² A few years later Bohadsch repeated and confirmed Nollet’s results. He found that 4 oz. of river-water exposed in a glass vessel of 4 inches diameter and electrized five hours lost in their weight 8 grains. But 4 oz. of river-water in the same kind of glass, but not electrized, lost in the same time only 3 grains. Hence he concluded that electricity augments the natural evaporation of liquids, and operates in vessels of metal more strongly than in those of glass.³

J. J. Thomson remarks that “few direct experiments on the evaporation of electrified water-surfaces seem to have been made. Mr. Crookes, from some experiments he made on this point, came to the conclusion that a negatively electrified surface of water

¹ *Phil. Trans.*, 1747.

² *Ibid.*, 1747.

³ *Ibid.*, 1751.

evaporated more rapidly than an unelectrified one. Mascart came to the conclusion that an electrified surface, whether the electrification was positive or negative, evaporated more rapidly than an unelectrified one; while Wirtz found that electrification diminished the rate of evaporation of dust-free water, and that positive electrification had more effect than negative.¹ Crookes's experiments, however, hardly seem to bear directly upon the question. The following are some extracts from his memoir, the first theoretical, the rest experimental:—"Electrical volatilisation or evaporation is very similar to ordinary evaporation by the agency of heat. . . . If we consider a liquid at atmospheric pressure—say, for instance, a basin of water in an open room—at molecular distances, the boundary-surface between the liquid and the superincumbent gas will not be a plane, but turbulent like a stormy ocean. . . . The intrinsic velocity of the molecules is intensified by heat and diminished by cold. If, therefore, we raise the temperature of the water without materially increasing that of the surrounding air, the excursions of the molecules of the liquid are rendered longer and the force of impact greater, and thus the escape of molecules into the upper region of gas is increased, and we say that evaporation is augmented. If the initial velocities of the liquid can be increased by any other means than by raising the temperature, so that their escape into the gas is rendered more rapid, the result may be called 'evaporation' just as well as if heat had been applied . . .

"*Evaporation of water.*—A delicate balance was taken and two very shallow porcelain dishes were filled with acidulated water and balanced on the pans. Dipping into each dish—touching the liquid, but not the dish—was a platinum wire, one connected with the induction coil and the other insulated. The balance was left free to move, but was not swinging, the pointer resting at the centre of the scale. The water in connexion with the coil was first made positive. After one and three-quarter hours there was scarcely any difference between the weight of the insulated water and that which had been exposed to the positive current. Equilibrium being restored, the current was reversed, the negative current being kept on the dish for two hours. At the end of this

¹ *Discharge of Electricity through Gases*, 1898, p. 16.

time the electrified water was decidedly lighter. . . . This experiment shows that the disturbing influence which assists evaporation is peculiar to the negative pole even at atmospheric pressures.”¹

Rowell, in his chapter on “Evaporation,” apparently accepting Nollet’s results, says:—“In accordance with the proposed theory I was led to think that evaporation would not go on so freely from an insulated vessel as from an uninsulated one, and, in 1841, I tried several experiments, the following account of which appeared in the *Phil. Mag.*, Jan., 1842:—‘In a warm room, over an oven in daily use, I suspended with silk threads two shallow vessels, eight inches and a half in diameter, containing eight ounces of water each; a small copper wire was hung from one vessel to the earth to take off the insulation, both vessels being similarly suspended in every other respect; after being suspended for twenty-five hours, the insulated vessel had lost two ounces, eleven dwts., and fifteen grains; and the other vessel three ounces, six dwts., showing an excess of evaporation from the non-insulated vessel of fourteen dwts., nine grains. I have tried similar experiments with water placed in the rays of the sun, and on all occasions the evaporation has been greatest from the non-insulated vessel. . . . And in the *Annals of Electricity*, vol. viii., p. 325, Mr. T. Spencer, in an article on Atmospheric Electricity, after referring to the foregoing experiment, says:—‘I have repeated a similar set of experiments, and with nearly similar results; always, at least, showing an excess in favour of the non-insulated vessels of water.’ Thus the agency of electricity in evaporation is shown in various ways; as electricity goes off during evaporation, an excess of it accelerates evaporation, and, as in the last experiments, the want of it retards evaporation.”²

Whether the surrounding conditions were such as to justify Rowell’s deductions is more than I know, although he seems to have got the same effect indoors and out. At any rate, I have not succeeded in getting it. During the dry, clear Kimberley winter of 1904, for about three months, I exposed four almost

¹ “On Electrical Evaporation,” *Proc. Roy. Soc.*, 1891, No. 302, p. 88.

² G. A. Rowell, Hon. Memb. Ashmolean Soc., *An Essay on the Cause of Rain, &c.*, 1859, p. 41.

identical, carefully-made, copper "evaporating gauges," with turned brass rims, in a large, louvered screen—one insulated, one connected to earth, one joined by an insulated wire to a (poor) collector suspended at a height of 45 feet; the fourth joined in the same way, but also earthed as well. The gauges were interchanged frequently, so as to eliminate their personal equations if such should exist. In the result, one gauge evaporated pretty much the same as another; when differences did show in the quantities evaporated, they were so small as to be most easily ascribed to errors of observation. This result applies only to the question whether an insulated gauge loses more or less than an uninsulated one; it does not touch the question whether electrified water evaporates faster or slower than unelectrified.

TABLE 24.—*Hourly Rates of Evaporation.*
 (Temperatures at the last Hour of the given Periods.) 15 days.

	Open Cup		One-foot Pipe		Two-foot Pipe		Three-foot Pipe		Air	Piche	Screened Tub	
	°	grains	°	grains	°	grains	°	grains	°	units	°	inch
8 a.m. to 11 a.m.	68.4	14.4	64.4	1.0	64.6	0.8	64.5	0.8	75.4	3.7	60.7	.013
11 a.m. to 2 p.m.	72.4	29.6	72.8	2.5	72.7	1.9	72.8	2.0	79.9	5.1	66.6	.014
2 p.m. to 5 p.m.	70.9	24.5	74.9	4.9	74.7	4.1	75.1	3.6	75.8	5.2	67.6	.012
5 p.m. to 8 p.m.	63.3	9.5	68.8	6.2	69.4	5.1	70.0	4.0	64.7	2.4	66.0	.005
8 p.m. to 11 p.m.	58.8	5.8	63.7	4.1	64.5	3.3	64.9	2.7	59.5	1.7	63.8	.007
11 p.m. to 8 a.m.	56.2	3.0	55.1	1.8	55.8	1.5	55.8	1.2	60.3	1.1	57.8	.004
5 days.												
8 a.m. to 8 a.m.	55.7	9.7	54.3	2.8	54.8	2.2	54.8	1.9	59.4	2.6	60.6	.008

TABLE 25.—Hourly Rates of Evaporation. (Temperatures at the last Hour of the given Periods.) 114 days.*

	Open Cup		One-foot Pipe		Two-foot Pipe		Three-foot Pipe		Air	Piche	Screened Tub	
	°	grains	°	grains	°	grains	°	grains	°	units	°	inch
8 a.m.—5 p.m.	60.7	15.3	63.2	1.2	63.4	1.0	63.6	1.1	62.4	3.4	54.7	.011
	76.9	23.3	80.5	3.3	80.6	2.8	81.1	2.4	83.8	4.6	76.2	.016
	75.3	21.2	79.2	2.8	79.3	2.3	79.5	2.1	81.3	4.1	73.8	.013
	72.1	17.9	75.1	2.2	75.1	1.8	75.4	1.6	76.9	5.7	69.9	.011
	67.3	15.6	70.0	1.8	70.0	1.4	70.2	1.3	70.8	3.3	63.1	.011
Mean,	70.5	18.7	73.6	2.3	73.7	1.9	74.0	1.7	75.0	4.2	67.5	.012
5 p.m.—8 p.m.	50.8	6.4	56.7	4.6	57.1	3.7	57.4	3.0	50.9	1.9	52.6	.005
	72.1	14.7	76.9	6.9	77.4	5.7	78.0	4.7	75.1	3.5	75.0	.014
	70.0	11.4	75.2	6.1	75.5	5.1	75.9	4.3	71.7	2.5	72.6	.011
	66.1	9.5	70.9	5.4	71.3	4.5	71.9	3.7	67.2	2.2	68.7	.007
	59.1	6.5	64.3	5.1	64.8	4.2	65.9	3.1	59.4	1.9	61.6	.005
Mean,	63.6	9.7	68.8	5.6	69.2	4.6	69.8	3.8	64.8	2.4	66.1	.008
8 p.m.—11 p.m.	46.4	4.3	50.9	3.1	51.7	2.3	52.0	1.9	46.9	1.5	(50.6)	(.004)
	67.8	8.4	72.4	4.7	73.1	3.8	73.4	3.1	69.7	2.4	72.7	.010
	65.6	6.5	70.2	4.3	70.9	3.4	71.2	2.9	66.8	1.9	70.6	.007
	62.1	5.1	66.3	3.7	67.0	2.9	67.3	2.3	63.1	1.6	66.7	.006
	54.2	4.1	58.9	3.2	59.6	2.4	59.9	2.0	54.4	1.4	59.4	.005
Mean,	59.2	5.7	63.7	3.8	64.5	3.0	64.8	2.4	60.2	1.8	64.0	.006
11 p.m.—8 a.m.	41.6	2.6	41.9	1.5	42.6	1.2	42.9	0.9	46.7	1.1	(45.6)	(.003)
	69.2	5.3	67.7	2.1	68.1	1.7	68.1	1.3	70.2	1.5	68.3	.007
	65.9	4.1	64.1	1.9	64.5	1.6	64.5	1.3	70.0	1.3	65.0	.006
	61.5	3.4	60.2	1.6	60.7	1.3	60.7	1.0	64.8	1.2	61.7	.005
Mean,	51.9	2.5	50.6	1.6	51.2	1.2	51.3	0.9	55.9	1.1	53.6	.004
Mean,	58.0	3.6	53.9	1.7	57.4	1.4	57.5	1.1	62.3	1.2	58.8	.005

* Series 1 = 19 days; Series 2 = 25 days; Series 3 = 24 days; Series 4 = 25 days; Series 5 = 21 days.

EXPLANATION OF PLATE IX.

PLATE IX.

A. Elevation.

B. Plan of Base showing how the Rubber Insertion is laid on.

C. Open Cup.

D. One-foot Pipe.

E. Two-foot Pipe.

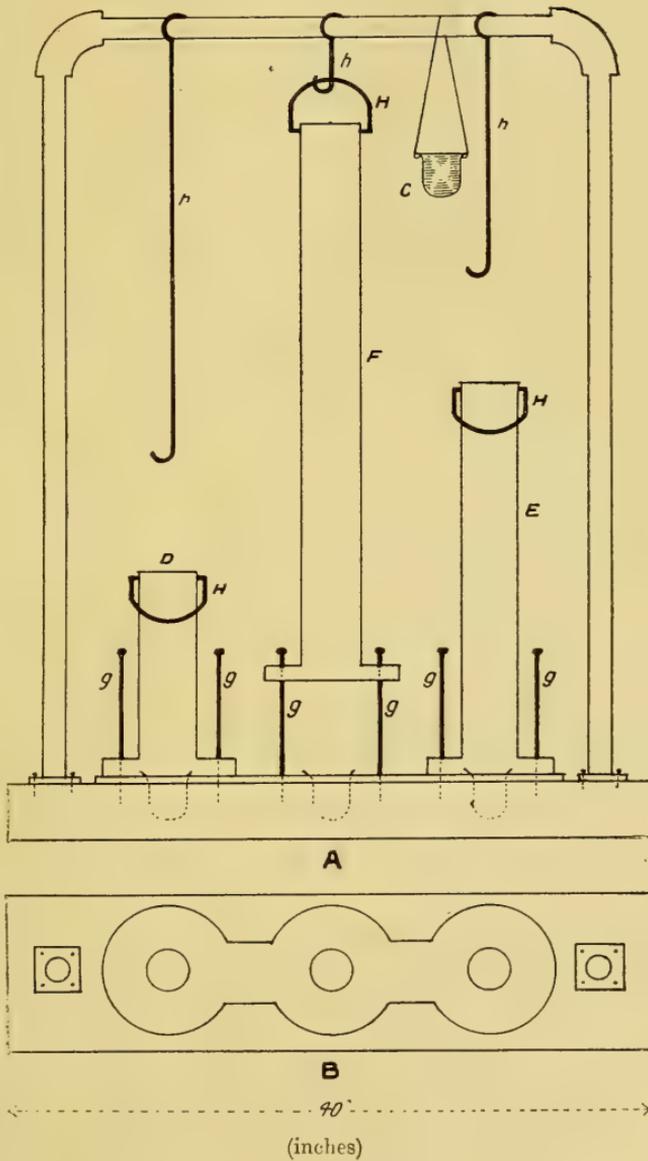
F. Three-foot Pipe.

g. g. Guides.

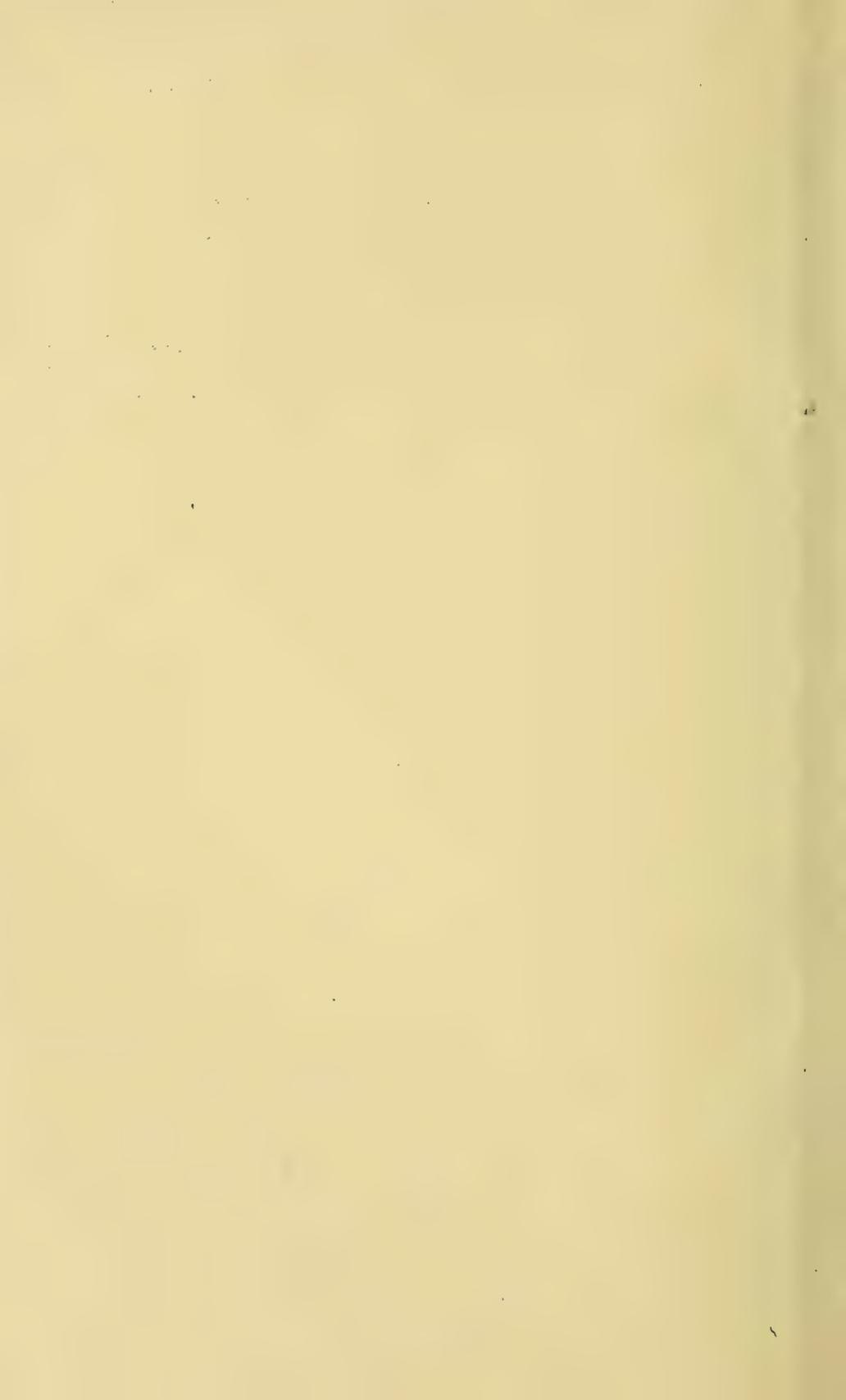
h. h. h. Supporting Hooks ; H. H. H. Handles.

Scale : one-tenth.

(The Elevation shows the one-foot and two-foot Pipes standing in place, and the three-foot Pipe raised and hung up for the purpose of getting at the water-vessel.)



APPARATUS FOR THE STUDY OF EVAPORATION IN IRON PIPES.



Royal Dublin Society.

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METHOD OF DETERMINING THE ABSOLUTE
DILATATION OF MERCURY.

BY

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XIV.

METHOD OF DETERMINING THE ABSOLUTE DILATATION
OF MERCURY.

By J. JOLY, Sc.D., F.R.S.,

Professor of Geology and Mineralogy in the University of Dublin ;
Hon. Secretary, Royal Dublin Society.[Read, JANUARY 15 ; Received for Publication, JANUARY 18 ;
Published, FEBRUARY 21, 1907.]

THE classical experiments of Dulong and Petit and of Regnault, whereby the absolute dilatation of mercury has been determined, necessitate the use of apparatus so complicated and costly as to render the experiments very difficult of repetition. A simple apparatus which will enable the teacher or student to make the determination with accuracy and ease is worth describing. The apparatus which I now describe was made by me many years ago, but no formal account of it has appeared.

The principle of the apparatus is as follows:—If a mercurial barometer be raised in temperature, it, of course, reads higher owing to the diminished density of the mercury. The amount of rise is independent of the expansion of the glass, and at once gives the absolute dilatation of the mercury, assuming that the pressure of the atmosphere has not varied during the progress of the experiment. In short, for the balancing column of mercury used in the experiments of Dulong and Petit, the steady pressure of the atmosphere is substituted.

In order to gain some idea of the degree of accuracy to be expected, I take the following figures:—

Let the initial temperature be 10°C , and the final temperature 100°C . The tables give us δ_{10} as $13\cdot5707$, and δ_{100} as $13\cdot3522$. If the initial height is 76 cms., then as $h_1\delta_1 = h_2\delta_2$, we find that h_2 is $77\cdot244$. The rise has been $1\cdot244$ cms.

If we read this with surety to $0\cdot005$ cms., the degree of

accuracy attained is very nearly 0·4 per cent.; or we know something of the magnitude in the third place of decimals. For purposes of demonstration or teaching, or for the study of the important principle involved, this is adequate.

The apparatus consists of a barometer-tube of thin glass, about 100 cms. in length, and about ·7 cms. bore, dipping into a bath consisting of a small, thin glass flask with two necks. A water-tight joint is made by means of a thin rubber collar, where the tube enters the flask. Enclosing the bath, and the barometer-tube for about 80 cms. of its length, is an outer tube of thin glass, 6 or 7 cms. in diameter, which can be filled with steam, which enters by a side tubulure below, and escapes by a tubulure above. Thus the entire mass of mercury is enclosed in the steam-jacket. As the entry of steam into the mercury-bath would be objectionable, the bath communicates with the external air by a glass tube which enters from the lower end of the steam-jacket, and is tightly attached to the second neck of the flask constituting the bath. Thus the bath, while raised to the temperature of the steam, is directly exposed to the atmospheric pressure.

About 20 cms. of the Torricellian vacuum extends above the steam-jacket. The object is to avoid the depression which would otherwise arise from the mercurial vapour-tension. If desired, an ice-jacket may envelop this upper part, and retain the vapour-pressure corresponding to 0° C.

A few minutes suffice to make the experiment. The heights of bath and column are read by a telescope, and to facilitate this the water is temporarily dried off the glass surface at the point of observation by warming the outer glass with a Bunsen burner.

Capillarity will cause but a small error if a tube of the diameter mentioned is used. A small correction for variation with temperature may be made if desired. As a precaution, if the barometric height is fluctuating at the time of observation, it is well to note the reading of a reference or standard barometer at the moments of observation. For ordinary usage this precaution is not required.

The method is available for certain other liquids; and of course when the barometric column is long the degree of accuracy attained is correspondingly increased.

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THE
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MARCH, 1907.

ON SERIES IN SPECTRA.

BY

ARTHUR W. CONWAY, M.A., F.R.U.I.,

PROFESSOR OF MATHEMATICAL PHYSICS, UNIVERSITY COLLEGE, DUBLIN.

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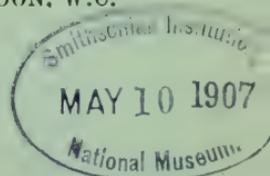
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XV.

ON SERIES IN SPECTRA.

By ARTHUR W. CONWAY, M.A., F.R.U.I.,

Professor of Mathematical Physics, University College, Dublin.

[Read, FEBRUARY 19; Received for Publication, FEBRUARY 26; Published, MARCH 25, 1907.]

IN the line spectra of various elements series of lines whose frequencies are connected by formulæ have been discovered. These formulæ have been put in various forms. A typical one is the formula of Kayser and Runge, in which the frequency of any line of the series is given by $A + Bn^{-2} + Cn^{-4}$, where n is one of the natural numbers 3, 4, 5, &c., and A , B , and C are constants depending on the substance in question. For example, in the case of hydrogen, $C = 0$ and $B = -4A$, which is Balmer's formula. It is probable that these formulæ require other terms to complete them, and that they represent only the first three terms of the expansion of a certain function.

According to modern ideas the atom is made up of positive and negative electrons in equilibrium, or in steady motion, and the spectrum is formed by the electromagnetic waves due to the motion of these electrons. The electrons may be sufficiently numerous to form a practically continuous body, or they may be comparatively few in number. In this paper an attempt is made to offer an explanation of a series on the supposition that it is due to the motion of one electron. A very slight modification will be required to deal with the case in which the number of electrons is small: for example, comparable with the atomic weight.

In the first place, let us consider a field of force isotropic with respect to a fixed point, and such that the electric force is along the line joining the point in question to the fixed point, and equal to $F(r)$ where r is the distance from the fixed point. Then, if

m is the mass of the electron, and $-e$ its charge, the equation of radial motion is

$$mr = -eF(r).$$

Let a be such that $F(a) = 0$, then the sphere $r = a$ is a position of equilibrium. To find the small radial oscillations about this sphere, put $r = a + x$, then

$$m\ddot{x} = -eF'(a) \cdot x,$$

so that for stable equilibrium $F'(a)$ must be positive. In this case the frequency is

$$2\pi \sqrt{\frac{eF'(a)}{m}}.$$

Hence, to produce a series of frequencies similar to a spectral series, we must find a function $F(x)$ such that for certain zeros a ,

$$F'(a) 4\pi^2 e' / m = (A + Bn^{-2} + Cn^{-4} \dots)^2,$$

where $n = 3, 4, 5 \dots$

A very general solution is obtained by taking $F(r)$ proportional to

$$\left(A + \frac{B}{v^2} + \frac{C}{v^4} \dots\right)^2 f'(v) \sin 2\pi v,$$

where $r = f(v)$ is an arbitrary function. For

$$F'(r) = \frac{\partial v}{\partial r} \frac{\partial F}{\partial v} = \frac{1}{f'(v)} \frac{\partial F}{\partial v},$$

and $v = n$ where n is a natural number, makes $F(r) = 0$, so that if

$$a = f(n),$$

$$F'(a) = \left(A + \frac{B}{n^2} + \frac{C}{n^4} + \dots\right)^2 2\pi k,$$

where k is a constant. If, for example, we put

$$v = ar + \frac{\beta}{r} + \frac{\gamma}{r^3},$$

where $a, \beta, \gamma \dots$ are arbitrary constants, we get a function of the form

$$\begin{aligned} & \sin mr \left(p_0 + \frac{p_2}{r^2} + \dots\right) \\ & + \cos mr \left(\frac{p_1}{r} + \frac{p_3}{r^3} + \dots\right). \end{aligned}$$

These are evidently "asymptotic" expansions of function which have a resemblance to the solutions of Riccati's equation which differ by factors from Bessel functions.

In the second place, we consider how this field of force might arise. Suppose that it is due to a sphere of electrical matter which for brevity we may call the atom. Suppose further that this atom is capable of itself vibrating much the same as an elastic sphere forming nodal surfaces, and that in consequence the electric force due to the disturbed motion is given by $E' \phi(r) \cos nt$, where $E' \cos nt$ is the amount of disturbed electricity, and

$$\phi(r) = K \left(\sin mr \left(p_0 + \frac{p_2}{r^2} + \dots \right) + \cos mr \frac{p_1}{r} + \dots \right),$$

and n/m is the velocity of these elastic vibrations, supposed slow compared with that of light. If the electric force in the undisturbed condition is $E\psi(r)$ where E is the charge, then, when oscillations are set up, the force becomes

$$(E - E' \cos nt) \psi(r) + E' \cos nt \phi(r),$$

so that at a node $r = a$, such that $\phi(a) = 0$, equilibrium is usually impossible until the amplitude of the "elastic" vibrations becomes so great that $E' = E$; then the node is a place of equilibrium when $\cos nt = 0$. As these oscillations are slow, an electron can remain at a node sufficiently long to give a great number of light vibrations.

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INDEX OF THE PRINCIPAL LINES OF THE
SPARK-SPECTRA OF THE ELEMENTS.

BY

JAMES H. POLLOK, D.Sc.

(PLATES X. AND XI.)

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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XVI.

INDEX OF THE PRINCIPAL LINES OF THE
SPARK-SPECTRA OF THE ELEMENTS.

By JAMES H. POLLOK, D.Sc.

[PLATES X. AND XI.]

[Read, DECEMBER 18 ; Received for publication, DECEMBER 21, 1906 ; Published,
JULY 22, 1907.]*Introduction.*

THE following index of the principal lines of the spark-spectra of the elements is compiled to facilitate the use of spectrum photography in chemical analysis, by helping an observer to quickly identify groups of lines with which he is not already acquainted. For analytical purposes a complete list of all the possible lines of a particular element is not required ; what is wanted is a selection of those lines which are certain to develop under specific conditions, so that their presence or absence may be taken as proof of the presence or absence of the element in question. To supply this want I have selected from Watts's "Index of Spectra"¹ the principal lines of all the elements, and arranged them in order of their wave-lengths, with the symbol of the element and the intensity as given by Watts. Greek letters are added to indicate the quantitative spectra investigated by Professor W. N. Hartley,² which are of the greatest importance. The quantitative spectra enable us to distinguish between the presence of a mere trace of an element and of a larger proportion, and even to determine the quantitative composition of a substance. Again, the absence of the residuary lines of an element conclusively proves the absence of that particular element, so that it is not necessary to consider other apparently coincident lines. Thus, if the aluminium lines 3092, 3082, and 2816, marked ω , are absent, aluminium

¹ See also "Introduction to the Study of Spectrum Analysis," by W. Marshall Watts, 1904.

² Proc. Roy. Soc., 1882, p. 81 ; also Phil. Trans., 1884, Part I., pp. 49-62 ; and Part II., pp. 325-342.

is absent, no matter how many other lines appear to agree with aluminium lines.

Analysis of Minerals.

To prepare minerals for spectrographic analysis they should be decomposed in the ordinary way—the solution separated into the various analytical groups, and these groups then dissolved in hydrochloric acid, or, if necessary, nitric acid, ammonia, or caustic soda, and made up to a fixed volume, such as 20 c.c. each for every two grams of sample taken, and these solutions then sparked. If only a small quantity of an element is present, much more of the original material must be taken, and the solution made of such a strength as to contain not less than 1 per cent. of the element sought for. Iron should be separated from the ammonia precipitate by tartaric acid and sulphide of ammonia, as there are so many iron lines that it is difficult to detect other elements when it is present. A somewhat similar difficulty occurs with cerium, but cerium can be completely removed by caustic soda and chlorine.

Silica gives no lines in an acid solution, but very characteristic lines when dissolved in caustic soda or with soluble silicates.¹ Tungsten gives its lines when dissolved in ammonia; the other metals may be sparked in acid solution. The non-metallic elements present do not give spectra when treated in this way; they must be sparked in the gaseous condition, at reduced pressure, in Geissler tubes.

Sparking.

In sparking solutions the most convenient electrodes to use in conjunction with this index are gold. A piece of glass-tube, about 6 inches long, and having a capillary bore, is bent into the form of a U with limbs of unequal length, and a small cup, like a miniature thistle-funnel, of about 2 c.c. capacity, blown at each end. The gold wire is then passed through the capillary bore of the tube, so as to project a little above the rim of the lower cup, and a small piece of thin-walled capillary tube slipped over the end of the gold wire, and made of such a length as just to reach the top of the wire, and thus draw up the solution and keep the top of the wire well wetted when sparking. Owing to the fusibility of

¹ Hartley, Proc. Roy. Soc., vol. xxxv., p. 301; also Brit. Assoc. Report, 1883.

gold, it is necessary to employ fairly thick wire; but economy can be effected by using only a short piece attached to a thin platinum wire, of sufficient length to pass through the capillary. When sparking, the electrode in the solution must be made the negative electrode. The upper or positive electrode may be held in any convenient manner, and the spark-gap should not be too long. A condensed spark should be used, and, if desired, a Hemsalech coil, to remove air-lines; a photograph is first taken with the electrodes alone, and a long slit, giving about one minute's exposure; the slit is then reduced to about one-third of its length, and the substance under examination also sparked for about one minute. The lines of the substance are then seen as short lines between the long lines of the gold electrodes, and are easily identified by aid of the gold lines. In all other respects the work should be conducted as described by Hartley in the *Journal of the Society of Arts*, March 12th, 1886; see also "*Thorpe's Dictionary of Applied Chemistry*," vol. iii., p. 536.

The first spectrum on Plate X. is that of cadmium with gold electrodes. Graphite and platinum electrodes can also be used, but are not so convenient for general purposes. Graphite has most of its lines concentrated in one part of the spectrum, so as to obscure any other lines there, and has too few lines in the other parts of the spectrum to assist in identification, and it is often very impure. Platinum has an inconveniently large number of fine lines; but where lines coincident, or nearly coincident, with gold lines are suspected, graphite or platinum can be used. The second and third spectra on Plate X. are those of platinum and carbon photographed on gold. The carbon spectrum is from Ceylon graphite, and shows the lines of silicon and magnesia, and many of the iron lines. The fourth spectrum shows the air-lines introduced by dispensing with the use of a Hemsalech's self-induction coil. The fifth and sixth spectra show the silver and copper lines photographed on a gold spectrum with short lines. Silver is practically always present in gold, and a very minute quantity gives certain lines quite strongly, as will be seen by comparison with the previous gold spectra; but this is rather a help than otherwise, as these lines are useful for reference, and fill up blanks in the gold spectrum. Copper is the only other element likely to be present as an impurity in gold electrodes.

Of course, if silver or copper is present in the electrodes, they cannot be used for testing solutions for those metals.

When the point at issue is the presence or absence of some impurity, or foreign substance, in a particular sample, a very convenient method is to photograph a pure sample of the substance, using a long slit, then shorten the slit, and photograph the suspected sample, when any new substance present will be seen at once by the short lines; and if no short lines are seen, the identity of the two samples is demonstrated. Spectrum 7 shows a sample of pure aluminium chloride, photographed against gold; and spectrum 8 shows a sample of aluminium chloride, containing beryllium, photographed against pure aluminium chloride and gold, the short lines indicating, at a glance, the nature of the new substance present.

Plate XI. gives the spectra of a number of other elements photographed against gold. The spectra extend from λ 5896.2 to about λ 2500; but the plates were not very sensitive below gold line No. 9. λ 4792.8. The two lines just before gold line No. 13 are the *H* and *K* lines of calcium, and are derived from the air, and also from the capillary glass tube placed round the gold electrode to supply the solution. They are, practically, always present, and are very useful, as they serve to at once identify aluminium, lanthanum, and a number of other elements, having lines that lie between them.

Unfortunately, the spectra are somewhat indistinct in the plates; but they are sufficient to indicate the general method of procedure.

Intensity.

The intensities given in the Tables refer, in some cases, to the spark-spectrum of the metal, and in others, to the spark-spectrum of a solution of the chloride. Some of the intensities are marked from 1 to 10, while others are numbered from 1 to 100; and there is a general want of uniformity in the standard of intensity adopted by different observers; but it will involve much labour, and take a long time to reduce the spectra of all the elements to a uniform standard of intensity. In the red and yellow end of the spectrum

one must distinguish between visible and photographic intensity; and so far as the latter is concerned, the intensity is purely a question of what plates are used. Probably the best plan would be to adopt the intensities of the gold spectrum as the standard, and compare other spectra with the lines of gold: this would give the standard of intensity on the same plate, with the spectrum under consideration, and photographed in the same way. It was not possible to deal with the question of intensity in the present paper, as it would require a detailed examination of the spectrum of each element. The various observers agree very well as to the measurements of the wave-lines of the various lines observed; but most serious differences of opinion exist as to the relative intensities of various lines; and there can be no doubt that in the spectra of many elements, lines have been carefully measured and recorded that are really due to impurities. I hope later to investigate a number of the coincident, or apparently coincident, strong lines, and lines of variable intensity.

Persistency.

Professor Hartley was the first to investigate the quantitative spectra of the elements, and point out that the persistency of a line was much more important than its intensity, and that the most persistent lines were not necessarily the most intense. Hartley's method is to take solutions containing 1 part of the element in 100, 1,000, 10,000, and 100,000 parts of solution, and spark them, using graphite electrodes; and he has given complete maps of the spectra drawn to a scale of wave-lengths, and also linear measurements, showing the successive disappearance of the lines of the spectra of magnesium, zinc, cadmium, aluminium, indium, thallium, copper, silver, mercury, tin, lead, tellurium, arsenic, antimony, bismuth, beryllium, and silicon.

For purposes of spectrographic analysis of minerals, nothing is so necessary as the completion of this work. When we have the dilution spectra of all the other elements, it will render the spectrographic identification of a substance a matter of rapidity and certainty, whether the substance be rare or common, old or new, and whether present in large or small quantity. I have

indicated Hartley's results by the use of the last letters of the Greek alphabet:—

ϕ = seen with 1 part in 100 of solution.

χ = seen with 1 part in 1,000 of solution.

ψ = seen with 1 part in 10,000 of solution.

ω = seen with 1 part in 100,000 of solution.

Thus the letter ψ after the intensity of an element indicated that this line is still visible when the solution contains .01 per cent. of the element, but that it is not visible for less quantities, such as .001 per cent.; whereas ω would indicate that even with this minute quantity in solution the line could still be seen. Of course, some elements do not give any ω lines, and some do not even give ψ lines. To determine whether an element is present or not, it is only necessary to look for the most persistent lines, and if these be absent the element is not present, even if there be several lines closely agreeing with a few of its lines; as already explained, they must be attributed to some other element. To determine the presence of an element, one need only look for the six most persistent lines; these lines we will call the residuary lines of the element, but they may be marked χ , ψ , or ω , accordingly as they are seen in a .1 per cent., .01 per cent., or .001 per cent. solution.

Identification.

To facilitate the identification of lines, I have marked strong electrode lines at convenient distances with numbers as shown on the gold cadmium spectrum on Plate X. These lines are similarly numbered in the index to enable lines that lie between them to be identified by inspection. Thus, if a line is observed a little beyond the gold line No. 20, the first of a very characteristic group of three lines, and its distance from the last of the group is just about equal to the space between each member, you can at once conclude that it is Al or Yt, and could not well be any other element. All the gold lines, and such silver lines as are usually shown by gold of an ordinary degree of purity, are printed in heavy type; and a list of those lines is given in a preliminary table, the wave-lengths of the gold

lines being taken from the measurements of Eder and Valenta.¹ As there are not many strong gold lines in the red, orange, yellow, and green part of the spectrum, one or two lithium, sodium, and nitrogen lines are added.

The easiest method of identification is undoubtedly to prepare a set of plates with spectra of all the elements, common and rare, and then identify lines by inspection and superposition of plates, and this method should be used when possible; but in searching for new substances, and when traces only are present, this method is often impossible, and a table like the present becomes almost indispensable.

Measurement of Lines.

In measuring lines, their position should be measured from two well-known gold lines on either side, and their wavelengths determined from an interpolation curve. In measuring a whole spectrum, all the principal gold lines should be measured at the same time as the others, their values compared with the curve values, and any corrections necessary applied to the values of the lines between. This will correct any errors caused by an alteration in the focus of the instrument, or inclination of the plate, or by the slit being slightly out of the perpendicular, or even by the curve being slightly erroneous; so long as the identity of the gold lines is absolutely certain, other errors will be eliminated. It is thus very desirable that an observer should make himself thoroughly acquainted with the position, intensity, appearance, and grouping of the gold lines, so that he may be readily able to identify any one of them. When this is achieved, it is possible by use of the index to identify most of the lines on a photograph without the necessity of measurement.

¹ Eder and Valenta: "Denkschr. kaiserl. Akad. Wissench. zu Wien," Bd. lxx., 1896; Bd. lxxviii., 1899.

TABLE OF STANDARD ELECTRODE LINES.

No.	Wave-Length.	Element and Intensity.	No.	Wave-Length.	Element and Intensity.
1	6708·2	Li 10	23	2641·6	Au 6
2	6457·0	Au 5	24	2590·2	Au 6
3	6278·4	Au 4	25	2544·3	Au 5
—	{ 5896·2	Na 10	26	2503·4	Au 8
	{ 5890·2	Na 10	27	2473·9	Ag 8
4	5837·7	Au 6	28	2447·9	Ag 8
5	5679·8	N 12	29	2437·8	Ag 10
6	5465·5	Ag 10	30	2428·1	Au 10
7	5230·5	Au 8	31	2413·2	Ag 10
8	{ 5005·7	N 10	32	2387·9	Au 4
	{ 5002·7	N 10	33	2364·8	Au 10
9	4792·8	Au 8	34	2352·7	Au 6
10	4488·4	Au 8	35	2331·3	Ag 8
11	4315·4	Au 8	36	2304·9	Au 8
12	4065·2	Au 15	37	2283·4	Au 5
13	3898·0	Au 10	38	2242·7	Au 5
14	3586·7	Au 7	39	2229·1	Au 6
15	3383·0	Ag 10	40	2201·4	Au 5
16	3280·8	Ag 10	41	2189·0	Au 5
17	3122·9	Au 10	42	2166·6	Ag 4
18	3029·3	Au 6	43	2145·7	Ag 3
19	2913·6	Au 9	44	2125·3	Au 5
20	2825·6	Au 6	45	2110·8	Au 6
21	2748·3	Au 5	46	2082·1	Au 5
22	2676·1	Au 12			

RED RAYS.

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
8949.9	Cs 10	6911.2	K 7	6584.2	C 4
8527.7	Cs 10	6908.0	In 6	6578.7	C 5
7699.3	K 8	6854.9	Fe 6	6575.2	Fe 6
7665.6	K 8	6843.6	Fe 6	6569.4	Fe 8
7515.1	Fe 6	6841.4	Fe 6	6563.0	H 20
7504.0	A 7	6827.8	Fe 6	6557.0	Ti 4
7500.0	Fe 6	6753.1	A 5	6550.5	Sr 4
7449.8	Fe 6	6741.2	Di 4	6546.4	Fe 10
7414.8	Fe 6	[No. 1,	Lithium.]	6527.6	Ba 6
7392.3	Fe 6	6708.2,	Li 10	6523.3	Pt 6
7384.2	A 5	6682.8	Br 2	6518.5	Fe 6
7281.8	He 3	6678.4	He 5	6504.2	Sr 8
7273.1	A 5	6678.1	Fe 8	6500.0	Se 9
7206.6	Fe 4	6677.6	A 6	6499.9	Ca 8
7187.2	Fe 8	6663.6	Fe 6	6497.1	Ba 10
7067.5	A 5	6657.3	Pb 10	6495.1	Fe 10
7065.5	He 5	6633.9	Fe 6	6494.0	Ca 10
7057.9	Al 6	6632.0	Br 5	6493.8	Bi 6
7042.5	Al 6	6609.3	Fe 6	6483.1	Ba 6
6973.9	Cs 6	6603.4	N 4	6480.8	N 5
6965.8	A 6	6600.3	Ri 4	6479.0	Se 9
6944.8	Fe 6	6594.0	Fe 6	6471.9	Ca 8
6938.8	K 8	6593.1	Fe 10	6470.0	Red ends.
6916.8	Fe 6				

ORANGE RAYS.

6467.4	Cd 6	6393.5	La 8	6302.8	Sb 8
6462.8	Ca 10	6389.0	S 7	6302.7	Fe 6
[No. 2,	Gold.]	6386.7	Sr 6	6301.6	Fe 10
6457.0	Au 5	6386.0	Di 4	6298.7	Rb 10
6453.5	Sn 10	6384.9	A 5	6297.9	Fe 6
6453.3	Pb 6	6383.1	Ne 8	6297.1	A 5
6451.0	Ba 6	6381.1	Cu 6	6291.1	Fe 6
6450.0	Ca 8	6380.9	Fe 6	6290.0	S 10
6439.4	Ca 10	6380.9	Sr 4	[No. 3,	Gold.]
6439.3	Cd 10	6364.0	Zn 10	6278.4	Au 4
6438.2	Te 10	6351.0	Br 10	6270.4	Fe 6
6432.0	Se 8	6344.8	Zr 6	6266.6	Ne 10
6431.0	Fe 8	6341.9	Ba 6	6265.3	Fe 8
6421.5	Fe 8	6337.0	Fe 10	6261.4	Ti 8
6420.2	Fe 6	6335.4	Fe 8	6258.6	Ti 10
6416.5	A 8	6328.3	Ne 6	6256.5	Fe 6
6412.4	Ga 6	6326.7	Ga 8	6254.4	Fe 6
6411.8	Fe 8	6319.0	S 8	6252.7	Fe 10
6408.6	Sr 10	6318.2	Fe 10	6250.0	La 8
6408.3	Fe 6	6311.3	Zr 6	6246.5	Fe 8
6406.7	Ne 6	6308.0	S 9	6245.7	Sb 4
6402.4	Ne 10	6307.9	A 5	6245.2	Al 8
6400.1	Fe 10	6305.1	Sc 10	6235.2	Al 8
6393.6	Fe 8	6304.9	Ne 8	6232.8	Fe 6

ORANGE RAYS—*continued.*

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
6230.9	Fe 10	6141.8	Zr 10	6042.2	Fe 6
6222.8	Fe 6	6137.8	Fe 10	6041.2	Pb 6
6222.0	Ti 6	6136.8	Fe 10	6038.0	Sc 10
6219.5	Cu 4	6133.8	Zr 6	6032.4	A 9
6219.4	Fe 8	6131.0	I 8	6030.2	Ne 10
6217.5	Ne 8	6130.4	Pd 2	6030.2	Mo 10
6216.1	A 6	6130.1	Bi 8	6027.2	Fe 6
6215.3	Fe 6	6129.6	Sb 10	6024.2	Fe 10
6215.2	Ti 6	6128.6	Ne 8	6023.5	Zn 8
6213.6	Fe 8	6128.1	Zr 10	6022.8	As 4
6212.7	A 6	6128.0	Fe 6	6021.8	Mn 10
6210.9	Sc 8	6125.4	Ti 8	6020.3	Fe 6
6210.1	Sb 4	6122.5	Ca 10	6020.0	Ge 10
6206.7	Rb 8	6122.5	Co 6	6019.7	Ba 6
6200.5	Fe 6	6111.0	Ba 6	6016.6	Mn 10
6194.4	Sb 4	6110.2	As 8	6013.6	Mn 10
6194.0	In 10	6105.9	A 6	6008.8	Fe 8
6191.7	Fe 10	6103.8	Li 10	6004.7	Sb 10
6182.3	Ne 10	6103.4	Fe 8	6004.7	Co 8
6180.3	Fe 6	6103.1	Zn 10	6003.2	Fe 6
6176.9	Ni 6	6103.0	Ca 8	6002.1	Pb 6
6173.3	Ar 6	6102.3	Fe 8	5997.3	Ba 0
6172.7	A 5	6099.0	A 6	5994.9	Ga 4
6171.9	O 5	6098.6	Ti 6	5987.6	A 5
6171.9	N 5	6096.3	Ne 10	5987.2	Fe 6
6170.6	Fe 6	6096.0	In 8	5985.0	Fe 8
6170.6	As 8	6091.6	Ti 7	5983.9	Fe 6
6170.4	Ar 5	6084.4	Ti 6	5980.6	Sb 4
6169.9	Ca 5	6080.0	Sc 10	5979.1	Ti 10
6166.8	Ca 5	6079.1	Sb 10	5976.9	Fe 8
6163.7	Ne 10	6078.6	Fe 6	5975.7	Ne 8
6162.5	Ca 10	6076.0	I 9	5975.5	Fe 6
6161.1	Na 8	6074.5	Ne 10	5974.7	Ne 6
6159.8	Rb 6	6072.6	Sc 8	5974.1	Te 10
6157.9	Fe 6	6071.2	Rb 6	5973.9	La 6
6156.2	Sb 4	6065.8	Ti 8	5971.9	Ba 6
6155.5	Ar 5	6065.6	Fe 10	5966.5	Ti 10
6154.6	Na 8	6065.1	Sc 8	5964.7	Pt 6
6152.3	Hg 9	6063.3	Ba 6	5961.0	I 10
6149.9	Br 10	6059.6	A 7	5957.2	Au 6
6145.6	Ar 6	6057.7	Bi 8	5956.9	Fe 6
6143.8	Co 6	6056.2	Fe 6	5952.9	Fe 1
6143.2	Ne 10	6053.0	A 6	5952.7	Ti 10
6141.9	Ba 10	6052.2	Sb 4	5950.2	N 4
6141.9	Fe 6	6043.5	A 8	5950.0	Orange ends.

YELLOW RAYS.

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
5948.0	Tl 6	5875.8	He 5	5800.5	Ba 6
5944.9	Ne 10	5875.0	Pb 6	5799.2	Sn 10
5942.6	N 10	5872.1	Hg 8	5795.8	La 6
5936.2	Te 8	5871.1	Kr 10	5792.5	Sb 4
5934.8	Fe 8	5866.7	Ti 10	5792.1	Mo 6
5933.0	N 10	5862.6	Bi 8	5791.5	La 6
5930.3	La 8	5862.5	Fe 10	5791.0	I 5
5930.2	Fe 10	5859.8	Fe 8	5790.5	Hg 10
5929.6	N 4	5858.5	Mo 8	5789.4	La 6
5916.4	Fe 6	5857.8	Ca 6	5782.7	K 3
5914.3	Fe 10	5853.9	Ba 10	5782.3	Cu ⁸
5914.1	Ur 8	5852.4	Br 5	5782.3	Fe 8
5910.1	Sb 8	5852.6	Ne 20	5781.0	I 10
5905.8	Fe 6	5851.5	Ga 4	5769.5	La 8
5899.6	Ti 10	[No. 4,	Gold.]	5769.6	Hg 10
5896.2	Na 10	5837.6	Au 6	5768.5	N 3
5894.8	Sb 8	5831.0	Br 7	5766.0	I 10
5894.6	Zn 8	5827.0	Er 8	5764.5	Ne 8
5893.1	Ni 10	5826.5	Ba 6	5763.2	Fe 10
5892.0	Ge 10	5821.0	In 8	5763.0	Er 6
5890.2	Na 10	5817.1	Bi 6	5760.1	Au 5
5889.1	Hg 8	5816.5	Fe 6	5756.1	Te 10
5888.6	Mo 10	5813.8	R 10	5751.7	Mo 6
5882.0	Ne 8	5804.3	Hg 10	5750.0	Yellow ends.
5876.1	He 1	5802.0	K 10		

GREEN RAYS.

5747.5	N 3	5686.0	I 10	5644.4	Ti 10
5741.0	I 10	5682.9	Na 6	5640.0	S 10
5734.1	W 6	[No. 5,	Nitrogen.]	5639.1	Sb 8
5723.5	Al 10	5679.8	N 12	5636.4	Ru 7
5717.6	Bi 8	5679.1	Hg 10	5631.9	Sn 8
5716.0	I 10	5676.9	Di 4	5631.0	I 10
5712.3	N 6	5676.0	N 5	5625.1	As 8
5711.6	Mg 8	5675.6	Ti 10	5623.3	Ag 4
5707.6	Te 10	5672.0	Sc 8	5620.5	Di 3
5700.5	Se 8	5672.0	S 7	5620.1	Ur 6
5700.4	Cu 6	5670.3	Pd 6	5619.7	Pd 6
5699.2	Ru 2	5667.1	N 9	5616.7	R 8
5697.0	Se 8	5662.4	Ti 10	5615.8	Fe 10
5696.6	Al 10	5661.0	S 8	5608.2	Pb 10
5696.0	I 9	5660.8	R 10	5605.0	S 10
5695.3	Pd 6	5658.9	Fe 10	5603.1	Ca 4
5689.4	Mo 6	5657.5	Sc 8	5601.5	Ca 6
5689.0	Di 4	5656.0	Au 9	5598.7	Ca 6
5688.7	Au 3	5652.1	As 8	5596.0	Se 8
5688.3	Na 6	5651.0	S 8	5596.0	Hg 8
5687.0	Sc 8	5648.1	Te 10	5594.6	Ca 8
5686.3	N 5	5645.0	In 8	5594.5	Di 4

GREEN RAYS—*continued.*

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
5590.3	Ca 4	5497.0	I 9	5413.9	Mn 6
5590.1	Br 8	5496.6	N 6	5410.3	Ce 8
5589.0	Ca 10	5495.2	Br 7	5410.0	Cr 8
5588.7	W 10	5494.6	Ur 10	5408.0	I 10
5588.7	Sn 10	5492.6	W 8	5406.8	R 8
5588.6	La 6	5490.2	Cd 6	5400.3	R 8
5588.0	Au 4	5489.0	Br 6	5397.3	Fe 10
5586.9	Fe 10	5486.4	Sr 6	5395.5	Pd 8
5585.8	Au 1	5485.9	Di 6	5395.7	Br 5
5582.2	Ca 4	5484.5	Ru 6	5393.5	Ce 8
5580.2	Ur 6	5482.5	Ur 10	5392.3	Cl 6
5578.7	Au 5	5481.1	Sr 10	5390.6	Pt 6
5575.2	Te 8	5480.5	Ur 10	5385.1	Ur 6
5573.0	Fe 10	5479.8	N 5	5383.5	Fe 10
5570.7	Mo 10	5478.7	Pt 4	5382.0	La 8
5570.5	Kr 10	5478.0	Ur 10	5381.2	La 8
5569.8	Fe 10	5477.1	Ni 6	5380.2	Sb 6
5568.7	Sb 8	5476.0	Pt 4	5379.8	C 2
5568.7	Sn 10	5474.1	Fe 6	5379.3	Cd 10
5568.6	Ur 6	5472.8	Ce 6	5377.8	Mn 6
5562.4	Kr 6	5472.5	Cd 6	5377.3	La 8
5562.0	S 8	5471.7	Ag 5	5375.5	Th 6
5560.0	Ru 6	5471.0	S 8	5373.6	Pb 10
5559.2	As 8	5471.0	I 10	5372.0	Di 6
5552.4	Bi 4	5466.4	Br 5	5371.6	Fe 10
5547.2	Pb 8	[No. 6,	Silver.]	5371.0	I 6
5547.2	Pd 6	5465.7	Ag 10	5369.5	Ga 4
5543.5	Sr 4	5464.5	Sb 6	5369.2	Pt 8
5543.0	Pd 6	5462.8	N 5	5361.5	Di 6
5540.3	Sr 6	5461.0	Hg 10	5359.9	K 8
5538.1	Th 6	5455.8	Fe 10	5357.5	Di 4
5535.7	Ba 10	5455.4	La 8	5353.3	Ce 10
5535.2	N 6	5455.0	Ru 6	5350.6	Tl 10
5535.0	Sr 8	5453.8	N 5	5350.5	Zr 6
5533.3	Mo 10	5452.0	S 9	5349.7	Ca 8
5529.7	Pd 6	5451.1	Sr 5	5349.0	I 10
5528.7	Mg 6	5451.0	Bi 8	5344.4	Er 6
5528.1	Ur 10	5448.5	Te 8	5343.0	S 10
5527.0	Sc 12	5448.0	I 10	5341.2	Mn 6
5522.0	Sr 8	5447.1	Fe 10	5340.8	La 8
5519.4	Ba 4	5447.0	Th 6	5340.1	K 8
5514.8	Ti 10	5439.0	S 8	5339.0	I 10
5514.1	W 10	5435.3	Br 5	5338.6	Cd 10
5512.7	Ti 10	5430.0	S 6	5335.3	Br 5
5510.9	Ru 6	5429.7	Fe 10	5333.1	Sn 8
5510.1	Ur 6	5428.9	Ga 2	5332.3	Br 10
5508.0	S 8	5426.5	Hg 10	5332.1	As 6
5507.0	Br 8	5425.2	Br 5	5331.1	Ce 6
5506.7	Mo 10	5424.8	Ba 6	5328.2	Fe 10
5504.5	Sr 8	5424.2	Fe 10	5322.9	Di 4
5504.1	W 10	5423.4	Cl 10	5320.0	S 10
5502.1	R 8	5423.0	Br 7	5319.9	Di 8
5501.6	La 8	5420.6	Mn 6	5305.0	Se 10
5499.1	As 6	5415.4	Fe 10	5304.3	Br 7

GREEN RAYS—continued.

Wave- Length.	Element and Intensity.	Wave- Length.	Element and Intensity.	Wave- Length.	Element and Intensity.
5302.8	La 8	5209.1	Bi 8	5110.9	Pd 8
5302.5	Fe 10	5208.6	Cr 10	5105.8	Cu 8
5302.1	La 8	5206.4	O 6	5104.5	As 5
5301.2	Pt 10	5206.2	Cr 10	5104.0	S 7
5297.4	Ti 10	5204.7	Cr 10	5102.8	Di 4
5295.7	Pd 10	5201.6	Pb 6	5101.4	Sn 6
5293.5	Di 8	5201.0	S 10	5094.0	Se 10
5292.8	Cu 6	5193.1	Ti 10	5086.1	Cd 10
5283.6	Ti 10	5192.5	Fe 8	5079.5	Ce 6
5274.3	Ce 10	5192.5	Di 6	5071.4	W 6
5273.5	Di 6	5191.7	Zr 6	5067.0	Se 6
5271.1	Bi 8	5191.5	Di 6	5066.0	I 8
5270.5	Ca 8	5190.6	O 4	5064.8	Ti 10
5270.4	Fe 10	5189.0	Er 6	5064.7	Au 5
5270.0	Se 10	5189.0	Ca 6	5057.4	Al 10
5269.6	Fe 10	5188.4	La 8	5053.9	W 10
5266.7	Fe 8	5187.8	Ce 6	5051.7	Fe 8
5265.8	Ca 6	5183.8	Mg 10	5049.9	Fe 8
5264.5	Ca 4	5183.7	La 10	5047.8	He 2
5259.5	Di 4	5182.6	Br 7	5045.7	N 7
5257.1	Sr 8	5180.0	Di 4	5045.9	Pb 8
5257.0	Er 8	5180.0	N 5	5044.6	Pt 6
5255.5	Di 4	5178.2	Sb 6	5041.9	Ca 8
5252.0	In 10	5177.5	La 6	5036.7	Ti 10
5251.0	Se 9	5176.3	O 3	5036.1	Ti 10
5249.5	Di 8	5176.0	Se 10	5035.6	Ni 6
5244.0	I 10	5173.9	Di 4	5033.0	S 10
5242.7	Sb 6	5172.9	Mg 9	5031.3	Sc 10
5240.0	Se 8	5171.2	Ru 6	5027.9	Ur 6
5238.8	Sr 10	5167.6	Mg 8	5026.7	N 8
5238.5	Br 8	5164.6	Br 5	5021.0	S 10
5235.0	Pd 8	5164.0	Pd 10	5017.7	Ni 6
5233.1	Fe 10	5159.0	I 10	5015.7	He 6
[No. 7,	Gold.]	5156.4	Sr 2	5014.9	W 6
5230.5	Au 8	5154.9	Cd 1	5014.4	Ti 10
5230.5	As 5	5153.7	Na 5	5014.0	S 8
5229.5	Sr 6	5153.4	Cu 10	5011.1	N 5
5227.8	Pt 8	5151.2	C 3	5007.9	W 6
5227.3	Fe 10	5149.2	Na 5	5007.8	N 5
5227.0	Fe 10	5144.9	C 3	5007.4	Ti 10
5225.4	Sr 6	5144.5	Bi 10	[No. 8,	Nitrogen.]
5225.0	Se 10	5143.0	S 7	5005.7	N 10
5224.5	Ti 10	5142.0	Se 9	5005.6	Pb 6
5224.2	W 10	5139.6	Fe 8	5002.7	N 10
5222.4	Sr 6	5139.3	Fe 8	4999.7	Ti 10
5221.5	Cl 6	5132.9	C 3	4996.6	La 6
5220.2	Cu 6	5130.7	Di 6	4995.2	Di 6
5218.4	Cu 10	5129.3	Ti 10	4995.0	S 6
5218.2	Te 8	5124.5	Bi 10	4994.9	N 6
5218.1	Cl 8	5123.1	La 6	4993.9	Bi 10
5218.0	Er 6	5120.6	Ti 10	4993.0	Se 10
5315.0	S 10	5117.2	Pd 8	4991.2	Ti 10
5210.6	Ti 10	5114.7	La 6	4983.5	Na 6
5209.2	Ag 8	5111.3	Di 4	4981.9	Ti 10

GREEN RAYS—*continued.*

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
4979·3	Na 2	4952·0	Er 8	4924·4	Di 6
4972·1	Li 4	4949·7	Sb 8	4923·2	X 6
4972·0	Se 10	4947·8	Pr 8	4922·1	He 4
4968·1	Sr 4	4944·0	Di 4	4922·0	La 10
4962·4	Sr 8	4934·2	Ba 10	4921·1	La 10
4959·0	Di 4	4930·8	Br 5	4920·6	Fe 10
4957·8	Fe 10	4929·0	Br 5	4920·0	Th 10
4957·4	Fe 10	4926·0	S 8	4920·0	Green ends.
4955·0	Di 4	4924·8	Zn 10		

BLUE RAYS.

4919·1	Fe 8	4843·1	W 10	4780·5	Br 6
4916·4	Hg 4	4842·0	Se 10	4780·1	N 10
4916·6	X 6	4840·4	Co 10	4780·1	Co 10
4912·3	Zn 10	4840·0	Se 10	4476·6	Br 7
4904·6	Ni 6	4832·2	Sr 6	4772·1	Zr 10
4901·9	Di 4	4826·1	R 10	4767·3	Br 8
4900·1	La 10	4826·0	Hg 8	4766·3	Br 5
4899·9	Er 8	4825·0	Di 4	4760·4	Mo 6
4897·4	Di 5	4824·2	La 10	4759·4	Ti 10
4892·2	Sr 1	4823·7	Mn 8	4758·3	Ti 10
4890·9	Fe 10	4820·0	Er 8	4754·2	Mn 6
4890·9	Di 5	4819·6	Cl 8	4752·2	Na 2
4888·5	W 8	4817·7	Pd 6	4748·9	La 8
4885·2	Ti 10	4817·0	S 8	4748·4	Na 2
4881·9	Di 5	4816·9	Br 8	4743·3	La 8
4880·1	A 8	4816·1	Zr 10	4742·9	Br 8
4878·6	Sb 6	4813·7	Co 10	4742·1	Sr 6
4878·3	Ca 6	4812·0	Di 4	4739·6	Zr 10
4876·3	Sr 6	4812·0	Sr 6	4735·7	Br 5
4875·6	Pd 6	4811·5	Au 5	4734·3	X 8
4873·6	Ni 10	4810·7	Zn 10	4732·0	Ur 6
4872·7	Sr 6	4810·2	Cl 9	4722·7	Bi 10
4872·4	Er 6	4809·7	La 8	4722·4	Sr 6
4872·3	Fe 8	4809·2	La 8	4722·3	Zn 10
4871·4	Fe 8	4807·1	X 6	4719·9	Br 8
4869·3	Ru 6	4806·2	A 8	4716·0	S 8
4868·9	Sr 2	4805·6	Ti 10	4714·6	Ni 10
4868·0	Co 10	4804·2	La 8	4714·1	Ce 8
4866·4	Ni 10	4803·6	N 7	4713·3	He 3
4864·6	Ga 6	4800·1	Cd 10	4710·3	Zr 10
4864·6	Th 6	4794·6	Cl 10	4710·1	O 5
4861·5	H 20	4793·0	Co 10	4709·9	N 2
4861·1	La 8	[No. 9, Gold.]		4709·7	Ru 6
4859·5	Di 4	4792·8	Au 4	4706·9	Di 4
4859·1	Sn 6	4788·3	N 6	4705·6	O 6
4856·2	R 8	4788·3	Pd 6	4705·2	N 2
4855·6	Ni 10	4785·6	Br 10	4705·0	Br 10
4855·3	Sr 2	4784·4	Sr 6	4704·8	Cu 5
4849·0	Br 6	4783·6	Mn 6	4703·3	Mg 1

BLUE RAYS—continued.

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
4699·4	O 8	4620·4	Ur 3	4562·5	Ce 5
4697·1	X 7	4619·9	V 10	4561·4	Bi 7
4693·5	Br 8	4617·4	Mo 10	4560·9	V 22
4692·7	La 8	4616·3	Cr 7	4559·0	Au 6
4688·0	Zr 10	4616·1	Tm 2	4558·9	Cr 10
4686·1	Ge 10	4614·9	Br 6	4558·7	La 6
4683·8	Au 2	4614·1	N 8	4555·8	Th 8
4683·4	Di 4	4609·5	K 6	4555·4	Cs 10
4682·4	R 50	4609·7	O 2	4555·3	Ur 4
4682·4	In 8	4607·8	Au 6	4554·7	Ru 10
4680·8	W 6	4607·5	Sr 10	4554·2	Ba 10
4680·4	Zn 10	4607·3	N 8	4554·2	W 8
4678·9	Br 8	4607·0	Ta 5	4553·5	Mo 6
4678·4	Cd 10	4606·0	Se 10	4552·6	Pt 8
4676·4	O 3	4605·4	Ur 3	4552·0	S 10
4675·8	Er 6	4604·0	Cs 7	4550·6	Os 8
4675·0	Cu 6	4603·9	Ur 4	4549·8	Ti 15
4673·2	Au 6	4602·4	Li 10	4549·8	V 12
4672·7	Br 6	4601·6	Br 5	4549·7	La 7
4672·0	La 6	4601·5	N 9	4549·6	Au 6
4671·4	Kr 10	4600·9	Cr 6	4546·1	Cr 7
4671·4	X 10	4600·3	V 10	4545·6	V 14
4669·4	Na 3	4596·3	O 6	4543·8	Ur 7
4669·1	La 6	4594·3	V 12	4543·1	Br 8
4668·7	Ag 2	4594·2	Eu 10	4542·8	Nd 5
4665·2	Na 3	4593·3	Cs 6	4540·9	Cr 5
4663·1	Al 10	4592·4	Sb 6	4540·7	Cr 5
4662·7	Cd 3	4591·6	Cr 5	4539·9	Ce 8
4662·1	Eu 5	4591·1	O 5	4538·9	Br 5
4660·0	W 6	4588·4	Cr 10	4538·4	Ur 4
4656·1	In 8	4587·9	Au 7	4536·1	Ti 6
4655·7	La 8	4587·2	Cu 8	4535·9	Cr 6
4652·2	Br 6	4586·6	V 12	4534·4	Pr 6
4651·3	Cu 8	4586·1	Ca 4	4533·3	R 10
4649·2	O 8	4585·4	Sn 8	4531·5	Sr 1
4646·2	Au 3	4584·6	Ru 8	4530·9	Cr 7
4643·4	N 9	4581·7	Ca 4	4530·5	Al 6
4642·0	K 1	4580·6	V 10	4530·0	Br 5
4641·9	O 9	4579·8	Ba 6	4528·6	Ce 8
4638·9	O 5	4578·8	Ca 4	4527·5	Ce 10
4637·8	In 8	4577·4	V 10	4526·6	Cr 7
4635·0	I 6	4575·9	Br 6	4526·3	La 5
4634·0	N 3	4575·1	La 6	4525·8	Br 8
4633·8	Di 4	4574·1	Ba 4	4525·5	La 7
4630·8	N 12	4573·9	Ur 3	4525·2	Ba 10
4630·1	Zn 2	4572·9	Be 1	4525·0	S 10
4628·3	Ce 10	4572·5	Ce 10	4524·9	Sn 10
4627·4	Eu 8	4572·0	V 10	4524·8	X 6
4627·3	Ur 5	4572·2	Ti 20	4523·2	Ce 8
4624·4	Kr 10	4570·1	Ur 3	4523·0	Ti 10
4624·4	X 15	4567·9	Ur 3	4522·8	Eu 15
4623·0	Br 8	4564·8	V 12	4522·7	Tm 2
4622·3	Di 4	4563·9	Ti 15	4522·5	La 8
4621·7	N 9	4563·5	Th 5	4515·5	Ur 4

BLUE RAYS—*continued.*

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
4513·7	Br 5	4510·5	Ur 3	4501·4	Ti 15
4512·9	Ti 10	4510·4	Pr 10	4501·1	Kr 7
4511·9	Al 6	4507·7	N 6	4501·1	X 10
4511·4	In 50 x	4506·1	Ba 6	4500·9	Er 6
4510·7	Th 5	4502·5	Kr 9	4500·0	Blue ends.

INDIGO RAYS.

4498·9	Pt 4	4454·1	Kr 10	4411·2	Nd 7
4497·1	Zr 10	4453·2	Mn 10	4410·2	Ru 8
4497·0	Cr 6	4452·2	V 14	4409·0	Pr 10
4496·7	Pr 10	4451·8	Mn 6	4408·9	Nd 5
4495·5	As 8	4451·7	Nd 10	4408·7	V 14
4494·6	Zr 10	4450·1	Pr 5	4408·4	V 10
4491·0	Ur 3	4449·5	Ce 4	4407·9	V 12
4489·6	Be ?	4449·3	Ti 10	4406·9	V 12
4489·1	V 16	4447·2	N 12	4406·0	Pr 10
[No. 10,	Gold.]	4447·1	O 4	4404·9	Fe 10
4488·4	Au 18	4446·5	Nd 8	4402·7	Ba 8
4486·0	S 10	4444·4	V 10	4401·0	Nd 5
4484·3	W 6	4444·0	Ti 15	4400·8	V 18
4481·3	Mg 10 x	4443·3	Zr 10	4400·1	Kr 6
4479·4	Al 6	4442·7	Pt 4	4399·9	Ti 10
4478·2	Br 8	4441·9	V 14	4399·6	Ir 8
4476·3	Ag 5	4441·9	Br 8	4398·2	Yt 15
4474·9	V 10	4438·2	Sr 3	4396·5	Br 5
4474·8	Mo 6	4438·0	V 12	4396·3	Pr 5
4474·3	V 10	4437·4	Au 4	4395·7	Au 3
4473·8	Pd 6	4436·5	Mn 4	4395·4	V 20
4472·8	Br 8	4436·5	R 20	4395·2	Pr 5
4472·6	Ur 6	4436·3	V 10	4395·2	Ti 15
4471·6	He 6	4435·7	Eu 30	4395·0	Os 8
4471·4	Ce 6	4435·1	Ca 10	4391·8	Ce 8
4469·9	V 12	4434·1	Ur 3	4391·3	Th 8
4468·9	Pr 7	4432·1	Ba 8	4390·9	Nd 6
4468·7	Ti 15	4430·1	La 8	4390·6	Ru 8
4466·8	As 8	4429·4	Pr 12	4390·1	V 30
4465·3	Ur 3	4427·7	La 5	4388·8	He 10
4465·0	S 10	4426·1	N 5	4388·1	He 3
4463·8	Kr 10	4425·6	Ca 10	4387·9	Th 5
4463·2	Nd 9	4425·3	Br 5	4387·3	Pb 9
4463·2	Ur 3	4422·8	Yt 10	4385·9	Nd 7
4462·6	V 14	4420·6	Os 10	4385·1	Cr 6
4462·2	Mn 6	4419·8	Er 8	4384·9	V 40
4460·4	Ce 8	4419·0	Ce 6	4383·7	Fe 10
4460·2	Ru 8	4417·1	O 9	4383·6	La 5
4460·0	V 14	4415·9	Cd 10	4382·3	Ce 8
4460·5	V 12	4415·3	Fe 8	4382·1	Th 8
4457·6	Ti 10	4415·1	O 9	4380·0	Zr 12
4456·6	Nd 5	4413·3	Cd 2	4379·4	V 40
4455·0	Ca 10	4411·9	Mo 6	4378·3	La 3

INDIGO RAYS—continued.

Wave- Length.	Element and Intensity.	Wave- Length.	Element and Intensity.	Wave- Length.	Element and Intensity.
4377.9	Mo 6	4339.8	Cr 8	4296.3	V 10
4376.3	Kr 10	4339.6	Cr 8	4296.2	La 8
4375.2	Nd 6	4338.8	Nd 8	4295.0	S 8
4375.1	Yt 100	4338.1	Ti 10	4294.8	W 8
4375.0	Rh 10	4338.0	Sr 1	4294.3	Ti 10
4373.1	Cl 8	4337.9	Ce 4	4294.1	Os 10
4372.4	Ru 8	4335.1	La 5	4292.0	V 10
4371.8	Pr 5	4334.2	Pr 10	4291.5	Br 6
4371.4	Cr 7	4333.9	La 15	4290.1	Ce 6
4371.1	Zr 10	4333.6	A 8	4289.9	Cr 10
4370.4	Au 8	4333.0	V 12	4289.5	Ca 8
4368.6	Pr 10	4330.2	V 12	4288.9	Rh 8
4367.0	O 6	4328.8	Os 6	4288.0	Ur 3
4365.8	Br 8	4328.1	Nd 6	4287.1	Ur 3
4363.8	Mo 8	4326.1	Ur 3	4287.1	La 20
4362.8	Kr 9	4325.9	Fe 10	4284.7	Nd 7
4361.9	Sr 3	4325.9	Nd 7	4284.2	V 12
4361.4	Ru 6	4319.8	O 3	4283.3	Ba 8
4359.9	Zr 10	4319.7	Kr 10	4283.2	Ca 8
4359.8	Cr 7	4318.8	Ca 8	4283.0	S 8
4358.9	Y 8	4318.7	Kr 8	4282.7	Pr 7
4358.6	Hg 10	4317.4	Zr 6	4282.7	Nd 7
4358.3	Nd 8	4317.3	O 3	4282.7	Ur 3
4356.1	Nd 5	4316.1	La 1	4282.2	Ur 3
4355.9	Ur 4	4315.8	Sc 15	4282.3	Zr 8
4354.6	La 7	[No. 11, Gold.]		4280.3	Pr 7
4353.0	V 12	4315.4	Au 8	4279.2	Mo 6
4352.4	Sb 7	4314.6	Nd 8	4279.1	V 10
4352.2	Mg 2	4311.7	Ir 6	4277.4	Mo 6
4352.1	Pr 7	4311.6	Os 8	4277.3	Cs 5
4351.9	Nd 8	4309.8	Yt 20	4277.1	Mo 6
4351.9	Cr 8	4308.0	Fe 10	4277.1	V 12
4351.5	O 6	4307.9	Ca 6	4275.3	Cu 10
4351.2	Nd 7	4307.7	Ru 6	4275.3	Nd 5
4350.6	Pr 5	4307.6	Cl 8	4275.3	Te 6
4350.5	Mo 6	4306.1	Ti 15	4274.9	Cr 10
4350.5	Ba 6	4306.0	Pr 10	4274.7	Sc 20
4349.6	O 8	4305.6	Sr 30	4274.2	Ur 3
4348.2	W 6	4304.6	Nd 5	4274.1	Kr 10
4348.1	A 9	4303.8	Nd 10	4273.4	Li 4
4347.7	Pr 6	4303.8	Pr 5	4272.5	Pr 7
4347.7	Hg 2	4302.7	Ca 10	4272.3	A 8
4347.6	O 5	4302.6	Bi 9	4271.9	Fe 10
4347.4	Ur 3	4302.3	W 6	4271.3	Fe 7
4346.7	N 6	4302.1	Te 5	4269.8	Ur 4
4345.7	O 6	4300.6	Se 20	4269.7	La 10
4344.7	Cr 8	4300.2	A 8	4265.5	W 6
4344.6	Pr 8	4299.2	Pr 5	4269.4	Mo 6
4343.8	Cl 10	4299.1	Ca 6	4269.0	S 7
4341.9	Ur 4	4298.0	Pr 8	4268.8	V 14
4341.2	V 14	4298.0	Nd 5	4268.3	Ir 6
4340.8	R 50	4297.9	Ru 8	4267.5	C 7
4340.7	H 15	4297.3	Ur 3	4266.4	A 8
4340.7	K 15	4296.9	Ce 10	4265.0	Sb 6

INDIGO RAYS—*continued.*

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
4263·7	La 8	4253·6	Cl 10	4243·2	Ru 6
4263·2	K 6	4252·1	Nd 7	4242·3	Tm 4
4262·1	Nd 5	4252·1	Er 5	4241·9	N 6
4261·0	Os 10	4251·0	S 7	4241·9	Ur 4
4261·0	Ge 10	4250·9	Fe 8	4241·8	Zr 6
4260·7	Fe 10	4250·9	Mo 6	4241·5	Nd 5
4260·5	Te 6	4250·3	Fe 7	4241·5	Cl 8
4259·9	Bi 9	4248·8	Ce 6	4241·3	Pr 15
4259·5	Ne 6	4247·8	Pr 8	4241·2	Ru 6
4259·5	A 9	4247·6	Nd 8	4240·1	Ce 5
4255·8	Ga	4247·0	Sc 100	4240·0	Nd 6
4254·6	Pr 6	4246·1	Ce 5	4240·0	Indigo ends.
4254·2	Cr 10	4245·2	Pb 10		

VIOLET RAYS.

4238·5	La 10	4211·3	Rh 10	4186·7	Ce 10
4237·0	Br 6	4210·9	Ag 8	4186·3	K 8
4236·7	N 6	4210·0	V 12	4185·7	O 7
4236·2	Ur 3	4209·8	Mo 6	4184·4	Yb 10
4236·1	Fe 8	4209·0	Th 5	4183·6	V 16
4235·3	Mn 6	4208·5	Pr 5	4182·7	Zr 8
4233·8	Fe 6	4206·9	Pr 20	4181·9	Fe 7
4232·5	Nd 6	4206·2	Ru 10	4179·6	Pr 20
4228·5	N 6	4205·5	Ta 5	4179·8	Br 8
4226·9	La 6	4205·2	Eu 50	4179·2	Ge 20
4226·9	Ca 10	4205·2	V 16	4177·7	Yt 50
4226·8	Ge 50	4203·9	Tm 4	4177·5	Nd 10
4225·7	K 6	4203·1	Ce 5	4175·9	Br 5
4225·5	Pr 20	4202·2	Fe 9	4175·8	Nd 5
4225·2	Sc 20	4202·0	Rb 20	4175·8	Pr 5
4224·0	Br 8	4200·7	A 10	4175·8	Os 8
4223·2	Pr 20	4200·1	Ru 10	4173·4	Os 8
4223·2	Nd 6	4199·3	Fe 8	4172·5	Pr 8
4223·1	K 6	4198·8	Ce 6	4172·2	Ga 10
4222·8	Ce 5	4198·5	Fe 6	4172·0	Pr 8
4221·7	Te 6	4198·4	A 10	4172·0	Ti 10
4221·0	Sc 20	4196·7	La 10	4171·1	Ti 10
4217·7	La 10	4196·7	Rh 6	4171·8	Ur 3
4217·4	Ru 6	4196·5	Ce 4	4170·0	Ce 5
4217·1	Cd 6	4193·7	X 8	4168·3	Nb 6
4216·8	Hg 2	4193·6	Br 6	4168·3	Ta 8
4215·7	Sr 100	4192·5	La 8	4168·2	Pb 6
4215·7	Rb 10	4191·8	Pr 6	4167·7	Ru 6
4215·6	W 6	4191·5	Ta 6	4167·0	Ce 5
4214·6	Ru 6	4191·0	A 10	4166·2	Ba 10
4214·3	Sc 30	4190·1	O 7	4165·7	Ce 10
4213·1	Pd 10	4189·7	Pr 20	4165·2	Nd 5
4212·2	Ru 10	4187·9	Fe 8	4164·9	Nb 7
4212·0	Os 10	4187·8	Tm 3	4164·8	Ta 8
4211·4	Nd 5	4187·2	Fe 7	4164·4	Pr 15

VIOLET RAYS—*continued.*

Wave-length.	Element and Intensity.	Wave-length.	Element and Intensity.	Wave-length.	Element and Intensity.
4163·8	Ti 20	4132·1	V 16	4100·9	Pr 20
4163·8	Nb 7	4131·0	Si 4	4099·9	V 16
4163·8	Ta 8	4130·9	Ba 10	4099·7	La 10
4162·0	Sr 20	4130·9	Pr 6	4098·5	Pr 7
4161·4	Zr 10	4129·9	Eu 100	4098·0	Ru 6
4158·6	A 10	4129·2	Pr 6	4097·7	Rh 6
4156·4	Zr 10	4129·1	Rh 8	4097·5	N 2
4156·3	Nd 10	4128·2	Si 4	4097·0	Pr 7
4155·6	Ur 3	4128·2	V 16	4095·6	V 12
4154·5	Rh 6	4127·1	Cd 6	4095·0	Cd 7
4153·6	O 6	4124·9	Ur 3	4094·3	Tm 3
4152·7	Ta 8	4124·3	O 5	4090·9	La 6
4152·1	La 10	4124·0	Ta 10	4090·7	V 16
4152·1	Ce 9	4124·0	Nb 7	4090·7	Zr 6
4151·9	N 5	4124·0	Ce 5	4090·3	Ur 4
4150·1	Ce 10	4123·4	La 30	4087·5	Pd 8
4149·4	Zr 20	4122·0	Bi 3	4087·0	Pr 5
4149·1	K 6	4121·9	Rh 6	4086·8	La 20
4148·5	Pr 7	4121·7	Bi 8	4084·3	Au 4
4146·7	Pr 7	4121·5	Co 8	4083·8	Mn 6
4146·0	N 4	4121·0	He 3	4083·5	Pr 10
4145·9	Ru 6	4120·9	Hg 8	4083·4	Ce 5
4145·2	Ce 7	4120·0	Ce 7	4083·1	Mn 6
4144·3	Ru 8	4119·5	O 5	4083·0	Rh 8
4144·0	Fe 7	4119·3	Nb 7	4082·1	Pr 10
4143·9	He 2	4118·9	Pt 6	4081·4	Zr 6
4143·7	Mo 6	4118·9	Co 8	4081·2	Pr 6
4143·3	Nd 8	4118·6	Pr 15	4080·8	Ru 8
4143·2	Pr 20	4118·3	Ce 6	4080·8	Ur 3
4143·1	Er 5	4118·3	V 10	4080·6	V 20
4142·6	Ce 5	4116·9	Th 5	4079·9	Pr 8
4141·9	La 10	4116·7	V 14	4079·9	Ta 12
4141·4	Ur 3	4116·3	Ur 3	4079·9	Nb 10
4141·3	Pr 10	4116·2	X 7	4079·4	Bi 10
4140·4	Br 6	4115·5	Ce 5	4078·9	X 10
4139·9	Nb 6	4115·3	V 16	4078·1	Hg 10
4139·9	Ta 8	4115·3	Hg 8	4077·9	Sr 100
4137·8	Ce 9	4112·9	Ru 6	4077·5	La 15
4137·3	Ta 7	4112·2	Os 8	4076·1	O 9
4135·9	Os 10	4109·9	V 14	4074·5	W 6
4135·8	Br 5	4109·6	Nd 8	4072·8	Zr 6
4135·5	Nd 7	4109·3	Nd 6	4072·4	O 9
4135·4	Rh 8	4106·9	Tm 3	4071·9	Fe 10
4135·2	Yb 10	4105·1	Ce 4	4070·1	Ir 6
4134·7	K 6	4105·1	O 5	4070·0	W 6
4134·6	V 14	4102·9	W 6	4070·0	O 9
4134·0	Ce 10	4102·5	Yt 6	4066·9	Os 10
4133·8	N 6	4102·3	V 10	4065·2	V 12
4133·7	Pr 5	4101·8	H 10	[No. 12, Gold.]	
4133·5	Nd 5	4101·9	In 50 x	4065·2	Au 15
4133·0	O 5	4101·1	Ce 5	4064·3	Zr 6
4132·7	Cl 9	4101·1	Ta 10	4063·8	Fe 10
4132·4	Li 6	4101·1	Nb 9	4063·0	Pr 10
4132·2	Fe 8	4100·9	Nd 5	4062·9	Cu 7

VIOLET RAYS—*continued.*

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
4062.4	Pr 6	4032.7	Ta 5	3995.5	Co 8
4062.3	Te 6	4032.5	Sr 1	3995.3	N 15
4062.3	Pb 6	4031.9	Nd 10	3994.9	Pr 8
4061.3	Nd 10	4031.8	La 20	3994.8	Nd 5
4059.1	Ta 15	4030.9	Mn 8	3993.6	Ba 8
4059.1	Nb 15	4030.5	Sr 7	3992.9	V 12
4058.0	Pb 10	4029.8	Pr 5	3992.3	Ir 6
4058.0	Zn 2	4028.5	Ti 10	3991.9	Nd 5
4056.7	Pr 10	4026.3	He 5	3991.3	Zr 15
4055.7	Mn 6	4026.0	La 4	3990.7	V 12
4055.6	Er 5	4025.7	Pr 5	3990.3	Nd 6
4055.4	Ag 6	4024.7	Ce 5	3989.9	Ti 20
4055.1	Te 6	4024.4	Hg 2	3989.7	Pr 9
4055.0	Pr 10	4024.2	Br 5	3988.7	La 30
4053.0	Au 7	4023.5	V 20	3988.4	Cd 5
4051.6	Ru 6	4023.3	Rh 6	3988.1	Yb 15
4051.5	V 10	4023.2	Nd 5	3986.7	Br 8
4051.3	Nd 6	4022.9	Pr 7	3984.7	Cd 3
4051.3	Pr 6	4022.3	Ru 6	3984.6	Rh 6
4051.1	V 10	4021.1	Pr 6	3984.5	Te 6
4050.3	La 10	4020.2	Ir 8	3984.1	Hg 10
4050.2	Ur 3	4019.7	Pb 8	3982.7	Yt 20
4048.9	Mn 6	4019.3	Th 10	3982.9	O 4
4048.8	Zr 10	4016.3	Au 5	3982.2	Pr 10
4047.4	K 10	4015.5	Pr 6	3981.9	Ti 15
4046.8	Hg 10	4012.6	Ce 10	3980.6	Br 10
4046.0	Fe 10	4012.4	Nd 10	3980.2	Br 5
4045.8	Zr 8	4010.7	Pr 5	3977.9	V 10
4045.0	Pr 8	4008.9	W 8	3977.8	Cd 6
4044.5	A 8	4008.9	Pr 15	3977.4	Os 4
4044.3	K 10	4008.9	Br 6	3976.8	Cd 6
4043.1	La 20	4007.4	Br 5	3976.8	Cr 9
4042.7	Ce 5	4006.7	Te 8	3976.7	Nb 6
4041.5	Mn 6	4005.9	V 16	3976.5	Ir 6
4041.4	N 6	4005.3	Fe 10	3975.7	Rh 6
4041.0	Au 4	4004.8	Pr 7	3974.8	Er 5
4040.9	Ce 7	4003.1	V 10	3973.8	V 16
4040.9	Nd 7	4001.2	K 6	3973.4	O 8
4037.2	As 30	3999.4	Ce 6	3973.9	Ca 4
4035.9	Mn 6	3999.2	Zr 25	3973.4	Nd 6
4034.6	Mn 6	3998.8	Ti 15	3972.3	Pr 6
4035.8	V 16	3997.3	V 10	3972.2	Eu 50
4035.3	N 5	3997.1	Pr 5	3971.8	Pr 5
4034.0	Pr 6	3996.7	Tm 3	3971.3	Pr 7
4033.7	Sb 8	3996.3	Rh 8	3970.2	H 8
4033.2	Mn 6	3995.9	Pr 5	3970.0	Violet ends.
4033.2	Ga 6	3995.8	Rh 6		

ULTRA-VIOLET RAYS.

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
3969.4	Fe 10	3940.4	Cd 8	3899.9	Fe 6
3969.4	Sr 1	3939.0	Nd 5	3898.1	K 8
3969.3	Te 6	3936.4	La 3	[No. 13, Gold.]	
3868.8	Br 5	3935.9	Ba 4	3898.0	Au 10
3968.6	Ca 80	3934.4	Rh 8	3896.5	Er 8
3968.3	Ag 5	3933.8	Ca 100	3895.8	Mg 6
3967.7	X 10	3933.6	Ag 5	3895.8	Ir. 6
3966.7	Pr 7	3932.2	Ur 3	3894.2	Pd 8
3966.5	Pt 6	3931.4	As 6	3894.2	Co 10
3966.4	Ta 5	3930.7	Eu 50	3892.0	Ba 10
3965.4	Pr 6	3929.4	La 15	3891.8	Br 8
3965.1	W 6	3928.8	Cr 6	3890.5	Ur 3
3965.0	Pr 8	3928.1	Fe 7	3889.5	Pr 5
3964.9	He 4	3925.6	Pr 8	3889.1	H 7
3964.4	Pr 5	3924.2	Br 8	3888.8	He 10
3963.9	Cr 10	3923.1	Pt 8	3888.6	Fe 6
3963.8	Os 6	3923.1	Fe 6	3886.5	La 15
3963.3	Nd 6	3922.6	As 100	3886.4	Fe 8
3961.7	Al 5 ψ	3921.7	La 10	3883.8	C 3
3961.7	Mo 10	3920.8	C 2	3880.6	Pr. 5
3960.7	Pr 5	3919.3	Cr 8	3879.3	Pr 5
3959.3	Au 5	3919.2	O 10	3877.8	Pr 10
3959.0	Rh 10	3919.0	Pr 10	3877.0	C 3
3958.9	Cd 7	3919.2	N 10	3876.7	Cs 1
3958.8	Pd 10	3916.1	Zr 8	3876.3	Pr 6
3958.3	Ti 10	3916.1	La 10	3873.2	Co 10
3958.3	Zr 15	3916.6	V 14	3872.6	Fe 8
3958.2	Nd 5	3916.1	Au 5	3872.0	C 3
3956.9	Pr 6	3915.2	Li 6	3871.9	La 20
3956.2	N 7	3915.5	Ir 6	3870.2	Rh 6
3955.5	Br 8	3914.4	Br 9	3868.0	Ru 6
3954.5	O 5	3914.4	Ur 3	3867.6	He 2
3953.6	Pr 8	3914.4	V 14	3865.8	Ir 6
3953.6	Nd 5	3913.6	Ti 30	3865.7	Fe 6
3952.7	Ce 7	3913.1	Pr 5	3865.6	Pr 10
3952.1	V 18	3912.2	O 5	3864.2	Mo 10
3951.1	X 10	3911.3	Nd 7	3863.5	Nd 8
3951.3	Nd 8	3910.1	Ba 6	3862.8	Si 4
3950.7	Br 7	3908.5	Pr 10	3862.8	Ru 6
3950.5	Yt 20	3908.2	Pr 6	3861.0	Cl 10
3949.6	Pr 8	3907.3	Eu 30	3860.1	Fe 9
3949.3	La 50	3907.4	Sn 8	3859.7	Ur 3
3949.1	A 8	3906.5	Er 10	3859.0	Rh 10
3948.8	As 6	3905.8	Ta 10	3858.4	Ni 8
3948.9	Fe 4	3905.8	Si 5	3857.7	Ru 6
3948.8	Ti 10	3905.0	Ti 10	3856.7	Rh 10
3947.8	Pr 8	3903.1	Fe 7	3856.5	Fe 8
3945.2	O 3	3903.1	Mo 10	3856.2	Si 5
3944.2	Al 9 ψ	3903.0	Er 5	3854.0	Pb 10
3942.9	Ce 5	3902.6	Ir 8	3853.7	Au 6
3942.9	Rh 6	3902.0	Nd 5	3852.9	Pr 6
3941.7	Nd 8	3901.1	Ti 10	3851.8	Nd 5
3941.7	B 2	3900.7	Ti 50	3851.7	Pr 5
3941.6	Mo 6	3900.4	Nd 6	3851.2	Cl 10

ULTRA-VIOLET RAYS—continued.

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
3851.0	Pr 6	3816.7	Pr 10	3774.5	Y 100
3850.7	A 8	3816.6	Rh 6	3773.1	V 10
3850.1	Fe 6	3816.5	Au 5	3771.1	V 20
3849.2	La 10	3816.0	Fe 9	3770.7	H 1
3848.2	Th 7	3815.6	V 10	3767.3	Fe 7
3847.5	V 10	3814.6	R 100	3767.0	Zr 12
3846.8	Pr 5	3810.6	Ag 3	3765.2	Rh 8
3845.8	Cl 8	3807.3	Ni 8	3763.9	Fe 7
3845.6	Co 10	3806.9	Mn 10	3762.1	Tm 4
3843.4	Cl 5	3806.1	Rh 6	3762.0	Pr 5
3842.0	Te 8	3805.4	Cl 6	3761.5	Tm 5
3841.2	Fe 8	3805.0	Pr 8	3761.5	Ti 50
3840.6	Fe 8	3804.2	Au 5	3761.5	Er 5
3839.9	Mn 4	3803.1	Ta 5	3760.4	V 10
3838.4	Mg 10 χ	3801.7	Ce 8	3759.7	Ta 5
3837.0	Zr 12	3801.3	Nb 7	3759.4	Ti 50
3835.6	H 1	3801.2	Sn χ 10	3759.2	La 20
3834.8	A 8	3800.5	Pr 5	3758.4	Fe 8
3834.4	Fe 8	3800.2	Ir 8	3757.8	Ti 10
3834.0	Rh 8	3799.7	Fe 7	3756.1	Ru 6
3833.5	Cl 6	3799.5	Rh 10	3754.4	Rh 6
3833.1	Zn 1	3799.5	Ru 8	3752.7	Os 10
3833.0	Yt 20	3799.3	Pd 8	3752.7	Th 6
3833.0	Pb 8	3799.0	Ru 8	3752.0	H 1
3832.5	Mo 6	3799.0	Cl 5	3751.8	Zr 12
3832.5	Mg 10 χ	3798.6	Fe 6	3750.1	Cl 5
3832.0	Ta 6	3798.4	Mo 10	3750.1	V 12
3832.0	Nb 6	3798.3	Ta 6	3749.7	O 6
3831.6	Ur 3	3798.0	H 1	3749.6	Fe 10
3830.9	Pr 6	3795.9	Tm 5	3748.4	Fe 7
3830.7	Er 6	3795.1	Fe 6	3747.4	Ir 6
3829.5	Mg 10 χ	3795.1	V 10	3746.2	Zr 10
3829.3	B 1	3795.0	La 50	3746.0	Fe 7
3828.6	Rh 8	3794.9	Li 4	3746.0	V 14
3828.0	Fe 9	3793.4	Rh 8	3745.7	Fe 7
3827.8	Cl 5	3793.0	Bi 8 ϕ	3745.5	La 8
3820.6	Fe 9	3791.4	Ta 6	3743.5	Fe 7
3825.8	Au 8	3791.0	La 50	3743.0	Ru 6
3824.6	Fe 7	3790.6	Ru 8	3742.6	Ta 5
3824.5	B 1	3788.8	Yt 30	3742.5	Mo 6
3823.6	Mn 6	3788.6	Rh 6	3742.4	Ru 6
3822.4	Rh 8	3787.6	V 16	3741.8	Ti 30
3822.1	Au 6	3787.2	Ta 5	3741.4	Th 6
3821.9	Pr 5	3786.4	Pb 10	3740.9	Nb 8
3820.6	Fe 9	3786.2	Ru 8	3740.1	Pb 10 χ
3820.4	Cl 5	3783.7	Ni 6	3739.9	Ta 5 χ
3819.8	Eu 50	3782.3	Os 8	3739.5	Sb 8 ϕ
3819.8	He 4	3781.4	Cl 5	3737.4	Rh 6
3819.0	Nb 10	3781.5	Nb 6	3737.3	Fe 8
3819.0	Ta 5	3780.1	Au 5	3737.2	Ca 15
3818.8	Pt 6	3778.8	V 10	3736.9	Ni 8
3818.5	Yt 10	3778.5	V 12	3736.5	Te 8
3818.4	Pr 7	3775.9	Tl 20 ψ	3736.4	W 6
3818.3	Rh 8	3775.7	Ni 6	3736.2	V 10

ULTRA-VIOLET RAYS—*continued.*

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
3735·8	Nd 5	3692·8	Er 10	3652·6	Mo 6
3735·4	Rh 8	3692·6	Th 6	3652·0	Sc 20
3735·0	Fe 10	3692·5	Rh 10	3651·3	Mo 6
3734·3	Tm 3	3692·4	V 10	3651·3	Ta 6
3734·1	H 1	3692·4	Ir 6	3650·3	Hg 10
3732·9	V 14	3691·5	H 10	3650·0	Te 6
3731·5	Zr 10	3690·9	Rh 8	3649·8	R 50
3731·5	Ir 6	3690·5	Pd 10	3648·0	Fe 9
3730·6	Ru 10	3689·5	Ir 6	3646·7	W 6
3729·7	Er 5	3688·6	Eu 10	3646·1	Er 7
3729·5	A 9	3688·4	Mo 10	3645·8	W 6
3728·5	V 10	3688·1	Ta 5	3645·8	Pr 7
3728·2	Ru 10	3687·6	Fe 6	3645·5	La 8
3727·5	O 4	3687·6	Pt 8	3645·5	Sc 15
3727·1	Ru 10	3686·9	H 10	3643·3	Pt 6
3726·4	Ta 5	3685·3	Ti 50	3642·9	Sc 50
3725·1	Eu 30	3683·7	Ta 8	3642·8	Ti 10
3723·5	V 16	3683·6	Pb 10 X	3641·6	W 8
3722·9	Sb 8	3682·9	H 10	3641·5	Ti 20
3722·7	Fe 6	3682·3	Fe 4	3639·7	Pb 10 X
3722·6	Ni 6	3681·2	Rh 8	3639·7	Os 8
3722·2	H 1	3679·9	Th 5	3639·0	Pt 6
3720·1	Fe 8	3679·4	H 10	3637·9	Sb 8
3719·1	Pd 10	3676·4	H 10	3635·3	Mo 10
3718·3	V 10	3675·2	Yb 10	3635·1	Ru 8
3718·0	Tm 3	3675·2	Ir 8	3634·8	Pd 10
3317·2	Nb 10	3675·0	Zr 10	3634·4	He 2
3717·2	Ta 8	3674·2	Pt 6	3633·7	Er 5
3715·2	V 20	3673·9	H 10	3633·7	Ne 6
3713·2	Ta 6	3672·2	Pt 6	3633·4	Au 5
3713·2	Rh 8	3671·7	Pb 8	3631·6	Fe 10
3712·9	O 2	3671·0	H 10	3630·9	Sc 100
3712·0	H 10	3670·3	Ur 3	3630·8	Ur 3
3710·4	Y 100	3669·6	V 16	3630·0	Sb 5
3709·5	Zr 10	3669·6	Ru 6	3629·0	Pt 6
3709·4	Fe 6	3666·4	Rh 8	3628·9	Yt 10
3707·7	Er 5	3664·7	Yt 20	3628·3	Pt 8
3706·2	Mn 4	3663·3	Hg 10 φ	3626·8	Rh 10
3706·2	Ca 10	3662·4	Ti 15	3625·0	Ti 15
3705·9	Sr 3	3661·7	Th 6	3622·9	Au 6
3705·2	He 3	3661·5	V 12	3621·3	Co 8
3704·1	H 10	3661·5	Ru 10	3620·0	Vb 10
3703·7	V 12	3659·9	Ti 15	3619·5	Ni 10
3702·7	Mo 8	3659·7	Ta 6	3619·1	V 12
3701·5	Tm 5	3659·7	Th 6	3618·9	Fe 10
3701·3	Ne 6	3659·7	Nb 8	3617·9	Er 5
3701·1	Rh 8	3658·1	Rh 10	3617·7	W 6
3700·5	V 12	3657·7	W 6	3617·6	Te 6
3700·4	Tm 5	3657·5	W 6	3617·2	Th 5
3698·4	Zr 10	3655·9	Sn 8	3616·7	Er 7
3697·4	H 10	3654·9	Hg 10 φ	3614·9	Zr 10
3695·6	Bi 10 φ	3653·6	Ti 15	3614·9	Rh 8
3694·3	Yb 200	3653·4	Ir 10	3614·0	W 8
3692·8	Mo 6	3653·3	Sr 1	3614·0	Sc 100

ULTRA-VIOLET RAYS—continued.

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
3613·9	Bi 4	3581·1	Sc 20	3535·6	Ti 20
3613·8	He 3	3580·4	Ta 6	3535·5	Ta 6
3613·0	Cd 8 ψ	3578·8	Cr 10	3534·0	Sb 5
3612·9	Rh 8	3578·0	Mn 6	3532·1	Mn 10
3612·9	Ni 6	3577·1	Zr 10	3532·0	Mn 10
3612·1	Zr 10	3576·8	Ar 8	3530·9	V 20
3611·8	Cs 1	3576·5	Sc 20	3529·9	Co 10
3611·2	Y 30	3576·0	Ta 6	3529·6	Tl 10
3610·7	Cd 10 ψ	3573·9	Ir 8	3529·1	Th 5
3610·6	Ni 8	3573·8	Sn 6	3528·8	Os 6
3610·4	Mn 6	3572·9	Pb 10 ψ	3528·2	Rh 10
3609·7	Pd 10	3572·7	Sc 50	3527·0	Co 8
3609·0	Fe 9	3572·6	W 8	3524·9	V 16
3608·6	Mn 6	3572·6	Zr 22	3524·7	Mo 6
3607·7	Mn 6	3572·0	Ni 8	3524·6	Ni 10
3606·0	Ir 10	3571·3	Pd 10	3523·6	Co 10
3606·0	Rh 6	3570·7	Ru 6	3522·0	V 12
3605·5	Cr 10	3570·3	Rh 8	3521·4	Fe 6
3602·1	Yt 20	3570·3	Fe 10	3521·0	Te 8
3601·2	Th 7	3570·2	Mn 8	3520·5	Ne 8
3600·9	Y 50	3569·7	Mn 6	3520·4	Ti 20
3599·9	Er 7	3569·5	Co 10	3520·2	V 14
3599·9	Ru 8	3567·9	Sc 20	3519·7	Sb 5
3599·6	Er 5	3566·7	Sb 6	3519·4	Tl 20 χ
3597·8	Ni 10	3566·5	Ni 10	3517·4	V 20
3597·7	Sb 8 ϕ	3566·3	V 12	3517·3	La 50
3596·3	Bi 10 ϕ	3565·5	Fe 8	3517·1	Pd 10
3596·3	Rh 10	3561·1	Os 8	3515·3	Ne 6
3596·3	Ru 8	3560·9	Yb 10	3515·2	Ni 10
3596·0	Ti 10	3560·0	Os 6	3513·8	Ir 6
3595·2	Mn 6	3559·7	Ar 8	3511·8	Th 6
3593·6	Ne 10	3559·5	Sb 6	3511·0	Ti 50
3593·6	Cr 10	3558·7	Sc 20	3511·0	Bi 8 ϕ
3593·5	V 16	3558·7	Fe 6	3510·5	Ni 8
3593·2	Ru 8	3557·0	V 20	3510·5	Ta 5
3592·6	W 8	3556·7	Zr 15	3508·9	W 6
3592·2	V 18	3554·6	Yb 10	3507·7	Th 10
3591·7	Rb 1	3553·7	Au 6	3507·5	Rh 8
3590·7	Sc 10	3553·2	Pd 10	3506·4	Co 10
3589·9	V 18	3552·2	Te 8	3505·0	Ti 50
3589·8	Sc 10	3552·1	Zr 10	3504·8	Sb 6 ϕ
3589·4	Ru 8	3549·7	Rh 10	3504·6	V 16
3588·6	Ar 9	3549·2	W 6	3502·7	Rh 8
3587·4	He 2	3549·2	Y 20	3502·4	Co 8
3587·3	Co 10	3548·2	Mn 10	3501·3	Ba 8
3587·2	Rb 1	3548·1	Mn 10	3501·3	Ne 6
3587·0	Al 10 ϕ	3545·3	V 20	3501·0	Ni 8
3586·7	Mn 6	3544·1	Rh 8	3499·3	Er 10
[No. 14, Gold.]		3542·9	Zr 12	3499·1	Ru 10
3586·7	Au 7	3541·6	V 16	3498·9	Rh 8
3585·0	Ur 3	3539·4	Ru 6	3498·6	Sb 6
3584·7	Yt 10	3538·9	Th 10	3498·1	Ne 6
3583·2	Rh 6	3538·3	Rh 8	3497·7	Mn 8
3581·3	Fe 10	3535·9	Sc 15	3497·1	V 14

ULTRA-VIOLET RAYS—*continued.*

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
3496.6	Te 8	3457.3	V 14	3404.7	Pd 10
3496.3	Zr 20	3456.6	Ti 15	3403.7	Cd 10 χ
3496.2	Yt 10	3454.3	Ne 6	3403.5	Cr 10
3496.0	Mn 8	3454.2	Yb 15	3402.0	W 6
3495.8	Co 10	3453.8	Tm 3	3399.1	W 6
3493.3	V 12	3453.6	Co 8	3397.3	Bi 10 ϕ
3493.1	Ni 10	3453.0	Ni 7	3397.2	Yb 10
3491.7	Ar 9	3451.3	B 6	3397.0	Rh 10
3491.2	Ti 10	3451.1	Bi 8	3394.7	Ti 30
3490.7	Fe 6	3447.8	Ne 8	3393.1	Ni 7
3489.9	Pd 8	3447.7	He 2	3392.4	Zr 15
3489.5	Co 10	3447.5	K 10	3392.2	Er 5
3488.8	Mn 10	3446.3	Ni 8	3392.2	Th 5
3486.1	V 12	3444.5	Ti 15	3390.5	Hg 8
3485.4	Pt 6	3442.1	Mn 10	3388.0	Ti 15
3483.0	Mn 10	3441.6	Tm 4	3385.4	K 6
3481.3	Zr 10	3441.5	Pd 10	3385.3	Er 7
3481.3	Pd 10	3441.1	Fe 6	3383.9	Ti 50
3479.6	Zr 10	3440.8	Fe 7	3383.2	Sb 6
3478.9	Yb 20	3440.7	Rh 6	[No. 15,	Silver.]
3478.0	Rh 8	3440.5	K 6	3383.0	Ag 10 ψ
3477.4	Ti 15	3438.4	Zr 15	3381.4	K 6
3476.8	Fe 5	3437.2	Ir 6	3381.0	La 10
3475.6	Fe 7	3436.9	Ru 10	3380.9	Sr 80
3475.0	Sr 20	3435.0	Rh 10	3380.7	Ni 7
3474.9	Rh 8	3433.7	Ni 7	3380.4	Ti 15
3474.2	Mn 10	3433.6	Pd 10	3377.6	Th 8
3474.1	Co 10	3432.9	Nb 8	3376.2	W 8
3474.0	Sb 6	3432.9	Ta 5	3373.1	Pd 10
3472.7	Ni 8	3430.7	Zr 10	3372.9	Ti 30
3472.7	Ne 8	3430.5	Cr 10	3372.9	Er 10
3471.0	Ce 5	3428.5	Ru 10	3372.4	Rh 8
3470.8	Rh 8	3426.7	Nb 8	3372.3	Sc 10
3470.1	Th 5	3425.9	Sb 6	3370.7	Os 6
3467.8	Cd 10 ψ	3425.6	Nb 7	3370.0	Ne 6
3466.7	Ne 6	3425.2	Tu 5	3369.7	Ni 8
3466.3	Cd 10 ψ	3425.2	Tm 5	3369.1	Sc 10
3466.0	Fe 7	3423.8	Ni 7	3368.5	Rh 6
3465.9	Co 8	3422.9	Cr 10	3368.3	Ba 8
3464.6	Sr 100	3421.4	Pd 10	3368.2	Cr 10
3464.8	Ne 6	3421.4	Cr 10	3367.7	Pr 5
3463.7	W 6	3421.3	Rh 8	3366.4	Sr 4
3463.2	Zr 12	3420.3	Rh 8	3362.8	Tm 4
3462.9	Co 8	3418.0	Ne 8	3362.7	Te 8
3462.7	Yb 10	3417.5	Ru 8	3362.1	Sc 10
3462.4	Tm 5	3414.9	Ni 8	3361.3	Ti 50
3462.2	Rh 8	3412.4	Rh 8	3361.3	Rh 6
3461.8	Ni 10	3410.4	Zr 8	3360.5	Cr 10
3461.7	Ti 15	3408.9	Cr 10	3359.8	Sc 8
3460.9	Pd 10	3408.3	Pt 6	3359.6	Pr 5
3460.6	Ne 6	3407.6	Fe 6	3359.2	Ru 6
3460.5	Mn 10	3407.0	Te 6	3358.7	W 6
3458.6	Ni 10	3405.3	Co 8	3357.8	Pr 5
3458.5	Ni 8	3405.0	Zn 6	3353.9	Sc 20

ULTRA-VIOLET RAYS—*continued.*

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
3353·4	Cl 5	3306·1	Fe 7	3261·2	Cd 8 φ
3352·5	Sn 10 χ	3306·1	Ur 3	3258·9	Pd 8
3351·3	Sr 3	3305·0	Sb 6	3258·7	In 3 φ
3350·4	Ru 6	3303·1	Na 10	3256·2	In 8 ψ
3349·7	Ti 10	3303·0	Zn 10 ψ	3256·0	Pt 4
3349·2	Ti 20	3302·7	Zn 10	3254·8	V 10
3345·5	K 8	3302·5	Na 10	3253·0	Ti 10
3345·5	Zn 10 ψ	3302·3	Pd 10	3252·6	Ag 5
3345·1	Zn 10 ψ	3302·0	Pt 8	3252·6	Cd 7
3342·8	Cr 10	3301·8	Sr 3	3251·9	V 10
3342·6	W 6	3301·6	Ag 5	3251·8	Pd 8
3342·0	Ti 20	3300·6	Th 10	3250·9	V 10
3341·7	Hg 10	3294·3	Ru 10	3250·5	Cd 7
3341·6	Pr 5	3292·5	Mo 6	3248·8	Ti 20
3340·6	Zr 6	3291·5	Ur 3	3247·7	Ni 7
3340·5	Ti 15	3291·1	Tm 3	3247·6	Cu 10 ω
3340·0	Cr 10	3290·7	Th 10	3247·4	Pt 6
3339·7	Th 6	3290·6	Cu 3 φ	3246·8	Te 10 ψ
3338·0	V 12	3290·4	Pt 4	3246·9	B 1
3337·6	La 15	3289·5	Yb 100	3244·7	Ag 4
3337·3	Sb 8 φ	3287·8	Ti 15	3243·2	Ni 7
3336·8	Mg 8	3283·7	Rh 6	3243·0	Pb 6
3335·4	Ti 20	3283·6	Sn 10 χ	3242·9	Pd 19
3332·3	Mg 8	3282·7	V 10	3242·4	Y 20
3332·2	Ti 15	3282·5	Ti 10	3242·1	Ti 20
3330·7	Sn 10 χ	3282·4	Zn 10 ψ	3241·7	Tm 3
3330·2	Sr 4	[No. 16, Silver.]		3241·3	Sb 8
3330·1	Mg 6	3280·8	Ag 10 ψ	3240·3	Pb 2
3329·6	Ti 20	3280·7	Rh 8	3239·2	Ti 10
3329·1	Cl 5	3280·0	V 16	3238·0	V 12
3328·0	Y 20	3279·1	Ti 10	3236·7	Ti 15
3326·9	Ti 10	3278·7	Fe 8	3234·6	Ti 20
3323·9	Pt 2	3278·4	Ti 10	3233·1	Ni 8
3323·2	Rh 8	3276·3	V 20	3232·8	Li 5
3323·0	Ti 30	3274·1	Cu 8 ψ	3232·6	Sb φ
3322·3	Sr 3	3274·0	Pt 6	3232·2	Os 10
3321·9	Ti 10	3273·8	Au 4	3232·2	Th 7
3321·7	V 10	3273·2	Zr 8	3230·7	Er 5
3321·5	Be 3	3272·5	Th 16	3230·7	Au 8
3321·3	Mo 6	3271·2	V 20	3229·9	Tl 6
3321·3	Mn 6	3270·2	V 10	3229·8	Mo 6
3321·2	Be 3	3269·7	Ge 10	3229·6	Ur 3
3321·0	Mn 6	3269·1	Tm 3	3228·6	Ru 8
3318·2	Ti 10	3268·1	Os 8	3228·2	Mn 6
3316·6	Er 5	3267·8	V 20	3228·0	Au 5
3315·4	Ru 6	3267·6	Sb 10 φ	3227·9	Fe 6
3313·9	Th 10	3267·5	Pd 6	3225·6	Ta 5
3312·6	Er 5	3267·4	Os 8	3225·6	Nb 7
3308·3	Au 3	3266·0	V 10	3223·0	Ti 10
3308·1	Cu 7 χ	3265·0	Er 5	3221·4	Th 12
3307·6	Sr 3	3263·3	Rh 6	3220·9	Ir 6
3307·2	Cr 10	3262·5	Os 8	3218·4	Ti 10
3206·6	Zr 6	3262·4	Sn 10 χ	3217·9	Ni 7
3306·5	Fe 7	3261·7	Ti 30	3217·3	K 2

ULTRA-VIOLET RAYS—*continued.*

Wave-length.	Element and Intensity.	Wave-length.	Element and Intensity.	Wave-length.	Element and Intensity.
3217·2	V 12	3139·5	Pt 4	3091·9	Tl _X 8
3217·2	Ti 10	3137·8	Pb 10	3091·7	Fe 2
3216·8	Yt 10	3137·8	Ir 6	3091·2	Mg 2 χ
3216·7	Th 8	3136·6	V 12	3089·2	Pb 6
3213·5	Os 10	3135·1	V 12	3088·2	Ir 6
3212·2	Ir 8	3134·3	Ni 8	3088·1	Ti 15
3207·4	Rh 6	3134·2	Fe 1	3087·7	Mo 6
3206·5	Nb 6	3134·0	Tm 3	3085·4	Cd 5
3204·7	Au 8	3133·5	V 10	3082·3	Al 9 ω
3204·2	Pt 6	3133·4	Ir 8	3081·0	Cd 5
3202·7	Ti 15	3133·3	Cd 8	3080·8	Ni 7
3200·4	Yt 8	3132·6	Fe 1	3077·7	Mo 6
3197·2	Cr 10	3132·2	Cr 10	3077·6	W 6
3195·1	Nb 8	3131·9	Hg 10 χ	3076·0	Zn 8 χ
3194·9	Au 5	3131·7	Hg 10	3073·2	Th 3
3191·0	Ti 20	3131·4	Tm 6	3072·2	Zn 10
3190·8	V 16	3131·2	Be 15	3071·7	Ba 6
3188·8/8·0	Rh 6	3130·6	Be 20	3069·2	Ir 6
3188·6	V 10	3130·4	V 12	3069·0	Ir 6
3188·4	Th 5	3130·1	Ag 2	3067·8	Bi 10 ψ
3187·8	V 10	3127·6	Nb 7	3067·2	V 10
3187·8	He 8	3126·3	V 10	3066·3	Al 8
3185·5	V 4	3126·2	Cu 6	3064·9	Ir 8
3184·1	V 4	3125·8	Hg 10 ϕ	3064·8	Pt 8
3183·5	V 4	3125·8	Fe 1	3064·7	Ni 7
3181·4	Ca 7	3125·1	Cr 10	3064·4	Al 8
3180·8	Cr 10	3123·0	V 10	3063·8	V 10
3180·4	Nb 6	[No. 17, Gold.]	Au 6	3062·4	K 6
3179·4	Ca 10	3122·9	Er 5	3060·0	Al 1
3177·2	Ru 10	3122·8	Mo 6	3058·8	Os 10
3176·6	Pb 10	3122·1	Cr 10	3057·7	Ni 8
3176·0	Flint glass transmission ends.	3120·5	Cr 10	3057·3	Al 8 ϕ
		3119·7	As 8	3056·9	Ru 6
		3119·3	Ba 6	3055·8	Rh 6
3175·4	Te 6	3118·8	Cr 10	3054·8	Al 8
3175·1	Sn 10 χ	3118·5	V 12	3054·4	Ni 8
3174·0	Os 8	3114·2	Pd 8	3053·5	V 10
3173·0	Tm 3	3110·8	V 12	3050·9	Ni 8
3171·8	La 20	3108·6	Cu 5	3050·2	Al 8
3168·7	Ti 15	3104·0	Ba 6	3049·0	Rh 6
3167·6	V 10	3102·4	V 12	3048·8	V 10
3165·8	Os 8	3102·0	Ni 8	3047·7	Fe 3
3163·5	Nb 8	3101·6	Ni 8	3047·4	Rh 6
3159·4	Rh 8	3101·0	V 10	3047·0	Te 10
3159·1	Ca 10	3100·6	Ir 6	3044·0	Pb 8
3156·7	Au 5	3098·0	Th 6	3042·8	Ir 8
3156·3	Os 10	3097·1	Mg 2 χ	3042·8	Os 8
3155·5	Rh 8	3094·3	V 12	3041·0	Os 8
3152·8	Ba 6	3094·3	Nb 10	3039·5	In 4 ψ
3151·2	Tm 3	3094·0	Ru 6	3039·2	Ge 20
3148·1	Th 5	3093·6	Rh 6	3038·0	Ni 7
3145·3	Nb 6	3093·2	V 6	3036·6	Ru 8
3141·9	Sn 8	3093·1	Mg 2	3036·6	Pt 4
3139·9	V 10	3092·8	Al 9 ω	3035·9	Zn 8

ULTRA-VIOLET RAYS—*continued.*

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
3034.2	Sn 10	2967.4	Hg 10 χ	2913.6	Au 9
3033.4	Au 1	2967.2	Te 4	2912.4	Os 8
3033.0	As 6	2965.7	Ru 8	2911.5	Yb 10
3032.9	Sn 10 χ	2963.7	Rh 10	2910.3	Rh 10
3032.3	Pd 6	2961.2	Cu 5 ϕ	2909.0	Os 10
3031.2	Mn 6	2959.8	As 10	2908.3	Ur 3
3030.8	Os 8	2957.7	V 10	2907.1	Au 5
3029.9	Sb 6 ϕ	2954.8	Co 8	2903.1	Mo 6
[No. 18, Gold.]		2954.6	Au 6	2899.0	Th 6
3029.3	Au 6	2952.1	V 10	2898.8	As 2
3028.0	Pd 6	2951.0	Nb 10	2898.1	Bi 10 χ
3024.8	Bi 8 χ	2949.6	Os 6	2896.2	Sn 8 ϕ
3023.7	Hg 10	2949.3	Mn 10	2895.6	Te 10 ϕ
3020.8	Fe 2	2948.0	Fe 2	2894.0	Pt 4
3020.7	Tm 5	2946.1	Y 20	2893.7	Hg 10
3020.0	Rh 6	2945.8	Ru 10	2893.5	Au 5
3020.0	Mn 6	2945.2	He 6	2893.5	V 10
3018.5	Zn 4	2944.7	V 10	2892.8	V 10
3017.9	Te 6	2944.1	Ni 6	2891.8	V 10
3012.1	Ni 8	2942.3	Te 4	2890.3	In 4
3009.2	Sn 10 χ	2942.2	Mg 1	2889.7	V 10
3009.1	Rh 6	2941.6	Nb 9	2889.5	Mn 6
3008.3	In 10	2941.5	V 10	2888.4	V 10
3005.9	Yb 10	2941.4	In 10 χ	2887.8	Sn 6
3003.7	Ni 8	2939.4	Mn 8	2886.4	Ag 5
3002.6	Ni 6	2938.5	Ag 3 ϕ	2884.9	V 12
3001.3	V 10	2938.4	Bi 10 ϕ	2883.3	Nb 7
3001.3	Pt 6	2937.0	Mg 10 ω	2882.6	V 19
3000.0	Solar spectrum ends.	2937.0	Fe 2	2882.2	Ru 6
		2933.1	Mn 8	2881.7	Si 10
2999.7	Pd 6	2932.7	In 1 ϕ	2880.9	Cd 10
2999.0	Ru 6	2932.6	Th 5	2880.1	V 10
2998.1	Pt 2	2932.3	Au 5	2879.5	Mn 6
2995.1	Au 8	2929.9	Pt 6	2879.1	Mo 6
2993.5	Bi 8 ϕ	2929.3	Ag 5	2878.0	Sb 7 ψ
2993.2	C 4	2928.7	Mg 10 ω	2877.6	Pt 6
2992.7	Ni 7	2927.9	Ru 6	2877.1	Nb 6
2991.7	Ru 8	2927.9	Nb 10	2875.5	Nb 6
2990.3	Au 6	2926.9	Rh 6	2873.6	Ag 5
2989.1	Bi 8	2926.5	V 10	2873.4	Pb 10
2989.0	Rh 6	2925.5	Hg 2	2871.6	Mo 6
2984.9	Fe 6	2924.9	Ir 8	2869.4	Tm 3
2983.5	In 8	2924.8	V 10	2869.2	V 12
2980.8	Cd 10	2924.1	V 10	2868.9	Te 8 ϕ
2980.8	Pd 8	2924.1	Rh 8	2868.4	Cd 5
2980.0	Crown glass transmission ends.	2921.6	Tl 8	2863.4	Sn 10 ψ
		2920.5	V 10	2860.5	As 10 ϕ
		2919.9	Os 8	2858.3	Te 10 ϕ
2978.8	Th 8	2918.4	Tl 10 ϕ	2854.4	V 12
2976.7	Ru 10	2916.4	Ru 6	2853.3	Mo 6
2976.6	V 10	2915.6	Mg 10	2852.9	Na 10
2972.3	V 10	2913.7	Ni 6	2852.2	Mg 8 ω
2968.4	V 12	2913.6	Sn 8 ϕ	2851.2	Sb 8
2967.6	C 3	[No. 19, Gold.]		2850.7	Sn 8 ϕ

ULTRA-VIOLET RAYS—continued.

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
2850.3	V 10	2802.1	Pb 10	2760.6	V 10
2849.8	Ir 6	2801.0	Zn 8 χ	2759.8	Hg 2
2848.4	Mo 8	2800.9	Ir 6	2756.5	Zn 6
2847.9	Hg 10 ϕ	2800.8	Ir. 6	2755.8	Fe 10
2847.6	V 10	2799.6	Ag 5	2754.7	Ge 20
2847.2	Au 5	2799.6	V 10	2754.0	In 1
2845.9	Rh 8	2798.2	Mg 8	2753.9	Ar 8
2844.4	Os 6	2795.6	Mg 10 ω	2753.5	V 16
2843.3	Cr 10	2795.6	Ni 7	2753.2	Nb 6
2841.8	Ru 6	2794.3	Pt 6	2752.9	Hg 2
2840.1	Sn 10	2793.1	Te 6	2750.9	Fe
2838.7	Os 8	2790.9	Mg 10 ω	2750.6	Yb 10
2838.1	Au 5	2790.6	Sb 8 χ	2749.4	Fe 10
2837.4	C 8	2788.1	Sn 1	2748.7	Cd 10 χ
2837.4	Th 5	2787.9	Ru 6	[No. 21, Gold.]	
2837.0	Cd 8	2783.8	Fe 7	2748.3	Au 5
2836.2	C 8	2783.1	Mg 4	2747.6	Fe 7
2835.7	Cr 10	2781.8	Rh 6	2747.6	V 10
2833.3	Ir 8	2781.7	V 12	2747.3	C 6
2833.2	Pb 10	2781.5	Mg 4	2747.1	Fe 7
2833.1	Zn 1	2780.6	Bi 4	2745.1	As 10
2831.0	As 8	2780.3	As 10 χ	2744.9	Ar 8
2830.4	Pt 4	2780.1	Mo 6	2744.1	Ru 6
2829.2	He 4	2779.9	Mg 6 ψ	2743.2	Fe 8
2828.3	Ti 10	2779.9	Sn 8 χ	2741.4	Li 2
2826.3	Tl 2	2778.5	Ru 6	2740.0	Rh 8
[No. 20, Gold.]		2778.4	Mg 4	2739.6	Fe 10
2825.6	Au 6	2778.2	Rh 6	2737.5	Rh 8
2823.3	Pb 10	2777.9	V 10	2734.4	Ru 8
2822.8	Au 5	2777.3	Fe 2	2734.1	Pt 4
2820.1	Au 9	2776.8	Mg 4 χ	2734.1	Sc 7
2819.3	Rh 8	2775.9	Rh 6	2734.0	Cd 3
2818.9	Yb 10	2777.5	Mo 6	2730.6	Bi 4
2818.0	Ti 10	2775.1	Cd 6	2729.8	V 10
2817.1	Yt 30	2775.1	Ir 6	2729.0	Rh 6
2816.4	Al 10 ω	2774.9	Pt 6	2727.6	Fe 8
2816.3	Mo 8	2772.2	V 10	2725.5	Ru 8
2815.5	Ag 5	2771.5	Ba 8	2724.9	Ru 6
2813.8	R 10	2771.0	Zn 8	2723.3	Er 5
2813.7	Sn 6 χ	2770.0	Sb 8	2719.1	Pt 4
2813.4	Fe 2	2769.8	Te 8	2719.0	Sb 6
2810.8	Ru 6	2769.7	Ar 8	2717.5	Ru 6
2810.7	Nb 6	2769.0	Ru 6	2715.8	V 16
2810.4	Ti 10	2768.7	V 10	2715.4	Rh 8
2810.4	V 12	2768.0	Tl 6 ψ	2714.5	Fe 7
2809.7	Bi 2	2767.6	Ag 8 χ	2714.0	In 1
2807.8	Mo 6	2767.6	Fe 7	2713.8	Cu 8 χ
2806.3	Ar 8	2766.6	Cr 10	2712.6	Zn 2
2805.0	Ti 10	2766.6	V 10	2712.5	Ru 8
2803.6	Yb 10	2765.8	V 14	2711.9	Ag 8 χ
2803.6	V 10	2764.0	Cd 4	2711.9	V 10
2802.8	Mg 10 ω	2763.9	He 2	2711.7	Te 4
2802.8	Ni 7	2762.7	Cr 10	2710.4	In 2 χ
2802.3	Au 10	2761.9	Fe 3	2709.7	Ge 20

ULTRA-VIOLET RAYS—*continued.*

Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
2709.3	Tl 3	2670.4	V 10	2632.3	Co 8
2709.0	R 8	2667.1	Yb 15	2632.1	Sn 8 χ
2708.4	Ar 8	2666.7	Fe 7	2631.4	Si 8
2708.0	V 10	2666.2	Yb 15	2631.4	Fe 4
2706.9	V 10	2665.7	Tl 3	2630.7	V 12
2706.6	Sn 10 ψ	2664.7	Fe 7	2629.9	V 10
2706.6	Zn 1	2663.8	Rh 6	2628.4	Fe 8
2705.7	Rh 10	2663.6	Co 8	2628.4	Pd 6
2705.7	Mn 6	2663.4	V 18	2628.2	Rh 8
2703.5	Cu 9	2663.3	Pb 10	2628.1	Pt 6
2702.5	Pt 6	2661.7	V 10	2628.0	Bi 4
2702.3	V 14	2661.3	Sn 2	2625.8	Fe 7
2701.7	Mn 6	2660.5	Ag 8 χ	2625.7	Mn 6
2701.3	Cu 10 ϕ	2660.5	Al 5 χ	2625.5	Rh 8
2701.2	V 10	2659.5	Pt 6	2625.4	Pt 6
2699.1	Sc 20	2659.2	Rh 8	2621.7	Fe 6
2698.5	Er 5	2658.9	Sn 10 χ	2620.7	Zr 8
2698.5	Pt 4	2658.8	Pd 6	2618.5	Cu 8
2698.1	Ur 3	2658.7	Os 6	2618.2	Mn 6
2697.7	Pb 2	2655.8	V 16	2615.5	Fe 1
2697.2	Nb 6	2655.3	Hg 2	2615.5	Yb 15
2696.8	Bi 4	2653.9	Hg 2	2614.5	Ag 6
2694.7	Co 8	2653.8	Yb 10	2614.3	Pb 10
2694.4	Au 2	2652.9	V 10	2613.9	Fe 9
2692.7	Fe 6	2652.6	Al 5 χ	2612.0	Fe 9
2692.1	Ru 10	2652.2	Hg 2	2609.4	Cu 7
2691.5	Ge 15	2652.0	Rh 10	2609.3	Rh 8
2690.9	V 12	2651.8	La 8	2609.1	Tl 2
2690.4	V 10	2651.6	Ge 15	2608.6	Zn 2
2690.0	V 10	2651.2	Ge 15	2607.2	Fe 9
2689.7	Cu 10 χ	2650.8	Pb 4	2606.2	Ag 6
2689.0	B 1	2650.7	Be 7	2605.8	Mn 6
2688.8	V 10	2649.5	V 16	2603.4	Yb 10
2688.3	Mn 6	2648.0	V 12	2601.8	In 1
2688.1	V 10	2647.6	Ar 8	2600.5	Cu 10 ϕ
2687.0	Th 6	2647.0	Pt 4	2599.5	Fe 10
2686.2	B 1	2645.9	V 14	2599.1	Cu 8
2684.8	Fe 6	2644.5	V 16	2599.0	Nb 10
2684.3	Zn 2	2643.8	Sn 10 χ	2598.5	Fe 9
2684.3	Rh 8	2642.7	Yb 10	2598.2	Sb 10 ψ
2683.7	Rh 8	2642.7	Hg 2	2597.0	Rh 8
2683.2	V 10	2642.3	V 14	2595.2	V 16
2683.0	V 10	[No. 23, Gold.]		2594.5	Sn 4 ϕ
2681.4	Ag 5	2641.6	Au 6	2593.2	V 16
2680.5	Na 8	2641.4	C 4	2592.9	Fe 6
2679.4	V 14	2641.0	V 16	2592.6	Ge 15
2678.8	Ru 10	2639.9	Mn 6	2592.2	Rh 6
2677.6	Cd 8	2639.6	Cd 3	2591.6	Fe 6
[No. 22, Gold.]		2637.1	Os 6	2591.1	Nb 7
2676.1	Au 12	2636.0	Pd 8	2590.4	Sb 7
2674.6	Rh 8	2635.9	Fe 2	[No. 24, Gold.]	
2672.8	Mn 6	2635.4	Rh 6	2590.2	Au 6
2670.7	Sb 7	2634.9	Ba 8	2588.1	Fe 5
2670.7	Zn 1	2632.5	Mn 6	2587.2	Co 8

ULTRA-VIOLET RAYS—continued.

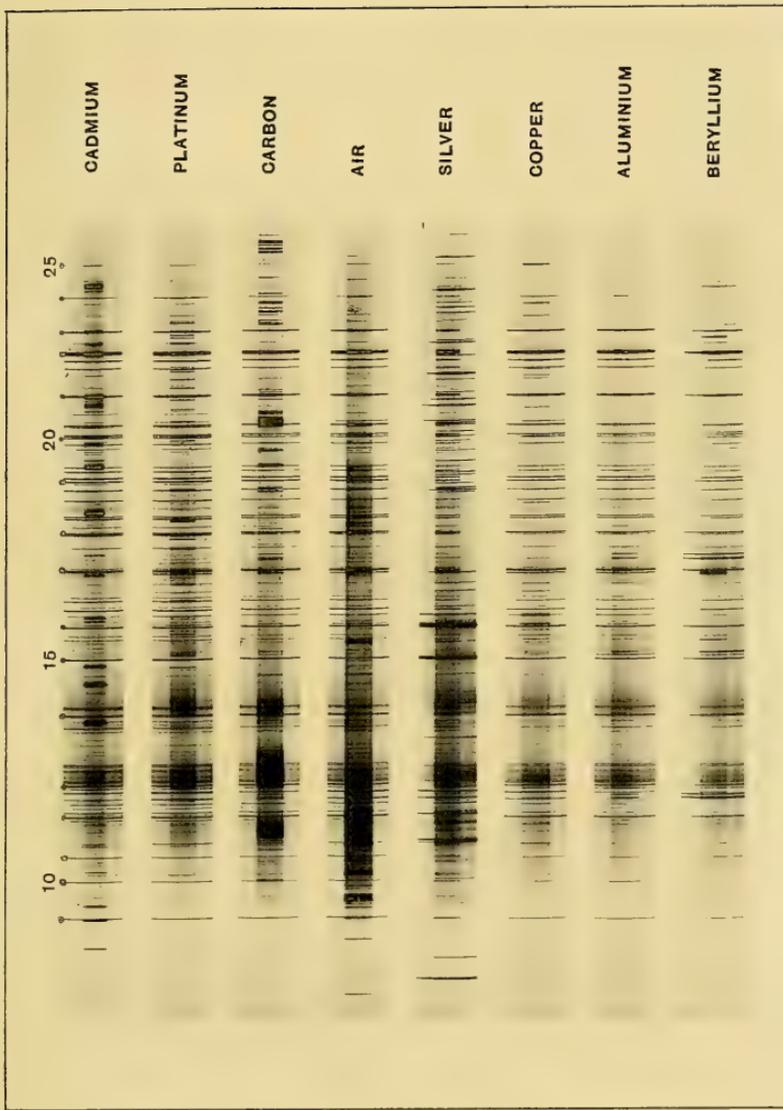
Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.	Wave-Length.	Element and Intensity.
2586.1	Ir 8	2545.1	Cu 10 χ	2510.6	Au 5
2586.0	Fe 8	2544.8	Fe 1	2508.0	C 6
2585.0	V 10	[No. 25,	Gold.]	2507.0	Si 8
2584.1	Nb 8	2544.3	Au 5	2506.8	Cu 10 χ
2582.6	Zn 2	2543.4	Ru 8	2506.7	Ag 9 χ
2582.4	Fe 7	2542.6	V 10	2506.5	Co 8
2582.3	Co 8	2542.5	Zn 1	2506.3	V 10
2580.7	Ag 8 ϕ	2542.0	Co 8	2505.8	Pd 6
2580.4	Co 8	2541.9	Si 8	[No. 26,	Gold.]
2580.2	Tl 3	2540.1	Ti 10	2503.3	Au 7
2579.6	Ir 6	2539.0	Fe 5	2503.1	V 10
2577.8	V 10	2538.6	Mo 6	2502.1	Zn 10 χ
2577.3	Pb 8	2536.7	Hg 6	2501.2	Th 5
2576.3	Hg 3	2535.5	Ag 6	2499.8	Nb 7
2576.2	Mn 10	2534.9	Hg 3 ω	2498.8	Pd 6
2575.7	Ag 1	2534.5	Fe 6	2497.7	B 10
2575.5	Al 7	2533.9	Fe 9	2496.8	B 10
2575.2	Al 7	2533.6	Au 6	2495.8	Sn 6 ϕ
2574.6	V 10	2532.4	Fe 1	2494.7	Be 3
2573.1	Cd 10	2530.9	Te 8	2493.3	Fe 8
2571.7	Sn 8 χ	2530.3	Zn 1	2493.0	As 8
2571.7	Th 5	2529.6	Fe 6	2492.2	Cu 6 ϕ
2571.5	Zr 8	2529.6	Cu 8 χ	2491.9	Rh 6
2571.2	Cu 7	2529.0	V 14	2491.7	Zn 2
2571.1	V 10	2528.6	Si 8	2491.0	A 6
2570.0	Zn 2	2528.6	Sb 10 χ	2490.9	Rh 8
2569.0	Zr 7	2528.0	V 18	2489.8	Cu 8 ϕ
2568.1	Al 10 χ	2526.8	V 16	2489.4	W 4
2567.7	Yb 10	2526.3	Fe 3	3489.0	Pd 8
2565.8	Au 5	2525.5	Fe 3	2488.9	W 4
2565.6	Pd 8	2525.1	V 10	2487.8	Mo 4
2564.5	Th 5	2524.6	Bi 2	2487.2	Pt 6
2564.2	Co 8	2524.2	Si 6	2486.6	Pd 6
2563.5	Ti 10	2522.9	Fe 6	2483.5	Sn 6 χ
2562.6	Fe 6	2521.6	V 12	2483.1	V 10
2562.6	Li 4	2521.3	V 10	2482.4	V 10
2562.3	Pb 8	2520.6	Rh 8	2481.3	Mo 6
2560.2	In 1 ϕ	2519.9	Co 8	2480.5	Ag 5
2559.5	Co 8	2519.3	Si 8	2480.4	Au 4
2558.0	Zn 10 χ	2516.8	Ar 8	2479.9	Zn 1
2557.3	Rh 6	2516.2	V 14	2479.6	V 12
2554.3	V 14	2516.2	Si 10	2479.2	A 6
2553.3	Fe 2	2515.7	Bi 1	2479.0	Ru 6
2553.1	V 12	2515.6	Ar 8	2478.7	Ur 3
2552.6	Tl 4	2514.7	V 12	2478.7	C 10
2552.5	Sc 8	2514.4	Si 7	2478.4	Sb 6
2552.0	Pd 8	2514.4	Fe 6	2477.9	W 4
2549.4	V 14	2514.0	Pt 6	2477.7	Mo 4
2548.8	V 12	2512.8	Th 8	2477.3	Ag 6 ϕ
2548.3	V 14	2512.7	Ir 6	2476.5	Pb 8
2546.6	Sn 6 χ	2511.8	C 7	2475.7	Rh 8
2546.3	Fe 6	2511.8	Fe 7	2475.1	Ll 4
2546.0	Ni 7	2510.9	Ni 8	2474.3	Mo 4
2545.4	Rh 8	2510.7	Rh 8	2474.1	Th 5

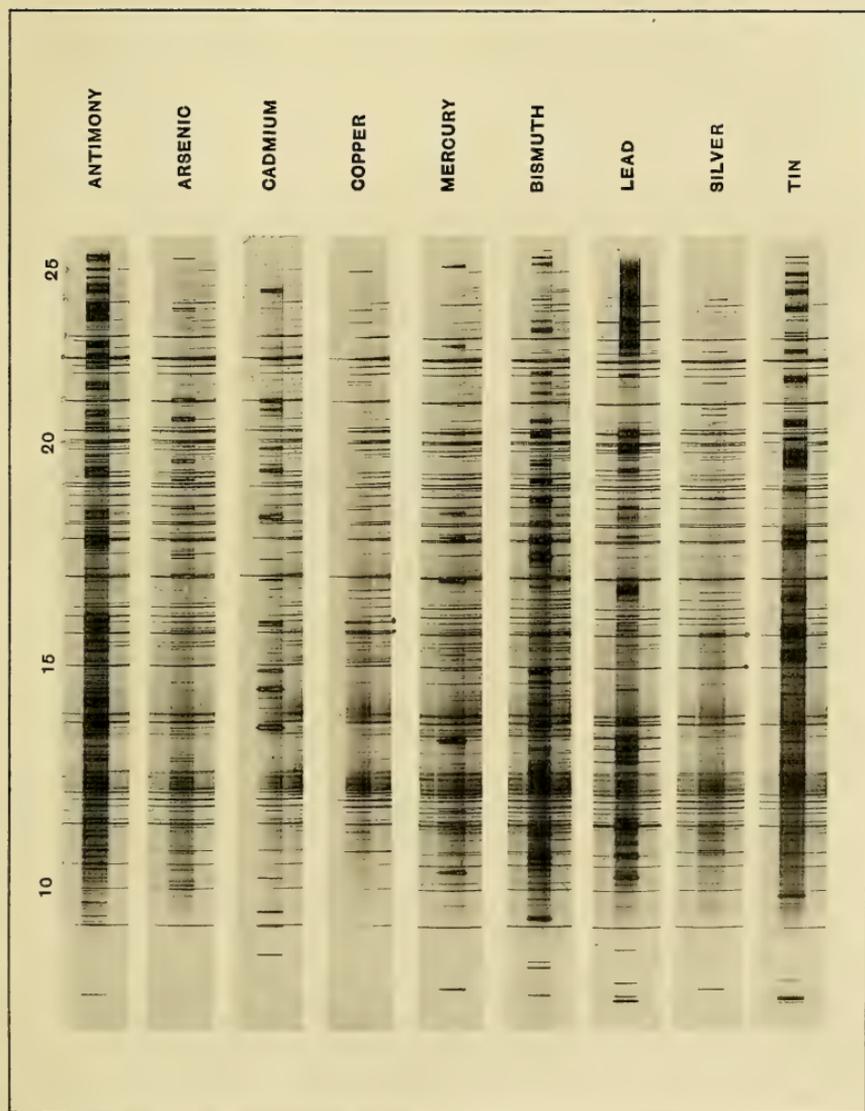
ULTRA-VIOLET RAYS—continued.

Wave-length.	Element and Intensity.	Wave-length.	Element and Intensity.	Wave-length.	Element and Intensity.
[No. 27]	Silver.]	2429.6	Sn 8 ψ	2393.9	Pb 4
2473.9	Ag 8 χ	2428.7	Pb 2	2393.7	V 18
2472.6	Cu 8 φ	2428.3	Ag 5	2392.4	Rh 6
2468.7	Cu 8	2428.2	Pt 1	2390.5	Ag 5
2467.5	Pt 6	2428.1	Te 4	2388.9	Co 6
2466.8	Mo 4	2428.1	Th 8	2388.5	B 1
2465.3	V 10	[No. 30	Gold.]	[No. 32	Gold.]
2464.2	Hg 2	2428.1	Au 15	2387.9	Au 4
2463.3	Th 7	2428.0	Mn 6	2387.0	Mo 4
2462.2	Ag 5	2425.0	Pt 6	2385.9	Te 8 χ
2461.1	Rh 8	2424.1	Mo 4	2384.9	Ir 6
2459.0	Rh 8	2422.2	Mo 4	2383.5	Co 5
2457.9	Mo 4	2422.0	Nb 5	2383.4	Te 8 χ
2457.5	Zr 6	2421.8	Sn 8 χ	2382.6	V 16
2457.1	Nb 8	2421.1	Rh 6	2382.1	Fe 9
2456.6	As 8	2420.8	Zr 4	2381.7	Ir 6
2455.8	Rh 8	2420.1	Ag 8 χ	2381.3	As 8
2455.6	Ru 4	2418.5	U 3	2381.0	V 10
2455.5	Mo 4	2417.6	V 10	2379.7	Tl 10
2454.5	A 6	2417.4	Ge 10	2379.5	La 10
2453.4	V 10	2416.2	Ni 7	2379.2	V 10
2453.3	Ag 7 φ	2415.9	Rh 6	2378.6	Co 7
2452.6	Mn 6	2415.7	A 6	2378.5	Al 1
2449.9	Zr 5	2414.8	Yt 15	2378.4	Hg 2
2448.9	Zr 6	2414.1	Ti 15	2377.3	Mo 4
2448.0	Pd 4	2414.0	V 14	2377.3	Pt 6
[N. 28	Silver.]	2414.0	Nb 5	2375.3	Ag 2 φ
2447.9	Ag 8 χ	2413.6	Th 6	2373.8	Fe 8
2447.7	V 10	2413.4	Fe 8	2373.4	Al 2
2447.0	Hg 2	[No. 31	Silver.]	2373.2	Al 2 φ
2446.5	W 4	2413.3	Ag 10 ω	2373.1	V 10
2446.3	Pb 6	2412.8	Mo 4	2372.2	Al 2
2445.7	Sb 6	2411.8	Pb 2	2371.2	V 18
2445.6	Au 4	2411.4	Ag 8 χ	2370.9	As 8
2445.0	V 10	2410.6	Fe 8	2370.0	Cu 10 χ
2444.3	Ag 5	2410.2	Mo 4	2369.7	As 8
2443.9	Pb 6	2408.3	Sn 1	2368.7	Fe 8
2442.2	Zr 4	2407.2	V 12	2368.1	Ir 8
2441.8	Ni 2	2405.3	V 16	2367.4	Os 6
2441.7	Cu 6	2403.7	Mo 6	2367.3	Yt 20
2441.4	Th 9	2402.8	Ru 8	2367.1	Al 2
2438.8	A 6	2402.0	Pb 2	2366.4	V 16
2438.2	Mn 8	2401.0	Bi 2	[No. 33	Gold.]
2437.9	Ni 7	2399.8	V 12	2364.8	Au 10
[No. 29	Silver.]	2399.3	Mo 4	2363.8	Co 7
2437.8	Ag 10 ψ	2399.3	Fe 8	2359.9	Mo 4
2437.8	Mo 4	2398.9	V 12	2358.9	Ag 6 χ
2437.3	As 8	2398.8	Ir 6	2358.8	V 14
2436.0	Mo 4	2398.7	Ca 2	2358.0	Ru 6
2435.2	Si 8	2397.4	Co 6	2357.9	Ag 8 χ
2432.6	Co 5	2397.1	W 4	2357.5	Zr 4
2431.8	Th 7	2396.6	Rh 8	2354.9	Sn 4 χ
2430.1	V 10	2395.6	Ag 5	2353.5	Co 5
2429.6	Ag 7 χ	2394.5	Ni 7	[No. 34	Gold.]

ULTRA-VIOLET RAYS—*continued.*

Wave-length.	Element and Intensity.	Wave-length.	Element and Intensity.	Wave-length.	Element and Intensity.
2352.7	Au 5	2298.2	Tl 7 χ	2228.3	Bi 1
2352.2	V 10	2296.8	C 6	2226.2	Ag 6
2349.9	As 10 ϕ	2295.0	Mo 4	2225.7	Hg 8 ϕ
2348.7	Be 3	2294.4	Cu 6 ϕ	2216.5	Ni 4
2347.7	Ba 4	2291.6	Au 6	2215.9	Au 3
2346.4	V 10	2290.1	Rh 8	2213.2	Au 4
2343.6	Fe 9	2288.2	As 10	2209.8	Sn 6
2343.2	V 10	2288.1	Cd 10 ψ	2207.1	Tl 2
2342.3	V 10	2286.8	Sn 1	[No. 40]	Gold.]
2341.7	Mo 4	2286.3	Co 5	2201.4	Au 5
2340.5	Mo 4	[No. 37]	Gold.]	2200.8	Ca 1
2340.3	Au 7	2283.4	Au 5	2199.5	Sn 1
2338.1	Fe 8	2280.0	Ag 8 χ	2194.7	Cd 5 ϕ
2335.3	Ba 4	2276.6	Bi 2	2194.6	Sn 1
2334.9	Sn 2 ϕ	2275.6	Ca 2	[No. 41]	Gold.]
2334.8	Rh 6	2275.4	Ag 5	2189.0	Au 5
2334.3	V 10	2271.5	As 6	2179.4	Cu 5
2332.9	Fe 8	2270.2	Ni 4	2179.3	Sb 6
2332.5	Cs 3	2269.2	Al 1 ϕ	2176.0	Sb 6
2331.9	V 10	2269.0	Sn 1	[No. 42]	Silver.]
[No. 35]	Silver.]	2267.6	Cs 3	2166.6	Ag 4
2331.3	Ag 8 ψ	2267.5	Cd 3	2165.6	As 8
2331.0	Mo 4	2267.3	Sn 1	2156.3	As 8
2330.5	V 12	2267.0	B 2	2151.2	Sn 2
2329.3	Cd 7	2266.8	As 3	[No. 43]	Silver.]
2325.6	Mo 4	2266.4	B 2	2145.7	Ag 3
2325.2	V 10	2265.1	Cd 10 ω	2144.5	Cd 5 ϕ
2324.7	Ag 8 ψ	2264.6	Ni 4	2134.4	As 8
2323.9	V 12	2263.8/5	Al ϕ	[No. 44]	Gold.]
2322.4	Au 7	2259.1	Te 6	2125.3	Au 5
2321.2	Cd 8 ϕ	2251.9	Sn 1	2113.9	Sn 4
2320.3	Ag 8 ψ	2248.8	Ag 6 χ	[No. 45]	Gold.]
2318.1	V 10	2247.1	Cu 7 χ	2110.8	Au 6
2317.3	Sn 2 ϕ	2246.4	Ag 5 ψ	2098.5	Sb 2
2317.1	Ag 8 ψ	2246.1	Sn 1 ϕ	2088.8	B 2
2316.0	Au 6	[No. 38]	Gold.]	2088.4	B 2
2316.0	Tl 4	2242.7	Au 5	[No. 46]	Gold.]
2314.8	Au 6	2242.6	Cu 7 χ	2082.1	Au 5
2313.0	Cd 10 ψ	2240.4	Au 4	2080.2	Sn 4
2311.6	Sb 2 ϕ	2239.9	Cd 3	2068.5	Sb 4
2309.7	Ag 4	2237.9	Tl 3	2066.2	B 2
2309.5	Au 6	2233.0	V 10	2064.6	B 2
2306.8	In 5 χ	2231.8	Sn 4	2044.7	Au 5
2306.7	Cd 5	2230.7	Bi 1	2000.8	Au 3
2306.6	Sb 1	2230.0	As 6	1931.7	Au 3
[No. 36]	Gold.]	2229.6	Ag 5	1921.4	Au 8
2304.9	Au 9	[No. 39]	Gold.]	1919.4	Au 6
2304.3	Ba 2	2229.1	Au 6	1861.7	Au 2





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JULY, 1907.

ON THE QUANTITATIVE SPECTRA OF IRON,
ALUMINIUM, CHROMIUM, SILICON, ZINC,
MANGANESE, NICKEL, AND COBALT.

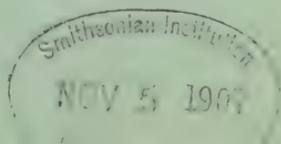
BY
JAMES H. POLLOK, D.Sc.,
AND
A. G. G. LEONARD, A.R.C.S.I.

(PLATES XII.-XVII.)

[Authors alone are responsible for all opinions expressed in their Communications.]

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XVII.

ON THE QUANTITATIVE SPECTRA OF IRON, ALUMINIUM,
CHROMIUM, SILICON, ZINC, MANGANESE, NICKEL,
AND COBALT.

BY JAMES H. POLLOK, D.Sc., AND A. G. G. LEONARD, A.R.C.S.I.

[PLATES XII.-XVII.]

[Read DECEMBER 18; Received for Publication, DECEMBER 21, 1906;
Published, JULY 22, 1907.]

INTRODUCTION.

THE following quantitative spectra of iron, aluminium, chromium, silicon, zinc, manganese, nickel, and cobalt, are, with slight modifications, taken after the manner devised by Professor W. N. Hartley, as published in the Philosophical Transactions of the Royal Society in 1884, vol. clxxv., pp. 49-62, and pp. 325-342.

For analytical purposes a knowledge of the residuary lines of spectra is of the greatest assistance, as on diluting a solution of a salt, the lines of the spark-spectrum disappear so rapidly, that with 0.1 per cent. solutions, the spectrum is difficult to identify by reference to an index where all the lines of the element are carefully recorded, especially as the last lines that disappear are not necessarily the most intense. On a plate giving the spark-spectrum of some chloride of beryllium, let us say, one might very well have a few foreign lines closely agreeing with lines of iron, manganese, or titanium, and without very exact measurement, it might be impossible to decide to which they belonged; but on the other hand, if we knew that these lines were the residuary lines of titanium, and that the residuary lines of iron and manganese were quite different, we should know definitely that a trace of titanium was present, and not iron or manganese. Again, if we know that the residuary lines of an element are absent, we know at once that the element is absent, so that it is only necessary to look for the residuary lines. Hartley investigated the dilution spectra of a large number of elements; but, with the exception of aluminium, silicon, and zinc, the

above are not amongst them, and as the authors are engaged in an investigation of the methods of separating the elements of the cerium and yttrium groups, they find that a knowledge of the residuary lines of all the common elements of the ammonia and ammonium sulphide groups is necessary. Gold electrodes have been substituted for graphite to bring the spectra into uniformity with other work by the authors, and in particular to make them readily comparable with the general index of spectra published by one of the authors in the Proceedings of this Society. On comparison of the dilution spectra of zinc and silicon with those of Hartley, it would seem that gold electrodes are not so sensitive as graphite. The results are otherwise substantially the same, a few more lines having been observed with a 1 per cent. solution of zinc, and all the lines disappear more rapidly; the last lines to disappear on dilution are identical with those observed by Hartley. That graphite should be more delicate than gold appears very natural, as the graphite tends to absorb the solution-sparks over a larger surface, and hence yields more vapour of the element under examination; but for all ordinary analytical purposes, gold is more convenient.

The work was done with a one-prism quartz spectrograph, by Hilger, using the spark produced by a Ruhmkorff's coil and condenser, with a Hemsalech self-induction coil placed in the circuit for the removal of air-lines. The plates were Rainbow Fast, made by the Warwick Photo Co., and in every case the exposure was 1'—this photographed clearly from λ 4792.8 to λ 2544 on one plate. To go farther down in the ultra-violet, it would be necessary to readjust the instrument and take another set of photographs.

The general method of procedure was to make a strong or saturated solution, of the chloride of the element under consideration; also solutions containing one gramme of the element in every 100, 1000, 10,000, 100,000 parts of solution. A photograph was taken of the gold electrodes with a long slit; the slit was then shortened and the metal sparked, thus giving the spectrum of gold with long lines, and the spectrum of the metal with short lines. The process was then reversed, the metal taken long, and the gold short, so that any lines coincident with gold lines might be seen. A photograph was then taken with both the strong solution and gold electrodes long, and the metals short, to show

any lines developed by the metals, but not by their solutions. Then in every case the last four spectra taken gave the gold electrodes long, with short lines between, of the spark spectra of solutions containing 1 per cent., .1 per cent., .01 per cent., .001 per cent. of the element under examination.

To distinguish briefly between the different phases of the lines, with diminishing concentration, use has been made of some of the letters of the Greek alphabet, with the following meanings:—

τ	=	seen with the metal, but not with strong solutions.
σ	=	strong solutions, but not with 1 % solutions.
ϕ	=	1 % " " " .1 % "
χ	=	.1 % " " " .01 % "
ψ	=	.01 % " " " .001 % "
ω	=	.001 % " "

No new measurements were attempted, the lines being identified by means of a finely graduated ivory scale, and the corresponding published lines tabulated. In the case of manganese, however, one of the residuary lines, λ 2594.0, was not found in the tables at our disposal, and our own measurement is given.

In the case of cobalt, Plate XVII., the solution was not diluted so abruptly, and this plate shows the gradual extinction of the lines with diminishing concentration better than the others; but as the whole object was to find the residuary lines, one passes directly from a saturated solution to a solution containing only 1 per cent. of the element under examination, and then dilutes until the lines entirely disappear. In the case of chromium, silicon, manganese, and zinc, all the dilutions are not given in the plates, as lines that can still be seen on the negatives cannot be seen in the reproductions at all, as will be obvious by comparing the tables with the plates. Even with 1 per cent. solutions, the lines do not come out by any means strongly with one minute's exposure, and with .1 per cent. they are always very faint, and very few substances give lines that will show at all with .001 per cent.

GOLD ELECTRODES.

To facilitate the identification of the lines, some of the strong gold lines have been numbered, from 10 to 25, and their wave-

lengths are given in the following table; and in the subsequent tables these numbers are inserted in their proper place. Thus in the case of chromium, we see from the table that the first triplet of persistency ψ lies between 11 and 12, and we know where to look for it on the plate.

NUMBERED GOLD LINES.

No.	Wave-length.	No.	Wave-length.
9	4792.8	18	3029.3
10	4488.4	19	2913.6
11	4315.4	20	2825.6
12	4065.2	21	2748.3
13	3898.0	22	2676.1
14	3586.5	23	2641.6
15	3383.0	24	2590.2
16	3280.8	25	2544.3
17	3122.9		

IRON. (Plate XII.)

Spectra 1 and 2 show the lines of the metal, with gold lines first long and then short, and there are so many coincident lines, that in the second spectrum the gold lines have almost all disappeared. Spectrum 3 shows the lines of a strong solution long, and the metal short; and as no short lines stand out it is clear that all iron lines are developed, both by the metal and a strong solution.

Spectrum 4 gives the lines of a strong solution short, with gold long, and is practically identical with spectrum 1.

Spectra 5, 6, 7, 8 show the lines of dilute solutions, and their progressive disappearance is given in the following table; but there are so many ϕ lines that it was not thought necessary to record more than the strongest. Some of the lines that show well with a strong solution, but are not seen with dilute solutions, are marked σ .

QUANTITATIVE SPECTRUM OF IRON CHLORIDE.

Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.
—10—		3631·6	10φ	2727·6	8χ
4415·3	8σ	3618·9	10φ	2714·5	7χ
4404·9	10σ	3610·3	4φ	2692·7	6φ
4383·7	10φ	3609·0	9φ	—22—	
4325·9	10σ	—14—		2684·8	6φ
—11—		3581·3	10χ	2666·7	7φ
4308·0	10σ	3570·3	8χ	2664·7	7φ
4271·9	10σ	3565·5	8χ	2631·4	4ψ
4260·7	10σ	3490·7	6φ	2628·4	8ψ
4250·9	8σ	3475·6	7χ	2625·8	7ψ
4071·9	10σ	3466·0	7χ	2621·7	6χ
—12—		3441·1	7χ	2617·7	7χ
4046·0	10σ	—15—18—		2613·9	9χ
4005·3	8σ	3021·2	2ψ	2612·0	9χ
—13—		3020·8	2ψ	2607·2	9χ
3860·1	9σ	2973·4	2χ	2599·5	10ψ
3828·0	9σ	2970·2	2χ	2598·5	9ψ
3816·0	9σ	2967·0	2χ	2586·0	8χ
3767·3	7φ	2965·4	1χ	2567·0	4χ
3758·4	8φ	—19—20—		2562·0	6ψ
3749·6	10φ	2783·8	7φ	2549·7	4χ
3745·7	7φ	2779·3	5φ	—25—	
3737·3	8ψ	2767·6	7ψ	2539·0	5χ
3735·0	10ψ	2755·8	10ψ	2533·9	7χ
3722·7	6ψ	2747·1	7φ	2529·6	6φ
3720·1	8ψ	2743·2	8χ	2526·3	6φ
3687·6	6φ	—21—		2525·5	7φ
3648·0	9φ	2739·6	10↓	2522·9	6χ
				2511·8	7χ

ALUMINIUM. (Plate XIII.)

Spectra 1, 2, 3, and 4 show the lines of the metal, and a strong solution as in the previous plate. There is a strong aluminium line at λ 3587·0, practically coincident with gold line No. 14 (λ 3586·5), and in consequence it cannot be followed in the dilution spectra. Quite a number of lines show strongly with the metal, but only very faintly, or not at all, with solutions. Of those the following belong to aluminium:—

4663·1	10 τ	3064·4	8 τ
4530·5	6 τ	3057·3	8 τ
4511·9	6 τ	3054·8	8 τ
4479·4	6 τ	3050·2	8 τ
3066·3	8 τ		

The rest between gold lines 22 and 24 belong to iron, and come from the small traces of iron in metallic aluminium, and they correspond with the most persistent lines of the iron solutions. Spectra 5, 6, 7, and 8 show the progressive disappearance of the aluminium lines on dilution.

QUANTITATIVE SPECTRUM OF ALUMINIUM CHLORIDE.

Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.
3961·7	9 ω	2816·4	10 χ
3944·2	9 ω	—21—22—	
—13—		2660·5	5 ϕ
3587·0	10 ϕ	2652·6	5 ϕ
—14—17—		—23—24—	
3092·8	9 ψ	2575·5	7 ϕ
3082·3	9 ψ	2568·1	7 ϕ
—18—20—		—25—	

CHROMIUM. (Plate XIV.)

Spectrum 1 shows the lines of an alloy of 50 per cent. chromium, and 50 per cent. iron short, with gold and iron lines long, the iron lines of the long spectrum thus cancelling the iron lines in the short, and showing only the chromium lines short. This plan was adopted owing to the difficulty of procuring or making chromium free of iron.

Spectra 2, 3, and 4 show the effects of dilution.

QUANTITATIVE SPECTRUM OF CHROMIUM CHLORIDE.

Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.
—11—		3030·4	
4289·9	10 ψ	—18—	} Group ϕ
4274·9	10 ψ	3015·3	
4254·5	10 ψ	2988·8	
—12-13—		2980·9	8 ϕ
3605·5	10 χ	2971·9	8 ϕ
3593·6	10 χ	2953·4	8 ϕ
—14—		—19—	
3578·8	10 χ	2843·3	10 ψ
3430·5	10 ϕ	2835·2	10 ψ
3422·9	10 ϕ	2830·5	10 ψ
3421·4	10 ϕ	—20—	
3408·9	10 ϕ	2766·6	8 ϕ
3403·5	10 ϕ	2762·7	8 ϕ
—15-16—		—21—	
3180·8	10 ϕ	2698·8	8 ϕ
3132·2	10 ϕ	—22—	
—17—		2663·6	8 ϕ
3050·9	8 ϕ	2659·0	8 ϕ
		2653·6	8 ϕ
		—23—	

SILICON. (Plate XIV.)

The last four spectra on this plate show the effects of diluting a solution of silicate of sodium. The line λ 3303 is a sodium one; and the subsequent lines are due to silicon. The lines of silicon do not develop in acid solutions, and quite large quantities may be present in acid solutions of other elements without giving any indication of their presence when sparked; so that for the detection of silicon, it is absolutely essential to spark an alkaline solution. The group a little beyond gold line No. 25 is very characteristic, and easily recognized.

QUANTITATIVE SPECTRUM OF SILICATE OF SODA.

Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.
4131.0	4 ϕ		
4128.2	4 ϕ	— 24-25 —	
— 12 —		2528.6	8 ψ
3905.8	5 ϕ	2524.2	6 ϕ
— 13 —		2519.3	8 ϕ
2881.7	10 ϕ	2516.2	10 ψ
— 20-23 —		2514.4	7 ϕ
2631.4	8 ϕ	2507.0	8 ϕ

ZINC. (Plate XV.)

Spectra 4, 5, 6, and 7 show the metal and three solutions. Zinc has a strong line coincident with gold line No. 16, and another with the gold line just beyond No. 20. As in the case of aluminium, quite a number of lines develop strongly with the metal and strong solutions, but not with dilute solutions; these are marked σ in the following table:—

QUANTITATIVE SPECTRUM OF ZINC CHLORIDE.

Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.
— 8 —		3035.9	8 σ
4810.7	10 ϕ	— 18 —	
— 9 —		3018.5	4 σ
4722.3	10 ϕ	— 19-20 —	
4685.4	10 ϕ	2801.0	8 ϕ
— 10-15 —		2771.0	8 ϕ
3345.3	10 χ	2756.5	6 ϕ
3303.0	10 χ	— 21 —	
3282.4	10 χ	2712.6	2 σ
		2684.3	2 σ
— 16-17 —		— 22-24 —	
		2582.6	2 σ
3076.0	8 σ	2570.0	2 σ
3072.2	10 σ	2558.0	10 χ

MANGANESE. (Plate XV.)

Spectra 1, 2, 3, and 4 show the lines of the metal, one strong, and two dilute solutions. The spectrum given by the metal is practically identical with that of a strong solution. The three ω lines in the region of gold line No. 24 form a very characteristic group, by which this element can be rapidly identified. The general results are as follows:—

QUANTITATIVE SPECTRUM OF MANGANESE CHLORIDE.

Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.
4823·7	8 σ	3460·5	10 ϕ
9		3442·1	10 ϕ
4783·6	6 σ	15-18	
10-11		2949·3	10 χ
4083·8	6 σ	2939·4	8 χ
12		2933·1	8 χ
4055·7	6 σ	19	
4048·9	6 σ	2879·5	6 ϕ
4041·5	6 σ	20-21	
4035·9	6 σ	2705·7	6 ϕ
4034·6	6 σ	22	
4033·2	6 σ	2701·7	6 ϕ
4030·9	8 χ	23	
13		2639·9	6 ϕ
3823·6	6 ϕ	2632·5	6 ϕ
3806·9	10 ϕ	2625·7	6 ϕ
14		2618·2	6 ϕ
3496·0	8 ϕ	2605·8	10 ω
3488·8	10 ϕ	2594·0	10 ω
3483·0	10 ϕ	24	
3474·2	10 ϕ	2576·2	10 ω

NICKEL. (Plate XVI.)

Spectra 1, 2, 3, and 4 show that the same lines are developed by the metal and strong solutions, as there are practically no outstanding short lines in the fourth spectrum, and the first and third spectra are identical; the relative rate of disappearance of the lines on dilution is shown in the table:—

QUANTITATIVE SPECTRUM OF NICKEL CHLORIDE.

Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.
3619.5	10 ϕ	3134.3	8 χ
3597.8	10 ϕ	—17—	
—14—		3102.0	8 χ
3566.5	10 ϕ	3101.6	8 χ
3524.6	10 χ	3064.7	7 ϕ
3515.2	10 χ	3057.7	8 ψ
3510.5	10 χ	3054.4	7 ψ
3493.1	10 χ	3050.9	8 ψ
3472.7	8 ϕ	3038.0	7 χ
3446.3	8 χ	—18—	
3433.7	7 χ	3012.1	8 χ
3423.8	7 ϕ	3003.7	8 χ
3414.9	8 ψ	—19-23—	
3393.1	7 ϕ	2546.0	7 ϕ
—15—		—24-25—	
3247.7	7 ϕ	2510.9	8 ψ
3233.1	8 ϕ		

COBALT. (Plate XVII.)

Spectrum 1 on this plate gives the lines of cobalt alone. 2, 3, and 4 give those of strong solutions; and the others give the dilutions as formerly. Like iron, manganese, and nickel, cobalt gives the same lines with the metal and strong solutions. The results of dilution are given in the table:—

QUANTITATIVE SPECTRUM OF COBALT CHLORIDE.

Wave-length.	Intensity and Persistency.	Wave-length.	Intensity and Persistency.
4531.1	4 σ	3412.8	7 ϕ
—10—		3405.3	8 ψ
4469.7	1 σ	—15-17—	
4121.5	8 ϕ	3086.9	6 ϕ
4118.9	8 σ	3072.5	6 ϕ
—12—		—18-21—	
3995.5	8 ϕ	2694.7	8 ω
—13—		—22—	
3894.2	10 ψ	2663.6	8 χ
3873.2	10 ψ	—23-24—	
3845.6	10 ϕ	2587.2	8 ϕ
—14—		2582.3	8 χ
3502.4	8 χ	2580.4	8 ψ
3489.5	10 ϕ	2564.2	8 ϕ
3474.1	10 χ	2559.5	8 χ
3465.9	8 ϕ	—25—	
3453.6	8 ψ		
3449.6	7 ϕ	2528.7	7 χ
3443.8	7 ϕ	2525.1	7 χ
3433.2	7 ϕ	2519.0	8 ω

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FERRIC CHLORIDE



METAL



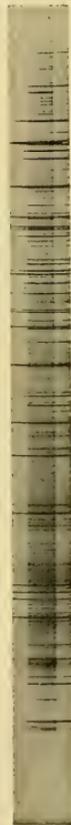
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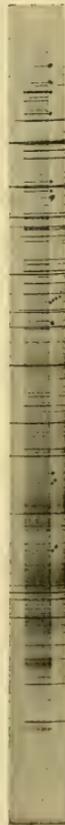
STRONG SOLN. + M.



10% FE



1% " " φ



.1% " " X



.01% " " γ



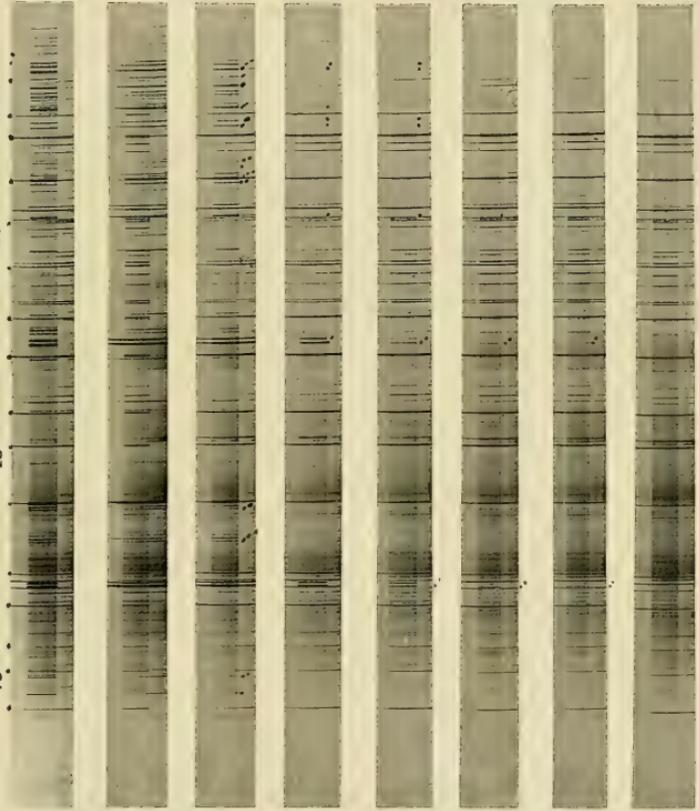
.001% " " ω

GOLD ELECTRODES.

ALUMINIUM CHLORIDE

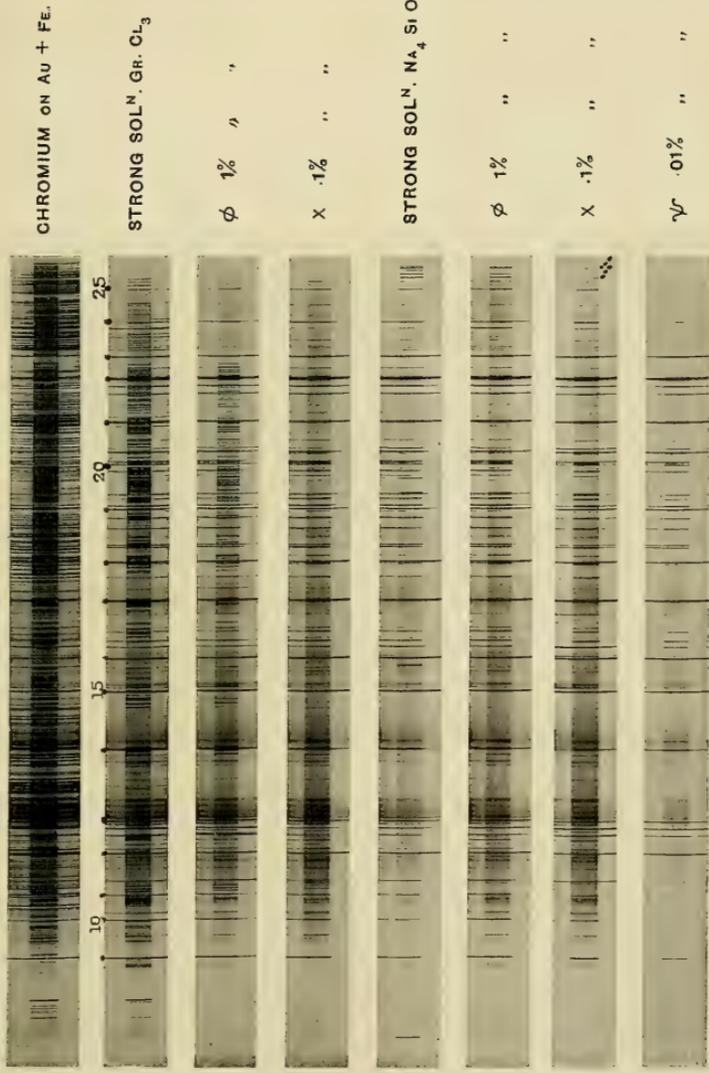
10
15
20
24

METAL
METAL
M. + S. S.
STRONG SOLN.
1% AL Ø
.1% " X
.01% " ψ
.001% " ω



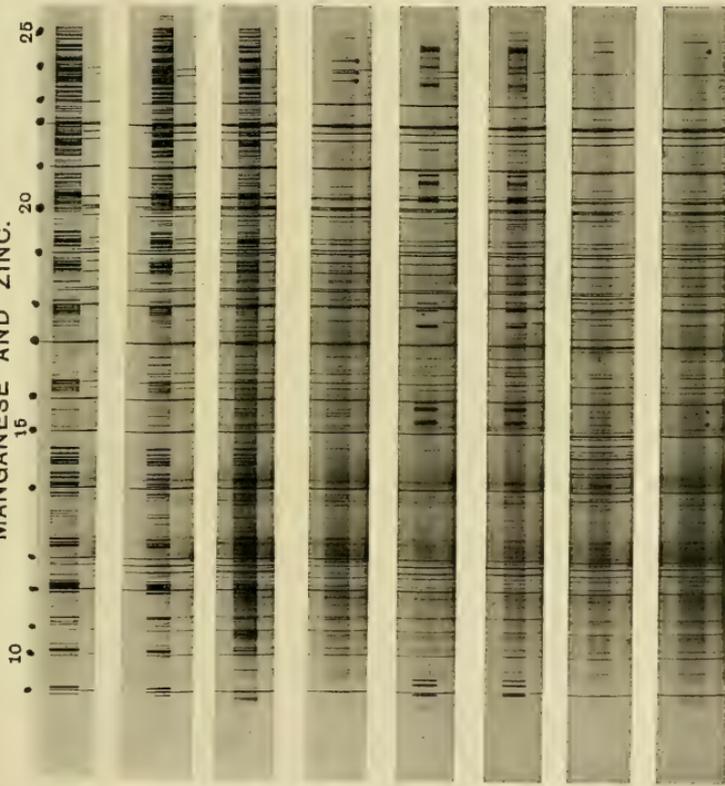
GOLD ELECTRODES.

CHROMIUM AND SILICON.



GOLD ELECTRODES.

MANGANESE AND ZINC.



METALLIC MANGANESE.

STRONG SOL'N, MN CL₂

φ 1% " "

x .1% " "

METALLIC ZINC.

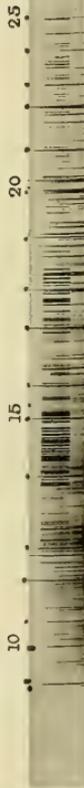
STRONG SOL'N, ZN CL₂

φ 1% " "

x .1% " "

GOLD ELECTRODES.

NICKEL CHLORIDE.



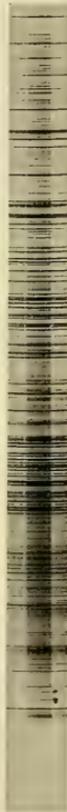
METAL



METAL.



STRONG SOL'N.



M. + S. S.



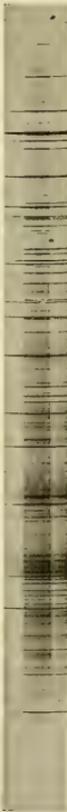
1% NI ϕ



1% .. x



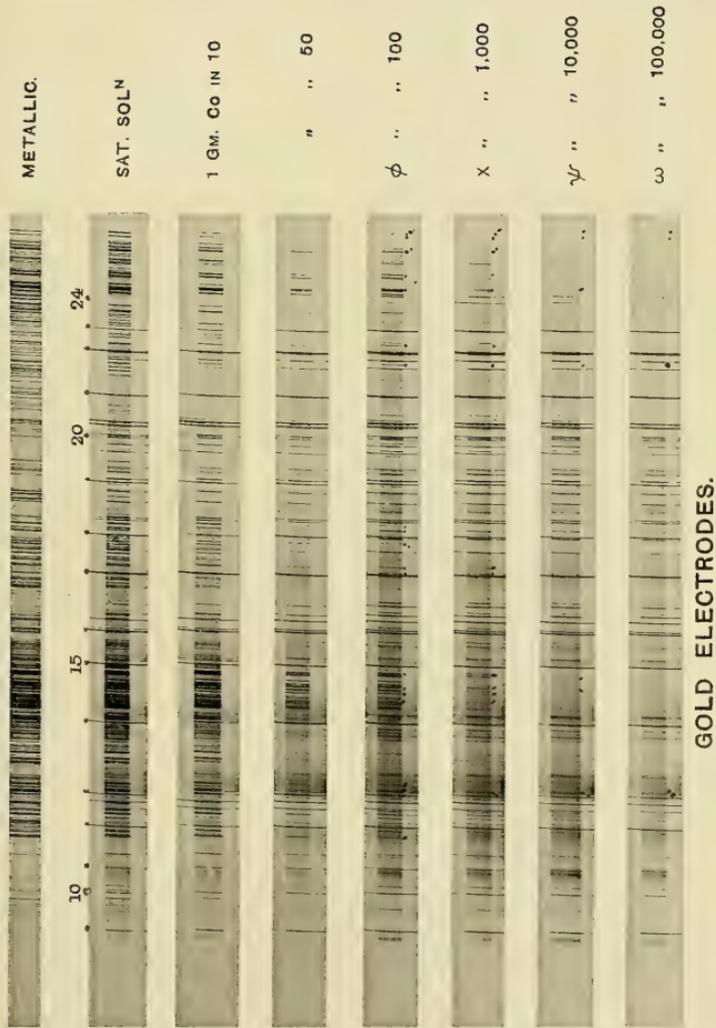
.01% .. γ



.001% .. ω

GOLD ELECTRODES.

COBALT CHLORIDE.



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THE
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JULY, 1907.

ON THE QUANTITATIVE SPECTRA OF BARIUM,
STRONTIUM, CALCIUM, MAGNESIUM,
POTASSIUM, AND SODIUM.

BY

JAMES H. POLLOK, D.Sc.,

AND

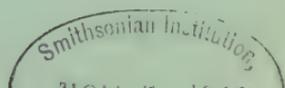
A. G. G. LEONARD, A.R.C.S.I.

(PLATES XVIII., XIX.)

[Authors alone are responsible for all opinions expressed in their Communications.]

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XVIII.

ON THE QUANTITATIVE SPECTRA OF BARIUM, STRONTIUM, CALCIUM, MAGNESIUM, POTASSIUM, AND SODIUM.

By JAMES H. POLLOK, D.Sc., AND A. G. G. LEONARD, A.R.C.S.I.

[PLATES XVIII., XIX.]

[Read, APRIL 23; Received for Publication, APRIL 26; Published, JULY 25, 1907.]

INTRODUCTION.

THESE spectra were taken after the manner devised by Professor W. N. Hartley,¹ with the modifications described in our previous paper on the quantitative spectra of the iron and zinc groups.² Gold electrodes were used, with a Rühmkorff's coil and condensed spark, a Hemsalech self-induction coil being employed for the removal of air-lines. A photograph was first taken of the electrodes alone, with a long slit; the slit was then shortened, and the solutions or metal sparked, the spectra of the various elements thus showing as short lines between the long lines of the gold electrodes. The second spectra can then be easily identified by reference to the dotted and numbered gold lines, the wave-lengths of which are given in a preliminary table.

When possible a photograph was first taken of the metal, with the lines of the metal long, and those of the electrodes short, to see if there were any lines coincident with the gold lines. Solutions were used saturated with the chlorides, and also containing 10 per cent., 1 per cent., .1 per cent., .01 per cent., and .001 per cent. of the element. In the tables the degree of persistency of the lines is indicated by the following Greek letters:—

τ	seen with the metal, not with solutions.
σ	strong solutions, not with dilute solutions.
ϕ	1% solutions, not with .1% solutions.
χ	.1% solutions, not with .01% solutions.
ψ	.01% solutions, not with .001% solutions.
ω	.001% solutions.

After sparking the strong solutions, it was found that in many cases the electrodes alone gave quite strong spectra of the metal

¹ Phil. Trans. Roy. Soc., vol. clxxv., 1884, Part i., pp. 49-62, Part ii., pp. 325-342.

² Proc. Roy. Dublin Soc., vol. xi., p. 217, 1907.

under examination, and at first it was supposed that the solutions had sprayed on to the fresh electrodes; but on keeping the fresh electrodes in another room, no difference was observed, and in the case of an element such as iron or calcium, the dilution spectra could not be followed beyond the $\cdot 1$ per cent. solution, as the electrodes then gave as strong spectra as the solutions. It was then seen that the atmosphere was charged with the element, and remained charged for a considerable time. In the following investigations the difficulty was got over by beginning with the most dilute solution, and working backwards towards the strong solutions, finally sparking the metal when it could be procured.

The photographs of spectra extend from λ 5900 to λ 2500; but the plates were not very sensitive below λ 4792 \cdot 8, nor was the instrument in perfect focus beyond λ 2590 \cdot 2.

It is a remarkable fact that the residuary lines of an element differ greatly with the method of excitation, and there is no guarantee that the residuary lines here tabulated would be the most persistent lines if the substances were vapourised by something other than the condensed spark; certainly, in the case of the oxyhydrogen flame, there is a notable difference; thus, with manganese, we have shown in a previous paper¹ that, when the condensed spark is used, the residuary lines are $\lambda\lambda$ 2605 \cdot 8, 2594 \cdot 0, and 2576 \cdot 2; but if the oxyhydrogen flame be employed to vapourise the element or its compounds, the residuary lines, as shown by Professor Hartley,² are $\lambda\lambda$ 4034 \cdot 6, 4033 \cdot 2, 4030 \cdot 9; and, in general, we note that, with the oxyhydrogen flame, the residuary lines tend to the less refrangible end of the spectrum; but with the condensed spark they tend to the more refrangible end. Apparently the nature of the dilutant has no effect on the residuary lines; thus the same residuary lines would be obtained whether the metal was in the form of a dilute solution or alloyed with another metal; but we have not yet investigated whether the degree of persistency is affected; probably it would be influenced by the relative volatility of the diluting metal in the alloy, and the sensitiveness greatly reduced owing to the vapour of the dilutant being itself a conductor, so that in an alloy one would not readily detect the presence of less than $\cdot 1$ per cent. of a substance. In tabulating the results, when the intensities were other than those usually accepted, they are enclosed in brackets.

¹ *Op. cit.*, p. 217. ² Hartley, *Phil. Trans.*, vol. *clxxxv.*, Part i., 1894, pp. 161–212.

BARIUM.

The salt used was barium chloride; and the most persistent lines were situated in the visible part of the spectrum, the residuary lines being $\lambda\lambda$ 4554.2, 4130.9. As metallic barium is not easily procured in a state of purity, we were unable to determine whether any lines are developed by the metal, but not by solutions.

Plate XVIII.—Spectra 4 and 5 show the spectra with a saturated solution, and a 1 per cent. solution of barium respectively; and the dots placed under lines indicate the lines that persist with further dilutions.

Quantitative Spectrum of Barium Chloride.

Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.	Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.
252.75	5535.7	10 ϕ	314.30	4283.3	8 σ
253.35	5519.4	4 ϕ	322.75	4166.2	10 ϕ
256.70	5524.8	6 σ	325.45	4130.9	10 ω
276.90	4934.2	10 ψ	330.80	[No. 12, Gold.]	
278.55	4900.1	[8] σ	336.80	3993.6	8 σ
283.83	[No. 9, Gold.]		344.25	3910.1	6 σ
287.32	4726.6	[3] σ	345.10	[No. 13, Gold.]	
289.20	4691.7	[3] σ	345.95	3892.0	10 ψ
293.80	4673.7	[3] σ	377.50	[No. 14, Silver.]	
296.85	4554.2	10 ω	387.95	3501.3	8 σ
298.63	4525.2	10 χ	403.55	[No. 15, Silver.]	
299.80	4506.1	6 σ	406.90	3357.0	[4] σ
300.85	[No. 10, Gold.]		506.20	[No. 20, Gold.]	
304.45	4432.1	8 σ	519.60	2771.5	8 ϕ
306.25	4402.7	8 σ	555.45	[No. 23, Gold.]	
309.70	4350.5	6 σ	557.40	2634.9	8 ϕ
312.10	[No. 11, Gold.]				

STRONTIUM.

Strontium chloride was the salt used. The most persistent lines were situated in the visible part of the spectrum, the residuary lines $\lambda\lambda$ 4607.5, 4305.6, 4215.7, and 4077.9 being faintly seen with a dilution of $\frac{1}{100000}$. As in the case of barium, we were unable to test the difference between the spark-spectrum of the metal and a strong solution.

Plate XVIII.—Spectra 6 and 7 show the spectra with 10 per cent. and 1 per cent. of the element respectively; and those lines that persist with greater dilutions are dotted.

Quantitative Spectrum of Strontium Chloride.

Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.	Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.
248.80	5535.0	8 σ	289.70	4607.5	10 ω
249.40	5522.0	8 σ	307.80	[No. 11,	Gold.]
249.90	5504.5	8 σ	308.50	4305.6	30 ω
250.80	{5486.4	6 } ϕ	314.80	4215.7	100 ω
	{5481.1		10 } ϕ	318.80	4162.0
251.85	5451.1	5 σ	325.30	4077.9	100 ω
259.10	5257.1	8 σ	326.35	[No. 12,	Gold.]
271.60	4962.4	8 ϕ	329.20	4032.5	[4] σ
275.75	4876.3	6 σ	340.80	[No. 13,	Gold.]
277.80	4832.2	6 σ	387.65	3475.0	20 ϕ
278.80	4812.0	6 σ	388.00	3464.6	100 ϕ
279.80	[No. 9,	Gold.]	399.00	[No. 15,	Silver.]
282.35	4742.1	6 σ	399.50	3380.9	80 σ
283.40	4722.4	6 σ	403.50	3351.3	3 χ

CALCIUM.

Calcium chloride was the salt used; and, as in the case of barium and strontium, the most persistent lines were situated in the visible part of the spectrum, the residuary lines being $\lambda\lambda$ 4226.9, 3968.6, and 3933.8. On taking the spark-spectrum of the metal, it was found to contain magnesium, manganese, and silicon; but in addi-

tion to the residuary lines of these elements, which are all situated in the ultra-violet part of the spectrum above gold line No. 18, the metal showed one or two very well-defined and intense lines that are either not shown at all by strong solutions, or only faintly shown: those lines are marked τ in the table. The dilution-spectrum of calcium was investigated by Sir William and Lady Huggins in a manner differing somewhat in detail from that adopted in the present experiments; but the conclusions are the same as regards the identity of the residuary lines.

Plate XVIII.—Spectra 1, 2, and 3 show the spectra of the metal, a 10 per cent. solution, and a 1 per cent. solution.

Quantitative Spectrum of Calcium Chloride.

Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.	Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.
250.85	5594.6	8 σ	313.80	4289.5	8 ϕ
262.70	5270.5	8 σ	314.30	4283.2	8 ϕ
279.60	4878.3	6 σ	318.25	4226.9	10 ω
283.80	[No. 9, Gold.]		330.70	[No. 12, Gold.]	
295.00	4586.1	4 σ	338.85	3968.6	80 ω
295.50	4581.7	4 σ	341.90	3933.8	100 ω
298.50	4527.2	[4] σ	345.10	[No. 13, Gold.]	
302.85	4455.0	10 ϕ	360.85	3737.2	15 ψ
304.05	4435.1	10 ϕ	364.05	3706.2	10 ψ
304.75	4425.6	10 ϕ	371.00	3644.5	2 ϕ
311.80	4318.8	8	372.50	3630.8	1 ϕ
312.00	[No. 11, Gold.]		377.50	[No. 14, Silver.]	
312.55	4307.9	6 σ	434.80	3179.4	10 χ
313.00	4302.7	10 σ	438.35	3159.1	10 χ
313.20	4299.1	6 σ	444.70	[No. 17, Gold.]	

MAGNESIUM.

Magnesium chloride was the salt used. Unlike barium, strontium, and calcium, the most persistent lines are situated in

the ultra-violet part of the spectrum, the residuary lines being $\lambda\lambda$ 2852·2, 2798·2, and 2790·9.

The metal gives one or two strong lines that are not seen, or only very faintly seen, with strong solutions. Those lines are marked τ .

The quantitative spectrum of magnesium was previously investigated by Professor W. N. Hartley, and his results are in accordance with the present observations; but as explained in a previous paper, Professor Hartley's method of observation gave a greater quantity of vapour, and an apparently greater persistency of the lines; but the relative persistencies are substantially the same, and the residuary lines are identical.

Plate XIX.—Spectra 1, 2, and 3 show the spectra of the metal, a 10 per cent. solution, and a 1 per cent. solution.

Quantitative Spectrum of Magnesium Chloride.

Linear Measurement, $\frac{1}{100}$ inch.	Wave-Length.	Intensity and Persistency.	Linear Measurement, $\frac{1}{100}$ inch.	Wave-Length.	Intensity and Persistency.	
253·13	5528·7	6 ϕ	444·45	[No. 17,	Gold.]	
265·90	5183·8	10 ϕ	449·00	3097·1	[8] ϕ	
266·80	5167·6	8 ϕ	449·85	3093·1	[8] ϕ	
283·85	[No. 9,	Gold.]	462·00	[No. 18,	Gold.]	
288·50	4703·3	[8] τ	480·85	2937·0	10 χ	
300·85	[No. 10,	Gold.]	482·50	2928·7	10 χ	
301·30	4481·3	10 σ	485·40	2915·5	10 σ	
309·45	4352·2	[8] τ	499·80	2852·2	10 ω	
345·00	[No. 13,	Gold.]	506·10	[No. 20,	Gold.]	
350·60	3838·4	10 σ	512·70	2798·2	8 ω	
351·30	{ 3832·5	10 σ	514·55	2790·9	10 ω	
	{ 3829·5	10 σ	516·50	{ 2783·1	4 ϕ	
403·40	[No. 15,	Silver.]	2781·5		4 ϕ	
409·95	3336·8	8 σ	to		2779·9	6 χ
410·60	3332·3	8 σ			2778·4	4 ϕ
411·05	3330·1	6 σ	518·20	2776·8	4 ϕ	

POTASSIUM.

Photographs were taken with metallic potassium in an atmosphere of hydrogen, and also with solutions of potassium chloride.

Potassium is characterized by a very feeble spark-spectrum, only two lines showing with one minute's exposure either with the metal or a saturated solution; and with a 1 per cent. solution they are scarcely visible. It is remarkable that the flame-spectrum is very intense; apparently the temperature of the oxyhydrogen flame, or even the Bunsen, gives a far more brilliant spectrum than the condensed spark. This is, no doubt, owing to the greater quantity of vapour produced.

Plate XIX.—Spectra 4 and 5 give the spectra of the metal and a saturated solution of the chloride respectively. With the metal the intensities of the lines $\lambda\lambda$ 3447.5 and 3446.5 are not nearly so great as in the case of the other two lines, so we have marked them 8, instead of 10, to show the difference.

Quantitative Spectrum of Potassium Chloride.

Wave-Length.	Intensity and Persistency.
4047.4	10 ϕ
4044.3	10 ϕ
3447.5	(8) σ
3446.5	(8) σ

SODIUM.

Sodium chloride was used for the solutions, and the metal was photographed in an atmosphere of hydrogen. Sodium gives a well-marked spectrum of three pairs of lines; but, with the exception of the D lines, they are not very persistent; and, as in the case of potassium, the sodium lines do not show with the spark nearly so strongly as with the oxyhydrogen flame, or even the Bunsen burner. It is also very remarkable that the D lines do

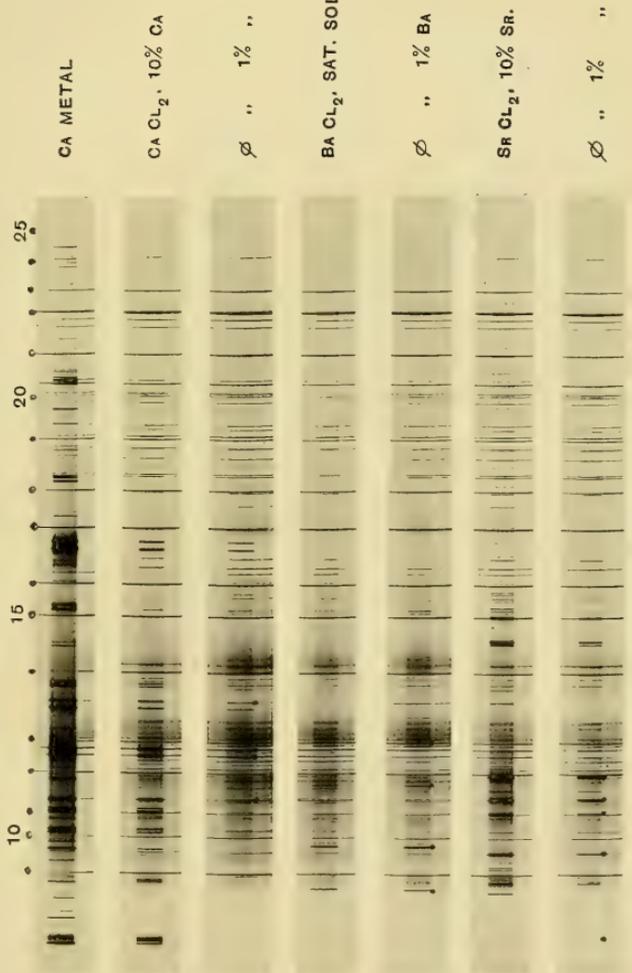
not seem to show as strongly with the metal as with a strong solution of the chloride.

Plate XIX.—Spectra 6 and 7 give the photographs of the metal in hydrogen, and of a 10 per cent. solution of the chloride.

Quantitative Spectrum of Sodium Chloride.

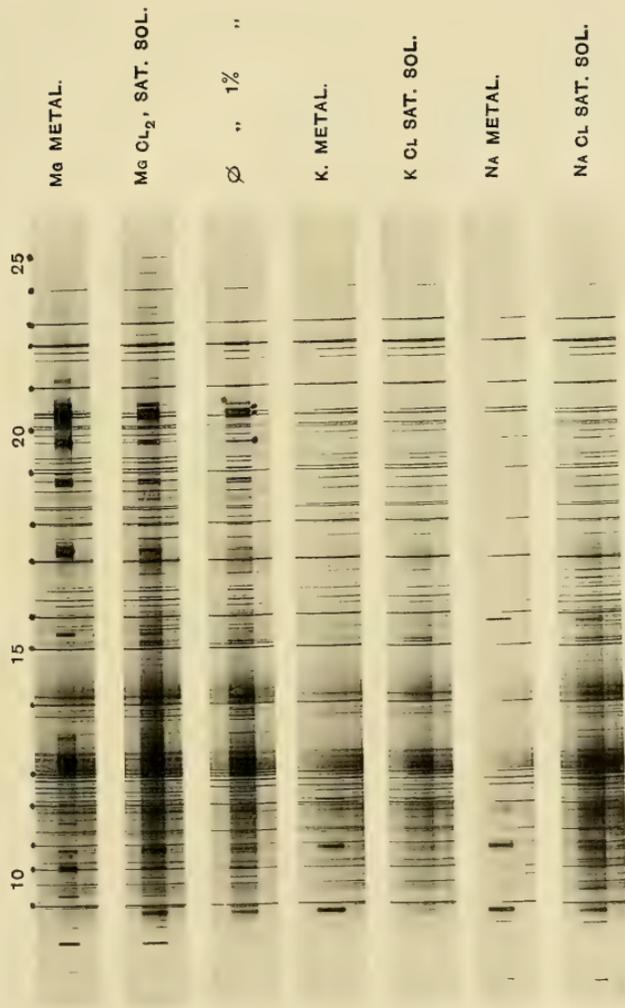
Wave- Length.	Intensity and Persistency.
5896·2	10 ω
5890·2	10 ω
5688·3	6 ψ
5682·9	6 ψ
3303·1	10 χ
3302·5	10 χ
2852·9	(6) σ

CALCIUM, BARIUM AND STRONTIUM.



GOLD ELECTRODES.

MAGNESIUM, POTASSIUM AND SODIUM.



GOLD ELECTRODES.

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Vol. XI. (N. S.), No. 19.

AUGUST, 1907.

ON SOME DEVICES FACILITATING THE STUDY
OF SPECTRA.

BY

WALTER NOEL HARTLEY, D.Sc., F.R.S.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

(PLATE XX.)

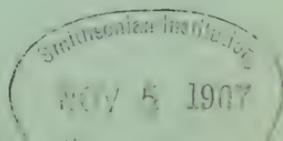
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XIX.

ON SOME DEVICES FACILITATING THE STUDY OF
SPECTRA.

By WALTER NOEL HARTLEY, D.Sc., F.R.S.,
Royal College of Science, Dublin.

[PLATE XX.]

[Read, MAY 21; Received for Publication, MAY 24; Published, AUGUST 17, 1907.]

It has been shown in previous communications that flame-spectra at high temperatures have a special value, inasmuch as minute traces of metallic and mineral substances may be readily detected, and their spectra photographed; for instance, from iron ores and pig-iron as many as ninety lines of the element are photographed at one exposure.¹

The source of heat being the oxyhydrogen flame, the temperature lies between 1400° and 2000°; and as 1775° is about the melting-point of platinum, some other support than that metal must be used for solid substances. Thin slips of Donegal cyanite and ashless filter-papers have been used almost exclusively, and their use described in the publications quoted. The cyanite consists of 98·0 per cent. of aluminium silicate, according to an unpublished analysis made in my laboratory; it merely softens in the flame, and it is useful for long exposures of half an hour or upwards. The lines of sodium and lithium in the yellow and red are the only impurities which are photographed. The filter-papers are useful for rapid exposures of one to two minutes; they yield the sodium line only; but atmospheric dust settles upon them, and consequently feeble red and green bands of calcium sometimes appear, especially when ten filter-papers are used for one

¹ "Flame-Spectra at High Temperatures," Hartley, *Phil. Trans.*, 1894, A, vol. clxxxv., part 1, pp. 161-211.

"A Simplified Method for the Spectrographic Examination of Minerals," Hartley & Ramage, *Chem. Soc. Trans.*, 1901, vol. lxxix., p. 61.

spectrum. Cyanite is not always procurable, but carborundum is now an article of commerce.

Carborundum.—This gives no spectrum in the oxyhydrogen flame; it is incombustible, and quite infusible. This material in a form adapted for supports is manufactured by the *Carborundum Company* for other purposes, the small crystals being mixed with porcelain clay, and fired at a high temperature. Thin, flattened pieces, four inches in length and $\frac{1}{16}$ of an inch in thickness, are sold as silversmiths' stones. It is advisable that this material be cautiously introduced into the flame.

Quartz fibres and thin rods.—At the melting-point of platinum quartz only softens; hence this material, which is now manufactured by Messrs. Johnson & Mathey, in the form of rod and tube, is available for use. The quartz, as a rule, gives no impurity lines.

The Mecke burner.—In all the various forms of smokeless burners which have been devised, the chief defect lies in the small area of the cross-section of the flame, which provides the maximum temperature; great variations in temperature arise from the irregularity of the flame, when subject to the influence of draughts, especially horizontal currents of air. From these defects the Mecke burner is entirely free; and for ordinary spectroscopic purposes I can recommend no other. Its construction is that of a Gifford's injector, the current of gas injecting into the tube the requisite amount of air necessary for its complete combustion. In order to admit of the gas and air being mixed together, two metallic gratings are placed within the tube of the burner; and about half an inch above the upper grating a cap consisting of a third grating is fitted. As the upper part of the tube is choked by the gratings, it is expanded to compensate for this. To ignite the mixture of gas and air, the match-flame must not be held above, but close to the grating. Supposing the diameter of the top of the burner be two centimetres, the gaseous mixture is seen to burn from about thirty-seven little jets, each of which shows a green cone if the air is excessive, but a blue one if the mixture is of the right nature to obtain the highest temperature. The maximum heating effect is from two to three millimetres above the grating; and it is equable across the whole diameter of the tube. Platinum wire of the ordinary thickness just

fuses upon the surface. The shape of the flame is a cone about 25 mm. high, and therefore pyramidal. Draughts do not affect the flame. In the Mecke burner, fused alkali and alkaline earth-salts are easily examined on platinum wire, hard asbestos fibres, quartz fibres, or on tobacco-pipe. It is, of course, necessary to ascertain what spectrum-lines the support yields, and eliminate the lines or bands from the spectra subsequently observed. Quartz fibres and platinum obviously yield nothing. Fusible silicates, such as lepidolite, show the spectra of potassium, lithium, and, with a wide slit, even of rubidium. A convenient way of examining solutions is to employ a clay tobacco-pipe, to plug the mouthpiece of the pipe with two or three asbestos fibres, and to pour the solution into the bowl. By inclining the pipe, the solution soaks through the asbestos, the water evaporates, and the salt fuses on the fibres. Similarly, a piece of quartz tube is drawn out to a capillary point, the end being left open; the solution then issues in drops, which dry upon the point of the tube; it is the solid salt, and also spray from the solution, which yields the spectrum. The quartz is unbreakable by the contact of the hot material with a cold solution. When even white-hot, it may be dropped into cold water without cracking, or into hydrochloric acid, in order to cleanse it.

The Mecke blast-burner.—This modification, in addition to the injector, has an air-jet placed higher up in the tube. The air-blast must be supplied with a regulated constant-pressure, which may be obtained in any way, as by bellows, a rotary fan, or tromp; but the pressure should not be less than two kilogrammes per square centimetre. With water direct from the high-pressure mains, the water-blower is satisfactory; but the instrument should be fitted with a pressure-gauge. A blower fitted up twenty-five years ago has been found generally effective. The essential parts are a Körting's jet, soldered on to a water-tap, to which again the inlet-tube of the blower is soldered. The air-reservoir is a tube 4 feet long by 3 inches broad. Platinum wire, of the usual thickness suitable for spectroscopy, is easily melted in the flame at its hottest part; and therefore quartz-fibres are a suitable material to use as supports. To convey some idea of the advantages gained by the use of these burners for spectroscopic work, I may mention that the use of fused salts or infusible compounds

is to be preferred to aqueous solutions, or to substances strongly acidified with hydrochloric acid. Thus the examination is simplified and made more cleanly in manipulation. Any salt previous to being examined should be heated in a covered porcelain crucible until it ceases to decrepitate or evolve water; it is then in a suitable condition to be placed on the support.

In the practical use of the flame-spectra there is no difficulty in recognizing traces of the alkalis by their lines; but with salts of the alkaline earth-metals, the most characteristic feature of their spectra are bands, and not lines. The usual mode of examination in the Bunsen flame is to moisten the solid substance with hydrochloric acid, to take some of this up on a platinum wire and place it in the flame, when a momentary brilliant flash follows; after a short interval very little of the spectrum remains to be seen, and what there is has an essentially different appearance. It is hardly necessary to point out that volatile metallic chlorides yield the first spectra; and those subsequently visible are the spectra obtained, first by the conversion of the chlorides into oxides, and secondly by the reduction of oxides to the metallic state and the coloration of the flame by the metals.¹

By employing the high temperature of the Mecke burner even of the simple pattern, the second spectra are rendered constant for a long period, even if the oxides or sulphates are employed. Accordingly, what distinguishes the least trace of calcium is a red band and a green band, one on each side of the sodium line. Strontium yields two red bands and one orange band. As a rule, neither the blue line of calcium nor the corresponding blue line of strontium is plainly seen. If any calcium salt be placed in the flame, the effect first seen is a strong sodium spectrum; but the heat is so intense that the sodium is soon volatilised; and nothing but the red colouration of the calcium remains; though this may continue for an hour or longer, and may be photographed. The red and green bands have been obtained from calcium chloride, calcium nitrate, calcium carbonate, calcium sulphate, and from quick-lime. The photograph of the bands, taken from calcium nitrate during one hour's exposure in a

¹ "On the Thermo-Chemistry of Flame-Spectra at High Temperatures," Hartley, *Proc. Roy. Soc.*, 1907, A, vol. lxxix., pp. 242-261.

simple Mecke burner shows the essential features of the calcium spectrum. The slit was sufficiently narrow to divide the two sodium lines when very minute quantities of sodium were present.

A Device for showing Chloride Spectra.—When an oxide is supported in the flame of a Mecke burner, it may be made to yield a chloride spectrum by introducing a few fibres of asbestos or tobacco-pipe upon which is crystallised some ammonium chloride. The effect is, however, evanescent; and to operate continuously over long periods, the burner is supplied with gas mixed with the vapour of chloroform in exactly those proportions which give the best effect. The gas may be taken from two separate taps, or from a tube with a by-pass; one-half of the gas to be burnt goes through a bottle containing sponge saturated with chloroform. The outlet tube from the bottle is joined to one end of a λ piece; the gas is joined to the other; while a single tube goes to the burner. By regulating the two taps, the most brilliant spectra may be made to continue for several hours without trouble; and the spectra may be photographed.

On measuring Spectra.—In making observations of the visible spectrum, measurements made with cross-wires in the eye-piece of the telescope are seldom quite concordant when series of measurements are made throughout the whole spectrum, first in one direction and then in the other; the differences are greater in the measurements of bands than in those of lines. This is due to two causes, the one an alteration in the focus of the eye; the second, slight variations in the width and intensity of the bands. To counteract the first difficulty I have had two instruments made with graduated draw-tubes, and have marked the focus as determined for red, yellow, green, blue, and violet lines, such as lines of potassium, lithium, sodium, thallium, strontium, calcium, and a spark-line of magnesium. Of course the focusing is adapted to only one eye-piece. In measuring green rays the telescope is adjusted for the thallium-line as marked upon the scale; and other measurements are easily made on either side of this. Each observer must focus for himself. In the measurements of bands the Mecke burner offers a decided advantage over the ordinary Bunsen flame, because it is not subject to fluctuations in temperature, and is on the whole hotter, being about 1400° C. throughout

the body of the flame; the bands are therefore of uniform brilliancy and width. But, above all, the bands may be photographed, so that with the same photographic plates and the same exposure a similar spectrum is obtained, which can be measured by applying an ivory scale divided into hundredths of an inch, or fourths of a millimetre; and measurements may be repeated and corrected. Eye-observations record the average effect of brilliancy and intensity of lines and bands; while photographs are a record of the aggregate effect over a given period of time. All difficulties arising out of inequality in sensitiveness of the prepared film to different colours are now overcome by the use of Wratten and Wainwright's panchromatic plates (see Plate XX., fig. 2, Potassium). The examples of flame-spectra of the calcium, strontium, and barium group show that, with a constant exposure, the width of the bands increases with the quantity of substance in the flame; with a constant quantity of substance and varying exposures, the width and intensity of the bands increase with the exposure. With certain elements the bands are widened and intensified more on the less refrangible side; with others, on the more refrangible. This explains what has been remarked by Von der Seipen,¹ namely, that, between his measurements of the bands of metallic tin and mine, there is a large though constant difference in the wave-length values; and he attributes this to the old normal wave-lengths of Ångström being used. The difference, however, between the two sets of measurements amounts to from 4 to 7 Ångström units, but over the same range of spectrum the maximum difference between Hartley and Adeney's wave-lengths (1884) and Rowland's (1893)² is, at most, + 1.1 Å. unit, the minimum being + 0.4, and the average something less than + 0.8.

There is no doubt that my spectrum was photographed from a much larger quantity of material; and the exposure was also longer; and therefore the bands were broader and more intense.

¹ "Über das Flammenspektrum des Zinns," *Zeitsch. f. wissensch. Photographie*, 1907, Bd. v., pp. 69-85.

² J. F. Eder, "Beiträge zur Spectralanalyse," *K. K. Akad. Wissensch., Vienna*, 1893, Bd. lx., p. 13.

EXPLANATION OF PLATE XX.

PLATE XX.

FIG. 1.

No.

1. The calcium spectrum as obtained from lime ignited in the flame of a simple Mecke burner for two hours.
2. The calcium spectrum as obtained from lime ignited in the flame of the smallest size of the Mecke blast-burner. Exposure, two hours.
3. The same, with chloroform in the gas, showing the chloride spectrum. Exposure, two hours.
4. The spectrum of copper oxide in the Mecke blast-flame. The sodium line only is distinctly seen. A green band from λ 5605 to 5560 is all but invisible. Exposure, two hours.
5. The same, with chloroform in the gas, showing the beautiful banded chloride spectrum. Exposure, two hours.

By comparing Nos. 4 and 5, it will be readily understood why traces of copper in the fuel show a blue flame when salt is thrown on to a fire of glowing coals.

FIG. 2.

Oxyhydrogen flame spectra of the alkali metals, as rendered by their carbonates.

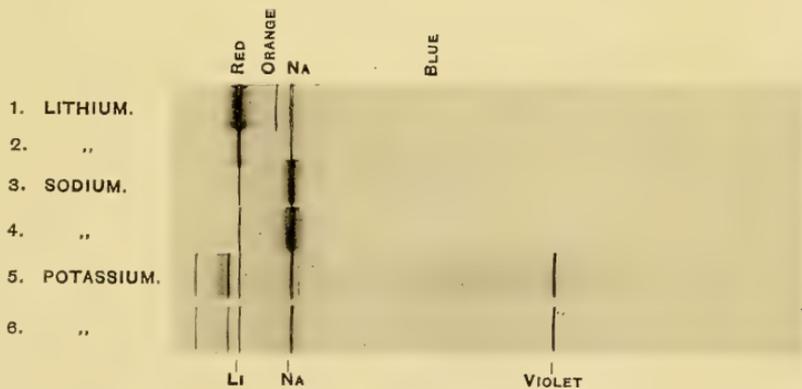
No.

1. LITHIUM. The red, orange, and blue lines are all photographed. Sodium appears as an impurity.
2. The same, with half the quantity of substance.
3. SODIUM, with the red lithium line as an impurity.
4. The same, with double the quantity of substance.
5. POTASSIUM, containing traces of lithium and sodium, as shown by the presence of the red and yellow lines. The potassium spectrum ranges from the pair of lines in the red, wave-lengths 7699.3 and 7665.6, to the pair 4047.4 and 4044.3 in the violet. The continuous spectrum and lines in the green are well shown. The band in the red fades away on the side of least refrangibility.
6. The same, with half the quantity of substance.

FIG. 1.



FIG. 2.





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THE
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AUGUST, 1907.

NOTE ON THE SPECTRA OF CALCIUM AND
MAGNESIUM AS OBSERVED UNDER
DIFFERENT CONDITIONS.

BY

WALTER NOEL HARTLEY, D.Sc., F.R.S.,

ROYAL COLLEGE OF SCIENCE, DUBLIN.

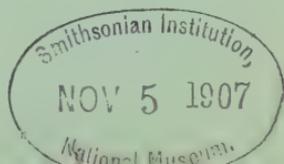
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XX.

NOTE ON THE SPECTRA OF CALCIUM AND MAGNESIUM
AS OBSERVED UNDER DIFFERENT CONDITIONS.

By WALTER NOEL HARTLEY, D.Sc., F.R.S.,

Royal College of Science, Dublin.

[Read, MAY 21 ; Received for Publication, MAY 24 ; Published, AUGUST 17, 1907.]

Calcium.—In photographing the spark spectrum of metallic calcium in an atmosphere of hydrogen, and also in a vacuum without a jar in the circuit, it was found very difficult always to obtain precisely the same spectrum, with the same exposure. The principal features were the bands in the red, orange, and green, and the line λ 4226·9, and also in one instance there appeared very feebly the lines at $\lambda\lambda$ 3968·6 and 3933·8. Occasionally the red and green bands were not so strong as they should have been ; and the pair of lines with the above wave-lengths appeared distinctly with λ 4226·9 stronger than usual. Sometimes other lines appeared ; and in one instance they overlaid the red and green bands, as if the band spectrum was being transformed into a line spectrum. On one photograph of the uncondensed spark between metal points in a tube, at a pressure of 7 mm., the only features presented were the representatives of the solar lines H and K, namely, $\lambda\lambda$ 3968·6 and 3933·8, the blue line λ 4226·9, also indistinctly λ 4300, with feeble indications of a line on each side of it. There were two other lines scarcely visible about wave-lengths 4420 and 4452, probably 4425·6 and 4455·0. Eye-observations were made at the commencement of the exposures when the red, orange, and green bands were brilliantly visible ; but the exposures varied from ten to twenty minutes, and in one case with a small coil the period was extended to one hour. In this last instance it was observed that no calcium spectrum was visible, but only the red and blue hydrogen lines, when the spark had passed for some time. On developing the plate there was practically nothing upon it. In yet another instance, after a

photograph had been taken in hydrogen, this gas was displaced by air, and another photograph secured. Here the spectrum was a continuous one, overlying and obscuring the red and green bands, just as if the rays had proceeded simultaneously from a white-hot solid substance and the flame of burning calcium. It is not improbable that the bright metallic electrodes had become oxidised on the surface, and that a trace of lime was the origin of the continuous rays. It was thought desirable that the spark should be examined again in a vacuum; and the result led to a red flame being seen to proceed from one electrode, half-way towards the other, upon which bright white scintillations were observed. The red flame yielded the calcium bands; the lines in the spectrum evidently proceeded from the bright scintillations. These changes in the spark-discharge were observed when the electrodes had become heated. The position of the red flame was reversed when the direction of the current was reversed. This behaviour of metallic calcium is apparently similar to that described by Ramage¹ in connexion with lithium carbonate fused to a platinum wire; but it is probably connected with the phenomenon described by Horton.²

It should be noted here that the red, orange, and green bands appear in the spark-spectrum with Hemsalech's self-induction coil in circuit, the characteristic spark-lines overlying the bands. On renewing the electrodes, and making a further series of experiments with a small motor-car sparking-coil, with the discharge between calcium electrodes in an exhausted tube at 5 mm. pressure, it was found that there was no direct passage of the spark. The metal points glowed with a violet light; bright stationary spots of white light were seen on the negative electrode, and a great number of scintillations less bright on the positive electrode, not at one spot, but all over it. At intervals, as in the previous instances, a small flame of red light, lasting only a few seconds, passed apparently from the positive electrode. With a more powerful coil, the sparks between the electrodes were fairly continuous for a time, but still showed irregularities.

¹ "On the Distribution and Spectra of Metallic Vapours in Electric Sparks." By Hugh Ramage, B.A., *Proc. Camb. Phil. Soc.*, 1904, vol. xii., pt. v., p. 349.

² "On the Discharge of Negative Electricity from Hot Calcium and from Lime." By Frank Horton, D.Sc. A Paper read on January 31st, 1907. *Proc. Roy. Soc.*, 1907, A, vol. lxxix., p. 96.

The question arises, To what extent can foreign substances in the calcium affect the spectrum? Traces of lithium and sodium are present; but such minute quantities of these metals can have no influence. The calcium undoubtedly contains a small quantity of carbide, because the gas which is evolved by its interaction with water has the odour of acetylene; but since the hydrogen burns without any perceptible illumination, such as would proceed from an admixture with a gas so rich in carbon, the amount is probably very small. There is a possibility of calcium hydride being an impurity; but to what extent this substance can affect the discharge of electricity is not known.

Magnesium.—When photographing magnesium metal with sparks passing in a closed vessel at a reduced pressure of 5 mm., similar observations were made of stationary bright spots and scintillations, with an occasional very brilliant green flame. The sparks passed with greater regularity than was the case with calcium in like circumstances.

When the current was first turned on, the sparks had a yellow or orange colour; the brilliant green rays appeared subsequently. With the eye, bands in the citron green and an orange line were visible with two brilliant green lines close together. A photograph taken of the spectrum of the spark without condenser, and an exposure of twenty minutes with a narrow slit, yielded nothing beyond the two intensely green lines, with wave-lengths approximately 5209 and 5200.

Another photograph taken in the same manner yielded the two lines in the green, with a faint indication of a narrow band a little more refrangible than 5200, and degraded on the more refrangible edge. This corresponds with the head of the fluted band in the magnesium spectrum on Plate XXX. of “Banded Flame Spectra of Metals”;¹ but there is, in addition, a series of nitrogen bands in the region lying between wave-lengths 4000 and 3600, and a group of bands like strong, broad lines, terminating in two lines.

The lines and bands have not been photographed from magnesium in an atmosphere of hydrogen at normal pressures. They appear to be variable even under apparently identical

¹ Hartley and Ramage, *Trans. Roy. Dublin Soc.*, 1901, vol. vii., part 12, p. 339.

conditions with respect to spark and pressure; but when the pressure is reduced to less than one millimetre, it is found that all the nitrogen bands have disappeared, and also the narrow bands, leaving just the two most refrangible of the lines $\lambda\lambda$ 3830 and 3837 approximately, which are a pair, with a similar pair $\lambda\lambda$ 5209 and 5200. From these changes, it appears more than probable that they are the spectrum of magnesium nitride, which is decomposed gradually until nothing but the two pairs of lines remain to represent the magnesium in the compound.

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THE
SCIENTIFIC PROCEEDINGS
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JANUARY, 1908.

THE SYNTHESIS OF GLYCOSIDES: SOME
DERIVATIVES OF XYLOSE.

BY

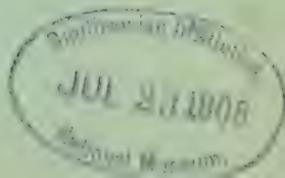
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CATHOLIC UNIVERSITY SCHOOL OF MEDICINE, DUBLIN.

[Authors alone are responsible for all opinions expressed in their Communications.]

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XXI.

THE SYNTHESIS OF GLYCOSIDES: SOME DERIVATIVES
OF XYLOSE.

By HUGH RYAN, M.A., D.SC., F.R.U.I., AND
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[Read, NOVEMBER 19; Received for Publication, NOVEMBER 22, 1907;
Published, JANUARY 13, 1908.]

IN 1870 Colley¹ obtained acetyl-chloro-glucose by the interaction of acetyl chloride and glucose in a sealed tube at the ordinary temperature; and by reacting on the alkaline derivatives of salicylic aldehyde, methyl-hydro-quinone, phenol, eugenol, and guaiacol with acetyl-chloro-glucose in alcoholic solution, Michael² synthesized the corresponding glucosides. Using a similar reaction, Drouin³ prepared the glucosides of thymol and *a*-naphthol. By the action of alcoholic potash on equi-molecular quantities of acetyl-chloro-glucose, the cresols, carvacrol, and β -naphthol, Ryan⁴ prepared the glucosides of cresol, carvacrol, and β -naphthol, which he afterwards converted into their tetracetyl derivatives.⁵

From acetyl chloride and galactose, Ryan and Mills⁶ obtained acetyl-chloro-galactose, and converted it into *a*-naphthyl-galactoside.

Koenigs and Knorr⁷ succeeded in obtaining a well-crystallized

¹ Ann. Chim. Phys., 1870, iv., 21, p. 363.

² Comptes Rendus, lxxxix., p. 355.

³ Bull. Soc. Chim., xiii. (3), p. 5.

⁴ Jour. Chem. Soc., 1899, vol. lxxv., p. 1054.

⁵ Proc. Roy. Dublin Soc., 1901, vol. ix., p. 508.

⁶ *Ibid.*, p. 506.

⁷ Sitz. Bayr. Akad. der Wissensch., 1900, p. 103.

substance (acetyl-bromo-glucose) by the action of acetyl bromide on glucose, and converted it into pentacetyl-glucose, alcoholic and phenolic glucosides.

By the action of phosphorus pentachloride and aluminium chloride on pentacetyl-hexoses, crystallized acetyl-chloro-hexoses were prepared by Skraup and Kremann.¹

Emil Fischer and Armstrong² found that anhydrous liquid halogen acids can convert pentacetyl-hexoses into well-crystallized acetyl-chloro-hexoses. From the latter β -phenyl-galactoside and its tetracetyl derivative were, amongst other glycosides, prepared.

The first crystallized acetyl-chloro-pentose was obtained by Ryan and Mills³ by the action of acetyl chloride on arabinose in an open or in a closed tube. From it Ryan and Ebrill⁴ synthesized the arabinosides of methyl alcohol, β -naphthol, carvacrol, and ortho-cresol.

Acetyl-chloro-arabinose was subsequently rediscovered by Chavanne,⁵ who converted it into a crystallized tetracetyl-arabinose, and at the same time succeeded in preparing a crystallized acetyl-bromo-arabinose by the action of acetyl bromide on arabinose.

The methyl-arabinoside obtained by us was identical with that previously obtained by Emil Fischer⁶ by a different method; and according to Purdie and Rose⁷ belongs to the α -series, the isomeric β -compound having been obtained by the latter workers.

In the present paper we describe the preparation of a crystallized acetyl-chloro-xylose, its conversion into a crystallized tetracetyl-xylose, and well-crystallized xylosides (α -naphthol and carvacrol). The tetracetyl-xylose, obtained by us, melted at a lower temperature (119° C.) (uncorrected) than that (124° C.)

¹ Monatsh. f. Chem. xxii., p. 375.

² Sitz. der k. Akad. der Wissensch., Berlin, 1901, Bd. xiii., p. 316.

³ Jour. Chem. Soc., 1901, vol. lxxix., p. 704.

⁴ Proc. Roy. Irish Acad., 1903, vol. xxiv., Sec. B., p. 379.

⁵ Comptes Rendus, vol. cxxxiv., 1902, p. 661.

⁶ Ber. Deutsch. Chem. Gesellsch., 1893, Jahrg. xxvi., p. 2400.

⁷ Jour. Chem. Soc., 1906, vol. lxxxix., p. 1204.

which has been given by Stone¹ and Bader² for the similar substance prepared by them from the interaction of xylose and acetic anhydride.

Though the constitution of our acetyl-chloro-pentoses remains unestablished, unless we assume that since the acetyl-chloro-arabinose is converted by methyl alcohol into a methyl-arabino-side which Purdie and Rose regard as an α -derivative, the parent-substance must be an α -compound, we can nevertheless regard the phenolic derivatives of them as β -compounds, since it has been shown by Fischer and Armstrong that both α and β acetyl-chloro-hexoses give in alkaline solution β -hexosides only. All the glycosides obtained from acetyl-chloro-hexoses in alkaline solution are, when the hexose is a fermentable one, with the single exception of the synthetical cane-sugar,³ capable of being hydrolysed by emulsin.

The phenolic compounds of non-fermentable sugars, such as the pentoses, are not hydrolysable by emulsin.⁴

In an unsuccessful attempt to isolate the disaccharide of amygdalin by the action of emulsin on the heptacetyl derivative of the glucoside, it was found by the authors⁵ that the conversion of the hydroxyl groups of a glucoside into the corresponding oxyacetyl groups rendered the substance incapable of being hydrolysed by emulsin even when the solubility of the acetyl compound was increased by addition of a moderate amount of alcohol. Caldwell and Courtauld⁶ have recently confirmed our results with regard to the inactivity of emulsin towards the acetyl-derivatives of the glycosides.

Preparation of Acetyl-chloro-xylose.

Well-dried xylose (5 grams) and acetyl chloride (10.5 grams) were placed in a sealed tube, and the tube was then immersed in

¹ Amer. Chem. Jour., vol. xv., p. 653.

² Chem. Zeit., Bd. xix., p. 55.

³ Marchlewski, Anzeiger Akad. der Wissensch., Cracau, 1899.

⁴ Ryan and Ebrill, Proc. Roy. Irish Acad., 1906, vol. xxvi., Sec. B., p. 53.

⁵ *Ibid.*

⁶ Jour. Chem. Soc., 1907, vol. xci., p. 671.

iced-water until the xylose had completely dissolved. This was completed in from two to three days, the solution becoming brown, and the reaction, as in the case of glucose, being attended by the production of a large amount of hydrochloric acid gas. The tube was then opened and the syrupy liquid, which had remained after the hydrochloric acid had escaped, was dissolved in chloroform. The solution was then washed first with cold water, and afterwards with dilute sodium bicarbonate, until the reaction was no longer acid. The chloroform solution was dried rapidly with calcium chloride, filtered, and the chloroform distilled off in vacuo.

The syrupy residue crystallized on the addition of absolute alcohol, and was purified for analysis by redissolving in chloroform and reprecipitating by addition of absolute alcohol. After drying in a steam-oven, the following results were obtained on analysis :—

0.1786 grm. subst.	0.0864 grm. AgCl
	Cl 11.96 per cent.
$C_{11}H_{15}O_7Cl$ required	Cl 12.02 per cent.

Acetyl-chloro-xylose melts at $101^{\circ}C$. It is scarcely soluble in cold methyl or ethyl alcohol, but dissolves in hot alcohol, and is reprecipitated on cooling. (Prolonged boiling with alcohol converts it into a non-reducing derivative.)

Conversion of Acetyl-chloro-xylose into β a-Naphthyl-xyloside.

To a solution of 0.28 gram of potash and 0.7 gram of α -naphthol in absolute alcohol, 1.5 grams of acetyl-chloro-xylose were added slowly with frequent shaking. Potassium chloride separated out; and the mixture smelt of acetic ester. Within twenty-four hours a white crystalline solid separated from the solution. The mixture was warmed until the solid had redissolved, and then filtered from the insoluble potassium chloride. On concentrating the solution on the water-bath, long needle-shaped crystals were obtained.

The substance was purified by recrystallization from dilute alcohol, and, when dried at $100^{\circ}C$., began to soften at $191^{\circ}C$.,

and melted at 192°–193° C. On analysis the following results were obtained:—

0.1260 grm. subst. gave 0.3001 grm. CO₂, and 0.0656 grm. H₂O.
C 64.96 H 5.78.

C₁₅H₁₆O₅ requires C 65.21 H 5.8.

Naphthyl-xyloside crystallizes from dilute alcohol in long branching needles, which dissolve slowly in cold, and readily in hot, absolute alcohol. It is very soluble in acetone and acetic ester, but almost insoluble in ether, carbon bisulphide, chloroform, and petroleum ether. Its solubility in water is not increased by addition of potash. The substance does not reduce Fehling's solution before, but does so readily after, hydrolysis, by boiling with dilute sulphuric acid. It is not hydrolysed by emulsin.

Conversion of Acetyl-chloro-xylose into Carvacryl-xyloside.

Acetyl-chloro-xylose was added to equimolecular quantities of potash and carvacrol, dissolved in absolute alcohol, and the mixture allowed to remain at the temperature of the laboratory for two days. It was next warmed for some time, filtered, and the alcohol evaporated from the filtrate. An oily mass was left, which became crystalline after evaporation a few times with water. It was boiled with water and a little animal charcoal, filtered and concentrated until the glycoside crystallized out. It was recrystallized several times from water. When dried in a vacuum over sulphuric acid, it melted at 105° C., and gave on analysis:—

0.1000 grm. subst. gave 0.0740 grm. H₂O and 0.2317 grm. CO₂.
C 63.2 H 8.22.

C₁₅H₂₂O₅ requires C 63.78 H 7.87.

β-Carcacryl-xyloside crystallizes from boiling water in long needles. It is soluble in hot alcohol, ether, chloroform, acetic ester, and acetone. It is insoluble in carbon bisulphide. Its behaviour towards Fehling's solution is similar to that of β-naphthyl-xyloside. In potash it dissolves much more readily than in water, resembling in this respect the corresponding glucose derivative.

Conversion of Acetyl-chloro-xylose into Tetracetyl-xylose.

Tetracetyl-xylose was prepared by mixing together 1 gram of acetyl-chloro-xylose, 0.8 gram of silver acetate, and 25 c.c. of glacial acetic acid. The mixture was shaken at the ordinary temperature until the clear upper layer was free from chlorine, and then filtered from the silver chloride, which had separated out. The filtrate was diluted with water, and sodium carbonate was added until the reaction became alkaline. The acetyl-derivative was extracted with ether. The crystals which remained on evaporating the ether were recrystallized from ether, and dried at 100° C. for analysis.

0.1000 grm. subst. boiled for three hours with 50 c.c. of decinormal sulphuric acid required for neutralization 62.75 c.c.s of decinormal potash, showing that the acidity due to the substance was equivalent to 12.75 c.cs. of decinormal acetic acid, whereas the calculated quantity of acetic acid obtainable from 0.1000 grm. of $C_5H_6O_5(CH_3CO)_4$ is 12.58 c.cs. of decinormal acetic acid.

Tetracetyl-xylose is soluble in ether, chloroform, acetic ester, and acetone. It dissolves readily in hot alcohol, and is scarcely soluble in petroleum ether, or carbon bisulphide. The melting-point 119° C. (uncorr.) is lower than that got by Stone (*loc. cit.*), 124° C., for the similar substance got by the action of acetic anhydride on xylose.

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JANUARY, 1908.

THE RADIOACTIVITY OF SEA-WATER.

BY

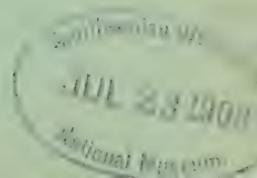
J. JOLY, Sc.D., F.R.S.,

PROFESSOR OF GEOLOGY AND MINERALOGY IN THE UNIVERSITY OF DUBLIN.
HON. SEC. ROYAL DUBLIN SOCIETY.

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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XXII.

THE RADIOACTIVITY OF SEA-WATER.

By J. JOLY, Sc.D., F.R.S.,

Professor of Geology and Mineralogy in the University of Dublin.
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[Read, NOVEMBER 19; Received for Publication, NOVEMBER 22, 1907;
 Published, JANUARY 15, 1908.]

I AM acquainted with only one determination of the radium in sea-water taken directly from the ocean—that recorded by A. S. Eve in his paper “On the Ionization of the Atmosphere over the Ocean.”¹ Strutt had previously determined the radium in sea-salt,² and obtained the value 0.15×10^{-12} in grams per gram of salt. This must be reduced, however, to about one-half, seeing that, at the time of this determination, the quantity of radium associated with a gram of uranium was believed to be about double as great as it has since been shown to be—this quantity entering into the calibration of the electroscope. It is necessary to add that Strutt gives his determination as “approximate only.”

The sea-water dealt with by Eve was collected in mid-Atlantic, between Montreal and Glasgow. The amount of radium found was 0.0003×10^{-12} grams per gram of sea-water. If we reckon sea-salts as composing 3 per cent. by weight of sea-water, Strutt’s determination would give 0.0023×10^{-12} grams per gram of sea-water.

Eve also made an experiment on sea-salt, using 400 grams of Omaha sea-salt guaranteed pure by the importers. He finds 0.02×10^{-12} grams per gram, or for the equivalent sea-water, 0.0006×10^{-12} .

We thus have the three divergent results:—

From radium in sea-salt (Strutt),	0.0023×10^{-12} .
From radium in sea-salt (Eve),	0.0006×10^{-12} .
From mid-Atlantic sea-water (Eve),	0.0003×10^{-12} .

¹ Phil. Mag., vol. xiii., Ser. vi., p. 248.
 SCIEN. PROC. R.D.S., VOL. XI., NO. XXII.

² Proc. R. S., vol. lxxviii., p. 151.
 2 L

In reviewing these figures Eve states that it is safe to conclude that sea-water does not contain more than 0.0006×10^{-12} grams radium per gram.

In April of the present year a friend sent me from Valencia, Co. Kerry, a sample of sea-water collected in the harbour at flood-tide. A very large volume of water enters this extensive harbour at each flood; and as there are no large rivers along the coast, water taken at the harbour mouth may be regarded as free from impurities derived from the shore. The quantity sent to me (in a stoppered glass bottle which I had transmitted, specially cleansed, for the purpose) was 2450 c.cs. This was evaporated on the water-bath to about 1200 c.cs., with every precaution against contamination, and in a part of the laboratory in which radioactive preparations had never come. The radium determined in this Valencia sea-water was 0.0356×10^{-12} grams per gram. The apparatus and mode of extraction I was using at this time were closely similar to those developed by Strutt as described in his paper (*loc. cit.*). The readings of the electroscope were standardised by the emanation from Joachimsthal pitchblende, a portion of which I had analyzed for the uranium.

This determination, showing more than ten times the amount of radium given in any evaluation known to me, I naturally regarded as requiring confirmation.

In the month of May I received from Mr. S. W. Kemp, of the Irish Fishery Department, 2800 c.cs. of sea-water taken in the Irish Channel a few miles to west of the Isle of Man, lat. $53^{\circ} 53' N.$, long. $5^{\circ} 16' W.$ This also was transmitted in bottles which I had supplied for the purpose. The water was evaporated down to about 800 c.cs., and when investigated yielded only 0.0038×10^{-12} grams per gram. This figure seemed to support sea-salt determinations; but I was so convinced of the genuineness of the first result that I provisionally concluded a real difference to exist between near-shore and more open-sea samples of water. I had, indeed, changed the mode of extraction of the emanation, substituting a method in which ebullition proceeds in a partial vacuum, and at its conclusion the space above the liquid in the flask is completely filled with distilled water, thereby securing that every trace of emanation is displaced into a receiver, from which it is transferred into the electroscope. I had found by comparative

experiments on known quantities of uraninite in solution, that this mode of extraction gives a somewhat lower constant for the electroscope, showing that it is capable of effecting a more complete extraction. The change in manipulation was therefore in favour of giving a higher, and not lower, result.

Shortly after this measurement, Mr. Kemp sent me three other samples of sea-water. Calling the two samples already referred to (*a*) and (*b*) respectively—

Sample (*c*) is from lat. $51^{\circ} 26' N.$, long. $12^{\circ} 5' W.$ A point about 65 miles due west of Valencia. Quantity, 2665 c.cs.

Sample (*d*) is from 1.5 miles south of Crow Head, Co. Kerry. Quantity, 2740 c.cs.

Sample (*e*) is from lat. $51^{\circ} 35' N.$, long. $10^{\circ} 43' W.$ —that is, about twenty miles west of Bantry Bay. Quantity, 2764 c.cs. The last two samples were collected on the same day, June 21st.

These were evaporated down as before, each to about 900 or 1000 c.cs. The results were as follows:—

$$(c) 0.0126 \times 10^{-12}.$$

$$(d) 0.0152 \times 10^{-12}.$$

$$(e) 0.0268 \times 10^{-12}.$$

It will be seen that all these figures are of the same order of magnitude as the result on the Valencia water. The discrepancy with the Isle of Man sample is considerable. While very sure that errors arising from contamination did not enter these results, it seemed probable that some other source of error existed. If this arose from any cause residing in the nature of the material dealt with, it could only be that there was in some way concealment of the emanation in the lower results, and that the higher results were the more nearly approximate to the truth. Sea-water is rich in sulphates; and the possibility of the process of concentration resulting in a precipitation of the radium in a non-emanating form occurred to me. There is a small quantity of barium in sea-water. A very minute precipitate of this might bring with it the radium; and, again, the calcium sulphate, which is one of the earliest substances to fall, might also be concerned. The emanation, which never increases beyond a certain amount, might be imprisoned in very fine precipitated particles. The flasks were examined with this possibility in view. None of them were perfectly clear of precipitate. In (*a*) it was least,

perhaps; but the dulling of the glass on the inside of the flasks showed that in every case some solid matter had come down. It is true that, in so far as this is redissolved on ebullition, it can do no harm; but the risk of error here was evident.

Accordingly all five were somewhat diluted, and transferred to larger flasks, and a few c.cs. of very pure HCl (which I had distilled from a nearly pure acid) added to each. This instantly cleared the precipitates away. They were then boiled and closed. When in due time the whole five came to be redetermined, the results came out as follows:—

(a) Valencia, taken in March,	$0\cdot0400 \times 10^{-12}$.
(b) Isle of Man, taken in April,	$0\cdot0386 \times 10^{-12}$.
(c) 65 miles W. of Valencia, June,	$0\cdot0314 \times 10^{-12}$.
(d) 1·5 miles S. of Crow Head, June,	$0\cdot0226 \times 10^{-12}$.
(e) 20 miles W. of Bantry Bay, June,	$0\cdot0393 \times 10^{-12}$.

These, with the exception of (d), are in close agreement; and I find it hard to believe that such a degree of uniformity could arise without a real basis for the results. The deficiency of (d) might originate in a loss of radium in the process of evaporation, the radium being in part left as a precipitate clinging to the evaporating dish. The higher results appear to be the more reliable; indeed, there is the possibility that, in a liquid so rich in sulphates, even these are not a full revelation. I do not regard this, however, as probable.

These results, of course, do not warrant the conclusion that mid-ocean sea-water is equally rich in radium. It might be that the acid-treatment is effective in bringing into solution suspended radioactive particles of coastal origin. Samples are, however, now reaching me through the kindness of friends in many parts of the world; and before long I shall be able to compare the above results with waters from various parts of the Ocean.

The bearing of the subject on many problems it would be premature to discuss. My object in publishing the few results given above is mainly to call attention to an insidious source of error in measurements of the kind. It will be evident also that measurements made on sea-salts must be unreliable; for there is no assurance that the sample used will contain its due share of the radium which would be carried down among the first constituents precipitated in the preparation of the salt.

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ON THE
SEPARATION AND QUANTITATIVE SPECTRA OF
CERIUM, LANTHANUM, AND YTTRIUM.

BY

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AND

A. G. G. LEONARD, A. R. C. S. I.,

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(PLATES XXI.-XXIII.)

[Authors alone are responsible for all opinions expressed in their Communications.]

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PHYSICS 311

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1.1. Kinematics

1.2. Dynamics

1.3. Energy

1.4. Angular momentum

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XXIII.

ON THE SEPARATION AND QUANTITATIVE SPECTRA OF
CERIUM, LANTHANUM, AND YTTRIUM.

By JAMES H. POLLOK, D.Sc., AND A. G. G. LEONARD, A.R.C.S.I.,
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[PLATES XXI.-XXIII.]

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PREPARATION OF THE PURE EARTHS.

TEN pounds weight of cerite was decomposed by fusion with its own weight of caustic soda in a large salamander crucible. The fusion was done in eight successive charges, and each charge took about one hour in an ordinary wind-furnace used for gold assays; after fusion the charge was perfectly liquid and poured well. This method of decomposing silicates of the rare earths on a large scale is preferable to fusion with the mixed carbonates of the alkalis, as much less flux is necessary, and consequently less chemicals in the subsequent decomposition, and the mixture does not froth so much in the crucible. The fusion was then ground, treated with excess of hydrochloric acid, the solutions decanted off, and the residue boiled with more hydrochloric acid by passing steam into it for some hours; the insoluble silica was then filtered off. On decomposing a small portion of the silica with hydrofluoric acid in the usual way, it was found to leave a residue of about 4 per cent. of its own weight. On dissolving this residue in strong hydrochloric acid, and photographing and examining its spectrum, it was found to consist principally of titanium and some of the cerite minerals that had not been completely separated, but nothing else. The hydrochloric acid solutions were mixed, diluted, and treated with sulphuretted hydrogen for the separation of a small quantity of lead and copper; they were then boiled and treated with excess of oxalic acid; and

the copious precipitate of the mixed oxalates of the rare earths filtered off, well washed, dried, and preserved for future treatment. The residual liquors were now rendered alkaline with ammonia, when a further precipitate came down, which, on spectroscopic examination, was found to consist of the rare earths mixed with much lime and magnesia. The alkaline precipitate was ignited, dissolved in the least possible quantity of hydrochloric acid and then precipitated by oxalic acid, and the precipitate filtered, washed, and dried. On examining photographs of the spark-spectra of the two oxalic acid precipitates, they were found to contain identically the same lines; so both oxalates were mixed. The residual liquors from this second oxalic acid precipitate contained all the lime and magnesia; but its spark-spectrum gave also many lines of the rare earths, showing that they were not completely precipitated; but as the quantity was comparatively small, and as there were no lines, other than those of lime and magnesia, that were not represented in the first two precipitates, the liquors were thrown out. The liquors from the alkaline oxalic acid precipitate on concentration and examination showed only the lines of magnesium, potassium, sodium, and traces of manganese and iron. We may therefore conclude that the earths are completely precipitated by oxalic acid in alkaline solution, but cannot be completely precipitated in an acid solution. The whole quantity of the mixed oxalates were now ignited in a muffle at a dull red heat, and yielded about 4 lb. weight of a light brown oxide, and a great number of experiments were made on small portions of these oxides to find the best and easiest method of separation, in every case photographs being taken of the spark-spectra of the precipitates and solutions, or of the successive fractions, and the lines in each photograph carefully compared. In all no less than thirty spectra were photographed; but the results may be briefly stated as follows:

PREPARATION OF PURE CERIA.

Preliminary experiments showed that the method of separating ceria by precipitating with excess of caustic soda, and then saturating the solution with chlorine, gave a sharp quantitative separation of ceria from all the other rare earths present, the

ceria being converted into the insoluble yellow dioxide and remaining suspended in the fluid, the oxides of lanthanum, didymium, and yttrium dissolving completely when the solution is absolutely saturated with chlorine. In operating on large quantities it is necessary to repeat the process three times. The whole quantity of the mixed oxides was dissolved in hydrochloric acid, treated with excess of caustic soda, and a steady stream of chlorine passed through the liquid for two days. The cerium was converted into dioxide and remained undissolved; all the other earths dissolved. After filtration and washing, the cerium dioxide was suspended in fresh caustic soda and again treated with chlorine, and the operation thereafter repeated a third time, when no more dissolved.

The dioxide after the third treatment was dissolved in hydrochloric acid, precipitated as oxalate, and ignited to oxide, and preserved for future experiments. The oxide was of a light reddish-brown colour; its solution in hydrochloric acid was quite free from absorption-bands, and, on sparking a concentrated solution, gave no trace of lanthanum, yttrium, or didymium lines. This preparation was used for the quantitative spectrum of cerium.

The solutions were boiled, then precipitated by oxalic acid, and the oxalates ignited, giving mixed oxides free from cerium; and these were used for the subsequent preparations. It was remarkable that the particular specimen of cerite operated on was not of the usual composition; for it contained over 50 per cent. of silica, and gave an almost equal quantity of oxalate of cerium, and of the mixed oxalates of the other rare earths. These latter consisted for the most part of lanthanum, with a large proportion of didymium, and a small proportion of yttrium. After a great number of preliminary experiments, in which the spectra of all the products were examined, the following method of preparing pure yttria and lanthana was adopted, but no efficient method for preparing neodymium and praseodymium free from lanthanum was discovered; and we did not get them in a sufficient state of purity to determine their quantitative spectra. Cerite of normal composition will not fuse with as little as its own weight of caustic soda, but is nevertheless completely decomposed, and easily soluble in hydrochloric acid, after treatment with this quantity of alkali.

PREPARATION OF PURE YTTRIA.

The preliminary experiments showed that, on fusing the mixed nitrates of lanthanum, didymium, and yttrium, and then dissolving in water, the whole of the yttria is contained in the insoluble or basic nitrates, the solutions being spectroscopically free from yttrium. There is also a marked concentration of didymium in the insoluble portion, as this portion gives much the most intense absorption-bands. The separation of the yttria can be readily followed by the presence or absence of the line λ 2817.1, just beyond gold line No. 20.

The whole of the oxides from which the ceria had been removed were dissolved in nitric acid, and evaporated down, then fused in a platinum basin until the oxides of nitrogen came off pretty freely, and the melt became stiff; but the temperature was never allowed to reach a red heat; on cooling, water was added, and the whole boiled up, and the insoluble basic nitrates filtered off. The filtrate was again boiled down, fused, and similarly treated, yielding two fractions. The solid or decomposed fraction, from the first treatment, was redissolved in nitric acid, evaporated to dryness, and fused with four times its weight of potassium nitrate, the latter being added to keep the mass in a fused state, facilitating the decomposition of the nitrates of yttrium and didymium, and retarding the decomposition of the lanthanum nitrate. On boiling the melt with water, and filtering off the basic nitrates, which amounted roughly to about one quarter of the whole quantity treated, they were found to contain all the yttrium; and this product was much richer in didymium than any of the other three fractions, as, with solutions of equal concentration, it gave much the most intense absorption-bands; but it still contained large quantities of lanthanum, and gave a strong spark-spectrum of that element, as well as the lines of the other two.

To remove the didymium and the remainder of the lanthanum, this fourth fraction was dissolved and treated with excess of potassium sulphate, a bag of crystals being hung in the beaker; after standing two or three days, the crystalline pink precipitate was filtered off, and found to be free from yttrium; but the solution still showed absorption-bands, so the bases were precipitated by

ammonia, filtered, washed, and redissolved in the least possible quantity of hydrochloric acid, a little water added, then a quantity of strong solution of potassium sulphate, a bag of crystals being suspended in the beaker as formerly; but the total volume of the solution was about one quarter of that present in the previous precipitation. After two days the precipitate was filtered off, and the solution found to be colourless, and almost free from absorption-bands. On precipitating with ammonia, washing, redissolving, precipitating with oxalic acid, filtering, washing, drying, and igniting, it gave an oxide of a pale buff colour; that, on sparking, gave a splendid spectrum of yttrium free from all lines of lanthanum or didymium, and containing only a trace of iron, the residuary lines of which can be seen in the ultra-violet end of the spectrum of the strong solutions of cerium and yttrium; but they disappeared in the dilution-spectra, and did not interfere with the determination of the quantitative spectra; but it is remarkable that even any iron should remain after so many precipitations with oxalic acid. This preparation was used for the quantitative spectrum of yttrium.

PREPARATION OF PURE LANTHANA.

The first fraction from the fusion of the nitrates—that is, that portion which had been twice fused without decomposition—was now further treated for the preparation of pure lanthana. The solution was nearly colourless, and gave no spark-spectrum of yttrium; and the lines of didymium shown by the spark-spectrum were very feeble; but when viewed through any depth, the solution gave quite strong absorption-bands. The oxides from this fraction were precipitated by ammonia, and weighed about 50 grams; they were dissolved in the least possible quantity of hydrochloric acid; then treated with one-half the quantity of sulphuric acid necessary to precipitate the whole. The solution gave no immediate precipitate in the cold; so an equal volume of alcohol was added, when a good precipitate came down; this was filtered off, washed with alcohol, dissolved in strong hydrochloric acid, precipitated by ammonia to get rid of the sulphuric acid present, then again dissolved in the least possible quantity of hydrochloric acid, diluted to about 500 c.c., then again treated

with half the quantity of sulphuric acid necessary for complete precipitation, and an equal bulk of alcohol added. On solution and precipitation by ammonia, about 10 grams of pure white hydrate of lanthanum were obtained, which gave a pure spectrum of lanthanum free from all lines of didymium; and the solution showed only very faint indications of absorption-bands. This preparation was used for the quantitative spectrum of lanthanum.

PREPARATION OF DIDYMIA.

As already mentioned, the didymium was concentrated in the fourth fraction of the fused nitrates, that is, that portion which was first to decompose in two separations. This fraction was dissolved, and the didymia precipitated by potassium sulphate for the preparation of pure yttrium. The precipitated basic sulphates were now fused with alkaline carbonates, boiled and filtered for the removal of the sulphuric acid, and then dissolved in hydrochloric acid.

The sulphates are not freely soluble in acid without this preliminary fusion with alkali, which is a great inconvenience in the use of this method of separation. The solution was now fractionally precipitated by sulphuric acid and alcohol, as in the case of lanthanum; but the precipitate was rejected, the alcohol distilled off, the didymium precipitated by ammonia, and the process repeated. This yielded about 8 grams of hydrate of a pink colour, which, on dissolving, gave a dark pink solution with very intense absorption-bands, and a strong spectrum showing the characteristic lines of neodymium; but the lines of lanthanum also showed strongly; and it was not possible to satisfactorily determine the quantitative spectrum of didymium, as its spectrum vanishes very rapidly on dilution, whereas that of lanthanum is very persistent.

METHOD OF TAKING THE SPECTRA.

The quantitative spectra were taken after the manner devised by Professor W. N. Hartley,¹ with the modifications described in our previous papers "On Quantitative Spectra,"² published in the Proceedings of this Society. In each case a weighed quantity of

¹ Proc. Roy. Soc., 1882, p. 81.

² Proc. Roy. Dub. Soc., 1907. Nos. 16, 17, and 18.

the oxide was dissolved in hydrochloric acid, and then diluted, so as to contain 10 per cent., 5 per cent., 1 per cent., .1 per cent., .01 per cent., and .001 per cent. of the element. These solutions were then successively sparked, using a Ruhmkorff coil, condenser, and self-induction coil for removal of air-lines, and photographs were taken of the spectra giving an exposure of 1 minute each. The photographs of all the dilutions of lanthanum are reproduced in Plate XXI.; but as the lines of the more dilute solutions do not show in the reproductions, only the spectra of the 10 per cent. and 1 per cent. solutions of cerium and yttrium are shown in Plates XXII. and XXIII. The most persistent lines are indicated by one, two, or three dots placed under them according to their persistency.

In the tables of wave-lengths, double lines, the wave-length of only one of which is given, are indicated by two dashes after the intensity; so 10'', the persistency of the lines, is indicated by Greek letters, thus:—

σ seen with a strong solution only.			
ϕ	" 1 %	"	not seen with 0.1 %
χ	" 0.1 %	"	" 0.01 %
ψ	" 0.01 %	"	" 0.001 %
ω	" 0.001 %	"	"

The photographs of spectra extend from λ 5890 to λ 2544.3 on Plates XXI. and XXII., and from λ 2825.6 to 2100 on Plate XXIII.; and they were taken by a one-prism quartz spectrograph by Hilger. A slow-motion tangent-screw was attached to the slit to permit of its rotation, so as to bring the slit absolutely perpendicular to the edge of the prism, and then clamp it there. This attachment was found of great advantage in practical work, and should be added to all spectrographs.

The measurements were made with a micrometer, also by Hilger; but a movable sub-stage, controlled by a slow-motion screw, was fitted to it, to enable the micrometer to be set to any particular reading. The plate was clamped on to the stage, and then any line could be brought exactly to position between the cross-wires of the microscope. This is the greatest possible convenience in conjunction with the use of gold electrodes in the measurement of spectra, as it greatly facilitates and expedites the reduction of the measure-

ments to wave-lengths by use of a curve. In the present set of measurements the micrometer was set at 280·0; and the gold-line, No. 9, brought into exact coincidence with the cross-wires, this being the reading corresponding to the wave-length of the line λ 4792·8 on the curve. The micrometer was then screwed back to the edge of the plate, and the measurements proceeded with. It will be noted that only in one case did the micrometer return exactly to 280·0 for line No. 9; but the instrument was not perfect. With a quartz spectrograph all measurements on the less refrangible side of gold-line No. 9 are of little value, as there is not sufficient dispersion in this region of the spectrum.

CERIUM.

Plates XXII. and XXIII., spectra 3 and 4, show the spectra of solutions of cerium chloride with 10 per cent. and 1 per cent. of cerium respectively. There are a great number of lines in the spectrum of cerium; but they are not well marked, and vanish very rapidly on dilution. Those lines marked χ , corresponding to 1 per cent. of Ce, are scarcely visible on the negative, and could not possibly be seen in a reproduction; but they are the easiest lines by which to identify the presence of cerium, and they stand out fairly strongly with a 1 per cent. solution.

QUANTITATIVE SPECTRUM OF CERIUM CHLORIDE.

Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.	Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.
249·6	5511·2	8 χ	289·9	4606·5	2 ϕ
251·1	5472·8	6 ϕ	290·7	4594·1	4 ϕ
255·3	5353·3	10 ϕ	291·9	4572·5	10 ϕ
258·4	5274·3	10 ϕ	292·6	4560·5	4 ϕ
261·9	5187·8	6 ϕ	293·9	4539·9	4 ϕ
266·5	5079·5	6 χ	294·5	4527·5	10" χ
279·9	4792·8	Au No. 9	297·0	4488·4	Au No. 10
284·0	4714·1	8 ϕ	298·0	4471·4	6 ϕ
288·7	4628·3	5 ϕ	298·6	4460·4	8 ϕ

QUANTITATIVE SPECTRUM OF CERIUM CHLORIDE—*continued.*

Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.	Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.
299.5	4444.5	4" ϕ	422.0	3234.4	1" ϕ
300.7	4428.1	3" ϕ	424.3	3219.1	1" ϕ
301.3	4419.0	6 ϕ	427.2	3201.9	1" ϕ
301.9	4410.8	2 ϕ	428.3	3195.0	1" ϕ
303.0	4391.8	5 ϕ	432.3	3169.4	1" ϕ
303.8	4382.3	5 ϕ	436.7	3144.1	2" ϕ
304.8	4064.8	4 ϕ	440.7	3122.9	Au No. 17
305.6	4352.9	3 ϕ	453.0	3056.7	2" χ
308.0	4315.4	Au No. 11	458.2	3029.3	Au No. 18
309.5	4296.9	8 ϕ	482.2	2913.6	Au No. 19
310.0	4285.5	3 ϕ	502.2	2825.6	Au No. 20
311.3	4270.9	3" ϕ	516.6	2768.5	1 ϕ
317.5	4181.3	3 χ	521.7	2748.3	Au No. 21
318.8	4165.7	10 χ	541.4	2676.1	Au No. 22
326.9	4065.2	Au No. 12	548.6	2651.1	1 ϕ
337.3	3940.5	3" χ	549.1	2649.5	1 ϕ
341.3	3898.0	Au No. 13	551.4	2641.6	Au No. 23
358.0	3730.1	1" ϕ	554.5	2635.3	1 ϕ
359.0	3720.0	1" ϕ	562.9	2603.7	3 χ
360.0	3709.5	3" ϕ	567.2	2590.2	Au No. 24
373.5	3586.7	Au No. 14	571.6	2578.4	1 ϕ
399.6	3383.0	Au No. 15	580.5	2548.9	1 ϕ
414.6	3280.8	Au No. 16	582.0	2544.3	Au No. 25
420.3	3243.6	1" ϕ			

LANTHANUM.

Plate XXI., spectra 1 to 6, shows the gradual extinction of the lines of lanthanum on dilution; and Plates XXII. and XXIII., spectra 5 and 6, show the spectra of lanthanum chloride in solutions containing respectively 10 per cent. and 1 per cent. of the element. Lanthanum has a strong characteristic spectrum, of

great persistency; and the lines marked χ and ψ show well in the original negatives in those dilutions.

QUANTITATIVE SPECTRUM OF LANTHANUM CHLORIDE.

Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.	Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.
247.5	5588.6	6 χ	341.1	3898.0	Au No. 13
251.5	5455.4	8 χ	351.6	3791.0	50 ϕ
254.6	5377.3	8'' ϕ	354.7	3759.2	20 ϕ
273.8	4921.1	10'' χ	373.3	3586.7	Au No. 14
274.7	4901.1	10 χ	382.0	3517.3	50 ϕ
280.0	4792.8	Au No. 9	399.4	3383.0	Au No. 15
282.6	4743.3	8 ϕ	405.0	3344.7	8 ϕ
285.2	4692.7	8 ϕ	406.0	3337.6	15 ϕ
286.8	4663.9	4 ϕ	411.0	3718.0	—
287.3	4655.7	8 ϕ	432.0	3171.8	20 ψ
294.8	4522.6	8 χ	501.9	2825.6	Au No. 20
296.9	4488.4	Au No. 10	506.1	2808.4	3 χ
300.6	4430.1	8 ϕ	535.6	2695.6	1 ϕ
306.9	4333.9	15'' ϕ	538.5	2685.1	1 ϕ
308.1	4315.4	Au No. 11	548.1	2651.8	8 ϕ
309.5	4296.2	8 ϕ	560.5	2610.5	5 χ
310.1	4287.1	20 ϕ	566.9	2590.2	Au No. 24
311.4	4269.7	10 ϕ	364.2	2641.6	Au No. 23
311.8	4263.7	8 ϕ	379.9	2596.2	1 ϕ
313.5	4238.5	10 ϕ	392.8	2560.5	1 ϕ
316.7	4196.7	10 ϕ	408.5	2519.3	2 ϕ
322.1	4123.4	30 ϕ	421.2	2487.6	1 ϕ
325.8	4077.5	15 ϕ	425.7	2476.8	7 χ
326.7	4065.2	Au No. 12	446.3	2428.1	Au No. 30
329.5	4031.8	20 ϕ	459.0	2399.7	1 ϕ
333.2	3988.7	30 χ	468.3	2379.5	10 ψ
336.6	3949.3	50 ψ	509.0	2297.9	7 χ

YTTRIUM.

Plates XXII. and XXIII., spectra 1 and 2, show the spectra of solutions of yttrium chloride containing respectively 10 per cent. and 1 per cent. of the element. Yttrium gives a strong characteristic spectrum, of great persistency; and the lines marked χ and ψ stand out well in those dilutions.

QUANTITATIVE SPECTRUM OF YTTRIUM CHLORIDE.

Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.	Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.
244.7	5648.7	5 ϕ	307.9	4315.4	Au No. 11
247.5	5582.1	5 ϕ	308.5	4309.8	20 ϕ
248.6	5544.8	5 ϕ	317.9	4177.7	50 ψ
250.3	5497.6	5 ϕ	320.6	4143.0	7 ϕ
251.4	5466.7	6 ϕ	321.6	4128.5	7 ϕ
253.7	5403.0	4 ϕ	323.8	4102.5	6 ϕ
261.2	5205.9	6 ϕ	326.8	4065.2	Au No. 12
266.1	5087.6	5 χ	333.6	3982.7	20 ϕ
274.6	4900.3	6 χ	341.2	3898.0	Au No. 13
275.3	4883.9	6 χ	347.3	3833.0	20 ϕ
276.8	4855.1	6 ϕ	351.6	3788.8	30 ϕ
279.9	4792.8	Au No. 9	353.1	3774.5	100 χ
286.1	4675.0	4 ϕ	360.0	3710.4	100 χ
287.9	4643.8	4 ϕ	364.7	3664.8	20 ϕ
294.5	4527.4	3 ϕ	370.7	3611.2	30 χ
296.9	4488.4	Au No. 10	371.8	3600.9	50 χ
301.0	4422.8	10 ϕ	373.6	3586.7	Au No. 14
302.5	4402.5	Yb ?	378.1	3549.2	20 ϕ
304.0	4375.1	100'' ψ	384.6	3496.2	10 ϕ

QUANTITATIVE SPECTRUM OF YTTRIUM CHLORIDE—*continued.*

Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.	Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.
399·6	3383·0	Au No. 15	482·1	2913·6	Au No. 19
407·6	3328·1	20 ϕ	502·3	2825·6	Au No. 20
414·6	3280·8	Au No. 16	504·4	2817·1	30 χ
420·6	3242·5	20 ψ	521·8	2748·3	Au No. 21
424·8	3216·8	10 χ			
427·5	3200·4	8 ϕ	432·3	2460·7	4 ϕ
428·2	3195·8	8 ϕ	446·3	2428·1	Au No. 30
431·9	3173·4	5 ϕ	448·9	2422·3	8 χ
440·6	3122·9	Au No. 17	452·2	2414·8	15 χ
458·2	3029·3	Au No. 18	453·0	2413·2	Au No. 31
475·1	2946·1	20 χ			

[DIDYMIUM.]

DIDYMIUM.

A photograph was taken with the solution rich in didymium, but still containing some lanthanum, and giving a strong spectrum of the latter element. The slit was then lengthened, and a photograph of the spectrum of pure lanthanum superimposed on the first. The long lines of the second spectrum thus cancelled all the lanthanum lines in the first spectrum, leaving the didymium lines as short lines between.

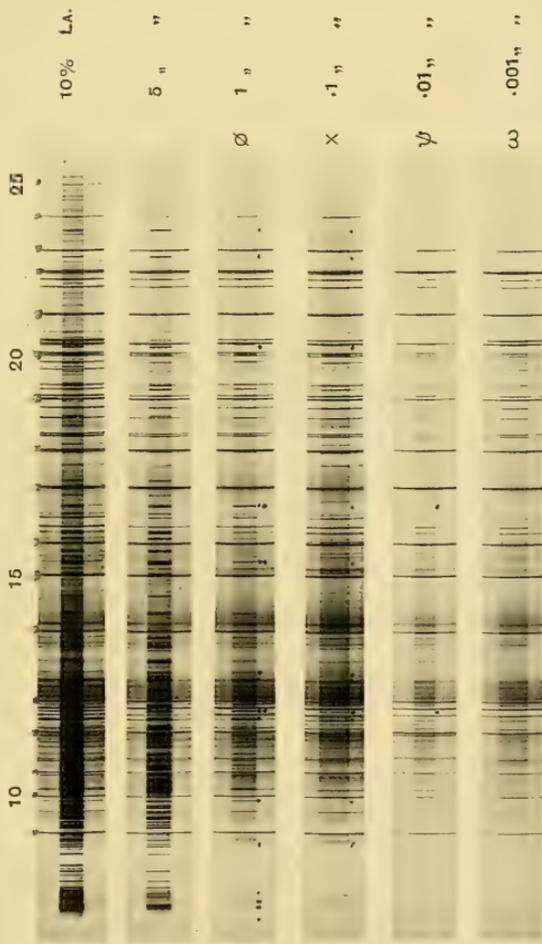
The following are the measurements of the most characteristic lines, and those marked with an asterisk appeared to be the most persistent :—

SOME PERSISTENT LINES OF DIDYMIUM CHLORIDE.

Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.
279·9	4792·8	Au No. 9
293·7	4542·8	5
298·1	4463·2	9
308·8	4303·8	10"
317·9	4177·5	10"
399·9	3383·0	Au No. 15
475·1	2946·8	3*
485·3	2899·9	3*
490·6	2876·1	3
502·4	2825·6	Au No. 20

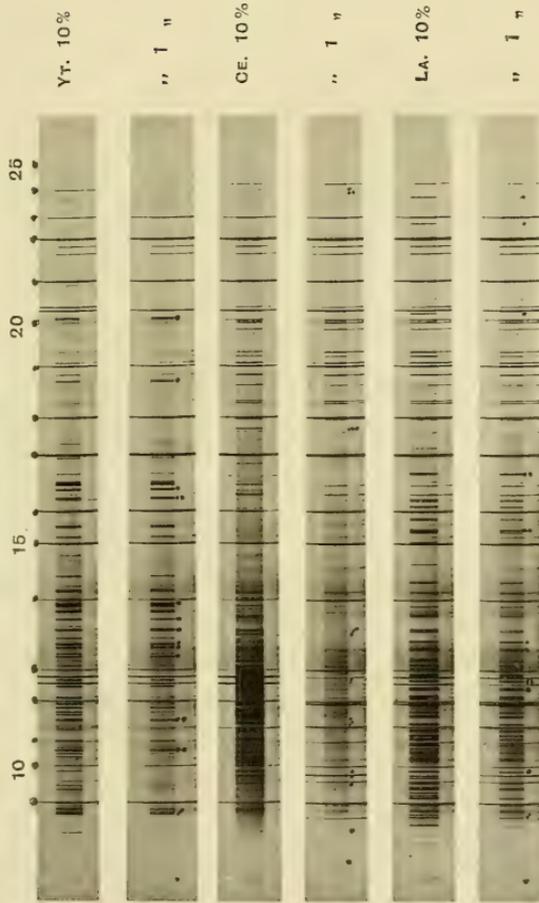
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QUANTITATIVE SPECTRUM OF LANTHANUM CHLORIDE.



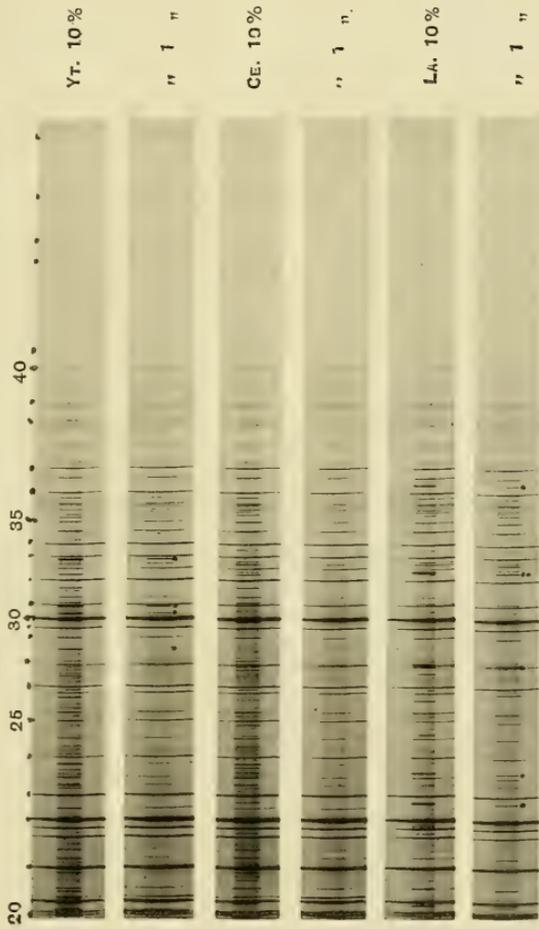
GOLD ELECTRODES.

QUANTITATIVE SPECTRA OF YTTRIUM, GERIUM,
AND LANTHANUM.



GOLD ELECTRODES.

QUANTITATIVE SPECTRA OF YTTRIUM, CERIUM,
AND LANTHANUM.



GOLD ELECTRODES.

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ON THE
QUANTITATIVE SPECTRA OF MOLYBDENUM,
TUNGSTEN, THORIUM, AND ZIRCONIUM.

BY

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(PLATE XXIV.)

[*Authors alone are responsible for all opinions expressed in their Communications.*]

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DIDYMIUM.

A photograph was taken with the solution rich in didymium, but still containing some lanthanum, and giving a strong spectrum of the latter element. The slit was then lengthened, and a photograph of the spectrum of pure lanthanum superimposed on the first. The long lines of the second spectrum thus cancelled all the lanthanum lines in the first spectrum, leaving the didymium lines as short lines between.

The following are the measurements of the most characteristic lines, and those marked with an asterisk appeared to be the most persistent :—

SOME PERSISTENT LINES OF DIDYMIUM CHLORIDE.

Linear Measurement, $\frac{1}{100}$ inch.	Wave-length.	Intensity and Persistency.
279·9	4792·8	Au No. 9
293·7	4542·8	5
298·1	4463·2	9
308·8	4303·8	10"
317·9	4177·5	10"
399·9	3383·0	Au No. 15
475·1	2946·8	3*
485·3	2899·9	3*
490·6	2876·1	3
502·4	2825·6	Au No. 20

CHEMICAL LABORATORY,
ROYAL COLLEGE OF SCIENCE,
DUBLIN.

XXIV.

ON THE QUANTITATIVE SPECTRA OF MOLYBDENUM,
TUNGSTEN, THORIUM, AND ZIRCONIUM.

By A. G. G. LEONARD, A.R.C.S.I.,
Royal College of Science, Dublin.

[PLATE XXIV.]

[Read, DECEMBER 17; Received for Publication, DECEMBER 20, 1907; Published,
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INTRODUCTION.

THE quantitative spark-spectra described in this paper have been investigated according to the method devised by Prof. W. N. Hartley,¹ certain modifications having been introduced in order to make the results readily comparable with previous work on the same subject.²

The object of the work is to facilitate the use of the spectro-scope for analytical purposes by determining the lines which characterize the spark-spectra of the elements when present in solution in small quantities, as without a knowledge of these lines the elements present are not easily identified.

The photographs were taken on a single prism quartz instrument made by Adam Hilger. The instrument when focussed for the less refrangible rays of the spectrum photographed from λ 5500 to λ 2500. A Ruhmkorff's coil, with a condenser and Hemsalech self-induction coil in circuit, was employed to obtain the spark. The plates were Cadett's Royal Standard; and these were found to give excellent results with one minute's exposure and subsequent development with hydroquinone. Gold electrodes

¹ Phil. Trans. Roy. Soc., vol. clxxv., 1884; Part I., pp. 49-62; Part II., pp. 325-342.

² Proc. Roy. Dublin Soc., vol. xi., 1907, pp. 184, 217, 229.

were employed throughout, the numbered lines from 9 to 25 serving as a ready means of identifying intermediate lines and of checking their measurements. In order to trace the gradual extinction of the lines, a solution was prepared containing 1 per cent. of the element; this was then diluted to contain 0.1 per cent., 0.01 per cent., and 0.001 per cent. With the last dilution, very few lines appear, and in some cases none at all are seen. The last letters of the Greek alphabet have been used as before to designate the relative persistencies of the lines. Thus:—

τ , seen with the metal, not in solutions.

σ , seen with strong solutions, not in 1 % solutions.

ϕ , " " 1 % " " " 0.1 % "

χ , " " 0.1 % " " " 0.01 % "

ψ , " " 0.01 % " " " 0.001 % "

ω , " " 0.001 % "

On examining all the quantitative spark-spectra which have been so far investigated, it is at once evident that the most persistent lines of the metals tend towards the more refrangible part of the spectrum. At first sight this might appear to be due to the greater sensitiveness of the photographic plate to the ultra-violet rays. On further examination of the plates, however, it is seen in general that, with 1 per cent. solutions, lines appear in the visible rays which are quite as strong as those in the ultra-violet; but on dilution they are much more rapidly extinguished. It seems, then, that the occurrence of the residuary lines at the more refrangible end of the spectrum cannot be put down to the greater sensitiveness of the plate for such rays, but must rather be attributed to these lines representing the wave-lengths of those vibrations which are most easily excited within the molecule. Furthermore, this affords an explanation as to why the ultra-violet rays are more chemically active than those of less refrangibility; for they can more readily set the atoms or molecules into vibration, and so induce chemical action.

MOLYBDENUM.

The spectrum of ammonium molybdate was photographed in both acid and alkaline solutions; the results so produced were identical.

The spectrum of molybdenum presents a great number of well-defined lines which are very evenly spaced, and extend throughout the plate; furthermore, the metal is a good conductor of electricity, does not oxidize readily when sparked in air, and can be obtained in a state of purity, so that it would be an excellent substance to employ as electrodes for calibrating a spectroscope or for the accurate determination of absorption-bands.

Spectra 1 and 2 give the lines of the metal with the gold lines long and short respectively. No. 3 gives the lines of a strong solution long and the metal short; and no lines are given by the metal which are not also given by the solution, so that the sample of molybdenum employed was quite pure. Spectra 5, 6, 7, 8 give the lines developed with solutions containing 1 per cent., 0·1 per cent., 0·01 per cent., and 0·001 per cent. of molybdenum; and there are quite a number of persistent lines.

QUANTITATIVE SPECTRUM OF AMMONIUM MOLYBDATE.

Scale Measurement.	Wave-length.	Intensity and Persistence.	Scale Measurement.	Wave-length.	Intensity and Persistence.
247·43	5570·7	10 σ	345·00	3864·2	10 ψ
248·71	5533·3	10 σ	351·41	3798·4	10 ψ
249·62	5506·7	10 σ	362·42	3688·4	10 χ
	—9—		370·53	3614·4	4 σ
281·65	4760·4	6 ϕ		—14—	
283·16	4731·6	4 ϕ	381·96	3524·7	6 χ
284·49	4707·4	4 ϕ	397·55	3402·9	2 χ
	—10—			—15-16—	
303·85	4381·8	4 χ	419·62	3254·8	4 χ
	—11—			3253·9	4 χ
317·55	4244·9	4 ϕ	421·42	3244·6	1 σ
	—12—		422·00	3240·8	4 χ
341·40	3903·1	10 ψ	422·47	3237·96	2 χ
	—13—		424·50	3223·1	2 σ

QUANTITATIVE SPECTRUM OF AMMONIUM MOLYBDATE—*continued.*

Scale Measurement.	Wave-length.	Intensity and Persistence.	Scale Measurement.	Wave-length.	Intensity and Persistence.
427·00	3209·0	2 σ	492·29	2871·6	6 ψ
	3200·4	} 4 χ	493·46	2866·8	5 σ
429·37	3196·0		494·08	2863·9	4 ψ
	3192·3	} 4 χ	496·50	2853·3	6 χ
433·29	3176·4		497·71	2848·4	8 ψ
	3175·2	} 4 χ		—20—	
	3173·0		505·31	2816·3	8 ψ
435·35	3159·4	2 σ	507·40	2807·8	6 ϕ
436·47	3155·8	4 σ	513·03	2785·1	4 ψ
437·55	3145·9	2 σ	514·26	2780·1	6 σ
438·36	3141·9	} 4 σ	515·46	2775·5	6 ω
	3141·6				—21—
438·92	3139·0	4 σ	523·00	2746·4	5 ϕ
439·86	3132·9	} 4 ϕ	530·68	2717·4	4 ϕ
	3132·7		539·83	2684·2	4 ψ
	—17—		540·10	2681·5	4 ψ
443·67	3111·0	4 ϕ		—22—	
447·27	3092·2	4 ϕ	543·00	2673·4	4 ψ
448·13	3087·7	6 ϕ	546·54	2660·6	4 ψ
449·93	3077·7	6 ϕ	548·70	2653·4	4 ϕ
	—18—		550·66	2646·6	4 χ
472·34	2963·9	4 ϕ	551·28	2644·4	4 χ
480·80	2923·5	4 ψ		—23—	
	—19—		553·00	2638·9	4 χ
483·28	2912·0	4 ϕ	563·83	2602·9	5 ϕ
485·21	2903·1	6 ϕ	564·87	2600·3	5 ϕ
487·18	2894·5	4 χ	566·73	2595·5	4 ϕ
488·00	2888·3	4 χ		—24-25—	
490·62	2879·1	6 ϕ			

TUNGSTEN.

Spectrum 1 shows the lines yielded by a strong solution of sodium tungstate; spectra 2, 3, 4, 5 give, as before, the effect of dilution. The lines of this element are not very persistent, few remaining with the .01 per cent. solution.

QUANTITATIVE SPECTRUM OF SODIUM TUNGSTATE.

Scale Measurement.	Wave-length.	Intensity and Persistency.	Scale Measurement.	Wave-length.	Intensity and Persistency.
	— 9 —		460.71	3017.6	2 ϕ
285.99	4680.8	6 ϕ	461.41	3014.3	1 σ
287.06	4660.0	6 ϕ	468.31	2980.0	2 ϕ
289.68	4610.1	2 σ	468.90	2977.3	2 ϕ
	— 10—11 —		475.18	2947.1	3 χ
309.21	4302.3	6 ϕ	475.66	2944.5	3 χ
309.72	4294.8	8 χ	477.72	2935.1	3 ϕ
311.51	4269.5	6 ϕ	480.23	2923.2	1 σ
326.25	4074.5	6 χ		— 19 —	
	4070.0	6 χ	486.10	2896.15	2 ϕ
	— 12 —		489.97	2879.5	2 \downarrow
331.66	4008.9	8 χ	493.03	2866.4	2 ϕ
	— 13 —		497.16	2848.2	1 ϕ
352.76	3780.9	4 ϕ	501.16	2831.5	2 ψ
353.85	3768.6	4 ϕ		— 20 —	
355.93	3750.9	2 ϕ	515.25	2774.6	3 ϕ
370.24	3617.7	6 ϕ	517.77	2764.4	4 χ
	— 14—16 —			— 21 —	
425.09	3215.7	4 χ	526.93	2729.69	4 ϕ
	— 17 —		528.26	2724.2	4 χ
454.18	3051.4	4 χ	532.58	2709.7	4 ϕ
454.45	3049.9	3 χ	534.32	2702.2	4 ϕ
	— 18 —		535.57	2697.8	4 χ
459.27	3024.5	4 ϕ	536.53	2694.5	2 ϕ

QUANTITATIVE SPECTRUM OF SODIUM TUNGSTATE—*continued.*

Scale Measurement.	Wave-length.	Intensity and Persistency.	Scale Measurement.	Wave-length.	Intensity and Persistency.
540·15	2679·8	4 χ	562·47	2608·5	1 χ
	—22—		563·47	2603·1	4 χ
545·07	2664·4	4 ϕ		—24—	
546·86	2658·1	7 χ	570·77	2581·2	4 ϕ
547·23	2656·6	2 χ	573·39	2572·3	4 ψ
547·87	2653·6	3 χ	576·15	2563·2	4 ψ
550·21	2647·8	4 χ	578·77	2555·1	4 ψ
	—23—		580·03	2551·5	3 ϕ
554·30	2632·9	2 ϕ		—25—	
558·19	2620·2	4 ϕ	586·93	2531·1	3 χ
560·24	2615·5	4 χ	590·13	2522·1	4 σ

THORIUM.

Thorium nitrate was employed for these solutions. This element gives a well-defined spectrum in strong solutions; but the lines are rapidly extinguished on dilution. Two of the last lines to disappear, $\lambda\lambda$ 4391·3 and 4382·1, are situated in the visible rays between gold lines 10 and 11. A number of lines were measured between gold 18 and 20 which could not at first be identified, but were afterwards found recorded in the arc-spectrum of Exner and Haschek.

QUANTITATIVE SPECTRUM OF THORIUM NITRATE.

Scale Measurement.	Wave-length.	Intensity and Persistency.	Scale Measurement.	Wave-length.	Intensity and Persistency.
	—9-10—		322·91	4116·9	5 χ
303·30	4391·3	8 ψ		—12—	
303·80	4382·1	8 ψ	330·80	4019·3	10 χ
	—11—			—13—	

QUANTITATIVE SPECTRUM OF THORIUM NITRATE—*continued.*

Scale Measurement.	Wave-length.	Intensity and Persistence.	Scale Measurement.	Wave-length.	Intensity and Persistence.
356·84	3741·4	6 χ	480·56	2923·1	1 ϕ
358·89	3711·5	3 χ		—19—	
	—14—		485·51	2899·0	6 χ
379·70	3538·9	10 χ	486·08	2895·3	2 ϕ
388·38	3470·1	5 χ	492·03	2870·5	3 ψ
395·14	3417·1	1 χ	493·13	2864·8	1 ϕ
397·44	3402·8	4 χ	494·12	2861·5	3 χ
	—15—		498·43	2842·9	2 ϕ
404·15	3354·8	8 σ	500·72	2832·5	4 χ
404·64	3351·4	4 σ		—20—	
407·10	3334·7	4 σ	515·90	2771·6	3 χ
408·47	3325·3	4 σ	516·55	2769·0	4 χ
412·01	3300·6	12 χ	517·75	2764·8	2 χ
413·32	3290·7	10 ψ	518·80	2760·5	2 χ
	—16—		520·00	2757·3	1 χ
429·94	3188·4	5 χ	520·86	2752·3	3 χ
432·16	3174·4	1 χ		—21—	
437·81	3141·9	2 σ	522·12	2747·3	3 χ
438·37	3139·4	4 σ	523·18	2742·4	2 χ
	—17—		526·90	2729·4	3 χ
443·82	3108·4	5 χ	528·85	2722·5	2 χ
448·96	3079·0	6 χ	530·36	2716·4	2 χ
449·15	3078·8	5 χ	530·90	2715·2	1 χ
457·72	3034·2	3 χ	532·56	2708·4	4 χ
	—18—		533·75	2704·1	3 χ
462·80	3008·6	2 χ	536·07	2695·3	2 ϕ
468·70	2978·8	8 χ	536·87	2692·5	3 ϕ
471·52	2965·6	1 χ	538·66	2687·0	6 ϕ
476·05	2943·0	3 ϕ	539·13	2685·0	1 ϕ
479·91	2925·2	3 ϕ		—22—	

QUANTITATIVE SPECTRUM OF THORIUM NITRATE—*continued.*

Scale Measurement.	Wave-length.	Intensity and Persistence.	Scale Measurement.	Wave-length.	Intensity and Persistence.
548·30	2652·2	1 σ	569·28	2583·5	4 χ
	—23—		573·09	2571·7	5 χ
556·51	2625·9	2 χ	575·32	2564·5	6 ϕ
559·00	2619·0	2 χ	578·51	2555·3	4 ψ
563·86	2601·0	1 χ		2554·8	4 ψ
564·95	2597·2	2 χ	580·41	2549·7	4 ψ
	—24—			—25—	

ZIRCONIUM.

A quantity of zirconium hydrate was dissolved in hydrochloric acid, and the resulting chloride solution employed. The two most persistent lines occur at $\lambda\lambda$ 3304·8 and 3392·4.

QUANTITATIVE SPECTRUM OF ZIRCONIUM CHLORIDE.

Scale Measurement.	Wave-length.	Intensity and Persistence.	Scale Measurement.	Wave-length.	Intensity and Persistence.
	—9—		304·40	4371·1	10 ϕ
281·03	4772·1	10 ϕ	305·12	4359·9	10 ϕ
282·73	4739·6	10 ϕ		—11—	
284·33	4710·3	10 ϕ	315·65	4209·2	20 ϕ
285·54	4688·0	10 ϕ	319·26	4161·4	10 ϕ
291·77	4574·8	4 ϕ	320·22	4149·4	20 ϕ
293·93	4535·9	5 ϕ		—12—	
296·48	4497·1	10 ϕ	329·75	4029·8	4 ϕ
	—10—		330·30	4025·1	3 ϕ
299·78	4443·3	10 ϕ	332·35	3999·2	15 ϕ
303·80	4380·0	12 ϕ	333·08	3991·3	15 ϕ

QUANTITATIVE SPECTRUM OF ZIRCONIUM CHLORIDE—*continued.*

Scale Measurement.	Wave-length.	Intensity and Persistence.	Scale Measurement.	Wave-length.	Intensity and Persistence.
335·85	3958·3	15 χ	399·18	3388	5 ψ
	—13—			—15—	
347·07	3837·0	12 χ	403·66	3356·3	4 ϕ
354·08	3767·0	10 ϕ	405·97	3340·6	6 ϕ
355·53	3751·8	12 ϕ	406·86	3334·4	4 χ
356·17	3746·2	10 ϕ	410·90	3306·4	6 ϕ
357·72	3731·5	10 ϕ	414·07	3284·8	4 ϕ
360·05	3709·5	10 ϕ		—16—	
361·13	3698·4	10 χ	415·17	3279·4	5 ϕ
363·57	3679·1	6 χ	415·93	3273·2	8 χ
363·82	3675·0	10 χ	420·88	3241·2	4 ϕ
372·08	3601·3	4 ψ	422·59	3234·2	2 ϕ
	—14—		425·24	3214·3	4 χ
374·68	3578·4	3 ϕ	430·45	3182·9	5 χ
375·03	3577·1	10 ϕ	433·28	3166·1	3 ψ
375·57	3572·6	12 ψ	438·04	3138·8	4 ψ
377·38	3556·7	15 ϕ	438·92	3133·6	4 ϕ
379·01	3542·9	12 ϕ	439·54	3129·9	4 ϕ
383·57	3505·6	10 χ		—17—	
384·50	3498·0	8 χ	443·68	3106·7	4 χ
384·88	3496·3	20 χ	453·25	3054·9	4 ψ
386·72	3481·3	10 χ	456·78	3036·6	3 ψ
388·96	3463·2	12 ϕ		—18—	
392·09	3440·5	2 χ	459·97	3020·5	2 χ
392·50	3438·4	15 ϕ	463·29	3003·9	2 χ
393·22	3430·7	10 ϕ	479·10	2927·1	4 ψ
394·83	3419·2	3 ψ		—19—	
396·11	3410·4	8 ψ	491·88	2869·8	3 χ
398·28	3394·8	2 ω	498·69	2844·7	4 ψ
398·73	3392·4	15 ω		—20—	

QUANTITATIVE SPECTRUM OF ZIRCONIUM CHLORIDE—*continued.*

Scale Measurement.	Wave-length.	Intensity and Persistence.	Scale Measurement.	Wave-length.	Intensity and Persistence.
503·91	2818·8	3 ϕ	538·39	2686·4	4 ϕ
505·77	2811·0	3 ϕ	539·59	2682·3	5 ϕ
514·93	2774·3	3 ϕ	540·58	2678·8	5 ϕ
516·26	2768·9	3 ϕ		—22—	
518·86	2758·9	3 ϕ	544·68	2664·4	5 χ
520·61	2752·3	3 ϕ	546·97	2656·6	4 χ
	—21—		550·65	2643·9	5 ϕ
522·21	2745·9	3 ϕ		—23—	
523·07	2742·7	4 ϕ	554·50	2631·0	4 ψ
525·18	2735·0	5 ϕ	555·27	2628·3	4 χ
525·65	2732·8	3 ϕ	557·65	2620·7	8 χ
527·36	2726·6	4 ϕ	557·95	2622·8	1 χ
528·41	2722·7	4 ϕ		—24—	
529·07	2720·1	2 ϕ	573·03	2571·5	8 ψ
530·30	2715·8	3 ϕ	573·78	2569·0	7 ψ
530·69	2714·3	3 ϕ	579·84	2550·9	4 ϕ
531·41	2711·6	3 ϕ		—25—	
532·11	2709·1	3 ϕ	582·67	2542·2	4 χ
534·60	2700·3	4 ϕ	584·57	2539·7	1 χ
537·21	2690·6	4 ϕ	586·03	2532·6	3 ϕ

1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100.

10 15 20 25

Mo. AND Au.

Ø 1.0% Mo.

STRONG SOL^N. W.

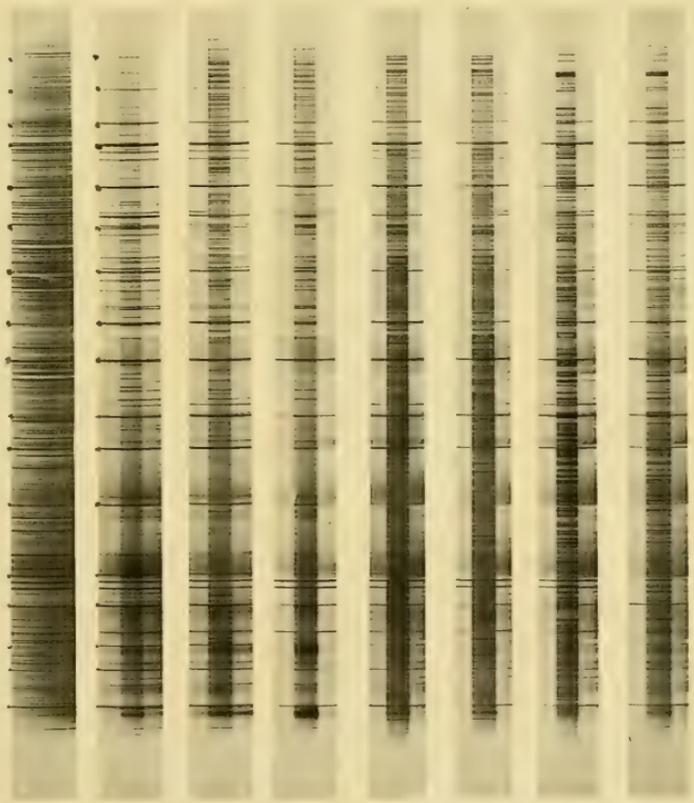
Ø 1.0% W.

STRONG SOL^N. Th.

Ø 1.0% Th.

STRONG SOL^N. Zr.

Ø 1.0% Zr.



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THE
SCIENTIFIC PROCEEDINGS
OF THE
ROYAL DUBLIN SOCIETY.

Vol. XI. (N. S.), No. 25.

FEBRUARY, 1908.

ON A SIMPLE FORM OF APPARATUS FOR
OBSERVING THE RATE OF ABSORPTION OF
OXYGEN BY POLLUTED WATERS, AND BY
OTHER FERMENTING LIQUIDS.

BY

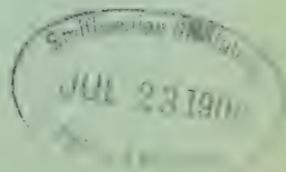
W. E. ADENEY, D.Sc., F.I.C.,

CURATOR AND EXAMINER IN CHEMISTRY IN THE ROYAL UNIVERSITY, DUBLIN.

[Authors alone are responsible for all opinions expressed in their Communications.]

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1908.

Price Sixpence.



QUANTITATIVE SPECTRUM OF ZIRCONIUM CHLORIDE—*continued.*

| Scale Measurement. | Wave-length. | Intensity and Persistence. | Scale Measurement. | Wave-length. | Intensity and Persistence. |
|--------------------|--------------|----------------------------|--------------------|--------------|----------------------------|
| 503·91 | 2818·8 | 3 ϕ | 538·39 | 2686·4 | 4 ϕ |
| 505·77 | 2811·0 | 3 ϕ | 539·59 | 2682·3 | 5 ϕ |
| 514·93 | 2774·3 | 3 ϕ | 540·58 | 2678·8 | 5 ϕ |
| 516·26 | 2768·9 | 3 ϕ | | —22— | |
| 518·86 | 2758·9 | 3 ϕ | 544·68 | 2664·4 | 5 χ |
| 520·61 | 2752·3 | 3 ϕ | 546·97 | 2656·6 | 4 χ |
| | —21— | | 550·65 | 2643·9 | 5 ϕ |
| 522·21 | 2745·9 | 3 ϕ | | —23— | |
| 523·07 | 2742·7 | 4 ϕ | 554·50 | 2631·0 | 4 ψ |
| 525·18 | 2735·0 | 5 ϕ | 555·27 | 2628·3 | 4 χ |
| 525·65 | 2732·8 | 3 ϕ | 557·65 | 2620·7 | 8 χ |
| 527·36 | 2726·6 | 4 ϕ | 557·95 | 2622·8 | 1 χ |
| 528·41 | 2722·7 | 4 ϕ | | —24— | |
| 529·07 | 2720·1 | 2 ϕ | 573·03 | 2571·5 | 8 ψ |
| 530·30 | 2715·8 | 3 ϕ | 573·78 | 2569·0 | ψ |
| 530·69 | 2714·3 | 3 ϕ | 579·84 | 2550·9 | 4 ϕ |
| 531·41 | 2711·6 | 3 ϕ | | —25— | |
| 532·11 | 2709·1 | 3 ϕ | 582·67 | 2542·2 | 4 χ |
| 534·60 | 2700·3 | 4 ϕ | 584·57 | 2539·7 | 1 χ |
| 537·21 | 2690·6 | 4 ϕ | 586·03 | 2532·6 | 3 ϕ |

XXV.

ON A SIMPLE FORM OF APPARATUS FOR OBSERVING THE RATE OF ABSORPTION OF OXYGEN BY POLLUTED WATERS, AND BY OTHER FERMENTING LIQUIDS.

By W. E. ADENEY, D.Sc., F.I.C.,

Curator and Examiner in Chemistry in the Royal University, Dublin.

[Read, JANUARY 21; Received for Publication, JANUARY 24;
Published, FEBRUARY 26, 1908.]

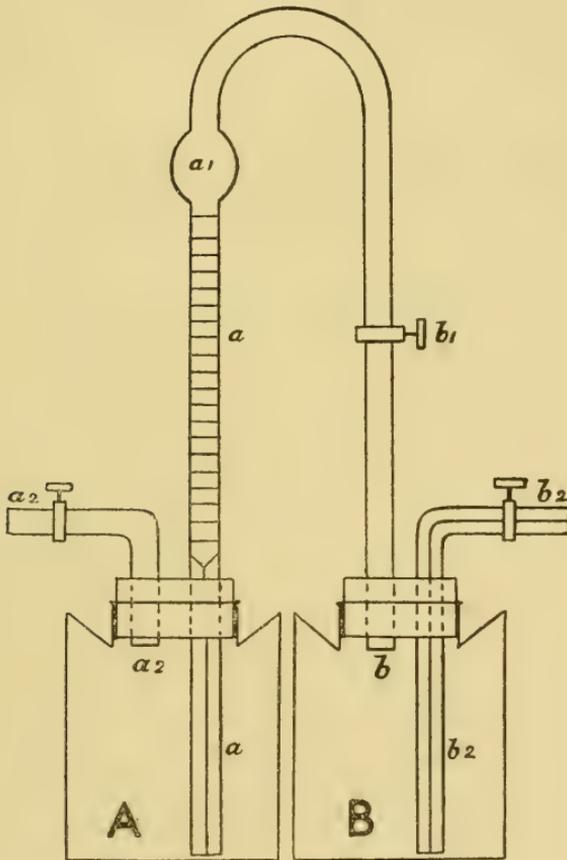
THE author has shown in a number of papers, which he has communicated to this Society from time to time during the past seventeen years, that the true significance of the presence of polluting matters in water depends not so much upon their quantity, as upon their fermentative properties; that is to say, it depends upon the rate at which they will undergo self-purification by fermentation under the influence of the mixed bacteria to be found in all polluted waters, except when antiseptics are present, and in all river- and sea-water; and upon the extent and rapidity with which the dissolved oxygen of the clean waters, with which they become mixed, will be absorbed during the process.

He has also demonstrated that the process of self-purification of waters, under natural conditions, when polluted within limits of fouling, takes place in two distinct and progressive steps. During the first, the carbon oxidisable substances, that is, the fresh polluting organic substances, are oxidised and otherwise changed by bacterial fermentation into carbon dioxide, water, ammonia, and organic substances of an excretory nature, which may be termed nitrifiable organic substances. During the second stage these last named substances and ammonium compounds are fermented to nitric acid and carbon dioxide.

The author has furthermore shown that the quantity of oxygen absorbed, and of products formed, on the completion of each stage of aerobic fermentation, is constant for similar

volumes of the same polluted water, and that this law is applicable to all polluted waters undergoing purification by bacterial fermentation, provided that the dissolved oxygen is in excess of the fermenting matters.

These results have been confirmed by other observers; and it is now agreed that the determination of the extent and rate of absorption of oxygen by polluted waters with reference to the



question of the protection of waterways from over-pollution is of fundamental importance. Unfortunately up to the present time the method employed for the purpose has been too elaborate and too slow for practical purposes; and the result has been that these important determinations are even now seldom made.

The apparatus which is the subject of this communication has been devised to meet this want. Its form is shown by the above diagram.

The bottles *A* and *B* are two flat and shallow bottles of similar capacity. Each bottle is fitted with an ordinary cork previously soaked in melted paraffin. Through the cork of *A* passes a capillary glass tube to the bottom of the bottle. This tube is continued above the cork by a graduated one of wider bore, the upper end of which is enlarged to a small bulb, a_1 , and then bent downwards as shown in the diagram, and continued downwards until it passes through the cork of the second bottle *B* at b ; it is furnished with a glass stopcock b_1 , just above the cork of *B*. By means of this connecting tube aa and stopcock, communication between the two bottles can be opened or closed at will. The cork of the bottle *A* is also fitted with a short tube and stopcock a_2 . The cork to the bottle *B* is likewise furnished with a second tube and stopcock b_2 . It is a capillary tube, and passes to the bottom of the bottle.

To work the apparatus, the bottle *B* is partially filled with a known volume of the polluted water, previously mixed with a little magnesium hydrate to fix free carbon dioxide, and a similar volume of distilled water is poured into the bottle *A*. As the two bottles are similar in capacity, the volumes of the air-spaces left in them are also similar. The polluted water and distilled water should have been left in the laboratory for some little time previously to allow of their assuming a common temperature. The plug of the stopcock b_1 is taken out; and the stopcock a_2 is closed, and b_2 is opened. The two corks are then inserted in their respective bottles, and the whole apparatus is put aside (or preferably immersed in a water-bath kept at the temperature of the laboratory) for a few minutes to ensure their contents assuming the same temperature as that of the laboratory. This is noted, and also the height of the barometer. The effect of keeping the stopcock a_2 closed during the operation of inserting the corks into their respective bottles, as above described, will be found to cause a rise of the water through the capillary tube a , and above the zero point of the graduated portion immediately above it. This stopcock is now cautiously opened to allow the water in the graduated portion of the tube to sink down to the zero-point; it is then closed. The stopcock b_2 is also closed, and the plug of b_1 is replaced.

The pressure in *B* will be that of the atmosphere, and in *A* that of the atmosphere plus that due to the column of water in the capillary tube *a*, less the height to which the water rises in it by capillary action. If the polluted water be a strong one, the apparatus is put into a mechanical shaker; and the contents of the two bottles are kept in gentle motion. If, however, it be a weak one, this will be unnecessary; an occasional shake of the two bottles will be sufficient. The apparatus should be kept at a temperature of 15° to 18° C.

The principle on which the apparatus works depends upon the fact that the atmosphere in the bottle *A* remains practically unchanged in composition during the time of the experiment; and the bottle *A* consequently acts as a standard pressure bottle. As the oxygen is absorbed in the bottle *B*, the pressure of its atmosphere will be reduced in direct proportion to the loss of oxygen, as no carbon dioxide will be evolved from the polluted liquid owing to its fixation by the magnesium hydrate previously added.¹ If, therefore, the stopcock *b*₁ be opened, the water will rise above the zero of the scale of the tube *aa* in proportion to the loss of pressure in *B*. The volume of water which so rises into the graduated portion of the tube *aa*, at any given time, and the height of it above the zero-mark, give the means of calculating the volume of oxygen absorbed by the polluted water in *B* during the period of observation; thus—

Let v' = volume of oxygen absorbed from atmosphere in *B*,
at initial temperature and pressure.

V = volume of air in *A* or *B* at commencement.

v = volume of water that rises above the zero of the
scale of the tube *aa*.

p' = height of water in the capillary tube *a* above the
level it assumes by capillary action.

p'' = height of water in the graduated tube above the
zero-mark on the scale.

$$p = p' + p''.$$

P = pressure of air in *B* at commencement, in terms of
the water-barometer. The pressure in *A* at
commencement will be $P + p'$.

¹ If crude sewage be the subject of examination, it should be diluted to five or ten times its volume with tap-water before being put into *B*; such dilution prevents

Then

$$v' = 2v + \frac{p}{P}V - \frac{p'}{P}(V - v).$$

Since v is generally small in comparison with V , it may be neglected, except in cases where the utmost accuracy is desired. The equation then becomes—

$$v' = 2v + \frac{V}{P}(p - p').$$

The reason for adjusting the level of the water at the zero of the scale at the top of the capillary portion of the tube aa , at the commencement of the experiment, will be understood from the last equation. It is evident from it that, if this were not done, a considerable absorption of oxygen would take place from the atmosphere of bottle B before the water in the tube aa would rise to the graduated portion of it. It may be here remarked that it is inconvenient to have the graduated portion of the tube aa inside the bottle A , owing to the difficulty of reading the scale when it is so placed.

As regards the dimensions of the apparatus, these must be varied to meet the object for which it is required:—whether, for instance, it is required (1) to control the pollution of waterways within standards necessary for safeguarding the interests of public health, or of fish-life; (2) to determine the quality of an effluent from a continuous filter-bed or from a contact bed; (3) to determine the strength of a sewage in a comparatively unpurified condition, e.g., tank-liquor.

For the first purpose, an apparatus will be required that will accurately indicate very small volumes of oxygen absorbed in B . The volumes allowable under the standards formulated for the protection of fish-life must obviously be small; they will vary with the physical conditions of the stream, with such conditions as depth, flow, tidal or non-tidal, and distance from the open sea. Under the least favourable physical conditions, the allowable absorption may be taken to be about 5·5 c.c. per litre of water at

the evolution of nitrogen into the atmosphere of the bottle B , which might otherwise occur if the sewage were examined in the undiluted condition, since crude sewage is generally supersaturated with free nitrogen.

temperatures from 15° to 18° C. in 48 hours. For tidal waters of the most favourable character for the disposal of sewage, the allowable absorption may amount to 3.5 c.c. per litre in $6\frac{1}{4}$ hours, or 4.0 c.c. per litre in $12\frac{1}{2}$ hours.

An apparatus capable of indicating volumes of these dimensions, and at the same time of permitting the use of volumes of polluted water sufficiently large for subsequent chemical analysis, if such be necessary, should be as follows:—*A* and *B* should each have a capacity of 1200 c.c., which permits the use of 1000 c.c. of polluted water, and provides for an air-space of 200 c.c. The capillary portion of *aa* should be as short as possible in all forms of the apparatus. The bottle should consequently be made as shallow as possible; and for this purpose it is advantageous to have the necks of the bottles depressed as shown in the diagram, but this is not essential. The graduated portion should have a capacity of 3 c.c.; and its fine divisions should give readings in $1/20$ th c.c. The tube would then be about 112 mm. long, and 5.5 mm. bore. The volume of the bulb a_1 should be about 1 c.c.

The total loss of oxygen in the atmosphere of *B* observable by means of an apparatus of these dimensions would slightly exceed 10 c.c. per litre of water before replenishing the oxygen absorbed in *B* by fresh oxygen in the manner to be described later on.

The dimensions of an apparatus required for the second purpose would be such that *A* and *B* would each have a capacity of 1500 c.c., and would allow of the employment of 1000 c.c. of the polluted water, and the provision of an air-space of 500 c.c. The graduated tube should measure a total volume of 5 c.c., and afford readings in $1/20$ th c.c. A tube of this capacity would be about 186 mm. long, and 5.5 mm. bore. The capacity of the bulb a_1 should be 5 c.c.

For the third of the above-enumerated purposes, *A* and *B* should each have a capacity of 1500 c.c. The graduated tube should give readings in $1/10$ th c.c., with a total of 10 c.c. Such a tube would be about 225 mm. long and 7 mm. bore. The bulb a_1 should have a capacity of 10 c.c.

The maximum volume of oxygen absorbed in *B*, which would be recordable by this last apparatus, would slightly exceed 50 c.c.

This would amount to nearly half the total volume of oxygen in the air-space, which should certainly be taken as the maximum allowable reduction of the oxygen in the air-supply in *B*. Hence if the polluted water to be examined be an unpurified sewage, it would be necessary either to dilute it to five or ten times its volume with tap-water, or to replenish the oxygen in the atmosphere of *B* by the addition of fresh oxygen, which can very easily be done in the following manner:—A store of oxygen is kept in an ordinary Lunge's nitrometer over a saturated solution of common salt. After a reading of the volume of water which has risen in the graduated connecting tube of the apparatus has been taken, the nitrometer is connected by a short piece of capillary rubber tubing to b_2 , and its pressure tube is raised so as to cause a pressure upon the oxygen a little greater than that of the atmosphere. The stopcock b_1 and that of the nitrometer are then opened; and the stopcock b_2 is cautiously opened, and oxygen is allowed to bubble up through the water in *B* into its air-space until the level of the water in the graduated tube sinks to that of the zero-mark on the scale. The stopcock b_2 is then closed; and if the operation has been correctly carried out, the atmosphere in *B* will have been restored to its original composition; and the volume of oxygen which the nitrometer has lost will also be a measure of the oxygen which had been observed by the polluted water in *B*. In this simple way the oxygen in the atmosphere of *B* may be replenished from time to time; and so the rate of absorption of the most highly polluted sewage may be observed until the sewage becomes entirely self-purified under aerobic conditions.

The above dimensions have all been adopted with the view of allowing the use of volumes of polluted water sufficiently large for subsequent chemical analysis, if such be necessary. If, however, this be not necessary, as in many cases it will not be, the apparatus may be reduced to one-tenth the sizes above given. *A* and *B* would then have a capacity of 120 to 150 c.c. each; and the graduated tube would read to 1/100th c.c., and have a total capacity of 0.3 c.c. Such a tube would be about 50 mm. long, and 2 mm. bore. The bulb a_1 should have a capacity of 1 to 2 c.c., according to whether it be required for the first or second of the above purposes.

Experiments with this apparatus have shown it to be capable of yielding accurate and extremely important results with a minimum expenditure of time and labour. The author hopes shortly to publish in a further communication some important results which he has already obtained by its means.

It may be well perhaps to state in conclusion that a Report on the "Pollution of Estuaries and Tidal Waters," by Professor Letts and the author, will very shortly be issued by the Royal Commission on Sewage Disposal, in which the most important work on the subject of the absorption of atmospheric oxygen by polluted waters has been recorded and discussed.

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Vol. XI. (N. S.), No. 26.

MARCH, 1908.

ON THE RADIUM-CONTENT OF DEEP-SEA
SEDIMENTS.

BY

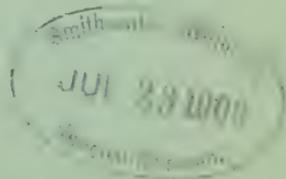
J. JOLY, Sc.D., F.R.S.,

PROFESSOR OF GEOLOGY AND MINERALOGY IN THE UNIVERSITY OF DUBLIN ;
HON. SEC., ROYAL DUBLIN SOCIETY.

[Authors alone are responsible for all opinions expressed in their Communications.]

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XXVI.

ON THE RADIUM-CONTENT OF DEEP-SEA SEDIMENTS.

By J. JOLY, Sc.D., F.R.S.,

Professor of Geology and Mineralogy in the University of Dublin ;
Hon. Sec., Royal Dublin Society.[Read, FEBRUARY 18; Received for Publication, FEBRUARY 20;
Published, MARCH 31, 1908.]

IN a recent paper communicated to this Society¹ I have recorded some experiments which appear to show that the sea-water round the coast of Ireland, and as far west as sixty-five miles west of Valencia, possesses a richness in radium not hitherto suspected. This result has been extended by recent measurements made on samples of water collected between Madeira and England, and also on water from the Arabian Sea.

Although the actual amount of radium per cubic centimetre is minute (approximating to 0.02×10^{-12} grams), the quantity distributed in the ocean is, of course, enormous. We do not as yet know in what state the radioactive matter exists in the water—whether in true solution, or as (possibly) a sulphate or dust in suspension; and, again, whether the uranium, which must be accountable for the continued supply of radium, is present in the water, or mainly in the sediments. To whatever views we may be led by the progress of research in these directions, it is certainly in harmony with the high radioactivity of sea-water to find that the deep-lying sediments of the ocean are exceptionally rich in radium—far richer than average terrestrial rocks.

The materials dealt with in the following experiments are partly from the 'Challenger,' partly from the 'Albatross' collections.

¹ Proc. R. D. S., vol. xi., p. 253.

I owe these to the kindness of Sir John Murray, F.R.S. For a specimen of *Globigerina* Ooze, brought up in trawling, I have to thank Mr. S. W. Kemp, of the Irish Fishery Department.

Although these materials have been in my possession for some months, most of the experiments are of recent date, and where two are recorded, the second is, in every case, a recent re-examination of the same material. The reason for this postponement was my desire to arrive at a fuller knowledge of the most reliable conditions of investigation before using up material of such value. In the process of acquiring experience of the experimental difficulties involved, various methods of extracting the emanation were tried. According to the nature of the substance these methods have been applied in the observations on deep-sea deposits. It would be out of place to consider these methods here, and their relative merits. A short list has to be given, however, of such as have been used in obtaining the data which follow. A reference letter attached to the experiment will then suffice to show the mode of extraction adopted.

(A.) The substance is fused in a platinum crucible with the mixed carbonates of sodium and potassium, and the melt leached in hot water. This is filtered, and the filtrate is closed as the alkaline solution. The residue is treated with hydrochloric acid, and closed as the acid solution. If the acid solution contains or develops a precipitate, this is filtered out and re-fused with the carbonates, the melt being treated as before, i.e. divided between the alkaline and the acid solutions. Both solutions are subsequently examined for radium. In a variation of this method the melt after leaching is acidified, and but one acid solution closed.

(B.) The substance is boiled in HCl, and the filtered solution enclosed the requisite time. This is applicable only when there is good reason to believe that the insoluble part contains but little radium.

(C.) The substance is fused with the carbonates, and the leaching effected as in (A). The thoroughly softened and diffused melt and solution are enclosed in the one flask without further treatment. After the lapse of the requisite period it is attacked with HCl, and the emanation withdrawn along with the CO₂ evolved in the process of decomposition. Vigorous boiling finishes the process of extraction. The arrangement of apparatus

is such as to secure the absorption of the CO_2 , the air and emanation only being transferred to the electroscope. This is a very effective method where the attack with acid secures complete solution.

(D.) The substance in the form of a fine powder is placed in a small flask, and acid run in upon it, the remainder of the treatment being as in method (C). It is, of course, only applicable to carbonates, or soluble substances like manganese dioxide, calcium sulphate, &c.

(E.) The substance is enclosed in a very thin blown glass bulb, which is sealed by the blowpipe. This is preserved for about twenty days. The bulb is then placed in a flask, and after this is attached to the train of receiving apparatus, the bulb is broken by shaking the flask. Acid is then run in, and the process proceeds as in (D). The object here is to correct the loss which attends the direct treatment of powders owing to the large surface and consequent escape of emanation. This loss is shown in experiment (2) on the *Globigerina* Ooze, from the 'Albatross' collection, when compared with experiment (1) on the same material.

The weights of material used in the several experiments are not corrected for contained hygroscopic moisture. The substances are in every case weighed "air-dry."

Blue Mud. Chall. Station, 45. Lat. $38^\circ 34'$ N., long. $72^\circ 10'$ W. 1240 fathoms. (Off the east coast of N. America.)

This deposit contains a considerable proportion of small rounded pebbles and sand, composed mainly of quartz.

On 8.86 grams treated according to method C.

Radium per gram in grams 3.1×10^{-12} .

Globigerina Ooze (from Mr. Kemp). Lat. $51^\circ 37'$ N., long. $12^\circ 5'$ to $12^\circ 14'$ W. 557 to 579 fathoms. (Brought up in trawling off west coast of Ireland.)

This Ooze is not quite free from mineral detritus derived from the land.

(1) On 20 grams by method B (soluble part 11 grams).

Radium in grams per gram of whole quantity 6.0×10^{-12} .

(2) On 10 grams by method A (all in solution).

Radium in grams per gram 6.6×10^{-12} .

Globigerina Ooze. Chall. Station, 338. Lat. $21^{\circ} 13' S.$, long. $14^{\circ} 2' W.$ 1990 fathoms. (Middle of South Atlantic.)

(1) On 25 grams by method B (soluble part 22.25 grams).
Radium in grams per gram 6.4×10^{-12} .

(2) Same; on fusing insoluble part and adding to acid extract.

Radium in grams per gram 6.7×10^{-12} .

Globigerina Ooze. Chall. Station, 296. Lat. $38^{\circ} 6' S.$, long. $88^{\circ} 2' W.$ 1825 fathoms. (Pacific Ocean, west of S. America.)

On 10 grams by method A (soluble part 9.44 grams).

Radium in grams per gram 7.4×10^{-12} .

Globigerina Ooze. Albatross Station, 4739. Lat. $22^{\circ} 11.1' S.$, long. $133^{\circ} 21' W.$ 2042 fathoms. (Central Pacific.)

(1) On 5.3 grams by method E.

Radium in grams per gram of whole sample 8.0×10^{-12} .

(2) On 7.1 grams by method D (soluble part 6.815 grams).

Radium in grams per gram of whole sample 7.1×10^{-12} .

Red Clay. Chall. Station 5. Lat. $24^{\circ} 20' N.$, long. $24^{\circ} 28' W.$ 2740 fathoms. (N. Atlantic, off coast of Africa.)

(1) On 20 grams, method A (14.5 grams soluble).

Radium in grams per gram 15.4×10^{-12} .

(2) On 10 grams of the first to settle from about 30 grams suspended in distilled water; by method A.

Radium in grams per gram 13.0×10^{-12} .

(3) On 10 grams of the last to settle from the 30 grams; by method A.

Radium in grams per gram, 28.0×10^{-12} .

(4) On 7 grams by method A, but all in one acid solution; some precipitate left.

Radium in grams per gram 13.9×10^{-12} .

Red Clay. Chall. Station, 276. Lat. $13^{\circ} 28' S.$, long. $149^{\circ} 30' W.$ 2350 fathoms. (Central Pacific, near region of Radiolarian Ooze, see under.)

(1) On 8.42 grams by method C. (Some precipitate and undecomposed particles remained.)

Radium in grams per gram 36.9×10^{-12} .

- (2) Same, but with re-fusion of undissolved particles; all in solution.

Radium in grams per gram 54.5×10^{-12} .

- (3) On 10 grams.

Part soluble in HCl (7.21 grams). By method B.

Radium in grams per gram of soluble part 64.3×10^{-12} .

Insoluble part (2.79 grams). By method A.

Radium in grams per gram of insoluble part 15.7×10^{-12} .

Mean radium content in grams per gram of whole amount
 50.7×10^{-12} .

Radiolarian Ooze. Chall. Station, 274. Lat. $7^{\circ} 25' S.$, long. $152^{\circ} 15' W.$ 2750 fathoms. (Central Pacific.) Magnetic particles had previously been removed from this Ooze by Sir John Murray.

- (1) On 20 grams by method A.

Radium in grams per gram 50.3×10^{-12} .

- (2) On 8 grams by method A.

Radium in grams per gram 50.7×10^{-12} .

- (3) On 6.33 grams, method A, but all in one acid solution.

Radium in grams per gram 49.8×10^{-12} .

Manganese Nodule. Chall. Station, 274 (as above).

On 25 grams by method B (nearly all dissolved).

Radium in grams per gram 24.0×10^{-12} .

Manganese Nodule. Albatross Station, 4658. Lat. $8^{\circ} 29' 5'' S.$, long. $85^{\circ} 36' 6'' W.$ 2370 fathoms. (Pacific Ocean, off coast of Africa.)

On 12 grams by method B, the hard manganese shell only used. Nearly all dissolved.

Radium in grams per gram 21.0×10^{-12} .

It will be seen that the deposits richest in radium are those which occur in the most central parts of the Pacific Ocean. From this region not only the Red Clay, but the Radiolarian Ooze, is remarkably radioactive. The Globigerina Ooze from the Pacific is also somewhat richer than Atlantic Ooze. The manganese nodules from the central Pacific are, again, rich in radium. The radioactivity of the Blue Mud of the Continental border region

is, on the other hand, comparable with that of many ordinary sedimentary rocks.

An interesting question arising in connexion with these measurements is as to the source of the radioactive substances in mid-ocean sediments. Are they chemically extracted from a true solution in the sea-water, much as are the manganese of the nodules and the potash of the glauconite? or, are they derived in whole, or in part, from suspended particles? It is almost certain that the greater richness in the more open parts of the ocean is traceable to the comparatively small amounts of calcareous materials which reach the depths; there being, on this account, less dilution of the radioactive substances. The lime-secreting organisms of the ocean appear to possess a power of rejecting to a great degree radioactive substances when secreting calcium carbonate. We may see this at once by considering the fact pointed out by Gustav Bischof in his *Chemical and Physical Geology*,¹ that an oyster will require the lime from some 27,000 to 76,000 times its weight of sea-water in order to secrete its shell. If the radioactive materials were secreted along with the lime, the calcareous rocks which are built of such calcareous remains would be very much more radioactive than experiment shows. Hence it is not remarkable that the tests of Foraminifera should act as dilutants of other radioactive products collecting at the ocean bottom. But this still leaves open the question as to the ultimate source of the radium or uranium of the ocean floor. Thus, if these were derived from an extra-terrestrial source, associated with meteoric dust, we should again find the deeper parts of the ocean, where Red Clay and Radiolarian Ooze accumulate with extreme slowness, characterized by conspicuous amounts of radium.

If we may assume that the radioactive substances are being laid down at a uniform rate over the Ocean floor, then the measurements given above afford an estimate of the relative amounts of other substances accumulating in a given time in various parts of the Ocean. Thus the deposit of Globigerina Ooze collects about eight times as fast as the Radiolarian Ooze or as the Red Clay: the two latter collecting at about the same rate.

It would be a matter of much interest if the radium could be

¹ “*Elements of Chemical and Physical Geology*,” vol. i., p. 180, English Trans.

traced to its true source among the several substances which enter into the composition of the deep-sea sediments. The further consideration of this point is, however, better deferred till more knowledge is obtained.

It is evident, however, that, if derived from the land, these rich deposits of radium go far towards supporting views as to the importance of radium in geological dynamics such as I have already outlined before the British Association at its last meeting, 1907. We are logically required to consider the thermal effects of these wide-spread deposits of uranium when concentrated in ancient rocks and terrigenous sediments. It is my view that the secret of the unrest attending sedimentary accumulations may be found in radioactive energy. Nor is it without significance that in the central Pacific, where by slow degrees much of the heat-producing substance has accumulated, the floor of the ocean has become disturbed by volcanic energy, and has given evidence of movements similar to those which have ordained and controlled the events of geological history. But, again, more detailed consideration is best postponed to another occasion.

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THE LINES OF FLOW OF WATER IN
SATURATED SOILS.

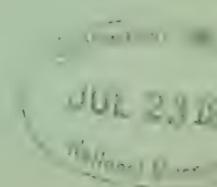
BY

LEWIS F. RICHARDSON.

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XXVII.

THE LINES OF FLOW OF WATER IN SATURATED SOILS:
 EXPLAINING A SIMPLE METHOD FOR DETERMINING THE RELATION
 BETWEEN THE DISTANCE APART OF DITCHES AND THE HEIGHT TO
 WHICH THE SATURATING WATER WILL RISE WITH A GIVEN RAIN-
 FALL, SPECIAL REFERENCE BEING MADE TO THE DRAINING OF
 PEAT-MOSSES.

By LEWIS F. RICHARDSON.

[Read, JANUARY 21; Received for Publication, JANUARY 24;
 Published, MAY 8, 1908.]

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§ 1. THE PROBLEM TO BE DISCUSSED.

In working a peat-moss for litter, it is customary to remove the excess of water by longish parallel drains 15 yards or so apart, intersected by deeper cross-drains.

The problem towards which this paper is devoted is as follows:—

Given the annual rainfall, how must the drains be cut in order to remove just the right amount of water? Or conversely, What will be the effect of any given cutting?

For this purpose it is proposed to consider the drainage of peat-mosses only as far as the saturated substance is concerned; that

which contains air as well as water is not here dealt with. For the purposes of mathematical analysis, the peat is treated as if it were a continuous medium. Thus, in what follows, the “*velocity of the water*” in any direction at a point does not refer to the actual mean velocity in the interstices, but rather to the quantity of water crossing a plane several square centimetres in area, normal to the said direction, divided by the said area.

In the present imperfect stage of the theory of drainage, there is no need to apologize for taking a simplified case. Thus, actual peat is always somewhat stratified; and its porosity will be different in different directions at the same point. But it is here assumed to be isotropic, so that the “*velocity of the water*” at any point is a simple vector, its magnitude in any direction being the projection of a certain line on to that direction.

Again, after heavy rainfall peat-mosses are known to swell, even to bursting. The peat has a velocity as well as the water. But it is here assumed that the peat remains unmoved. This will be true either if the excess of rainfall over evaporation is steady, or if the peat has an inextensible porous structure.

§ 2. THE LAW: FLOW PROPORTIONAL TO FORCE.

The equations for the percolation of water in a non-expanding porous soil are given by Boussinesq (1904e). They are founded on the supposition that the general velocity of the water is proportional to the pressure-gradient, which, on the theory of viscous liquids, would imply that the motion of the water through the interstices is steady, not turbulent. In order to test whether this assumption held good for peat, I made the following experiment:—

A glass tube 150 cm. long and 2·8 cm. uniform internal diameter had one end expanded, as in the figure (fig. 1). Into this end there was squeezed a plug of litter-peat taken from the Bog of Allen, Ireland, below the water-line, and preserved in the wet state. The plug was secured by a piece of muslin tied over the expanded end.

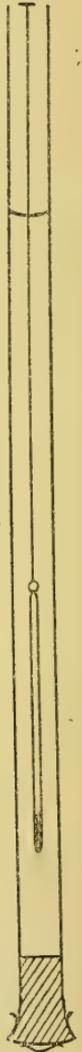


FIG. 1.

The tube was now filled with filtered water and set upright; and the rate of depression of the water-level was observed. The total difference of pressure tending to drive water through the plug is proportional to the height of the water-surface above some level in the plug. Just where this level comes in the plug depends on the proportion of water and solid therein. At a guess I took it as the section AB in the figure (fig. 2). Then calling z the height of the water-surface above AB , the pressure-difference is $g\rho z$, where g is acceleration of gravity, and ρ the density of water. The mass-acceleration is found to be entirely negligible.

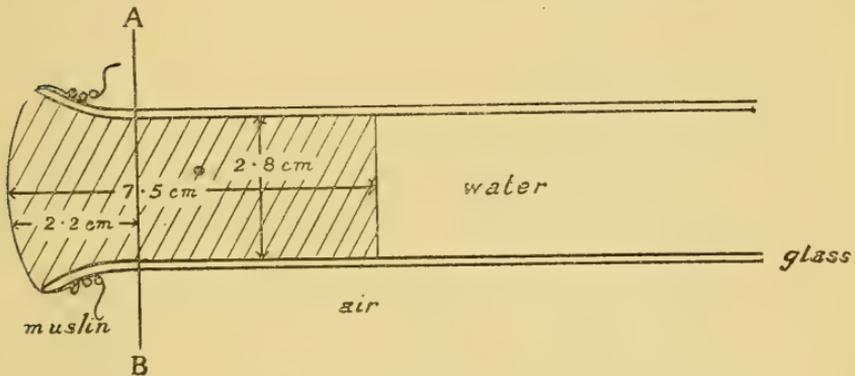


FIG. 2.

The flux is $\frac{dz}{dt}$ c.c. per sq. cm. per second. So that, if the flux is proportional to the pressure-difference, we have $\frac{dz}{dt} = -kz$, where k is a positive constant, namely, the conductance of tube 1 sq. cm. area cut longways from the plug. Integrating $z = Ae^{-kt}$. If in the observations z_1 corresponds to t_1 , and z_2 to t_2 , then by dividing we have

$$\frac{z_1}{z_2} = e^{-k(t_1-t_2)},$$

whence

$$k = \frac{1}{t_2 - t_1} \log_e \frac{z_1}{z_2} = \frac{2.30}{t_2 - t_1} \log_{10} \frac{z_1}{z_2}.$$

In the following table the irregular variation of the last column shows that the law, "flux is proportional to pressure-difference," is probably the best.

| Temperature of the water. | Time, | | Water level = z . | $\frac{1}{t_2 - t_1} \log_{10} \frac{x_1}{x_2}$ |
|--------------------------------|-------------|-------------------|---------------------|---|
| | by clock. | mins. difference. | | |
| 10.5° C. | P.M. 7h 11m | 49 | 151.4 cms. | .552 × 10 ⁻³ |
| | „ 8h 0m | | 142.2 „ | |
| Now some water was tipped out. | | | | |
| | P.M. 8h 16m | 119 | 84.6 „ | .500 × |
| | „ 10h 15m | | 73.8 „ | |
| Filled up again. | | | | |
| 9° C. | A.M. 8h 3m | 37 | 153.4 „ | .650 × |
| | „ 8h 40m | | 145.1 „ | |
| Some water poured out again. | | | | |
| 9.5° C. | A.M. 8h 45m | 122 | 63.3 „ | .580 × |
| | „ 10h 47m | | 53.8 „ | |
| | P.M. 1h 32m | 176 | 45.5 „ | .470 × |
| | „ 4h 28m | | 176 | |
| 9.5° C. | „ 8h 39m | 251 | 26.5 „ | .481 × 10 ⁻³ |
| | | | | |
| mean about | | | | .50 × 10 ⁻³ |

It is to be noticed that the head of water here bears a far greater proportion to the thickness of the wall of peat resisting it than would usually be the case in a bog. So that in the actual case we shall be still farther removed from Osborne Reynolds' criterion of turbulency; and therefore the flux will be inversely in the viscosity, that is, directly as $(1 + .0231T)^{1.542}$, where T is the temperature centigrade.¹

Next to work out the *porosity in absolute units*, that is, in c.c. of water per second passing through 1 sq. cm. of a slab when the pressure gradient is one dyne per sq. cm. every centimetre and the lines of flow are normal to the surfaces.

¹ Poynting and Thomson, "Properties of Matter."

Call this K_T at T degrees centigrade,

$$\text{then} \quad K_T = K_0(1 + .0231T)^{1.5+2}.$$

Now if the plug had been parallel instead of widening, I would guess that a reduction to 6.5 cm. long would make its conductance the same again. Now, the conductance of a tube of 1 sq. cm. cross-section in the plug is given by the last column of the foregoing table as

$$.50 \times 10^{-3} \times \frac{2.30}{60},$$

when seconds are the unit instead of minutes ;

$$\therefore \frac{K_{9.5}}{6.5} = .50 \times 10^{-3} \times \frac{2.30}{60},$$

whence it is found $K_{9.5} = 1.3 \times 10^{-7}$ C.G.S. units.

This, however, is not a good way of measuring the porosity of the peat as it lies in the bog, because the structure is destroyed when it is pressed into the tube. A better method will be worked out later on.

§ 3. THE DIFFERENTIAL EQUATIONS.

As has been stated, these are given by Boussinesq (1904e). He treats their solution in very considerable detail, but only when the lines of flow are nearly horizontal. In what follows the general equations are the same, except that capillarity is neglected, and the porosity supposed constant ; but they are solved for certain cases of steady motion in an entirely different manner, which can be applied when the slope of the surface is steep, and the lines of flow strongly curved, so that this method supplements Boussinesq's.

The particular examples dealt with in this paper could not have been worked out by Boussinesq's method, with the possible exception of fig. 3. But for all that concerns nearly horizontal flow the reader cannot do better than refer to Boussinesq's papers, a list of which is given at the end.

After the experiment with the glass tube described above, it is fairly obvious that at any point in the peat

$$\frac{\text{velocity}}{\text{porosity}} = \text{total impressed force} = \text{bodily force} + \text{slope of pressure,}$$

that is, in the usual symbols of hydrodynamics,

$$\left. \begin{aligned} \frac{u}{K} &= X - \frac{\partial p}{\partial x} \\ \frac{v}{K} &= Y - \frac{\partial p}{\partial y} \\ \frac{w}{K} &= Z - \frac{\partial p}{\partial z} \end{aligned} \right\} . \quad (1)$$

Take the z -axis vertically downwards; then $X = 0 = Y$, and $Z = g\rho$, where ρ is the density of water, namely, 1.00 grams per c.c. The equations may now be written

$$\left. \begin{aligned} u &= \frac{\partial}{\partial x} K(g\rho z - p) \\ v &= \frac{\partial}{\partial y} K(g\rho z - p) \\ w &= \frac{\partial}{\partial z} K(g\rho z - p) \end{aligned} \right\} , \text{ or in vectors } \mathbf{v} = \nabla K(g\rho z - p). \quad (2)$$

Therefore $K(g\rho z - p)$ is the velocity-potential, and the motion is irrotational.

$$\text{Put} \quad \phi = K(g\rho z - p). \quad (3)$$

We have also $\text{div } \mathbf{v} = 0$, which becomes

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0. \quad (4)$$

On account of the small porosity, the effects of acceleration are negligible; and the above is true for varying motion as well as steady.

All over the outside and upper water-surface p is atmospheric; and therefore

$$\phi = K g \rho z - K \times (\text{atmospheric pressure}).$$

Since adding a constant to ϕ has no effect on the motion, we may take the atmospheric pressure as zero, so that over the surface exposed to the air

$$\phi = K g \rho z. \quad (5)$$

Over a water-tight bottom with normal having direction-cosines l_1, m_1, n_1 , we have

$$O = l_1 \frac{\partial \phi}{\partial x} + m_1 \frac{\partial \phi}{\partial y} + n_1 \frac{\partial \phi}{\partial z}. \quad (6)$$

If l_2, m_2, n_2 apply similarly to the upper surface, then the flow per unit area across it is

$$l_2 \frac{\partial \phi}{\partial x} + m_2 \frac{\partial \phi}{\partial y} + n_2 \frac{\partial \phi}{\partial z}.$$

Now a vertical pipe of unit cross-section abuts on $\frac{1}{n_2}$ units of sloping surface at the water-level. Therefore, if the surface is steady, the total flow in the said pipe is $\frac{1}{n_2}$ of the above, that is,

$$\frac{l_2 \partial \phi}{n_2 \partial x} + \frac{m_2 \partial \phi}{n_2 \partial y} + \frac{\partial \phi}{\partial z} = W.$$

Here W is the excess of rainfall over evaporation in volumes per area. If, on the other hand, the water-surface is moving, then we must take account of the capacity of the soil for moisture. Call it μ volumes of free water per unit volume of soil and water. Then, if $z = h$ be the equation for the free surface,

$$W - \mu \frac{\partial h}{\partial t} = \frac{1}{n_2} \left(l_2 \frac{\partial \phi}{\partial x} + m_2 \frac{\partial \phi}{\partial y} + n_2 \frac{\partial \phi}{\partial z} \right). \quad (7)$$

However, in what follows, I will only treat the case $\frac{\partial h}{\partial t} = 0$.

As usual, before attempting to solve a set of differential equations in detail, it is well to make a linear transformation of the variables.

Let ϕ_1 be determined as $F(x, y, z)$ by equations (4), (5), (6), and (7), and imagine that its values are recorded upon, or fixed into the substance of, an elastic medium of the size and shape of the piece of peat considered. Now, let this medium be stretched b times every way, while the coordinate axes remain graduated in centimetres as before. Then (4) is still satisfied. But the space-rate of ϕ_1 is everywhere reduced to $\frac{1}{b}$ of what it was. Now, suppose that the value of the function everywhere in the expanded

medium is multiplied by $\frac{b}{Kg\rho}$. Call the product ϕ_2 ; then the space-rate is now $\frac{1}{Kg\rho}$ times its original value at the same particle of the medium. Consequently it still vanishes over the bottom; and over the top surface n_2 , which depends on the form, but not on the size, being unchanged, we have from (7)

$$\frac{W}{Kg\rho} = \frac{1}{n_2} \left(l_2 \frac{\partial \phi_2}{\partial x} + m_2 \frac{\partial \phi_2}{\partial y} + n_2 \frac{\partial \phi_2}{\partial z} \right). \quad (8)$$

The value of ϕ_1 over the top was by (5) equal to $Kg\rho z$. Therefore the value of ϕ_2 over the same surface, now stretched, is bz —that is to say, it is proportional to the height of the stretched medium as ϕ_1 was to that of the unstretched.

Now, because b does not appear in the formula (8), it is clear that W does not depend on the size of the mass of peat, but only on its shape, and on $Kg\rho$.

To determine ϕ_2 we have the following four relations :

$$\left\{ \begin{array}{l} \nabla^2 \phi_2 = 0 \text{ everywhere.} \quad (9) \\ \phi_2 \text{ is equal to the height on the water-air-surface.} \quad (10) \\ \text{The water-tight bottom is a surface of flow.} \quad (11) \\ \frac{W}{Kg\rho} = \frac{1}{n_2} \left(l_2 \frac{\partial \phi_2}{\partial x} + m_2 \frac{\partial \phi_2}{\partial y} + n_2 \frac{\partial \phi_2}{\partial z} \right) \text{ over the upper water-surface.} \end{array} \right. \quad (8) = (12)$$

§ 4. SOLUTION OF THE DIFFERENTIAL EQUATIONS.

As the drains in peat-moss are commonly long in comparison with their distance apart, we will, for simplicity, consider the flow in a section normal to the smallest drains, and neglect altogether the flow across the plane of the section, and, with it, the coordinate y .

An attempt to solve the equations (9), (10), (11), (12) by a series of terms of the type $\phi_2 = \cos mx \sinh mz$, led to great complications on account of the awkward surface-conditions (10) and (12), and was given up as hopeless.

Instead of algebra, a freehand graphic method has been employed. One draws two sets of lines, namely, stream-lines, marking off tubes of equal flow, and contours drawn at equal intervals of the

velocity-potential ϕ_2 . The lines of these two families must cut one another at right angles, forming rectangular chequers.

In order that the body equation, $\nabla^2\phi_2 = 0$, may be satisfied,

the ratio:
$$\frac{\text{length of chequer along normal to contour of } \phi_2}{\text{breadth of chequer along contour of } \phi_2},$$

which we may call the "chequer-ratio," must be constant along the normals to the contours of ϕ_2 ; and further, because each tube carries the same total flow, the chequer-ratio must be constant all over the field. The diagrams were sketched in pencil, rubbed out and repeatedly amended in the attempt to make the corners square and the chequer-ratio constant, with such success as you see. For a fuller account of the freehand graphic solution of $\nabla^2V = 0$, the reader is referred to a paper by the author published by the Physical Society of London, vol xxi. (also printed in *Phil. Mag.*, Feb., 1908).

The equations peculiar to this theory of drainage lead to the following conditions at the upper surface:

By equation (12) The tubes of flow start from points which are equidistant horizontally—that is, each tube carries the same amount of rain-water.

By equation (10) The equipotentials start from points which are equidistant vertically, as indicated by the faint lines on fig. 5.

One finds, on making the drawings, that these conditions determine the shape of the surface very closely, in those figures in which the tubes of flow are somewhat horizontal.

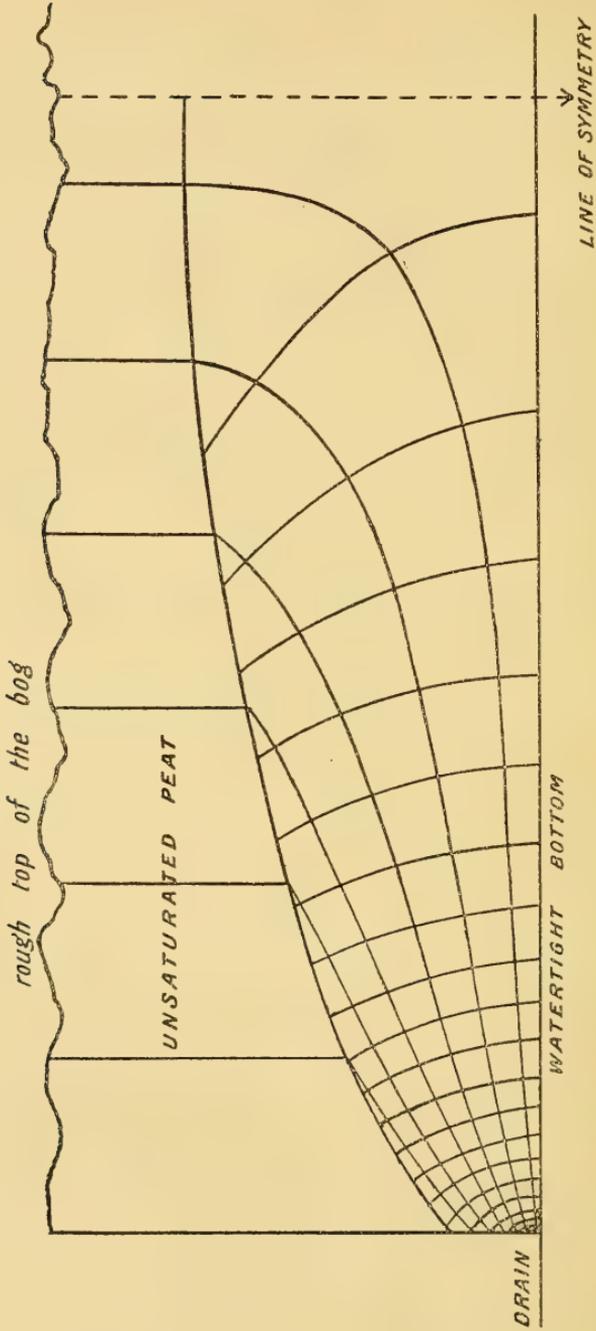


FIG. 3.

Reciprocal of chequer-ratio { mean = 0.85,
 "standard deviation" = 0.1 } $\frac{W}{K_{gp}} = 0.085$

THE FORM OF THE WATER SURFACE IS INDETERMINATE BY THIS METHOD
IN THIS INSTANCE.

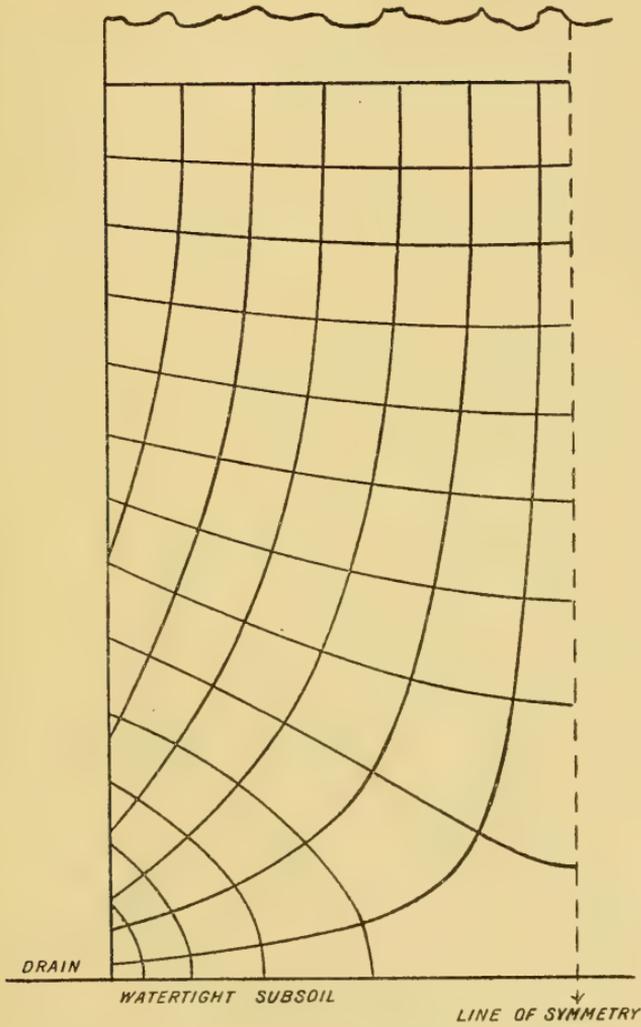


FIG. 4.

$$\text{Reciprocal of chequer-ratio} \left\{ \begin{array}{l} \text{mean} = 0.96 \\ \text{S. D.} \doteq 0.1 \end{array} \right. \quad \frac{W}{Kgp} = 0.96$$

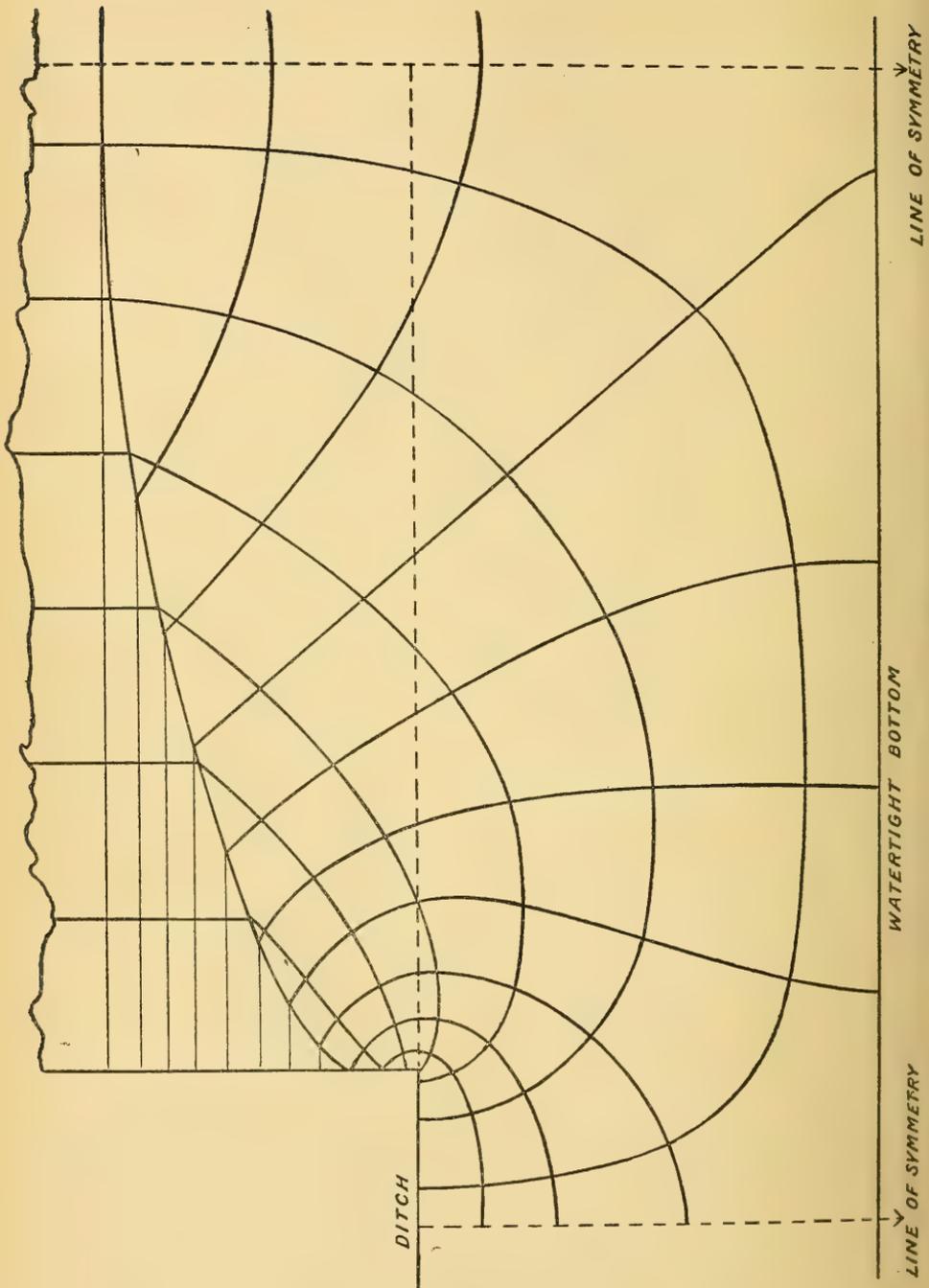


FIG. 5.—Reciprocal of chequer-ratio { mean = 1.13 $\frac{W}{K_{gp}} = 0.226$
 S. D. = 0.13

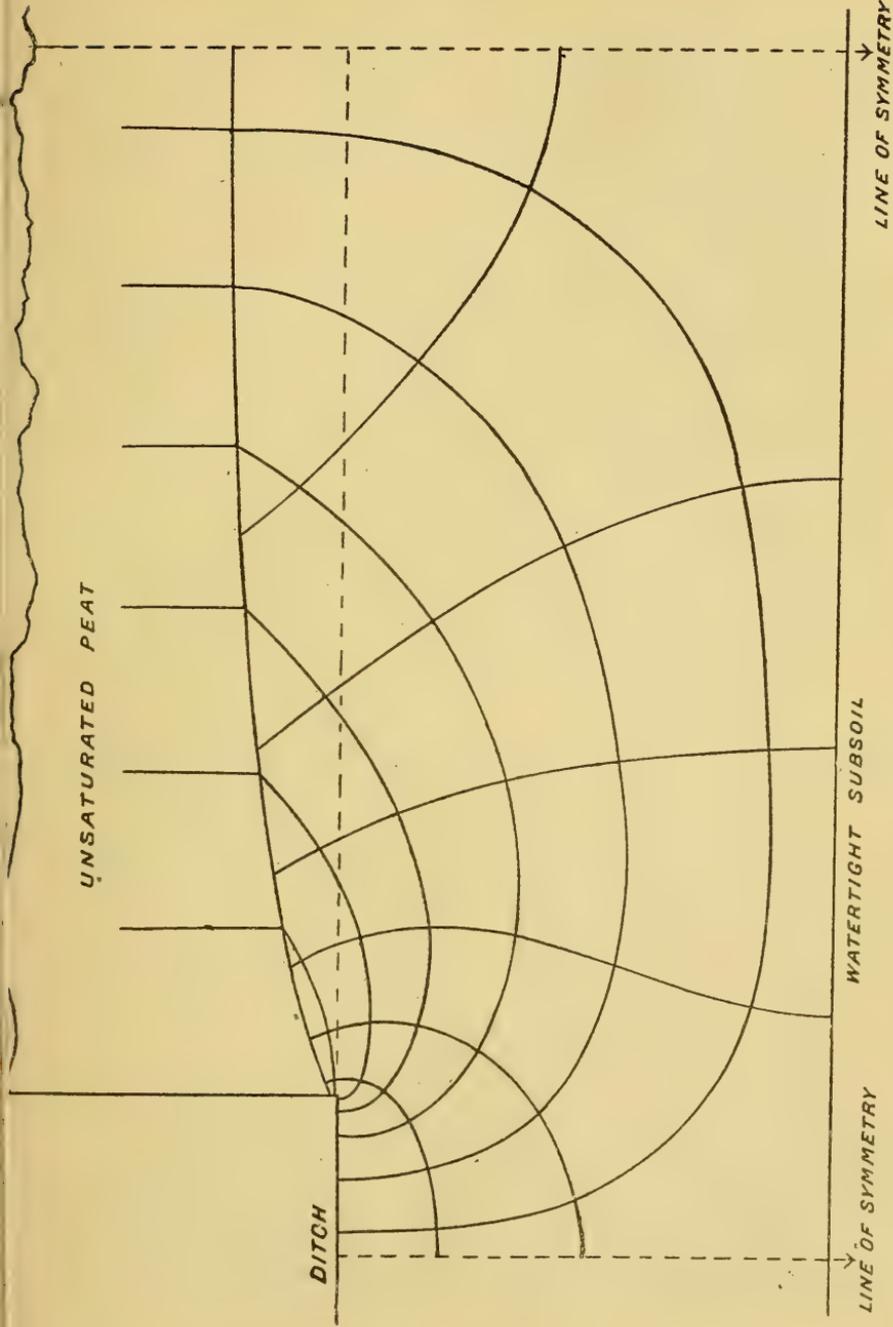


FIG. 6.—Reciprocal of chequer-ratio

In these an alteration in the height of the surface at any part, equal to $\frac{1}{30}$ of its greatest elevation above the bottom of the ditch, was found to throw the chequer-work decidedly out of shape. On the other hand, in fig. 4, where the tubes are nearly vertical at the surface, the form of the latter cannot be determined by this graphic method. It is, however, an unpractical case, and so it need not concern us.

The excess of rainfall over evaporation, which we called W , is determined from the diagrams in the following manner. All through we must remember that in the transformed equation (8) the peat has been replaced by a hypothetical medium. The flow in the unsaturated medium above the "water-line" is $\frac{W}{Kg\rho}$ per unit horizontal area. We will here suppose a diagram to represent a slab of unit thickness, so that horizontal length is equivalent to horizontal area. Now, in the diagrams, vertical tubes in the unsaturated medium are carried on into curved tubes in the saturated part; and the total flow in a tube must, of course, be the same all along it. Whence, equating the flows in unsaturated and saturated portions, we have

$$\frac{W}{Kg\rho} \times (\text{horizontal width of tube in unsaturated portion}) \text{ is equal to} \\ (\text{diff. of potential between contours}) \times \frac{(\text{width of chequer across flow})}{(\text{length of chequer along flow})}.$$

No specific resistance appears in this, because the flow referred to is not a flow of real water, but only of the auxiliary flux $\nabla\phi_2$. Now by equation (10) the difference of potential between successive contours is simply the difference of level between the ends of the equipotentials, where they crop out on the upper surface. Therefore

$$\frac{(\text{diff. of level of outcropping equipotentials})}{(\text{horizontal width of tube in unsat. portion})} \\ \times \frac{(\text{width of chequer across flow})}{(\text{length of chequer along flow})} = \frac{W}{Kg\rho}.$$

The left-hand side can be obtained at once from the drawings. Its value is independent of the unit of measurement. The greatest error is that due to the chequers not having all the same ratio of

length to breadth, nor corners that are quite square. The former irregularity has been estimated by measuring the length and breadth of a number of chequers—say, a dozen—and finding the variability of the ratio in a rough way by observing what deviation from the mean has $\frac{2}{3}$ of the observed deviations less than it, and $\frac{1}{3}$ greater. This corresponds in a very rough way to the “standard deviation” of the ratio from its mean, and is recorded on the diagrams in the form

$$\text{reciprocal of chequer ratio} = 1.13 \pm .13, \text{ or else S. D.} = .13.$$

But the effect of this error, and of the corners not being quite square, upon the value of $\frac{W}{Kg\rho}$ needs investigation. They must largely average out. I feel confident that the error is less than 7 per cent. of $\frac{W}{Kg\rho}$, probably about 3 per cent. One’s best guide is to attempt to improve the drawings, and to observe the consequent changes in $\frac{W}{Kg\rho}$. The value of $\frac{W}{Kg\rho}$ found is recorded on each diagram, so that the diagram may be applied to any uniform soil by putting in the specific value of K , and the absolute size may be neglected.

§ 5. DISCUSSION OF RESULTS.

Figs. 5 and 6 represent similarly placed ditches. It is interesting to notice how $\frac{W}{Kg\rho}$ is related to the height of the surface above the ditch-bottom. The ratio of $\frac{W}{Kg\rho}$ in fig. 5 to that in fig. 6 is $\frac{.226}{.068} = 3.3$, while the ratio of the heights runs as follows:—

| | | | | | | | | |
|---------------------|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|------|
| $x = \frac{1}{2}aX$ | $\frac{13}{13}$ | $\frac{11}{13}$ | $\frac{9}{13}$ | $\frac{7}{13}$ | $\frac{5}{13}$ | $\frac{3}{13}$ | $\frac{1}{13}$ | 0 |
| Ratio of heights, | 4.0 | 2.80 | 2.73 | 2.85 | 2.85 | 2.90 | — | 2.80 |

The ratio of the heights is remarkably constant about a mean of 2.82. The reason why this ratio is less than 3.3 must be because,

in fig. 6, there is less room for the tubes to crop out in the side of the ditch. For a still lower surface than that of fig. 6, the flowing area in the side of the ditch will be so small in comparison with the ditch-bottom that any variation in it may be neglected. Also the length of each tube above the level of the ditch-bottom is in the longer ones a small fraction of its total length. That is to say, its resistance does not alter much. From this, and from the observed similarity of the surfaces in figs. 5 and 6, it is clear that a further diminution of $\frac{W}{Kg\rho}$ will not cause the surface to alter its form, and that its central ordinate will be proportional to $\frac{W}{Kg\rho}$. This greatly generalizes the graphic method. Any lower rainfall can be calculated from fig. 6.

Further, we see that if $\frac{W}{Kg\rho}$ suddenly stops and remains zero, then the whole surface will begin to fall at the same rate. The portion half-way between the two ditches will subside according to the equation, height = Exp $\{-k(\text{time})\}$, where the constant k can be reckoned when the capacity of the soil for free water is known. The lower parts of the original surface must subside at a more rapidly diminishing rate, as all must reach the level of the ditch-bottom together.

The following is an example of the application of the foregoing diagrams:—In a country where the rainfall is 40 inches per year, how far apart must surface-ditches on a deep bog be cut in order that the level of saturation of the peat may not rise higher than one foot above the bottom of the ditches?

Well, 40 inches per year is 3.2×10^{-6} centimetres per second. We will neglect evaporation, and take this as the value of W . Then taking the porosity K as 10^{-7} C.G.S. units (see § 7), we have

$$\frac{W}{g\rho K} = \frac{3.2 \times 10^{-6}}{981 \times 10^{-7}} = .032.$$

Now, in fig. 6 $\frac{W}{Kg\rho} = .068$, and the water-surface rises to $\frac{0.7}{15}$ of the distance between the centres of two adjacent ditches above the level of their floor. Further, we have shown above that $\frac{W}{Kg\rho}$ is proportional to the height of rise for forms like fig. 6, with equal

or less values of $\frac{W}{g\rho k}$. Therefore, to make $\frac{W}{g\rho K} = \cdot 032$, the maximum height of rise must be $\frac{\cdot 032}{\cdot 068} \times \frac{0\cdot 7}{15}$ of the distance between the ditch centres, which is equal to $0\cdot 022$ of the same. But the maximum rise allowed is 1 foot. Therefore, the distance between the ditches must not exceed $\frac{1}{\cdot 022}$ feet = 15 yds. This is the answer required.

It seems a likely value. But we see from fig. 2 that, if we take the distance between the ditches to be 15 yards, we thereby assume that the ditch is 2 yards broad, and that there is 3 yards' depth of peat between the ditch-bottom and the clay. If these conditions are seriously different from the actual ones, a new figure must be sketched. The time taken to draw a figure increases very rapidly with the accuracy attempted. Those given here took me 4 hours or so each. Half the accuracy could probably be attained in a quarter the time.

Usually the lower parts of the soil are less porous. In this case let the paper be prepared by chequers of the proper shape before beginning the diagram. (See the paper on "Freehand Method," section v.)

It may indeed be justly doubted whether the foregoing results will apply to the practical draining of peat-mosses as they stand. The hypothesis of easy vertical flow in the unsaturated upper layers does not seem quite satisfactory. And the effect of capillarity is probably considerable (see the section thereon). But at any rate the present paper illustrates a method of solving the equations which can probably be adapted to deal with more correct hypotheses.

§ 6. DETERMINATION OF THE POROSITY.

The porosity of the peat, as it lies in the bog, to the flow of water, can only be satisfactorily determined from a sample in which the original structure has been preserved, or, at least, any other method must be standardized against one using such samples. As it did not seem easy to make a water-tight joint between a block of peat and a vessel of glass or metal without crushing the softer body, I determined to make the whole apparatus of peat, cutting the substance into a cup-shape, putting water inside, and

noting the rate at which it ran through. As the result would have to be compared with calculation, it was necessary to cut the peat into a solid of revolution, so that the flow could be completely specified by a single section, and the graphic method could be employed.

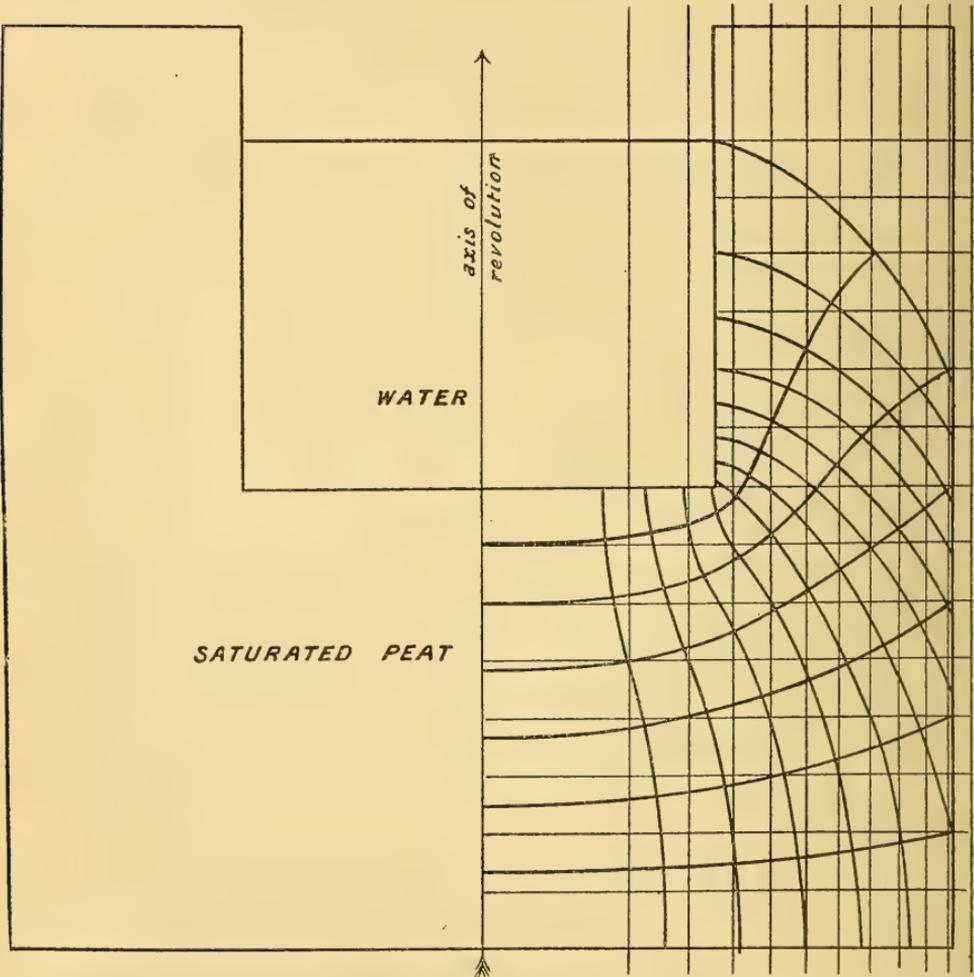


FIG. 7.

For simplicity and strength I chose the form which can be made as follows:—Cut a cube; then pare down four edges until you have a cylinder with diameter equal to its length; then in one end of this cut out a cylindrical hole similar in form to the

outside, and of exactly half the linear dimensions. This must be done with a sharp, narrow-bladed knife.

A section of this solid by a plane through the axis is shown in the annexed diagram. The faint lines would be contours at equal intervals of the stream-function and potential if the flow were parallel to the axis. The black lines are contours of the actual stream-function and potential, found by hand-sketching until each black chequer bore the same proportion of length by breadth to the same ratio in the pink chequer underneath. (See the paper referred to above.) As a matter of fact, the proportion is nearly unity. On measuring seventeen pairs of chequers the quantity:

$$\frac{\text{width of black chequer across flow}}{\text{length of black chequer}} \times \frac{\text{length of faint chequer}}{\text{width of faint chequer}}$$

was found to have a mean of $\cdot 92$ (and a standard deviation $\cdot 10$). This implies that if the drop in potential per contour is the same for faint and black, then the flow in every black tube is $\cdot 92$ of the flow in every faint one; and as there are twelve black tubes, the total flow is equal to $\cdot 92$ of that through twelve faint ones. Now, if the difference in level of the black equipotentials at the points where they crop out on the air-surface be taken as a unit of z , then by equation (5) the difference of potential is $Kg\rho$ per black contour. And therefore $\frac{Kg\rho}{2}$ per faint contour, as the figure shows. Further, twelve faint tubes form a cylinder of $4\cdot 35$ radius measured in the said units.

$\therefore \cdot 92$ (flow in 12 faint tubes) = total flow from the cavity

$$= \cdot 92\pi(4\cdot 35)^2 \cdot \frac{Kg\rho}{2} \text{ cubic units per second.}$$

Now there are $\pi \times 2^2$ square units of water-surface in the cavity.

So that the surface will fall at the rate of $\cdot 92 \times \frac{(4\cdot 35)^2}{2^2} \cdot \frac{Kg\rho}{2}$

units per second. But there are 8 units in the height of the block.

Therefore it will fall

$$\cdot 92 \times \frac{(4\cdot 35)^2}{8} \times 981 \cdot K \times \frac{\text{height of block}}{8} \text{ per second}$$

$$= 16,200 \times K \times (\text{height of block}) \text{ per minute.}$$

That would be one way of measuring K . Errors will arise owing

to the upper surface not remaining always at the level shown in the drawing. I have preferred to keep the water-surface nearly steady against a needle-point, and to measure the flow by a burette. In this case let the height of the block be h centimetres. Then

one of our cubic units is $\left(\frac{h}{8}\right)^3$ c.c.; and

$$\begin{aligned} \text{the total flow} &= \cdot 92 \times (4\cdot35)^2 \times \frac{Kgp}{2} \cdot \left(\frac{h}{8}\right)^3 \times 60 \text{ c.c. per minute} \\ &= 3140Kh^3 \text{ cc. per minute.} \end{aligned}$$

By this method I measured the conductivity of some peat brought from the Lochar Moss, near Dumfries. It was a slightly muddy litter-peat. It was cut from a wet part of the bog, and preserved in a damp-tight box until required four months later. Three blocks were cut, of the form shown in the diagram, and 8 cms. high; that is, $h = 8$. They had better have been twice or thrice this height, but I was short of material. They were placed on perforated zinc; and the flow measured with a burette and needle as described.

The values found for $K_{13\cdot5}$ were:

$$1\cdot30 \times 10^{-7} \text{ C.G.S. units,}$$

$$0\cdot93 \times 10^{-7} \quad ,, \quad ,,$$

$$11\cdot1 \times 10^{-7} \quad ,, \quad ,,$$

The first two resemble the value found by the glass tube experiment, namely $K_{9\cdot5} = 1\cdot3 \times 10^{-7}$ C.G.S. units.

The third was obviously more open in structure.

§ 7. CAPILLARITY IN PEAT.

Boussinesq (1904e) assumes that the capillary attraction in a uniform soil has the effect of reducing the pressure at the water-air surface by an amount which is constant all over the surface. This is clearly the most reasonable assumption when the surface is everywhere sinking. But if the surface is rising into dry soil, the innumerable water-air surfaces will then be convex upwards, and the pressure will be increased instead of diminished. And if

the surface is steady, as in the cases discussed in the foregoing section on drainage, it is not easy to foresee what shape they will be, except in certain instances—for example: the surface of a wall of peat from which water is oozing out is covered by a layer of water outside the peat, and of negligible curvature, so that the surface-tension there is of no effect. But what of the upper surface in the cylindrical block used in determining the conductivity? The theoretical water-line shown in the diagram had no real existence; the whole block was saturated. Some principle is required to determine the pressure due to capillarity as a function of position on the surface, and thus to find the corrected flow out of the cavity.

§ 8. CONCLUSION.

In conclusion, I should like to thank Dr. Gilbert J. Fowler, who has kindly given me the reference to Pennick's paper quoted in the bibliography.

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44, QUEEN'S ROAD,

TEDDINGTON,

MIDDLESEX.

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MENDELIAN CHARACTERS AMONG
SHORT-HORN CATTLE.

BY

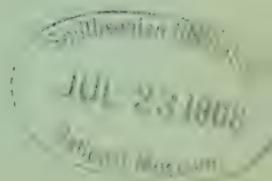
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[Authors alone are responsible for all opinions expressed in their Communications.]

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XXVIII.

MENDELIAN CHARACTERS AMONG SHORT-HORN CATTLE.

BY JAMES WILSON, M.A., B.Sc.,

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IN a paper "On the Inheritance of Coat-colour in Cattle," published in *Biometrika*, volume iv., pp. 427-464, Miss A. Barrington and Professor Karl Pearson have collected statistics taken at random from volumes xxxvii. to xlix. of the "Short-horn Herd-book" as to the colours of 2172 calves and their parents. From these statistics it can be shown that, as regards colour, short-horns display Mendelian characters: the whites and the reds being the pure ancestral races, and the roans the hybrids.

The following table (see p. 318) is Miss Barrington and Professor Pearson's second and third tables combined: the calves of both sexes being collected in one instead of being separated in two tables.

But this table is framed with regard rather to the colours under which short-horns are entered in the Herd-book than to the origin and history of the breed.

The short-horn breed of cattle originated in the eighteenth century on the borders of Durham and York, in a part of the country which was the meeting-ground of the three races of cattle then existing in Britain—the Celtic, the Roman, and the Saxon.

In pre-Roman times the Celtic race inhabited the whole of the island. Its modern representatives are the black breeds of Scotland, Wales, and Ireland.

The Romans introduced a white race which they distributed throughout the parts of the country under their occupation. Its modern representatives are the white cattle of Wales, the "wild"

white cattle of Chillingham, Cadzow, and other parks, and the white short-horns.

| COAT-COLOUR OF DAMS. | COAT-COLOUR OF SIRES. | | | | | COAT-COLOUR OF CALVES. |
|------------------------|-----------------------|------------------------|----------------|-------|--------|------------------------|
| | Red. | Red with little white. | Red and white. | Roan. | White. | |
| Red. | 156 | 23 | 10 | 126 | 1 | Red. |
| | 23 | 12 | 6 | 20 | — | Red with little white. |
| | 11 | 3 | 3 | 15 | 1 | Red and white. |
| | 6 | 1 | 5 | 167 | 40 | Roan. |
| | — | — | — | 4 | — | White. |
| Red with little white. | 18 | 8 | — | 22 | — | Red. |
| | 13 | 6 | 1 | 10 | — | Red with little white. |
| | 5 | 4 | 2 | 8 | — | Red and white. |
| | 1 | 1 | 1 | 43 | 10 | Roan. |
| | — | — | — | — | — | White. |
| Red and white. | 31 | 4 | 6 | 20 | 1 | Red. |
| | 12 | 4 | 1 | 15 | — | Red with little white. |
| | 23 | 10 | 18 | 21 | — | Red and white. |
| | 4 | 5 | 1 | 81 | 18 | Roan. |
| | — | — | — | — | — | White. |
| Roan. | 117 | 19 | 14 | 86 | — | Red. |
| | 26 | 9 | 3 | 31 | — | Red with little white. |
| | 24 | 9 | 5 | 35 | — | Red and white. |
| | 157 | 42 | 31 | 278 | 14 | Roan. |
| | — | — | — | 84 | 9 | White. |
| White. | — | — | — | 1 | — | Red. |
| | 1 | — | — | 1 | — | Red with little white. |
| | 2 | — | 1 | 1 | — | Red and white. |
| | 45 | 7 | 8 | 33 | — | Roan. |
| | — | — | — | 15 | 3 | White. |

The Anglo-Saxons introduced a red race which occupied England south of a line dipping southwards in the middle and drawn

approximately from Herefordshire to Lincolnshire till about the middle of the eighteenth century: the mixed Celtic and Roman races having been driven northwards and westwards. The modern representatives of the red race are the Hereford, Devon, Sussex, Norfolk, and Lincoln breeds.

There was thus established a red race, holding the south of the island, and a black race with an admixture of white, holding the rest.

Where the southern red race met the northern black and white races, there sprang up a new kind of cattle—the long-horn—which is now almost extinct, but which, at the middle of the eighteenth century, occupied some of the midland counties and pressed northwards on both sides of the Pennine range into south Lancashire and south-west Yorkshire. These cattle were a mixture possibly of all the three races; but they are not concerned in the present question.

During the seventeenth century and part of the eighteenth, and also probably at a somewhat earlier period, many cattle were imported from Holland to the east of England, especially to Durham, York, and Lincoln. These cattle were red-and-white and black-and-white flecked. The red-and-whites were most appreciated, and eventually swamped the others. These red-and-white cattle were of the same race as the red cattle brought over a thousand years before by the Anglo-Saxons.

Although the cattle of the south of England were called “red,” they were not all entirely red any more than the black cattle now in Wales and Scotland are all entirely black. Notwithstanding a tendency on the part of breeders to breed it out, a patch of white on the under-line is not uncommon among the red breeds; and the Herefords have white not only on the under-line, but also on the face and along the back. It is not probable that old Anglo-Saxon cattle were as highly flecked as the red-and-white cattle imported later from Holland. The point is of no present importance, however.

The earliest progenitors to which present-day short-horns can be clearly traced were white cattle belonging to the Aislabies of Studley Royal¹ near Ripon, whose herd dated back to the

¹ Storer suggested that the Studley Royal herd “originated from the cattle of the monks of Fountains Abbey close by.”

beginning of the eighteenth century. Studley Royal bulls were used by farmers in the neighbouring districts.

Celtic blood was also introduced to the stream from which modern short-horns are descended; and at least two instances are on record, viz.: through *Lady Maynard*, calved in 1789, who was "descended from a black cow with white belly and white legs to the knee"; and through *Grandson of Bolingbroke*, calved in 1794, whose grandam was a "red Galloway."

But the main stream consisted chiefly of Saxon cattle, more especially of the branch introduced from Holland in the seventeenth and eighteenth centuries. It would not be safe to say that there were none of the old Anglo-Saxon red cattle near the birth-place of the short-horn in the eighteenth century; but, if they were there, they were in a minority. The whole of the recruits drawn in to the short-horn breed during the last hundred years have been drawn from the two branches of the Saxon race, although, perhaps, as time went on, the red branch has been drawn upon more eagerly.

It happens among polygamous pure-bred stock that, in a few generations, unless it be specially eliminated, a progenitor's blood runs in the veins of numerous descendants. An illustrious sire gets, perhaps, twenty sons; his sons again get three or four hundred; these again get four or five thousand; and so on until it may be difficult to find an animal which is not the illustrious sire's descendant. Thus at the present day there are not many short-horns which are not descended from Cruickshank's *Champion of England*, born in 1860, and none which are not descended from Charles Colling's *Comet*, born in 1805, and descended from Studley Royal stock and also from *Lady Maynard*. Thus the blood of the old Studley Royal white cattle, of the old Saxon red and red-and-white cattle, and of the Northern black cattle flows in every short-horn alive to-day. But the black colour, if it can be said ever to have been bred within the breed, was soon bred out. It was unpopular even in the eighteenth century. Mendel's law shows how easily a foreign colour or any other outward signs of a foreign cross may be bred out.

Thus, in the matter of colour at any rate, the modern short-horn is descended from two races, the White Roman and the Red Saxon: the "red" including red, red with little white, and red-and-white.

The table of coat-colours on page 318 ought therefore to be reconstructed on the basis that the Saxon "reds" are one of the ancestral races, and the Roman white cattle the other. The table then becomes as follows :—

| COAT-COLOUR OF DAMS. | COAT-COLOUR OF SIREs. | | | COAT-COLOUR OF CALVES. |
|----------------------|-----------------------|-------|--------|------------------------|
| | Red. | Roan. | White. | |
| Red, } | 413 | 257 | 3 | Red. |
| | 25 | 291 | 68 | Roan. |
| | 0 | 4 | 0 | White. |
| Roan, } | 226 | 152 | 0 | Red. |
| | 230 | 278 | 14 | Roan. |
| | 0 | 84 | 9 | White. |
| White, } | 4 | 3 | 0 | Red. |
| | 60 | 33 | 0 | Roan. |
| | 0 | 15 | 3 | White. |

Expressed in the usual Mendelian manner, these figures show that—

| | Reds. | Roans. | Whites. |
|------------------------------------|-------|--------|---------|
| 438 Reds, crossed by reds, produce | 413 | 25 | — |
| 3 Whites, „ whites, „ | — | — | 3 |
| 135 Whites, „ reds, „ | 7 | 128 | — |
| 514 Roans, „ roans, „ | 152 | 278 | 84 |
| 1008 Roans, „ reds, „ | 483 | 521 | 4 |
| 74 Roans, „ whites, „ | 3 | 47 | 24 |

These figures do not come out in Mendelian ratios with perfect accuracy; but the discrepancies can be explained. They are the result of three causes, viz. :—

(a) Sometimes it requires a close examination to tell whether a calf is really red or roan. Breeders have not hitherto examined

the colours of their calves with a view to greater accuracy than commerce required; and so some errors of description have crept into the herd-book.

(b) White short-horns are of smaller money value than roans or reds, and consequently many are not registered at all. This happens especially with animals of little merit.

(c) Among unscrupulous breeders the substitution of a coloured calf for a white one is not unknown: a white calf's pedigree being bestowed upon a roan or a red.

To eliminate these sources of error as far as possible, I have collected a new set of data which is made up of every entry in volume lii. (published in November, 1906) of the Short-horn Herd-book by a number of breeders who may be expected, because of the high value of their cattle, to register a very high proportion of their calves, and who would not substitute one calf for another.

Two of the sources of error cannot, however, be entirely eliminated, viz.: the error of wrong description and the error arising from some white calves not being registered. For instance, a bull standing now at the Albert Agricultural College, Glasnevin, was registered in the herd-book by his breeder, who is the most distinguished breeder in England, as being red. This bull's sire was white; his dam was red; and he ought therefore to be roan. He has bred several white calves from roan cows; and on this ground also he ought to be roan. On close inspection *he is a roan*, but such a roan as might easily be mistaken for a red.

Amongst breeders the prejudice against white cattle is very strong, but especially against an animal some of whose ancestors were white. There is an impression that a white animal from roan parents may produce some white calves, but that a white animal from one or two white parents will produce many white calves. Consequently even in the best herds some white calves are not registered at all, more especially if they have a white parent.

For the reason that white calves are not desired, two white animals are very seldom mated. Among the 2172 matings collected by Miss Barrington and Professor Pearson, only three such cases occur. In the 1023 matings which I have collected

only one case occurs. The paucity of white matings detracts from the completeness of the data; but the necessary numbers can be made up from other data collected by Miss Barrington and Professor Pearson. They searched the herd-book for white matings, and found that 91 such cases produced 1 red calf, 4 roans, and 86 whites. In view of the causes of error above mentioned, and the regularity with which the Mendelian law operates, these 5 coloured calves may be set down as substitutes or the progeny of erroneously described parents.

Expressed in Mendelian form, the data I have collected give the following results:—

| | Reds. | Roans. | Whites. |
|-----------------------------------|-------|--------|---------|
| 95 Reds, crossed by reds, produce | 90 | 5 | 0 |
| 1 White, „ white, produces | 0 | 0 | 1 |
| 78 Reds, „ whites, produce | 0 | 78 | 0 |
| 370 Roans, „ roans, „ | 90 | 178 | 102 |
| 426 Roans, „ reds, „ | 214 | 209 | 3 |
| 53 Roans, „ whites, „ | 0 | 34 | 19 |
| <hr/> | | | |
| 1023 | | | |

Remembering the sources of error, the above figures approximate sufficiently closely to Mendelian ratios to show that the roan short-horn is a hybrid between two races—one white, the other “red.”

It may be of some interest to show the colours of the calves when reds are crossed by roans—first, when the bull is red, and secondly, when the bull is roan. They are as follows:—

| | Reds. | Roans. | Whites. |
|--|-------|--------|---------|
| 150 Red bulls produced from 150 roan cows, | 86 | 63 | 1 |
| 276 Roan bulls „ 276 red cows, | 128 | 146 | 2 |

The short historical sketch of British cattle in this paper is based chiefly upon the following:—Bede’s *Ecclesiastical History* and *The Anglo-Saxon Chronicle*; Green’s *The Making of England*; Boyd Dawkins’s *Early Man in Britain*; an article in “*Archæologia*” by M’Kenny Hughes, *On the more important Breeds of Cattle which have been recognized in the British Isles in successive periods*; Storer’s *Wild White Cattle*; Harting’s *Extinct British*

Mammals; Youatt's *Cattle : their Breeds, Management, and Diseases*; a number of English agricultural books published in the seventeenth and eighteenth centuries; Low's *Domesticated Animals of the British Islands*; an article in the *Journal of the Royal Agricultural Society of England* for 1899 by Cadwallader J. Bates, on *The Brothers Colling*; and Sinclair's *History of Short-horn Cattle*.

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JULY, 1908.

DEPOSITS OF UNBROKEN MARINE SHELLS
AT HIGH LEVELS IN THE CARRAUN
PENINSULA, COUNTY MAYO.

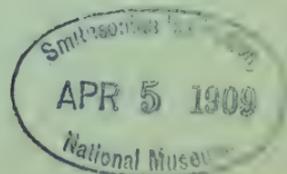
BY

T. E. GORDON, M.B., AND A. F. DIXON, Sc.D.

[Authors alone are responsible for all opinions expressed in their Communications.]

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XXIX.

DEPOSITS OF UNBROKEN MARINE SHELLS AT HIGH LEVELS IN THE CARRAUN PENINSULA, COUNTY MAYO.

BY T. E. GORDON, M.B., AND A. F. DIXON, Sc.D.

[Read, JUNE 16 ; Received for Publication, JUNE 19 ; Published, JULY 23, 1908.]

DURING the Easter holidays of 1907 we discovered a large deposit of shells a few miles west of Mulrany at about 100 feet above the present sea-level. The shells are all of modern littoral type, and of so fresh an appearance as to suggest that they were placed there very recently. Limpets form the large majority; but we found many periwinkles (*L. littorea* and *L. obtusata*), and in less numbers *Purpura*, *Trochus* (two species), small mussels, cockles; we also found a single *Solen*. These shells were for the most part unbroken, even in the case of the small fragile mussels, and one cockle had the ligament still intact. The number of shells was remarkable; we might easily have filled a wheelbarrow from any of the recesses of the rocks in which they lay.

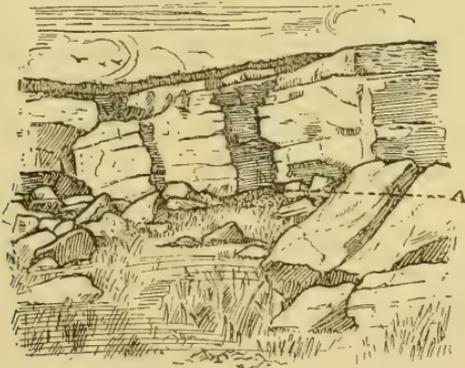


FIG.—Cliff of Old Red Sandstone. The dotted line A indicates the clefts, at the base of the cliff, in which the shell-deposits occur. (From a photograph.)

The position of this deposit can be easily determined by anyone who walks along the road that leads from Mulrany to

Achill, skirting the north shore of Clew Bay. This road, at about three and a half miles from Mulrany, passes between low cliffs of Old Red Sandstone, which are, as we have said, about 100 feet above the sea. Immediately bordering the road on the south side is a small peat bog, with a turf cutting in which we found some shells; and beyond the bog there lie in tumbled ruin many blocks of sandstone partially concealed by peaty deposit and vegetation. In the hollows under these blocks we found great numbers of shells. The cliffs themselves were much undercut, so as to form deep, narrow recesses from which we scooped out many limpets. On the north side of the road we found under the cliffs similar deep excavations, and in front similar scattered blocks. Here also we found large shell-deposits, a portion of a crab's claw, and some fish-bones, the latter like the shells of quite modern type. The fish remains included portions of a Wrass's skeleton.

Last Easter (1908) one of us made further explorations in the immediate district, and found shell-deposits at 150 feet, at 300 feet, and at about 750 feet above sea-level. In each case the shells lay in horizontal pockets or clefts, at the base of cliff-like rock-terraces of Old Red Sandstone. The largest deposits were found in recesses at the base of a rocky cliff 300 feet above the sea, and about a quarter of a mile to the north of the little village of Dooghbeg. Here many shells are exposed on the surface in hollows beneath the cliffs, and others occur deep in the narrow clefts, beneath the rocks, from which we were able to extract them by means of a small long-handled rake. Near Lough Ard on the mountain slope, 700 to 750 feet above sea-level, shells were obtained in large numbers in similar positions.

We record these observations because we think that the occurrence of large deposits of shells at heights varying from 100 to 750 feet above sea-level, on the hills to the north of Clew Bay, demands explanation from geologists.

The shells of course differ entirely from those obtained in drift, which are scattered and broken, while these are unbroken and grouped in vast numbers. Moreover the types are not mixed, for all the shells are littoral. It is impossible to believe that the shells were carried to their present position by birds. Their number, their unbroken condition, and their presence in deep

narrow recesses, or clefts, under the cliffs are sufficient to dispose of this suggestion. We find it alike impossible to believe that they have been carried by human agency. The land hereabouts is barren uncultivated mountain, without even a hovel near; and if it be thought suggestive that the shells were first found near the road, it must also be remembered that others were found, under similar conditions, about half a mile inland, and over 700 feet up the side of the mountain.

The aspect of the rocks, together with the fact that the shells are all shallow-water forms, naturally suggests to the ordinary observer that the explanation is to be found in a receding sea-level, and that the deposits should be regarded as raised beaches. No geologist, however, we fancy, would for one moment entertain this suggestion, yet we have no other to offer.

The shells found are exactly those kinds which at present occur in large numbers at the existing coast-line; and the extremely perfect state of preservation which may be observed in many of the limpets, leads one to doubt if they could possibly have been torn while alive from the rocks to which they clung. The intact condition of the edges of many of the shells harmonizes more readily with the idea that with the death of their inhabitants they had fallen down into the clefts of the rocks, and been protected from erosion and injury. Shells equally well preserved are to be found packed away in the rock-crevices which occur between the existing tide-marks near where the shell-deposits were found.

We hope that these observations, although extremely incomplete, may be of some geological importance or interest.

Royal Dublin Society.

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THE
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Vol. XI. (N. S.), No. 30.

JULY, 1908.

CURIOUS WATER-WORN MARKINGS ON ROCKS
AT DOOGBEG, CO. MAYO.

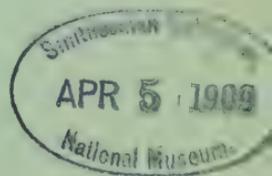
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XXX.

CURIOUS WATER-WORN MARKINGS ON ROCKS AT
DOOGBEG, CO. MAYO.

BY T. E. GORDON, M.B., AND A. F. DIXON, Sc.D.

[Read, JUNE 16; Received for Publication, JUNE 19; Published, JULY 23, 1908.]

THE curious markings here described and illustrated are to be seen on the red sandstone rocks close to the coast road near the little village of Dooghbeg, on the north of Clew Bay. The marks have attracted the notice of the inhabitants, who have invented a legend to account for their presence; but, so far as we have been able to find, they have not received the attention of geologists. They occur on a great flat surface of sandstone, which, like the other beds of this rock in the neighbourhood, is tilted so as to slope to the south, forming an angle of about 20 degrees with the horizontal. It is possible to refer all the markings, of which there are about twenty to twenty-five more or less defined examples, to a single type. In each mark there is a curved or arched portion, the convexity of which is always directed towards the north, i.e., up the slope of the rock on which it occurs. In the concavity of the arch there is always to be found a pit-like depression of varying size and depth. The limbs of the arch, as they pass down the slope of the rock, on each side of the pit, vary in their disposition. In some cases they run nearly parallel to one another, or are but slightly incurved; and then, if they are short, the whole mark has a somewhat horseshoe-shaped outline. In other cases the limbs of the arch gradually approach one another and become confluent. As a result a somewhat pear-shaped outline is present. Each marking may be made up of a large number of parallel, fairly deep, but narrow scratches, or the outline of the mark may consist of a single groove a quarter to half an inch in depth and half an inch wide. In size the markings vary from $4\frac{1}{2}$ inches to 12 inches in transverse diameter.

The figures illustrate some of the varieties of markings which may be observed.



FIG. 1.—Surface of Sandstone Rock, showing a group of the markings. In the upper part of the figure the drift, which covers much of the rock-surface, is seen. (From a photograph.)

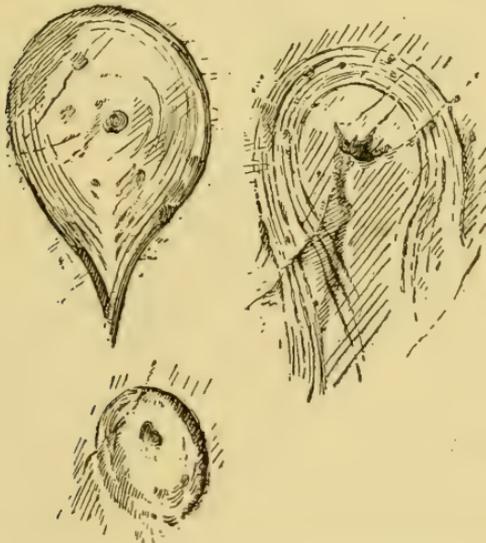


FIG. 2.—Three varieties of the markings drawn on a larger scale. The largest of these measures 12, the smaller $4\frac{1}{2}$ inches across. (Drawn from casts taken in plaster of Paris.)

We believe that the markings are water-worn. An examination of the neighbouring rocks leads us to believe that the surface of the bed on which the marks occur lay immediately

beneath a stratum of conglomerate. Such strata are conspicuous features of the rock-formation of the district. The pit-like depressions in the centre of the markings were no doubt occupied at one time by projecting pieces of vein-quartz, like those to be seen in the beds of conglomerate near at hand. The markings almost certainly were formed gradually, about the time that the overlying conglomerate was nearly all removed. A stream of water containing sand or grit, flowing over the sandstone bed, would be arrested and deflected by the few remaining upstanding pieces of quartz; and the grinding action of the grit would give rise to marks like those to be seen on the rocks. The outline of the mark, that is, the form of the arch and the direction of its limbs, appears to have been influenced in great measure by the size and shape of the obstructing piece of quartz. The drift, which at present lies over much of the mountain side and is being constantly washed over these rocks, would have furnished excellent material for cutting the grooves or markings. In wet weather at the present time, there is just such a flow of water and drift sand over the rock as would, we believe, be likely to produce the markings. Unfortunately there are now no projecting pieces of quartz sticking up to deflect the stream; and hence the flow, which at present occurs after heavy rain, tends to erase the existing marks.

If we prepare a flat sloping slab of plaster, with projecting embedded pebbles, and arrange that a thin stream of water flows evenly over it, we can easily demonstrate that particles of sand, or heavy, insoluble powder, carried in the stream, as they reach and are carried past the obstructing projections, can be made to describe figures quite comparable to those cut on the rock at Dooghbeg.

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FEBRUARY, 1909.

ON THE QUANTITATIVE SPARK-SPECTRA OF
TITANIUM, URANIUM, AND VANADIUM.

BY

JAMES H. POLLOK, D.Sc.,

ROYAL COLLEGE OF SCIENCE, DUBLIN.

(PLATES XXV., XXVI.)

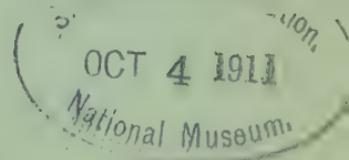
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XXXI.

ON THE QUANTITATIVE SPARK-SPECTRA OF TITANIUM,
URANIUM, AND VANADIUM.

BY JAMES H. POLLOK, D.Sc., Royal College of Science, Dublin.

[PLATES XXV.-XXVI.]

[Published FEBRUARY 25, 1909.]

OWING to the very large number of lines in the spectra of titanium, uranium, and vanadium, a knowledge of their quantitative spectra is absolutely necessary for analytical purposes; and as titanium is a very common constituent of minerals, its residuary lines are continually found in the course of spectrographic analysis.

The quantitative spectra of those elements were determined by the method devised by Professor W. N. Hartley,¹ with the modifications described by Mr. A. G. G. Leonard and me, in our various papers on Quantitative Spark-Spectra,² published in the Proceedings of this Society. Purchased samples of the metals and oxides were used, and in each case a weighed quantity of oxide was dissolved in hydrochloric acid, then diluted so as to contain 10 per cent., 1 per cent., .1 per cent., .01 per cent., and .001 per cent. of the element. These solutions were then successively sparked, using a Ruhmkorff coil, condenser, and self-induction coil for the removal of air-lines; and photographs were taken of the spectra, giving an exposure of one minute each. Photographs were also taken of the spectra given by the fused metals; and it was found that, in each of the three cases, the solutions gave all the lines given by the metallic electrodes.

¹ Proc. Roy. Soc., 1882, p. 81.

² Proc. Roy. Dub. Soc., 1907. Nos. 16, 17, and 18; and 1908. Nos. 23 and 24.

It was not considered necessary to reproduce the photographs of all the spectra; but Plate XXVI. shows the spectra given by a strong solution and a dilute solution of each of the three elements; and the most persistent lines are indicated by one, two, or three dots placed under them, accordingly to their persistency, and Plate XXV. shows the complete series of photographs for vanadium.

In the Tables of wave-lengths, double lines, the wave-lengths of only one of which is given, are indicated by two dashes after the intensity: thus 10''; the persistency of the lines is indicated by Greek letters, thus:—

| | | | | | |
|----------|-----------|-----|----------|---------------|-------|
| ϕ | seen with | 1 % | solution | not seen with | 0.1 % |
| χ | '' | '' | 0.1 % | '' | '' |
| ψ | '' | '' | 0.01 % | '' | '' |
| ω | '' | '' | 0.001 % | '' | '' |

The photographs of spectra extend from λ 5890 to λ 2544.3, and were taken by a one-prism quartz spectrograph by Hilger. The measurements were made by one of Hilger's micrometers, and these were afterwards reduced to wave-lengths by use of a curve for the identification of the lines. In each case the micrometer was set so that gold line No. 9 was at 280.0, that point corresponding with its position on the curve used. The wave-lengths given are those generally accepted, but in every case the measured wave-lengths agreed very closely, so that there could be no possible doubt of the identity of the lines.

QUANTITATIVE SPECTRUM OF TITANIUM CHLORIDE.

| Linear Measurement, $\frac{1}{100}$ inch. | Wave-length. | Intensity and Persistency. | Linear Measurement, $\frac{1}{100}$ inch. | Wave-length. | Intensity and Persistency. |
|---|--------------|----------------------------|---|--------------|----------------------------|
| 261.05 | 5210.6 | 10 ϕ | 366.35 | 3654.7 | 5 ϕ |
| 267.10 | 5064.4 | 10 ϕ | 367.70 | 3642.8 | 10 ϕ |
| 269.85 | 5014.4 | 10 ϕ | 374.00 | 3586.7 | Au No. 14 |
| | 5007.4 | 10 ϕ | 383.20 | 3511.0 | 50 χ |
| 270.40 | 4999.7 | 10 ϕ | 383.95 | 3505.0 | 50 χ |
| | 4991.2 | 10 ϕ | 387.50 | 3477.4 | 15 ϕ |
| 270.85 | 4981.9 | 10 $\frac{1}{2}\chi$ | 389.55 | 3461.9 | 15 ϕ |
| 274.00 | 4919.0 | 6 ϕ | 391.75 | 3444.5 | 15 χ |
| 279.40 | 4805.6 | 10 ϕ | 398.50 | 3394.7 | 30 χ |
| * 280.00 | 4792.8 | Au No. 9 | 399.40 | 3388.0 | 15 ϕ |
| 280.70 | 4779.0 | 6 ϕ | 400.00 | 3383.0 | Au No. 15 |
| 281.70 | 4759.4 | 10 ϕ | 401.60 | 3372.9 | 30 ω |
| | 4758.3 | 10 ϕ | 403.20 | 3301.3 | 50 ω |
| 292.10 | 4572.3 | 20 ϕ | 405.00 | 3349.2 | 20 ω |
| 292.60 | 4563.9 | 15 ϕ | 406.15 | 3340.5 | 15 ψ |
| 293.50 | 4549.9 | 20 ϕ | 407.00 | 3335.4 | 20 ϕ |
| 294.25 | 4534.2 | 6''' χ | | 3329.0 | 20 ϕ |
| 297.10 | 4488.4 | Au No. 10 | 408.00 | 3326.9 | 10 ϕ |
| 298.35 | 4468.7 | 15 χ | 409.00 | 3321.9 | 10 ψ |
| 303.10 | 4395.2 | 20 χ | 414.15 | 3287.8 | 15 ϕ |
| 308.35 | 4315.4 | Au No. 11 | 415.20 | 3280.8 | Au No. 16 |
| 309.45 | 4300.2 | (8) χ | 418.20 | 3261.7 | 30 ψ |
| 336.15 | 3958.3 | 10 χ | 419.55 | 3253.0 | 10 ψ |
| 336.95 | 3948.8 | 10 χ | 420.20 | 3248.8 | 20 ϕ |
| 354.90 | 3761.5 | (50) ω | 421.30 | 3242.1 | 20 χ |
| | 3759.4 | 50 ω | | 3239.6 | 10 χ |
| 355.70 | 3753.0 | 7 ϕ | | 3236.7 | 15 χ |
| 356.90 | 3741.8 | 30 χ | 422.60 | 3234.6 | 20 χ |
| 362.90 | 3685.3 | 50 ω | 423.35 | 3229.4 | (3) ψ |

QUANTITATIVE SPECTRUM OF TITANIUM CHLORIDE—*continued.*

| Linear Measurement, $\frac{1}{100}$ inch. | Wave-length. | Intensity and Persistency. | Linear Measurement, $\frac{1}{100}$ inch. | Wave-length. | Intensity and Persistency. |
|---|--------------|----------------------------|---|--------------|----------------------------|
| 424·20 | 3223·0 | 10 ϕ | 502·95 | 2825·6 | Au No. 20 |
| | 3224·4 | 10 ϕ | 504·80 | 2818·0 | 10 ϕ |
| 425·15 | 3218·4 | 10 ψ | 506·70 | 2810·4 | 10 χ |
| 427·55 | 3202·7 | 15 χ | 507·95 | 2805·0 | 10 ϕ |
| 429·65 | 3191·0 | 20 ψ | 521·50 | 2751·8 | 8 ϕ |
| 433·30 | 3168·7 | 15 χ | 522·35 | 2748·3 | Au No. 21 |
| 434·40 | 3162·7 | 6 ψ | 522·90 | 2746·8 | 6 ϕ |
| 441·20 | 3122·9 | Au No. 17 | 524·10 | 2742·4 | 4 ϕ |
| 447·55 | 3088·1 | 15 ψ | 224·75 | 2739·9 | 1 ϕ |
| 449·30 | 3078·7 | 6 χ | 542·10 | 2676·1 | Au No. 22 |
| 450·50 | 3072·2 | 3 χ | 550·70 | 2646·2 | 5 χ |
| 451·65 | 3066·4 | 3 χ | 551·30 | 2644·3 | 3 ϕ |
| 453·20 | 3058·2 | 5 χ | 552·10 | 2641·6 | Au No. 23 |
| 458·70 | 3029·3 | Au No. 18 | 567·80 | 2590·2 | Au No. 24 |
| 461·15 | 3017·4 | 6 ϕ | 573·85 | 2571·2 | 4 ϕ |
| 467·60 | 2984·9 | 10 ϕ | 575·00 | 2567·6 | 7 χ |
| 473·00 | 2959·1 | 5 ϕ | 575·65 | 2565·5 | 8 ϕ |
| 475·80 | 2945·6 | 5 ϕ | 576·30 | 2563·5 | 10 ϕ |
| 476·60 | 2942·1 | 4 ϕ | 582·75 | 2544·3 | Au No. 25 |
| 482·65 | 2913·6 | Au No. 19 | 584·20 | 2540·1 | 10 χ |
| 489·30 | 2884·3 | 8 ϕ | 585·65 | 2536·9 | 5 ϕ |
| 490·75 | 2877·5 | 5 χ | 586·05 | 2534·7 | 6 ϕ |
| 494·25 | 2862·5 | 3 χ | 587·10 | 2531·4 | 8 χ |
| 499·05 | 2842·0 | 4 χ | 588·35 | 2527·9 | 15 ϕ |
| 502·25 | 2828·3 | 10 χ | 589·15 | 2525·7 | 10 χ |

QUANTITATIVE SPECTRUM OF URANIUM CHLORIDE.

| Linear Measurement,
$\frac{1}{100}$ inch. | Wave-length. | Intensity and Persistence. | Linear Measurement,
$\frac{1}{100}$ inch. | Wave-length. | Intensity and Persistence. |
|--|--------------|----------------------------|--|--------------|----------------------------|
| * 280.00 | 4792.8 | Au No. 9 | 416.60 | 3270.3 | 2 ϕ |
| 290.30 | 4605.4 | 4 ϕ | 420.75 | 3244.4 | 2 ϕ |
| | 4603.9 | ϕ | 441.15 | 3122.9 | Au No. 17 |
| 293.70 | 4543.8 | 7 ϕ | 446.55 | 3093.1 | 2 χ |
| 297.00 | 4488.4 | Au No. 10 | 450.35 | 3072.9 | 2 ϕ |
| 301.65 | 4415.4 | 2 ϕ | 453.10 | 3058.0 | 2 χ |
| 304.50 | 4371.9 | 2 ϕ | 455.70 | 3044.3 | 2 χ |
| 305.60 | 4355.8 | 4 ϕ | 458.60 | 3029.3 | Au No. 18 |
| 306.50 | 4341.9 | 4 ϕ | 462.90 | 3006.9 | 1 ϕ |
| 308.30 | 4315.4 | Au No. 11 | 469.50 | 2974.2 | 1 ϕ |
| 313.40 | 4241.9 | 4 ψ | 470.00 | 2971.2 | 2 ϕ |
| 318.60 | 4171.8 | 3 ϕ | 470.50 | 2969.6 | 1 ϕ |
| 324.90 | 4090.3 | 4 χ | 476.50 | 2941.9 | 2 χ |
| 326.90 | 4065.2 | Au No. 12 | 482.60 | 2913.6 | Au No. 19 |
| 333.60 | 3979.9 | 2 ϕ | 488.00 | 2888.3 | 1''' ϕ |
| 336.30 | 3954.9 | 2 χ | 493.50 | 2865.7 | 2 χ |
| 341.45 | 3898.0 | Au No. 13 | 502.15 | 2828.1 | 1 ϕ |
| 343.65 | 3874.2 | 2 ϕ | 503.00 | 2825.6 | Au No. 20 |
| 345.00 | 3859.7 | 2 ϕ | 510.85 | 2794.0 | 2 ϕ |
| 352.60 | 3783.0 | 2 ϕ | 511.70 | 2790.8 | 1 ϕ |
| 361.90 | 3693.9 | 2 χ | 518.00 | 2766.0 | 1 ϕ |
| 364.35 | 3672.7 | 2 ψ | 518.75 | 2763.0 | 1 ϕ |
| 373.90 | 3586.7 | Au No. 14 | 522.45 | 2748.3 | Au No. 21 |
| 377.90 | 3552.4 | 2 ψ | 523.90 | 2742.7 | 1 ϕ |
| 390.35 | 3453.7 | 2 ϕ | 526.30 | 2733.4 | 1 ϕ |
| 392.60 | 3436.9 | 2 ϕ | 554.30 | 2635.6 | 2 χ |
| 400.00 | 3383.0 | Au No. 15 | 568.15 | 2590.2 | Au No. 24 |
| 406.55 | 3337.9 | 2 χ | 580.35 | 2552.5 | 1 ϕ |
| 415.05 | 3280.8 | Au No. 16 | 581.10 | 2549.5 | 1 ϕ |

QUANTITATIVE SPECTRUM OF VANADIUM CHLORIDE.

| Linear Measurement, $\frac{1}{100}$ inch. | Wave-length. | Intensity and Persistency. | Linear Measurement, $\frac{1}{100}$ inch. | Wave-length. | Intensity and Persistency. |
|---|--------------|----------------------------|---|--------------|----------------------------|
| * 280.00 | 4792.8 | Au No. 9 | 378.45 | 3545.3 | 20 χ |
| 298.75 | 4462.6 | 14 ψ | 381.90 | 3517.4 | 20 χ |
| | 4460.0 | 14 ψ | 389.50 | 3457.3 | 10 ϕ |
| 302.00 | 4408.7 | 15 ψ | 399.50 | 3383.0 | Au No. 15 |
| 402.50 | 4400.8 | 18 ϕ | 414.45 | 3280.8 | Au No. 16 |
| 302.80 | 4395.4 | 20 ϕ | 415.15 | 3276.3 | 20 χ |
| 303.20 | 4390.1 | 30 ϕ | 415.90 | 3271.2 | 20 χ |
| 303.60 | 4384.9 | 40 ϕ | 416.40 | 3267.8 | 20 χ |
| 303.90 | 4379.4 | 40 ψ | 424.40 | 3217.2 | 12 ϕ |
| 308.10 | 4315.4 | Au No. 11 | 428.78 | 3190.8 | 16 ϕ |
| 321.40 | 4132.2 | 10 ϕ | 429.15 | 3187.8 | 10 ϕ |
| 321.70 | 4128.3 | 10 ϕ | 429.80 | 3185.5 | 4 χ |
| 322.75 | 4115.5 | 4 ϕ | | 3184.1 | 4 χ |
| 323.05 | 4110.9 | 10 ϕ | 436.90 | 3142.7 | 3 ϕ |
| 326.70 | 4065.2 | Au No. 12 | 437.30 | 3139.9 | 8 ϕ |
| 330.25 | 4023.6 | 20 ϕ | 437.90 | 3136.7 | 7 ϕ |
| 331.70 | 4006.0 | 20 ϕ | 438.15 | 2135.5 | 7 ϕ |
| 341.20 | 3898.0 | Au No. 13 | 438.45 | 3133.5 | 5 ϕ |
| 344.20 | 3864.0 | 4 ϕ | 439.00 | 3130.3 | 10 ϕ |
| 345.10 | 3856.1 | 3 ϕ | 440.30 | 3122.9 | Au No. 17 |
| 346.70 | 3840.9 | 2 ϕ | 441.10 | 3118.5 | 15 ψ |
| 355.45 | 3751.1 | 4 ϕ | 442.50 | 3110.8 | 12 ψ |
| 356.00 | 3746.0 | 20 ϕ | 444.00 | 3102.4 | 12 ψ |
| 357.35 | 3733.0 | 20 ϕ | 445.60 | 3093.2 | 12 ψ |
| 357.95 | 3727.6 | 20 ϕ | 450.50 | 3067.2 | 5 ϕ |
| 359.20 | 3715.7 | 20 ϕ | 451.10 | 3063.4 | 4 ϕ |
| 360.30 | 3709.5 | 3 χ | 451.70 | 3060.7 | 1 ϕ |
| 372.80 | 3593.5 | 15 ϕ | 452.45 | 3057.2 | 1 ϕ |
| 373.45 | 3586.7 | Au No. 14 | 453.00 | 3053.5 | 10 χ |

QUANTITATIVE SPECTRUM OF VANADIUM CHLORIDE—*continued.*

| Linear Measurement, $\frac{1}{100}$ inch. | Wave-length. | Intensity and Persistency. | Linear Measurement, $\frac{1}{100}$ inch. | Wave-length. | Intensity and Persistency. |
|---|--------------|----------------------------|---|--------------|----------------------------|
| 454.06 | 3048.8 | 10 χ | 502.00 | 2825.6 | Au No. 20 |
| 457.70 | 3029.3 | Au No. 18 | 505.65 | 2810.4 | 12 ϕ |
| 461.75 | 3008.7 | 5 ϕ | 513.85 | 2777.9 | 10 ϕ |
| 462.75 | 3003.6 | 4 ϕ | 514.60 | 2775.8 | 3 ϕ |
| 463.25 | 3001.3 | 10 χ | 516.15 | 2769.8 | 10 ϕ |
| 468.25 | 2976.6 | 10 ϕ | 516.90 | 2766.6 | 10 ϕ |
| 470.00 | 2968.4 | 12 ϕ | 518.15 | 2760.8 | 3 ϕ |
| 472.25 | 2957.7 | 10 ϕ | 520.10 | 2753.5 | 16 χ |
| 473.40 | 2952.1 | 10 ϕ | 521.35 | 2748.2 | Au No. 21 |
| 475.00 | 2944.7 | 10 χ | 523.00 | 2742.5 | 3 ϕ |
| 475.70 | 2941.5 | 10 χ | 523.70 | 2739.8 | 3 ϕ |
| 479.30 | 2924.8 | 10 ψ | 526.60 | 2729.8 | 4 χ |
| 480.20 | 2920.5 | 10 ϕ | 530.15 | 2715.8 | 16 χ |
| 481.60 | 2913.6 | Au No. 19 | 530.55 | 2714.3 | 2 ϕ |
| 482.35 | 2910.5 | 4 ϕ | 532.65 | 2706.9 | 10 χ |
| | 2910.0 | 4 ϕ | 533.85 | 2702.3 | 14 χ |
| 482.75 | 2908.9 | 7 ϕ | 537.10 | 2690.9 | 10 ϕ |
| 484.00 | 2903.2 | 4 ϕ | 539.15 | 2683.2 | 10 χ |
| 485.60 | 2896.4 | 4 ϕ | 540.20 | 2679.4 | 14 ϕ |
| 486.30 | 2891.8 | 10 ^m ϕ | 541.15 | 2676.1 | Au No. 22 |
| 487.00 | 2889.7 | 10 ϕ | 542.35 | 2672.1 | 14 χ |
| 487.35 | 2888.4 | 10 ϕ | 544.80 | 2663.4 | 18 χ |
| 489.20 | 2880.1 | 10 ϕ | 547.00 | 2655.8 | 16 ϕ |
| 489.75 | 2877.8 | 2 ϕ | 548.90 | 2649.5 | 16 ϕ |
| 491.70 | 2869.2 | 10 ϕ | 551.20 | 2641.6 | Au No. 22 |
| 495.15 | 2854.4 | 12 ϕ | 554.45 | 2630.7 | 12 ϕ |

XXXII.

ON THE SPECTROGRAPHIC ANALYSIS OF A SPECIMEN
OF COMMERCIAL THALLIUM.

BY JAMES H. POLLOK, D.Sc., Royal College of Science, Dublin.

[PLATE XXVII.]

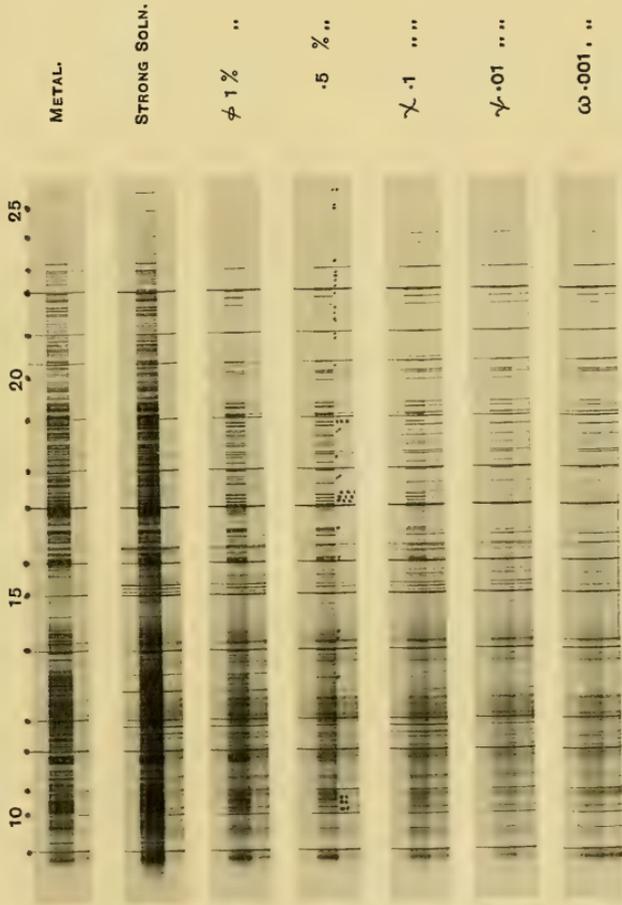
[Published FEBRUARY 25, 1909.]

THE following spectrographic analysis was made to determine the mineral impurities present in a specimen of commercial thallium received from Professor Hartley, and is a convenient illustration of the general method of procedure in any analysis of the kind, and the details of the measurement and identification of the lines may be of use to others engaged in similar work.

The difficulty in determining traces of impurities is, that the lines due to those impurities are necessarily faint and few in number, and there are always a great number of faint lines due to an element that are not recorded in ordinary tables of wavelengths, or, if recorded, may very possibly be due to the same impurity in the photograph of the original observer. To distinguish between faint lines due to impurities and those due to the element itself, a photograph is first taken with a pure specimen of the metal, or a solution of some pure salt of the metal, using a long slit. The slit is then shortened to a third of its length, and a photograph of the metal under examination taken on top of the last; in this way the first photograph cancels all the lines due to the metal and electrodes, and only lines due to impurities show in the short spectrum, and can thus be very quickly picked out, measured, and identified.

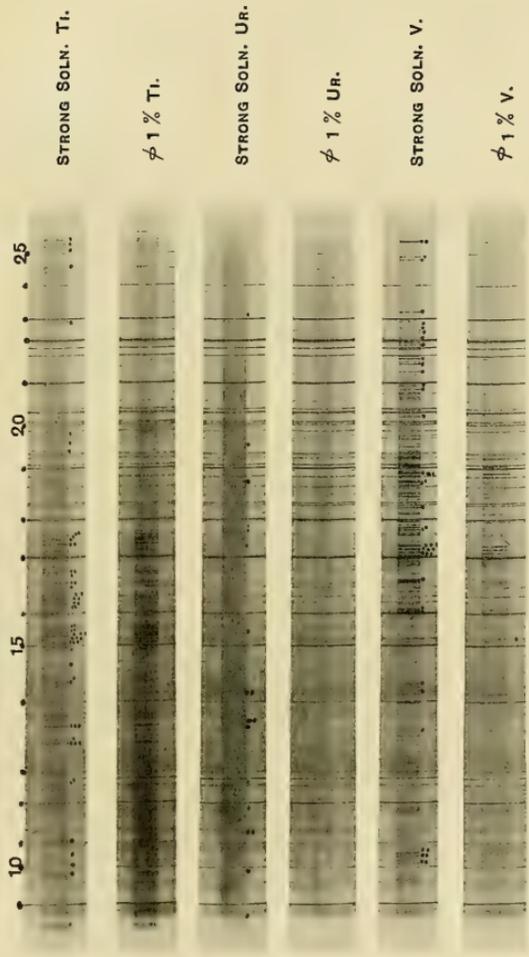
The first spectrum on Plate XXVII. shows a short spectrum of the sample of commercial thallium, superposed on a long spectrum of a solution of pure nitrate of thallium sparked between gold electrodes, and the lines of the impurities present

QUANTITATIVE SPECTRUM OF VANADIUM.



GOLD ELECTRODES.

QUANTITATIVE SPECTRA OF TITANIUM, URANIUM,
AND VANADIUM.



GOLD ELECTRODES.

Royal Dublin Society.

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SCIENTIFIC PROCEEDINGS
OF THE
ROYAL DUBLIN SOCIETY.

Vol. XI. (N. S.), No. 32.

FEBRUARY, 1909.

ON THE SPECTROGRAPHIC ANALYSIS OF A
SPECIMEN OF COMMERCIAL THALLIUM.

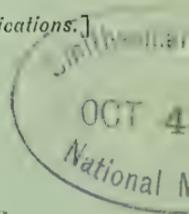
BY
JAMES H. POLLOK, D.Sc.,
ROYAL COLLEGE OF SCIENCE, DUBLIN.

(PLATE XXVII.)

[Authors alone are responsible for all opinions expressed in their Communications.]

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The difficulty in determining traces of impurities is, that the lines due to those impurities are necessarily faint and few in number, and there are always a great number of faint lines due to an element that are not recorded in ordinary tables of wavelengths, or, if recorded, may very possibly be due to the same impurity in the photograph of the original observer. To distinguish between faint lines due to impurities and those due to the element itself, a photograph is first taken with a pure specimen of the metal, or a solution of some pure salt of the metal, using a long slit. The slit is then shortened to a third of its length, and a photograph of the metal under examination taken on top of the last; in this way the first photograph cancels all the lines due to the metal and electrodes, and only lines due to impurities show in the short spectrum, and can thus be very quickly picked out, measured, and identified.

The first spectrum on Plate XXVII. shows a short spectrum of the sample of commercial thallium, superposed on a long spectrum of a solution of pure nitrate of thallium sparked between gold electrodes, and the lines of the impurities present

are seen as short lines between the long lines of gold and thallium. To facilitate identification, some of the strong lines of gold are dotted and numbered from 10 to 25, as in my "Index of the Principal Lines of the Spark-Spectra of the Elements."¹ Some of the lines of the impurities are also marked by dots placed over them, the elements identified being lead, tin, copper, and aluminium. The second spectrum on the plate shows the thallium superposed on a short spectrum of gold. The third spectrum shows the thallium superposed on a long spectrum of gold. The fourth and last spectrum is the metallic spark-spectrum of the specimen of commercial thallium alone. The last three spectra are not absolutely necessary, but are useful to distinguish between the lines of the gold electrodes and the thallium, and in case of coincident, or nearly coincident, lines would enable such lines to be detected.

In measuring the plate to determine the wave-lengths of the lines by use of an interpolation curve, and thus to identify them, only the position of the short lines need be noted, together with a sufficient number of the gold or thallium lines, for purposes of interpolation. To prevent confusion when the negative is dry, first dot the gold lines from 9 to 25, placing the dots just over the spectrum; then, if necessary, mark the lines it is specially required to identify by dots or other marks placed preferably under the spectrum, and not as shown in the Plate.

The interpolation curve used was drawn on ruled paper divided into inches and tenths of an inch, on a scale of an inch to every $\frac{1}{100}$ of an inch measured on the spectrum, and $\frac{1}{10}$ of an inch to each Angström unit of wave-length, and the position of the gold line No. 9 corresponded with the reading 283·85 on the curve. The measurements of the spectrum were made with a Hilgar micrometer reading to $\frac{1}{10000}$ of an inch, and with a movable sub-stage to facilitate the adjustment of any line to a particular reading; and the gold line No. 9 was thus adjusted to the reading 283·85 on starting the measurement of the plate. In plotting and measuring, an inch-scale will be found much more convenient for accurate reading, and not nearly so trying to the eye-sight, as a millimetre-scale.

¹ Scientific Proceedings of the Royal Dublin Society, vol. xi., pp. 184–216. 1907.
SCIENT. PROC. R.D.S., VOL. XI., NO. XXXII.

In drawing the curve, the spectroscope was adjusted to the best possible focus, and a photograph taken of the spark-spectrum of metallic cadmium, then of cadmium superposed on gold, and lastly of gold. The gold-cadmium spectrum was accurately measured, and the first pencil curve drawn from the cadmium measurement. The gold measurements were then dotted in very carefully with red dots, and the curve drawn accurately in ink to the gold dots. After drawing a curve, the particulars of the spectroscope used, the adjustments of the instrument, and the measurements of the fiducial lines, should all be carefully recorded on the first sheet of the curve, and an actual print of the negative, from the measurements of which it was drawn, pasted on.

No matter how accurately a curve is drawn, it will be found practically impossible always to bring the spectroscope back to exactly the same adjustment; and even if the instrument is not touched, temperature changes, in both the spectroscope and the micrometer, will introduce errors in the measurement of lines of quite a serious character. So that, from one cause or another, with photographs of spectra of 4 or 5 inches in length, an apparent change of dispersion of $\frac{1}{100}$ of an inch will be quite common, and would introduce a very serious error of a wave-length or so. It is, therefore, absolutely essential, in measuring spectra for purposes of identification of lines, to measure a number of the fiducial lines at the same time; and on every plate on which measurements may ever require to be made, a photograph of the gold or cadmium spectrum should appear at the top of the plate, if they do not occur on the plate as electrodes or otherwise. It is then always possible to verify measurements, and curve, from the photograph itself. In making measurements, it is very convenient to have foolscap sheets ruled and headed on which to record the measurements, intensities, and subsequent reduction to wave-lengths, and the final identification of the elements to which the lines are due. The Table at the end is an exact reproduction of the original sheet of measurements, corrections, and identifications of the lines of the first spectrum on the plate.

Column one, headed "Measurement, $\frac{1}{100}$ inch," gives the readings of the micrometer in hundredths of an inch, the line

to which the micrometer was adjusted being marked by an asterisk.

Column two, headed "Mark and Intensity," gives the marks over or under the lines if any, dots, dashes, and triangles, being the most convenient marks to use, and the intensity of the lines indicated by the letters S., M., and f., for strong, medium, and faint, corresponding roughly with intensities 10, 6, and 2; very strong lines may be marked S.S., and very faint ones, no more than visible, ff.

Column three, headed "Curve Reading," gives the readings on the curve corresponding to the actual measurements on the micrometer for the fiducial gold lines, and the amounts to be added to or subtracted from the various micrometric measurements to adjust them to the curve.

Column four, headed "Wave-Length, Rowland Scale," gives the wave-length given by the curve corresponding to the corrected measurement.

Column five, headed "Element and Accepted Wave-Length," gives the symbol of the element to which the line is due, its accepted wave-length, intensity and persistency, and any other notes that may be necessary.

From the list of identifications, it is obvious that the impurities are lead, tin, copper, and aluminium; and it will be noted that the lines showing correspond with the residuary lines of these elements as determined by Professor Hartley.¹ The relative persistency of the lines is represented by the letters ϕ , χ , ψ , and ω respectively, and the intensities, ordinarily accepted, are shown enclosed in brackets.

One or two lines were not identified with certainty, and are left blank.

¹ Phil. Trans., 1884; Part I., pp. 49-62; Part II., pp., 325-342.

MEASUREMENTS OF SPECTRA.

| Measurement
$\frac{1}{100}$ inch. | Mark and
Intensity. | Curve
Reading. | Wave-Length
Rowland
Scale. | Element and Accepted
Wave-Length. |
|--------------------------------------|------------------------|-------------------|----------------------------------|--------------------------------------|
| 259.35 | S | - .15 | 5350 | Tl 5350.6 (10) |
| 264.00 | Au No. 7 | 263.85 | 5230.58 | Au |
| 267.10 | M | - .15 | 5153 | Tl 5152.7 |
| 270.40 | • f. | - .15 | 5078 | Tl 5078.6 (6) |
| 271.00 | | 271.00 | 5064.7 | Au |
| 274.60 | • f. | 0.0 | 4984 | Tl 4981.6 (6) |
| * 283.85 | Au No. 9 | 283.85 | 4792.8 | Au |
| 286.65 | S | 0.0 | 4738.5 | Tl 4738.0 (6) |
| 301.00 | Au No. 10 | 301.00 | 4488.4 | Au |
| 307.65 | f. | 0.0 | 4385.0 | Pb 4387.3 (9) |
| 312.20 | Au No. 11 | 312.35 | 4315.4 | Au |
| 330.90 | Au No. 12 | 331.15 | 4065.2 | Au |
| 331.40 | • M. | + .25 | 4059.0 | Pb 4058.0 (10) χ |
| 339.65 | • M | + .25 | 3962.0 | Al 3961.7 (9) ψ |
| 341.20 | f | + .25 | 3944.0 | Al 3944.2 (9) ψ |
| 345.03 | Au No. 13 | 345.55 | 3898.0 | Au |
| 357.15 | S | + .25 | 3774 | Tl 3775.9 (20) |
| 362.90 | f | + .25 | 3719 | ? |
| 367.90 | • M | + .35 | 3672 | Pb 3671.7 (8) |
| 371.65 | • M | + .35 | 3639 | Pb 3639.7 (10) χ |
| 377.80 | Au No. 14 | 378.25 | 3686.7 | Au |
| 384.70 | S | + .45 | 3530 | Tl 3529.6 (10) |
| 386.00 | S | + .45 | 3519 | Tl 3519.4 (20) |
| 404.05 | Au No. 15 | 404.25 | 3383.0 | Au |
| 419.00 | Au No. 16 | 419.35 | 3280.8 | Au |
| 420.10 | S | + .35 | 3274.0 | Cu 3274.1 (6) ψ |
| 424.30 | S | + .35 | 3246.0 | Cu 3247.6 (10) ω |
| 427.10 | S | + .35 | 3228.5 | Tl 3229.9 (6) |

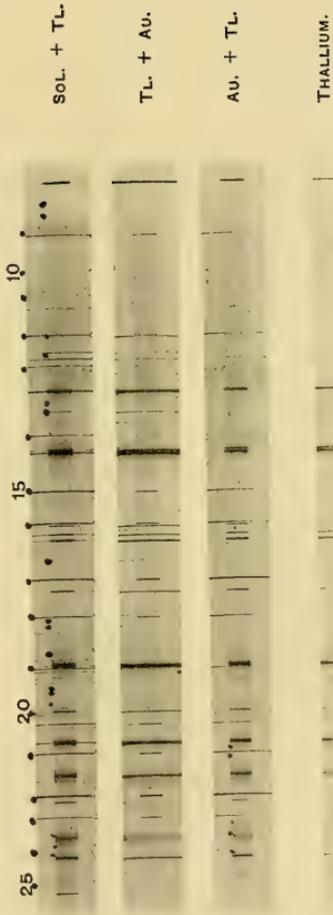
MEASUREMENTS OF SPECTRA—*continued.*

| Measure-
ment
$\frac{1}{100}$ inch. | Mark and
Intensity. | Curve
Reading. | Wave-Length
Rowland
Scale. | Element and Accepted
Wave-Length. |
|---|------------------------|-------------------|----------------------------------|--------------------------------------|
| 436·20 | • M | 0·0 | 3174 | Sn 3175·1 (10) χ |
| 445·25 | Au No. 17 | 444·09 | 3122·9 | Au |
| 450·95 | S | — ·35 | 3091·5 | Tl 3091·9 (8) |
| 462·65 | Au No. 18 | 462·85 | 3029·3 | Au |
| 464·40 | • M | + ·2 | 3020 | ? |
| 466·80 | • M | + ·2 | 3008·5 | Sn 3009·2 (10) χ |
| 484·90 | S | + ·2 | 2921 | Tl 2921·6 (8) |
| 485·75 | S | + ·2 | 2918 | Tl 2918·4 (10) ϕ |
| 486·80 | Au No. 19 | 486·85 | 2913·6 | Au |
| 490·85 | M | + ·05 | 2895 | Sn 2896·2 ϕ |
| 495·90 | • f | + ·05 | 2872·5 | Pb 2873·4 (10) χ |
| 498·10 | • M | + ·05 | 2862·5 | Sn 2863·4 (10) ψ |
| 501·05 | f | + ·05 | 2849·5 | Sn 2850·7 (8) ϕ |
| 503·65 | • S | + ·05 | 2839·5 | Sn 2840·1 (10) |
| 505·30 | S | + ·05 | 2833·0 | Pb 2833·2 (10) χ |
| 506·90 | S | + ·05 | 2826·5 | Tl 2826·3 (2) |
| 507·00 | Au No. 20 | 507·00 | 2825·6 | Au |
| 521·40 | SS | 0·0 | 2767 | Tl 2768 (8) |
| 524·65 | f | 0·0 | 2754 | ? |
| 526·55 | Au No. 21 | 526·15 | 2748·3 | Au |
| 528·85 | f | — ·4 | 2734 | ? |
| 536·90 | S. | — ·4 | 2709·5 | Tl 2709·3 (3) |
| 546·30 | Au No. 22 | 546·10 | 2676·1 | Au |
| 549·30 | S | — ·2 | 2666 | Tl 2665·7 (3) |
| 550·50 | f. | — ·2 | 2662 | Pb 2663·3 (10) χ |
| 556·45 | Au No. 23 | 556·20 | 2641·6 | Au |
| 559·45 | • f | — ·25 | 2631 | Sn 2632·1 (8) χ |
| 564·70 | • m | — ·25 | 2601 | Cu 2600·5 (10) ϕ |

MEASUREMENTS OF SPECTRA—*continued.*

| Measure-
ment
$\frac{1}{100}$ inch. | Mark and
Intensity. | Curve
Reading. | Wave-Length
Rowland
Scale. | Element and Accepted
Wave-Length. |
|---|------------------------|-------------------|----------------------------------|--------------------------------------|
| 572·15 | Au No. 24 | 571·35 | 2590·2 | Au |
| 573·50 | · f | — ·8 | 2586 | ? |
| 575·50 | S | — ·8 | 2580 | Tl 2580·2 (3) |
| 587·05 | Au No. 25 | 586·55 | 2544·3 | Au |
| 591·80 | S | — ·5 | 2531 | Tl 2530·9 (3) |

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