On that form of chemical hygrometer in which sulphuric acid has been used as the absorbent : the Johnson memorial prize essay for 1891 / by M.S. Pembrey.

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7.

THE JOHNSON MEMORIAL PRIZE ESSAY FOR 1891.

BY

M. S. PEMBREY, B.A.,

Radcliffe Travelling Fellow; late Fell Exhibitioner of Christ Church.

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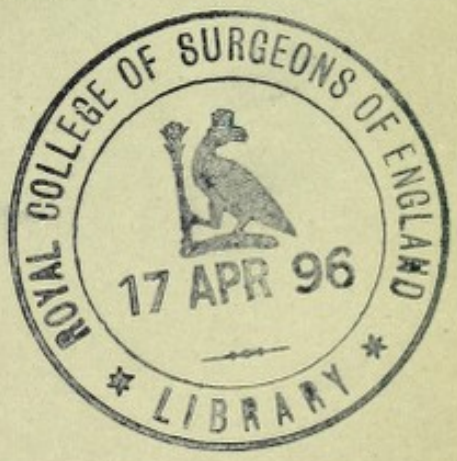

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On that Form of Chemical Hygrometer in which Sulphuric Acid has been used as the Absorbent.

THE object of the present essay is to trace, as far as possible, the various stages through which the sulphuric acid form of chemical Hygrometer has passed, and also to criticise the various forms, especially as regards their practical value in Meteorology.

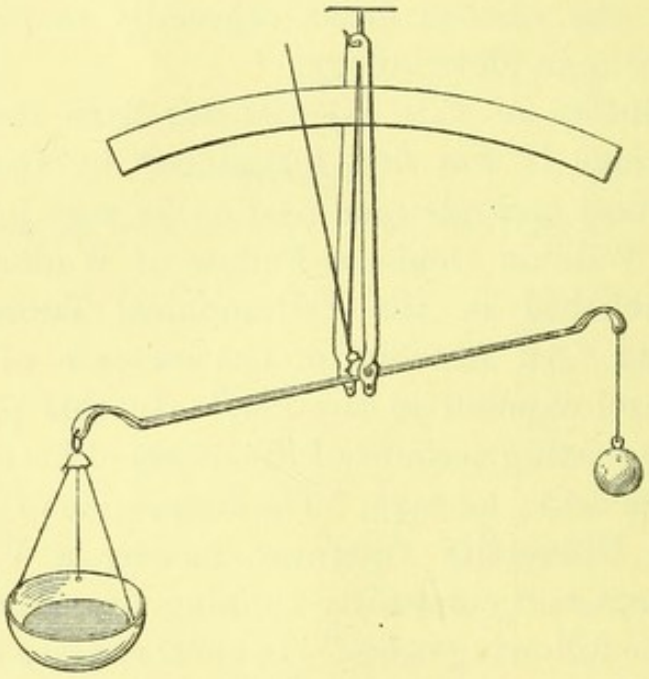
The evolution of this Hygrometer from the primitive form, in which it was first introduced by Gould, to the latest and most accurate modification, is very interesting.

In 1683 William Gould, a Fellow of Wadham College, Oxford, published in the Philosophical Transactions[1] a paper giving "An Account of the increase of weight in Oyl of Vitriol exposed to the Air." In this paper Gould gives an interesting account of the origin of his experiments on sulphuric acid; he says, "The Industrious Chymist Mr. White our University Operator, having a Viol of that liquor unstopt and constantly running over, first gave occasion to the following notes." In another place he remarks, "that liquids such as seem Saturated with their own moysture should nevertheless imbibe more from the Air is not mentioned by any Author I know of, except the aforesaid Learned person (Robert Boyle), who in his Tract of Aerial magnets advices tryals upon the liquid preparations of Vitriol: I have heard indeed some Druggists have accidentally taken notice of this encrease in Oyl of Vitriol, (and perhaps have improv'd it to their own gain though to the detriment of the buyer,) but the observation never was prosecuted with any method or certain account how

[1] *Philosophical Transactions*, vol. xiv. p. 496.

much the said increase was, and what the substance gain'd." From this it might appear that to Boyle is due the credit of first recognising the practical value of sulphuric acid in Hygrometry, but this is doubtful, to judge from his remarks in his paper "Of Celestial and Aerial Magnets[1]." He there says, "even liquid preparations of vitriol may be peculiarly affected by the air, and thereby perhaps be useful to discover the present constitution, or foretel some approaching changes of it."

Gould made his first experiments at Oxford with three drachms of strong oil of vitriol exposed to the air in a marmalade glass of three inches diameter and placed in a pair of scales. The air examined was that of a room, in

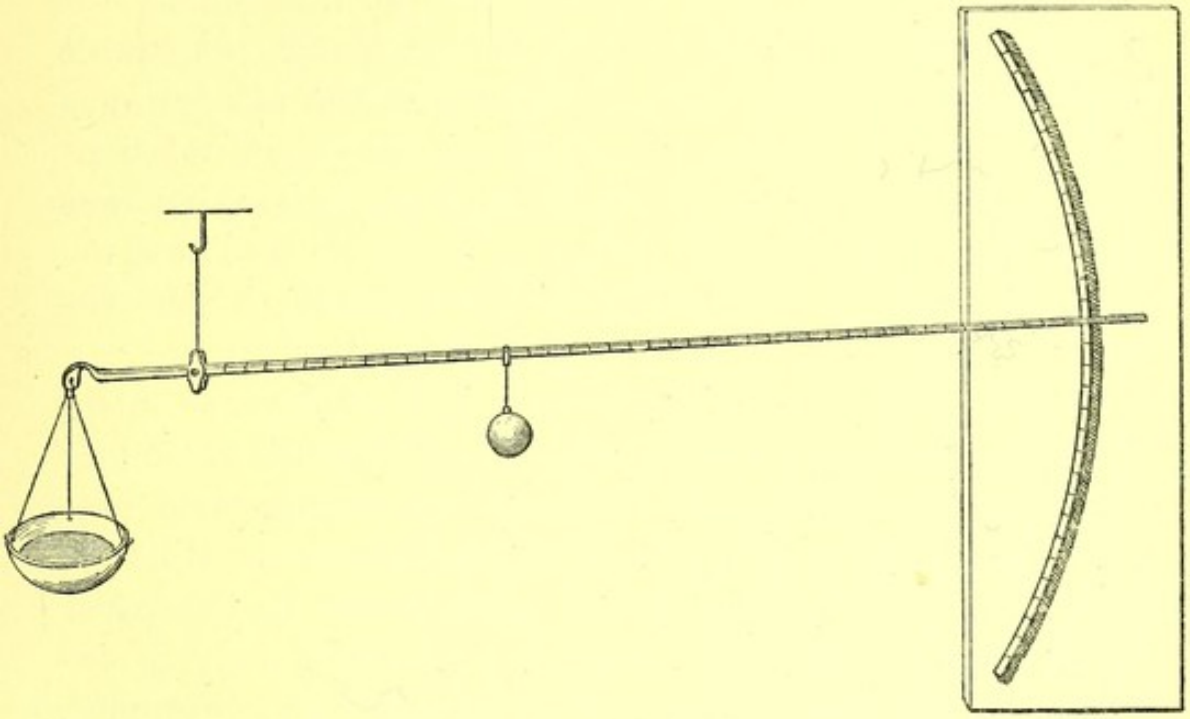


GOULD'S APPARATUS.

which there was no fire, and which was not exposed to the sun. From November 9, 1682, to January 4, 1683, he kept a daily chart, showing the increase in weight of the sulphuric acid, and the changes in the weather, as regards rain, wind, and sunshine. The conclusions, which Gould drew from these observations, were, that "the increase was

[1] *The Works of the Hon. Robert Boyle.* By Thomas Birch, 1772, vol. iv. p. 99.

more in a Moist, Rainy, Misty and Snowy, but less in a Frosty, Clear and Dry Season, as also was more in a Cold than in a Warm Air;" that "when the Wind was Northerly



GOULD'S APPARATUS.

or Easterly, the gain was less caeteris paribus than when Southerly or Westerly, and was less in the day than in the night."

From these experiments and also from the results, obtained by distilling the sulphuric acid, which had been exposed to the air, Gould concluded that the only cause of the increase was the moisture of the air. He found that the more diluted the acid was, the less attractive it proved; that the greater or less the surface, the quicker or slower the increase. The depth of the glass and the more or less free access of the air were, he considered, important factors.

Gould did not consider that his apparatus was chiefly to be valued as a hygrometer, by which the amount of moisture gained should be determined, but as a hygroscope, to show any alteration in the moisture of the air. He based the construction of his hygroscope upon the following observation, that "when the oyl of vitriol is

satiated, in the moistest weather; it afterward retains or looses its acquired weight as the Air proves more or less moist."

Although Gould's method was by far the most accurate of the other forms of hygroscope used at that time, yet it is evident that it could never give exact and comparable indications. Its chief defects were that the air during a series of observations was not brought into equal relationship with the absorbing liquid, that no precaution was taken to entirely deprive the air of moisture, and that the absorbing surface was soon rendered defective by the absorption of water.

No other form of sulphuric acid hygrometer was introduced until about 130 years after the publication of Gould's paper, when, according to Symons[1], the arrangement proposed by Gould was re-introduced by Guyton de Morveau in 1808. This apparently is a mistake, for in the paper by Guyton de Morveau[2] chloride of calcium only is described as the absorbent, and both Schmid[3] and Brunner[4], when speaking of the hygrometer of Guyton Morveau, only name chloride of calcium.

In 1819 John Livingstone[5], of Canton, published an "Account of an Improved Hygrometer," which was indeed only the re-introduction of the method employed by Gould. The apparatus described by Livingstone consisted of a watch glass, which contained 2·1 grains of pure sulphuric acid and 2·9 of water, and was placed in a balance. The arc described by the balance was graduated, so that it was possible from the readings to calculate the amount of moisture absorbed. The instrument was enclosed in a glass cover, sufficiently open below to admit the air freely. This hygrometer had all the defects of Gould's apparatus.

Again in 1824 Gould's apparatus was re-introduced by Kastner. This statement is made on the authority of

[1] "A Contribution to the History of Hygrometers," *Meteorol. Soc. Quart. Journ.*, vol. vii. p. 171.

[2] *Annales de Chimie*, t. lxviii. p. 5.

[3] *Lehrbuch der Meteorologie*, Schmid, p. 604.

[4] *Annalen der Physik und Chemie*, Poggendorff, Band xx. p. 274.

[5] *Edinburgh Philosophical Journal*, vol. i. 1819.

Symons, for it has unfortunately been impossible to obtain Kastner's paper.

It was not until 1830 that a successful attempt was made by Brunner[1] to construct a sulphuric acid hygrometer free from the defects which were necessarily inherent in the apparatus first introduced by Gould. The essential part of Brunner's hygrometer (Fig. A) was a glass tube

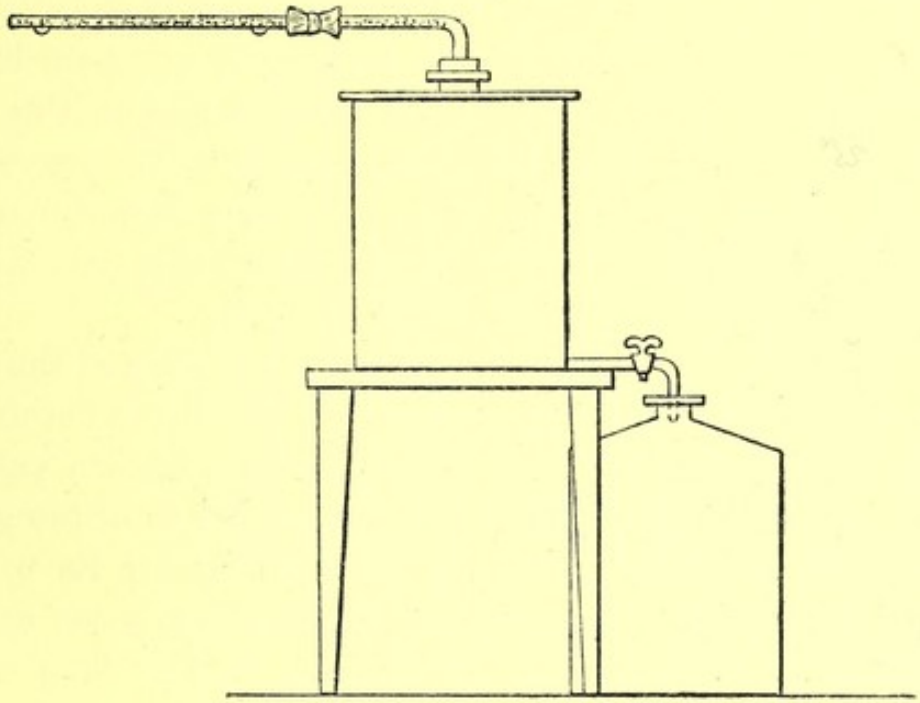


Fig. A.

11 (French) inches long and $3\frac{1}{2}$ /// in diameter, in which about one inch from each end had been made a small pocket to hold any superabundant liquid. This tube was filled with asbestos soaked in strong sulphuric acid, a small space being left between the upper surface of the asbestos and the glass to allow a free passage to the air. Through this tube the air to be examined was drawn by means of an aspirator, constructed on the principle of Mariotte's bottle. In order to prevent any absorption of water from the aspirator Brunner interposed a tube containing chloride of calcium between the absorption-tube and the aspirating bottles.

[1] "Ueber die Bestimmung des Wassergehaltes der Atmosphere," *Annalen der Physik und Chemie*, Poggendorff, Band xx. p. 274.

The determination of the moisture in air was made in the following manner; the absorption-tube was weighed and then connected with the aspirator, by means of which a known volume of air was drawn through the tube. The absorption-tube was disconnected and weighed. The increase in weight gave the amount of moisture absorbed from the air, the volume of which was calculated, after the necessary corrections for barometric pressure, temperature and vapour tension, from the capacity of the aspirator. Brunner used an aspirator with a capacity of 14–15 litres. The absorption was found to be complete when the rate of aspiration was 1300 cc in a minute. To prove the accuracy of his method Brunner gives one experiment, in which the calculated gain in weight was 0·122 grm, whilst the amount actually gained was 0·121 grm.

In Brunner's apparatus Meteorologists possessed the first accurate hygrometer—one based upon the direct determination of the weight of water contained in a known volume of air. It is true that the absorption-tube was of too great a size and too inconvenient a form to render its use in daily work possible, and that, to eliminate to some extent the errors of weighing, an experiment was of long duration; yet it is evident that, when once the principle of the hygrometer was made known, these defects would be removed.

From Gould until Brunner, a period of a century and a half, no real advance was made in the construction of the chemical hygrometer, but upon the introduction of Brunner's method there followed various improved forms and many important series of observations, especially those of Regnault.

In 1845 Regnault published his "Études sur l'hygrométrie[1]," the second series of which appeared in 1853. In these experiments Regnault used a modification of Brunner's hygrometer, in order to determine the weight of the vapour in a known volume of air saturated at different temperatures, and also as a standard hygrometer for his comparative experiments. His apparatus (Fig. B), similar to one

[1] *Annales de Chimie et de Physique*, tome quinzième, 1845.

introduced by Schmeddink[1], consisted of U-tubes, 18 cm in height, filled with pieces of pumice soaked in sulphuric acid. Three of these tubes were employed during an experiment; the first (1) absorbed the moisture, the second (2) caught any moisture which might escape absorption in the first tube, whilst the third (3) prevented any moisture from the aspirator being absorbed by the second tube. The first tube generally absorbed all the moisture; it was rare for the second tube to gain one or two milligrammes.

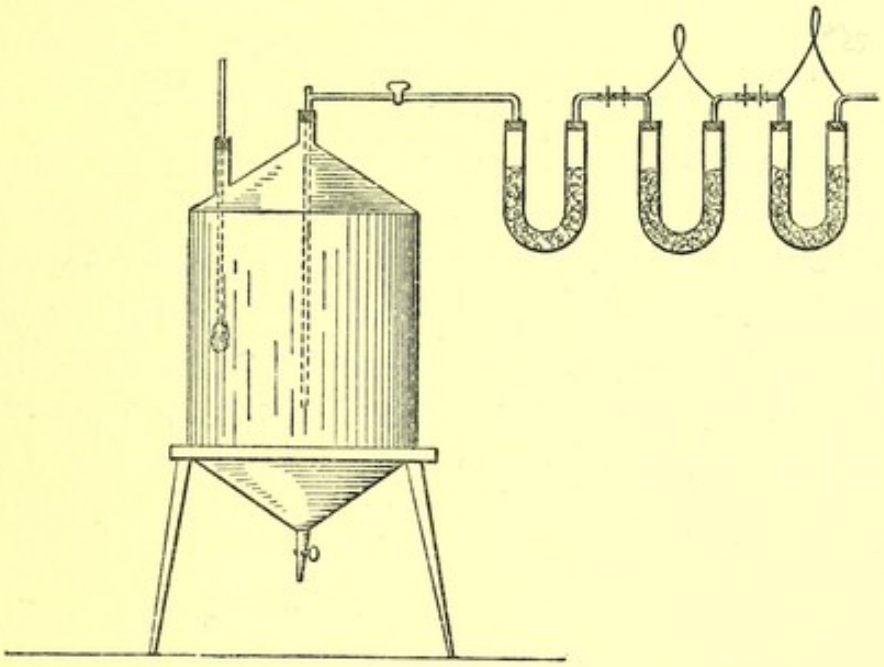


FIG. B.

Regnault tested the completeness of the absorption by the first tube in two series of experiments. He connected the second tube with a third tube plunged in ice, and with this a fourth placed in a mixture of ice and chloride of calcium; several litres of air were drawn through the tubes, which were then disconnected, dried over quicklime and weighed, when their temperature had reached that of the surrounding air. The result was that the first tube gained 1·235 grammes, whilst the second, third, and fourth had not altered in weight. The second series of experiments were made in the following manner. Three absorption-tubes *A*, *B*, and *C*, each 1 metre long, were connected

[1] No reference given.

together, and to the third was joined a tube *D*, containing moistened sponge, and following this there were two more absorption-tubes *E*, *F*. The air drawn through the tubes was completely deprived of its moisture by the tubes *A*, *B*, and *C*, but passing through the moist sponge it absorbed a certain weight of water, which in turn it lost in the tubes *E* and *F*. The tubes *D*, *E*, and *F* were carefully weighed both before and after the experiment with the following result:—

The tube *D* containing the moist sponge had lost ·767 grm.
The absorption-tube *E* had gained . . ·767 grm.
The absorption-tube *F* had not altered in weight.

These experiments convinced Regnault of the completeness of the absorption, but at the same time he recognised several defects in the method, which would prevent its general use in Hygrometry. He says [1], "Je dirai en passant que je pense qu'en multipliant beaucoup les appareils destinés à absorber des gaz ou des vapeurs, dans l'espoir d'obtenir une absorption plus complète, on commet, dans les pesées, des erreurs beaucoup plus grandes que celles que l'on cherche à éviter. En effet, lorsque le volume des appareils absorbants est considérable, on ne peut plus négliger dans les pesées les changements qui surviennent dans la nature de l'air extérieur dans l'intervalle des deux pesées. Or, ces changements ne peuvent pas être déterminés avec quelque précision. La moindre différence entre la température de l'air extérieur et celle des appareils au moment de la pesée, différence impossible à éviter, occasionne une erreur sensible. Enfin, la surface vitreuse éminemment hygroscopique des appareils peut se couvrir d'une quantité d'humidité inégale dans les deux pesées." Further he remarks [2], "Cette méthode est, du reste, tout à fait rigoureuse, et elle est très utile pour étudier la marche des autres hygromètres . . . . . Mais elle est trop embarrassante et elle exige une manipulation trop longue pour qu'on puisse l'employer souvent dans les observations météorologiques."

[1] *Annales de Chimie et de Physique*, p. 153 (1845). [2] Ibid. p. 164.

Regnault employed his chemical hygrometer in the series of experiments which he carried out to test the accuracy of the Dry- and Wet-Bulb Psychrometer. The results of these experiments will be given later (p. 34) with the account of the comparative experiments made by other observers.

Regnault's modification of Brunner's apparatus rendered the sulphuric acid hygrometer more accurate and also more suitable for hygrometric observations. But as regards its defects no one has so plainly pointed them out as Regnault—the long duration of an experiment, due to the slow rate of absorption; the uncertainty of the weighings in the case of small quantities of moisture. To remove these defects Regnault made many endeavours, but they were not successful. The substitution of the U-tube for the straight tube rendered the absorption more complete and rapid, and also made the hygrometer much more portable, but at the same time it increased the resistance, especially when much water was absorbed and collected in the bend of the tube.

In 1849 Lefebvre[1] made a series of comparative experiments with the chemical method and Regnault's hygrometer and also with Daniel's. He used an apparatus (Fig. C)[2] similar to that introduced by Regnault, and during an experiment he took all the precautions given by that observer.

In one series of experiments he made simultaneous determinations with two sulphuric acid hygrometers, the results of which are given in the following Table:—

Experiment.	Chemical Hygrometer No. 1.	Chemical Hygrometer No. 2.
1.	36·08	36·15
2.	40·85	40·27
3.	41·48	41·79
4.	46·01	46·17
5.	63·55	64·10
7.	46·05	46·21
8.	44·89	44·72
10.	46·37	46·41
11.	74·41	74·14
12.	57·20	56·89

[1] *Annales de Chimie et de Physique*, Troisième Série, t. xxv. p. 110 (1849).

[2] See p. 12.

Lefebvre used an aspirator with a capacity of 4 litres 278 cc. The duration of each determination with the chemical hygrometer was at least half an hour. The length of time necessary for a determination Lefebvre considered to be

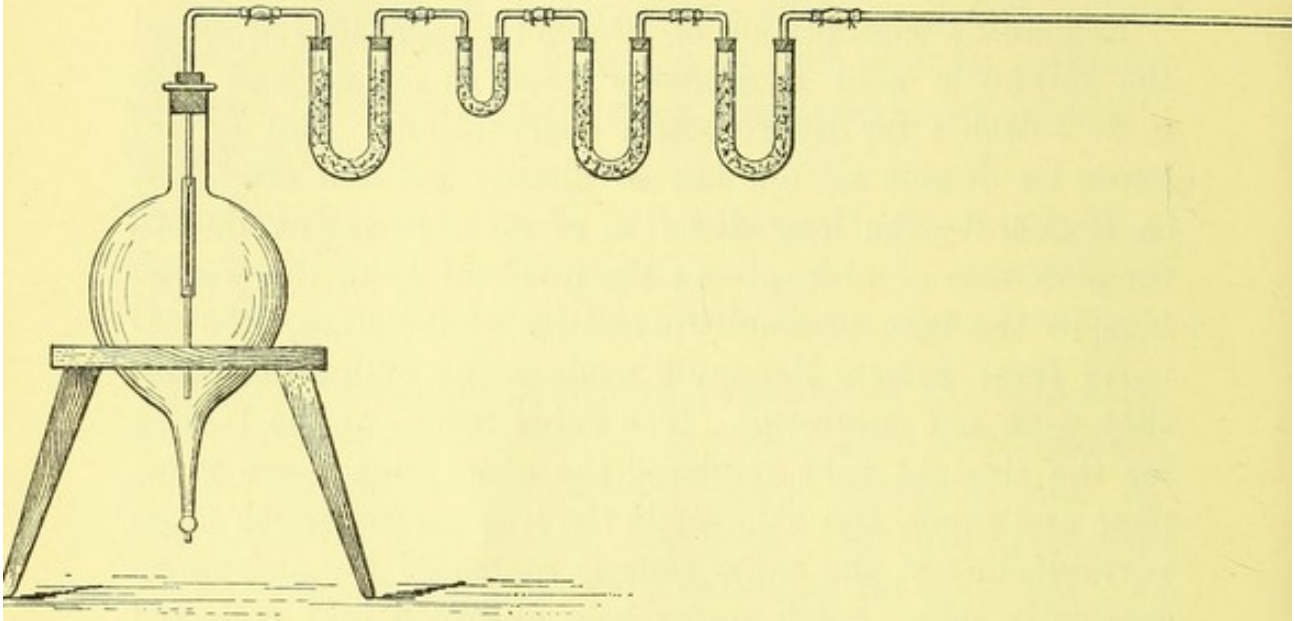


Fig. C.

a great objection to the method. He says, "L'hygromètre par absorption est le plus exact, et c'est à lui que l'on compare tous les autres ; mais quelle que soit la simplicité à laquelle on réduise l'appareil, une expérience demande encore beaucoup de temps, ce qui rend cet hygromètre peu propre à des recherches qui n'ont de valeur que par leur multiplicité."

Kamtz[1] in 1861 published a series of twenty-nine comparative experiments with the chemical method and the psychrometer. He used a U-tube containing pumice soaked in sulphuric acid,—an apparatus similar to that used by Regnault. The aspirator had a capacity of 12 litres, but frequently the amount of air drawn through the absorption-tube during an experiment was twice that quantity. The vapour pressure varied from 2·645 to 8·939 mm. The differences between the psychrometer and the chemical method ranged from −0·477 to +0·490, and they apparently

[1] "Bemerkungen über Hygrometrie," *Repertorium für Meteorologie*, Kamtz, Band ii. p. 341 (1862).

had no relation to the amount of moisture present in the air during the various experiments.

In 1871 Regnault published another important paper on hygrometers, among a series of papers entitled, "Instruction pouvant servir à l'établissement des Observatoires Météorologiques[1]." Here he gives the preference to the chemical method above all other hygrometers, and maintains that it ought to replace them in daily observations. He describes a method of making a continuous observation, in which the amount of moisture absorbed from a known volume of air is determined every three hours. The absorption-tube (Fig. D) is constructed in a similar manner to the ones employed in his first experiments, but he mentions several important details. The pieces of pumice are freed from powder, then soaked in weak sulphuric acid, and ignited to redness before being finally soaked in the strong sulphuric acid. The corks are covered with a resin to prevent absorption of moisture.

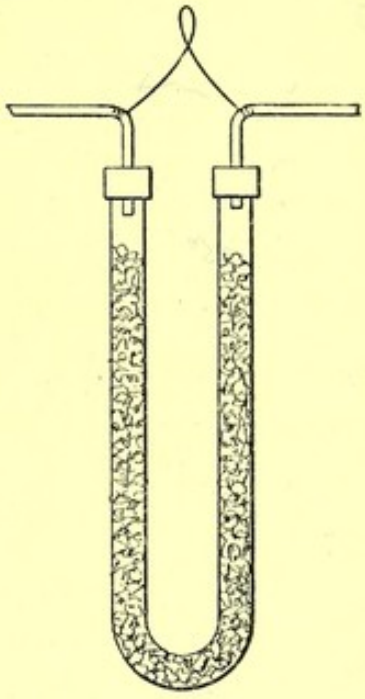


Fig. D.

But the most important detail—one by which, I now (March 1891) find for the first time, Regnault has anticipated Dr. Haldane and myself—is that of weighing one absorption-tube against another. Regnault's words are—"On fait une pesée préliminaire du tube, en faisant la tare avec un autre tube semblable, déplaçant à peu près le même volume d'air. Cette précaution ne donne aucun embarras, puisque le même tube taré sert indéfiniment, et elle permet de ne pas se préoccuper de la petite erreur que pourrait produire, sur les deux pesées, une variation notable survenue dans la densité de l'air extérieur entre les deux pesées." The value of this comparative weighing is so great that I shall in the concluding part of this paper take

[1] *Archives des Sciences Physiques et Naturelles*, Genève, t. xl. p. 201 (1871).

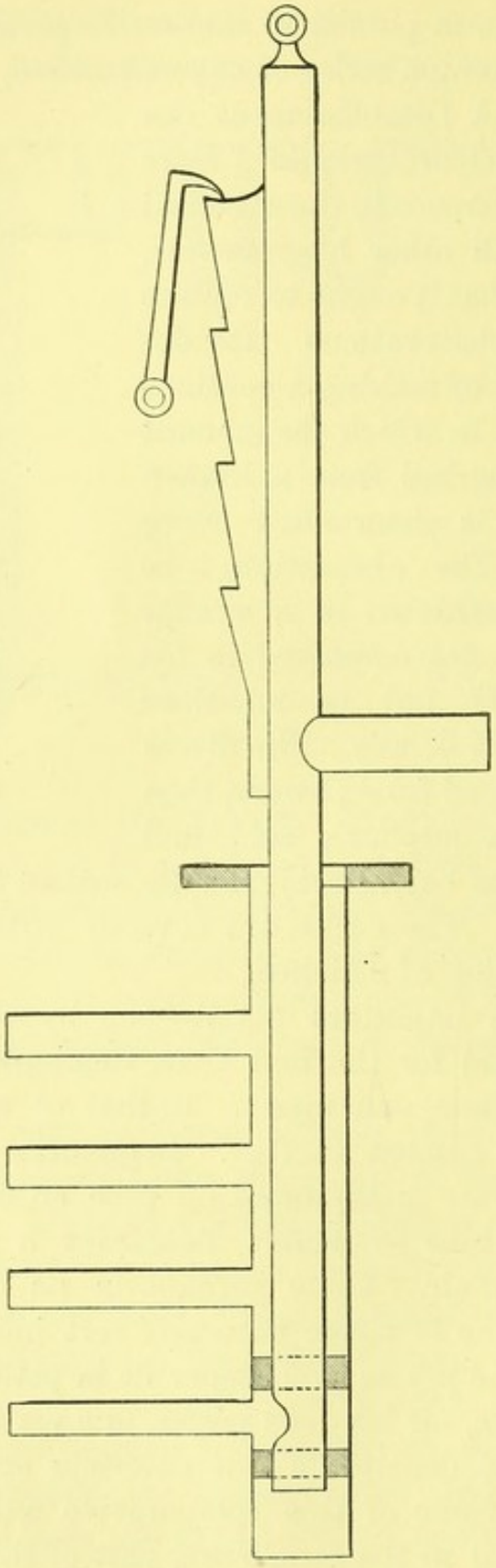


Fig. E.

the liberty of quoting fully the experiments, which led Dr. Haldane and myself to adopt it, at a time when we were ignorant that it had been employed twenty years before by Regnault.

The apparatus (Fig. E) for the continuous observation consisted of a clock-work mechanism, whereby at the end of every three hours the number of litres of air aspirated through one absorption-tube was indicated, and the aspirator was connected up for another three hours with a fresh absorption-tube. This arrangement is not free from defects, and all the advantages of a continuous observation might be obtained by a simple system of relays of modified absorption-tubes, so arranged that determinations could be made every two or three minutes, if required.

In 1871 Baumhauer[1] also described a sulphuric acid hygrometer for continuous observations. He had even as early as 1854 described an apparatus similar in all respects except that the absorbent was chloride of calcium. This hygrometer (Fig. F)[2] consists of a glass bulb containing pumice soaked in strong sulphuric acid and floating in a vessel of pure olive oil. The entrance and exit tubes are covered by two cone-like glass jars, the bases of which dip into the olive oil. One of the glass jars opens by a narrow mouth into the air, the other is connected with the aspirator. By this arrangement it is said to be possible to draw air through the pumice without causing any change in the position of the bulb except those due to the increasing weight of the absorbent. From the apex of the bulb springs a rod carrying a small capsule for weights and a screen with a hole in it for photographic record. The height of the instrument is regulated by weights in the capsule, and by varying the load a scale can be constructed for the photographic record. Baumhauer does not give any test experiments or series of determinations with his hygrometer.

Against the practical value of Baumhauer's hygrometer

[1] "L'hygrométrie dans les Observations Météorologiques," *Archives Néerlandaises des Sciences Exactes et Naturelles*, t. vi. p. 419 (1871).

[2] See p. 16.

there are several serious objections. Snellen, after observations made with this hygrometer for several months, found that even when no air is being aspirated through the apparatus it is far from remaining in one position.

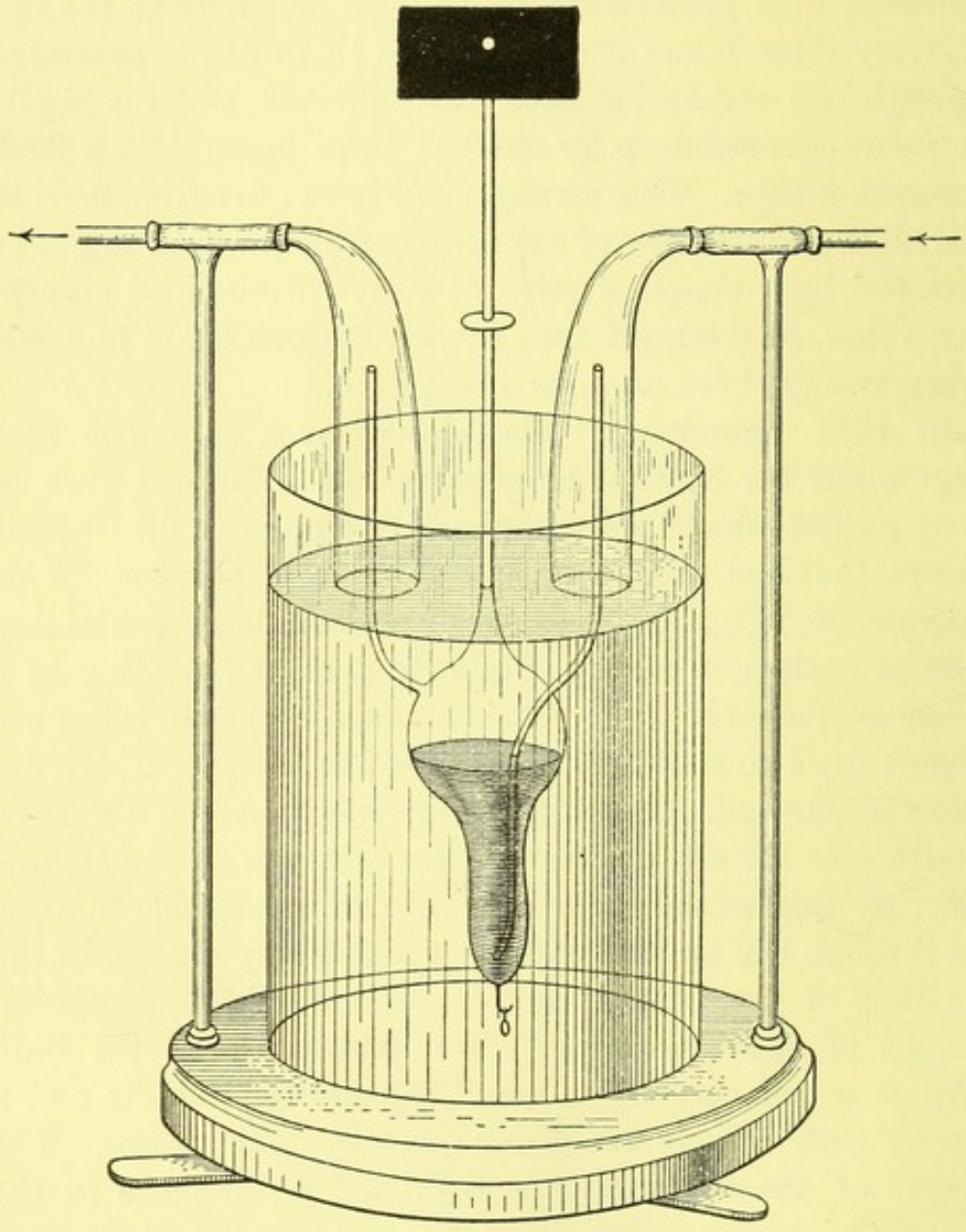


Fig. F.

This irregularity he believed to be due to extensive and irregular variations in the density of the oil—variations which could not be eliminated by any correction for temperature. This objection was admitted by Baumhauer

himself, but he thought that other liquids might be found for floating the bulb. Against the fragility of the instrument its inventor protests that it may be made of metal.

Snellen[1] in 1874 described another form of sulphuric acid hygrometer. It consisted of a U-tube containing pumice soaked in sulphuric acid and with the entrance and exit tubes each bent through two right angles, so that their free extremities, which were enlarged, might dip into vessels of olive oil. The absorption-tube was fixed to one arm of a balance and counterpoised by weights. As in Baumhauer's hygrometer air was drawn through the apparatus by means of glass tubes passing through the oil and opening into the bulbous ends of the entrance and exit tubes.

Snellen gives no figure of his hygrometer, nor does he describe any observations to test its accuracy or practical value.

A serious objection to this instrument is that variations may arise from changes in the density of the oil.

In 1879 an important research on hygrometric methods was undertaken by Shaw at the request of the Meteorological Council, and in 1888 the first part of his valuable report was published in the Philosophical Transactions[2]. This observer made a number of experiments on the chemical method, employing drying tubes of a special form (Fig. G)[3]. The U-tubes, about 6 inches long and ½ inch internal diameter, were fitted with wide glass connexions, one extremity of which was ground into the U-tube, while the other passed over narrow tubes coming through small mercury cups, and thus forming the connexions between the drying tubes and the other parts of the apparatus. These mercury joints Shaw considers superior to india-rubber connexions.

The drying tubes were filled either with coarse fragments of pumice saturated with the strongest sulphuric acid or

[1] "Sur un Hygromètre à Balance," *Archives Néerlandaises des Sciences Exactes et Naturelles*, t. ix. p. 477 (1874).

[2] *Philosophical Transactions*, 1888, vol. A, p. 73.

[3] See p. 18.

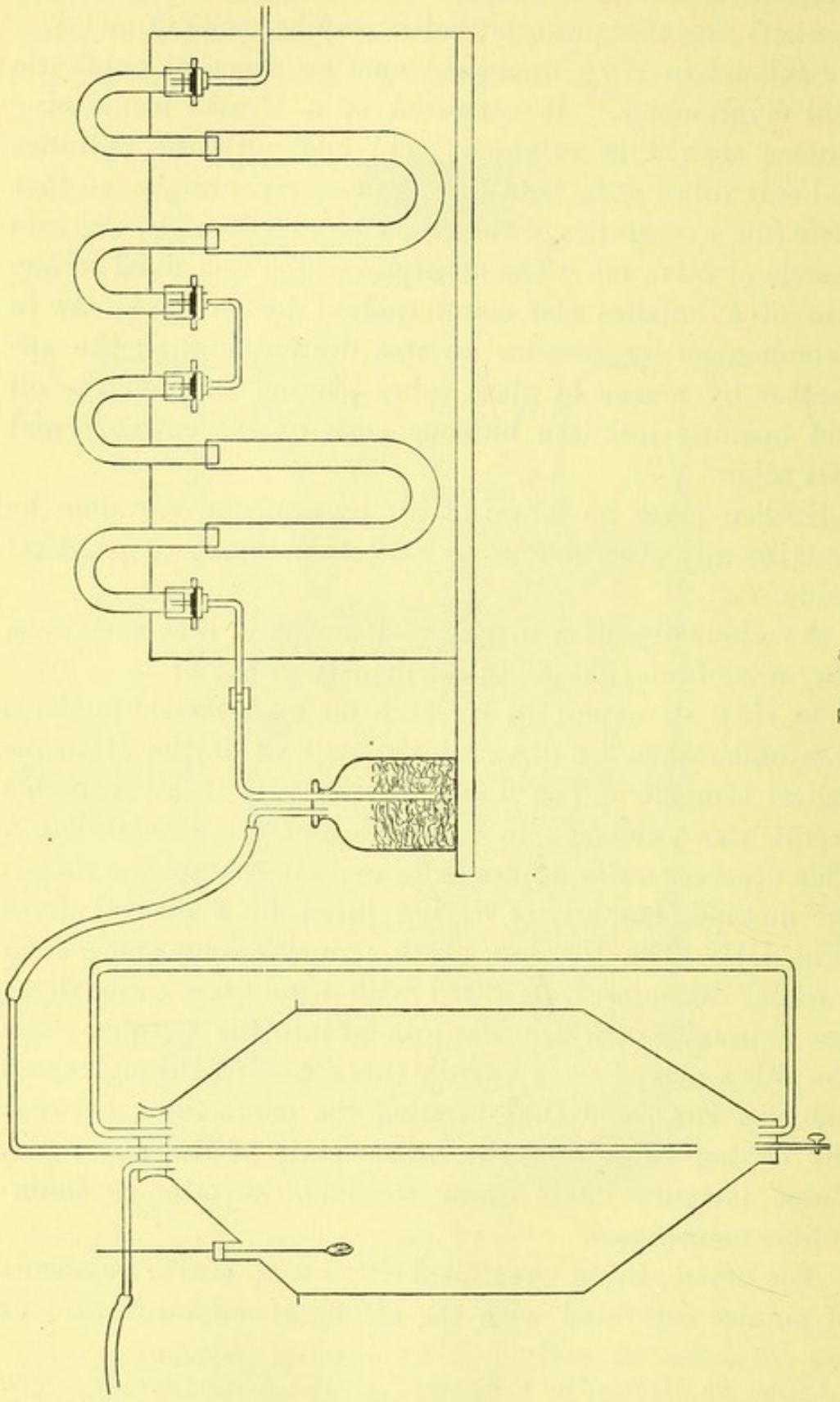


Fig. G.

with pieces of phosphoric anhydrite. Shaw states that "the variations of pressure and temperature between the successive weighings of the tubes during the observations were not sufficient to produce any appreciable effect upon the results;" but that this is not strictly accurate appears probable from his own experiments and also from those by Regnault, by Dr. Haldane and the Author of this Essay.

Shaw tested his method by a series of experiments in which saturated air was drawn through four absorption-tubes connected up in series. The results of these experiments are given in the following Table :—

Experiment.	Aspirator.	Gain in tube 1.	Gain in tube 2.	Gain in tube 3.	Gain in tube 4.	Duration of experiment.	
		Phosphoric acid.		Sulphuric acid.		H.	M.
1.	B	·2915	−·0050	+·0048	+·0028	1	20
2.	A	·2928	+·0008	+·0117	+·0018	2	15
3.	,,	·2916	+·0023	+·0080	+·0040	2	23
4.	,,	·2944	+·0005	+·0011	−·0008	2	3
5.	,,	·3074	+·0023	+·0033	+·0017	2	7
6.	,,	·2931	+·0007	+·0022	+·0006	2	45
7.	,,	·3020	−·0001	−·0002	−·0009	1	15
		Sulphuric acid.		Phosphoric acid.			
8.	,,	·2870	+·0027	+·0019		3	2
9.	B	·2785	−·0005	+·0018		2	0
10.	,,	·2702	+·0016	+·0018		1	55
11.	,,	·2557	+·0013	+·0010		2	0
12.	,,	·2682	+·0023	+·0013		2	0

Volume of aspirator A at 0° = 16384 cc.
B at 0° = 16400 cc.

As regards the variations in the weights of the second, third, and fourth tubes, Shaw says, "that amount is very irregular and is about the same whether the phosphoric acid tubes or the sulphuric are placed first, and the calculated tension is in nearly every case within 1 per cent. of the tabulated tension. This being about the same error as that which occurs in Regnault's observations, we may take it that the first tube was sufficient to completely dry the air passed through it, and that the increase of weight of the other tubes was due to some other causes."

To discover these causes Shaw made a few experiments on the condensation of moisture in glass and in india-rubber tubes, and from the results he concludes "that the increase in weight of the drying tubes after the first, in the Table of results given, was due for the most part to moisture derived from the india-rubber connexions. For the last three observations in the Table, the connexions were made as short as possible, so that the amount of india-rubber surface exposed to the dry air might be small. With the apparatus in that form the drying tubes gained very much less in weight than before, and we may give the results obtained from these three observations as instances of the accuracy which may be expected by the method." It is probable, however, that Shaw's absolute weighing is the chief cause of these differences of weight, for it is to be noted that in some cases the tube lost in weight, and that even in the last three experiments the variations are about 16 decimilligrammes.

I think that the following objections may be fairly urged against Shaw's chemical hygrometer; that, notwithstanding the complication of the apparatus, it does not give such accurate results as Regnault's simple U-tubes, when the system of comparative weighing is employed; that the mercury joints render the apparatus unfit for travelling and may introduce errors of weighing; that the rate of aspiration, 8 litres per hour, is extremely slow, and makes a determination very tedious.

In 1889 an improved method of determining moisture in air was worked out by Dr. Haldane and the writer of this paper. The investigation was suggested by Dr. Haldane, to whom the credit of the method is chiefly due, and arose out of some experiments with a new form of respiration apparatus introduced by him. In order to fully explain the method and to show how we came to adopt the precaution of comparative weighing—a precaution observed, unknown to us, twenty years before by Regnault—I shall take the liberty of inserting here a portion of the original paper [1].

[1] "An Improved Method of Determining Moisture and Carbonic Acid in Air." By J. S. Haldane and M. S. Pembrey. *Phil. Mag.*, April 1890.

"The absorption apparatus which we finally adopted is shown in Fig. 1. We shall describe it in detail because, as will be seen below, the disadvantages of the chemical method, as ordinarily used, are dependent on a want of attention to details. It consists of a pair of test-tubes, containing pumice soaked in sulphuric acid. The test-tubes are 4×1 inch, and made of thin glass. Each tube is provided with a double-bored cork about $\frac{1}{2}$ inch thick, which is fitted with glass tubing of about $\frac{3}{16}$ inch internal diameter, and in the form shown in the figure[1]. The tubing must fit firmly. The corks are covered with a layer of hard paraffin inside and out. They are pushed down a very little below the tops of the tubes, the end of each tube being first wiped inside free of acid, and then warmed to soften the paraffin on the cork and to facilitate its entrance. To enable the longer limb of the tubing to be pushed down, a passage should first be cleared in the pumice with a piece of glass rod. A layer of paraffin is spread smoothly over the top of the cork until it is just level with the edges of the tube. The apparatus must be absolutely tight, and should allow air to pass perfectly freely when suction is applied. It should finally be carefully cleaned with a wet cloth to remove any traces of acid, and then dried.

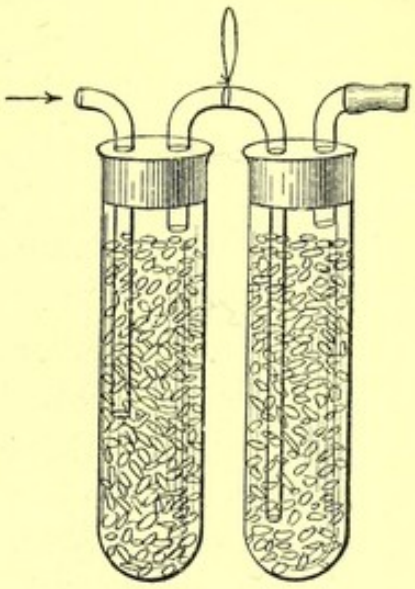


Fig. 1.

The pumice is sifted through a wire sieve with about 7 meshes to the inch, and shaken in a fine one to remove the powder. It is then heated to redness by playing on it with a large blowpipe-flame, and thrown still hot into 'pure

[1] The longer piece of glass tubing in the first sulphuric acid absorption-tube is made somewhat shorter than the corresponding tubing in the other absorption-tube. The inconvenience arising from the collection of water in the first tube is thus avoided.

Since writing the above we have been supplied by Messrs. Gallenkamp with pairs of tubes made in one piece. These are more brittle, but otherwise very convenient.

redistilled' sulphuric acid. The superfluous acid is then poured off, and the pumice preserved for use in a stoppered bottle. Before using the tubes for experiments we have always taken the precaution of washing them out with air, as the air passed through them at first usually tastes slightly of sulphurous acid.

Each pair of tubes when filled weighs about 80 grammes, and can therefore be weighed on any ordinary balance.

To diminish to a minimum errors arising from accidental variations in weight of the tubes, we adopted the plan of weighing against a counterpoise consisting of a similar absorption-tube, and of about the same weight. This counterpoise is always kept in the same place as the absorption-tubes. Since during an experiment the absorption-tubes will have been warmed above the temperature of the counterpoise, the weighing must be deferred for half an hour, so as to allow their temperatures to become equal again. The tubes are weighed unstoppered. If several tubes are to be weighed the stoppers[1] are removed before weighing from the whole of the tubes, including the counterpoise, and not replaced until the last tube has been weighed. No absorbent is kept inside the balance-case. The tubes should be lifted by the wires attached to them for hanging on the balance.

We found the following form of aspirator very convenient, especially when the apparatus had to be carried to a distance. Two bottles (Fig. 2), each holding about 3200 cub. cent. up to a mark in the neck, were arranged as shown in the figure, and connected together by a piece of stout, non-collapsing rubber-tubing provided with a screw-clip for regulating the rate of aspiration. The burette clips are for starting or stopping the flow. The bottles are covered outside with a layer of felt, to keep the temperature of the air and water equal during an experiment, and also to prevent breakage. A vertical strip on each bottle is, however, left uncovered, so that the height of the water may be watched during the experiment and the reading of the thermometer taken. It is convenient to graduate the bottles roughly by pasting strips of paper

[1] The stoppers used are the ordinary ones, consisting of a short piece of black rubber about $\frac{3}{4}$ inch long, closed at one end by a piece of glass rod.

at intervals of half a litre up the uncovered strip of glass. With the help of this graduation it is easy to ascertain if the aspirator is running at about the proper rate.

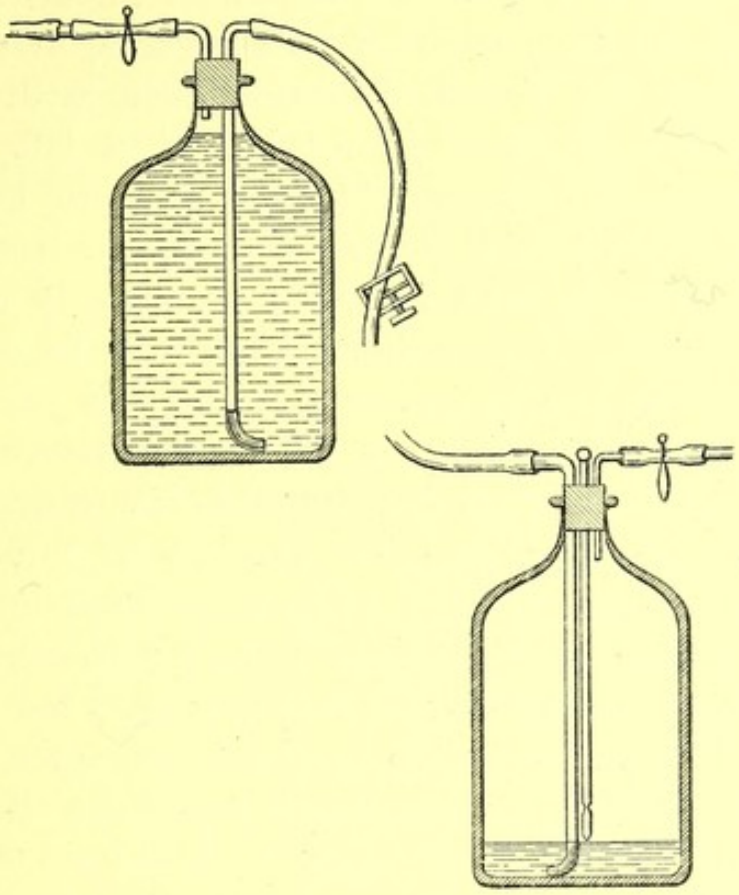


Fig. 2.

To graduate the aspirator, one of the bottles is allowed to drain for a minute, and is then weighed accurately. The two bottles are now connected and the weighed bottle is filled with distilled water to the mark, the tubing also being filled with water. The cork of the weighed bottle is then removed, care being taken to let no water escape from the end of the long piece of glass tubing. The bottle filled with water is then weighed again; and by deducting this weight from that of the empty bottle and allowing for air displaced &c., as in the graduation of a measuring-flask, the amount of water held by the bottle filled to the mark with the tubing in it, is obtained. The difference between this amount and some round number of cub. cent., such as 3000, is then measured into the bottle, which has been previously emptied and drained for a minute. The cork is then replaced, care being taken, as before, not to spill

any of the water in the tubing. The aspirator is now ready for use, and measures off with the utmost exactness 3000 cub. cent. of air each time it is reversed.

We are now in a position to consider the advantages of the method as thus modified. As regards, firstly, errors of weighing, we found, in accordance with previous observers, that an absorption-tube, when left to itself, varies considerably in weight from hour to hour. The same is true of a tube through which dry air from another absorption-tube is passed[1]. There is usually a gain in weight, but sometimes a loss. This may be due partly to variations in temperature and barometric pressure. It is also due to gradual penetration of moisture into the tubes and to the varying amount of moisture deposited on the surface of the glass. The amount of this variation in weight was often two milligrammes or more, both in Shaw's experiments and our earlier ones with other absorption-tubes. With the method just described the tubes did not vary in apparent weight by more than three decimilligrammes in a day; and these slight variations were in part accounted for by small imperfections in our set of weights.

The advantages of using a counterpoise are illustrated by an experiment in which weighings with the counterpoise were compared at intervals with ordinary weighings during several days. The differences found are shown in the following Table:—

Intervals between weighings.		2 hours.	3 hours.	4½ hours.	42 hours.
Counter-poise tube	Ordinary (66·9230 grms.)	+0·0012	+0·0010	+0·0008	+0·0024
Tube 1	Ordinary (77·7075)	.....	+0·0009	+0·0008	+0·0018
	Comparative (10·7840)	.....	±0·0000	±0·0000	−0·0004
Tube 2	Ordinary (87·6274)	+0·0007	+0·0015	.....	+0·0023
	Comparative (20·7041)	−0·0001	+0·0002	.....	+0·0002
Tube 3	Ordinary (69·6367)	+0·0009	+0·0010	+0·0006	+0·0018
	Comparative (2·7136)	±0.0000	−0·0002	±0·0000	−0·0005

[1] *Cf.* the data on this point given by Shaw, *loc. cit.* p. 84.

With regard, secondly, to the rate of aspiration possible and the lasting powers of the tubes, we made a number of experiments.

When a single absorption-tube was used, instead of the double ones described above, the absorption in the first tube was perfect (at least with rates up to two litres per minute) for a considerable time, as shown by the following experiments.

Experiment No. 1.

90 litres of air were aspirated at a rate of 1 litre per minute through two single absorption-tubes connected together by a very short piece of rubber tubing. The aspirator in this and the following experiment was a glass filter-pump, the air being measured by a gas meter:—

Tube 1	+0·5142.
Tube 2	+0·0000.

Experiment No. 2.

90 litres aspirated at 1 litre per minute.

Tube 1	+0·4712.
Tube 2	+0·0002.

Experiment No. 3.

50 litres aspirated at $1\frac{3}{4}$ litres per minute.

Tube 1	+0·4057.
Tube 2	+0·0001.

Experiment No. 4.

21 litres aspirated at 2 litres per minute.

Tube 1	+0·2334.
Tube 2	+0·0000.

Experiment No. 5.

50 litres aspirated at 1 litre per minute.

Tube 1	+0·4163.
Tube 2	−0·0003.

The same tubes were not used through all these experiments, as tube No. 1 had become spent in the middle of

the series. The use of double tubes enormously increases the lasting powers, so that, as shown by the following experiment, a double tube may be used for 300 determinations or more without being recharged.

Experiment No. 6.

The number of analyses possible without refilling a double absorption-tube was determined by aspirating air through two of them at a rate of 1 litre a minute, and weighing the second pair at intervals. 120 litres had previously passed through pair No. 1.

Litres of air aspirated through pair 1.	Variation in weight of pair 2.
235	−0·0005[1]
354	−0·0002
418	+0·0000
568	−0·0001
753	−0·0003
1046	+0·0000
1225	
1346	+0·0001
1588	+0·0003
1767	−0·0002
1994	+0·0000
2200	−0·0001

At the end of the experiment the first pair had absorbed 12·8255 grammes from 2320 litres of air. Although this pair was still absorbing moisture completely we did not continue the experiment further, on account of the inconvenient accumulation of dilute acid in the first tube.

As in determining moisture we have generally made a carbonic-acid determination simultaneously, our usual rate of aspiration has (for reasons given, p. 321) been about 1 litre per minute. The following were test experiments with faster rates:—

Experiment No. 7.

25 litres aspirated at 3 litres per minute.

Pair (1) . . . . +0·2012.
Pair (2) . . . . +0·0004.

[1] Weighed by mistake five minutes after experiment.

Experiment No. 8.

25 litres aspirated at 4 litres per minute.

Pair (1) . . . . . +0·3453.
Pair (2) . . . . . +0·0003.

Experiment No. 9.

21 litres aspirated at 7 litres per minute.

Pair (1) . . . . . +0·2142.
Pair (2) . . . . . +0·0001.

The rate of aspiration may thus be, if required, 7 litres per minute.

With the view of determining whether there is any appreciable constant error due to incomplete absorption of moisture by the first tube, we have added up the variations in weight of the second tube in all our experiments in which a second absorption-tube was used.

Total moisture absorbed by first tube.	Sum of variations of second tube.
13·0522 grms.	−0·0007 grms.

The mean variation in weight of the second tube was thus only 0·0065 per cent.; and a constant error of this order would be quite inappreciable in ordinary experiments.

Additional evidence of the accuracy of the method is afforded by the fact that in the simultaneous determinations recorded below (pp. 322 and 327) the two sets of results are practically identical. We have also made for another purpose two experiments in which air dried by sulphuric acid was passed through a weighed vessel containing water, and then again through a drying apparatus. The apparatus used was on a much larger scale, and the rate of aspiration was in one case 7 and in the other 15 litres per minute. The balance employed weighed to centigrammes. The vessel containing water lost 4·86 and 3·62 grammes, and the drying vessels gained 4·86 and 3·61 grammes respectively.

If the modified method described above be compared with the old method as investigated by Shaw, it is seen that by the modified method the rate of aspiration may be more than 20 times as fast and the accidental errors in weighing

are reduced to a sixth or less. Thus for a given duration of experiment the error in the modified method is less than a hundredth of that by the older method. In other words, an experiment of one minute's duration by the modified method is equal in accuracy to a two hours' experiment by the older method.

It is perhaps hardly necessary to refer to the great convenience of the modified method. For experiments in the open air sets of weighed tubes can be carried even for long distances in a box with places arranged for the tubes. We have found that no variation in weight is caused by the shaking, &c. (see p. 317). No precautions beyond the very simple ones above mentioned are necessary in weighing; and with a good short-beam balance not more than three minutes are occupied in the whole of the manipulations connected with weighing. Once an absorption apparatus is filled it is always ready for use, and may be used every day for nearly a year. The fact that only a small quantity (usually about 6 litres) of air is needed for an analysis makes it possible to use an easily portable aspirator, such as that described above."

I may here insert, even at the risk of some repetition, the original account of a short series of experiments which I made in the summer of 1889. These experiments will show the practical use of the sulphuric acid hygrometer in Meteorology.

"*Comparative Experiments with the Dry- and Wet-Bulb Psychrometer and the Apparatus described above. (Made at the Radcliffe Observatory, Oxford.)*

This series of experiments was undertaken with a view to test the degree of accuracy attainable by ordinary observations with the dry- and wet-bulb psychrometer; and also with the object of obtaining independent evidence as to the accuracy of the different tables used in connexion with the psychrometer.

The chemical method has been recognised by Regnault and others as the standard with which to compare all other

hygrometers. How important the first of these observers considered the method is shown by the following extracts from his *Études sur l'hygrométrie*:—'. . . j'attachais un grand intérêt à rendre cette méthode éminemment pratique et facile à employer dans toutes les expériences hygrométriques[1].'

'La méthode chimique convient éminemment à la vérification des autres méthodes hygrométriques et à la détermination des constantes numériques que plusieurs d'entre elles exigent. J'en ai constamment fait usage, à ce point de vue, dans les recherches qui font l'objet de mon premier Mémoire[2].'

Although Regnault proved by experiment that the absorption of moisture was complete with the chemical method, yet he was prevented from bringing it into general use in hygrometry by two difficulties. These were the inaccuracy of the weighings, and the slow rate at which the air could be aspirated through the absorption-tubes[3]. All other observers who have used the chemical method have had to encounter these same difficulties. Even the mercury-joints and glass-stoppered absorption-tubes used by Shaw have not removed the errors arising from these causes[4]. Each determination made by these observers required about one hour, and generally longer. By what simple means these serious errors can be avoided has been shown above.

I must here express my hearty thanks to the Radcliffe Observer for giving me every facility to carry out these experiments. To his assistants Messrs. Wickham, Robinson, and Bellamy, my thanks are also due.

Two determinations were made each time and as nearly simultaneously as possible. Two aspirators similar to the

[1] *Annales de Chimie et de Physique*, t. xv. p. 152 (1845).

[2] Ibid. t. xxxvii. p. 257 (1853).

[3] *Ann. de Chim. et de Phys.* t. xv. pp. 153 and 164. "La méthode chimique est trop embarrassante, et elle exige une manipulation trop longue pour qu'on puisse l'employer souvent dans les observations météorologiques."

[4] Shaw on Hygrometric Methods, *Phil. Trans.* 1888, vol. A, pp. 83 and 84. The variations in weight range from −·0009 to +·0023 gram. or still higher.

one described above were used. Four pairs of absorption-tubes were employed each time:—pair 1 for determination *A*; pair 2 for determination *B*; pair 3 as a test pair to show if any alteration in weight was caused by carrying the tubes from the Physiological Laboratory (where the tubes were weighed) to the Radcliffe Observatory and back; whilst pair 4 was the counterpoise.

The tubes were carried in a small box with partitions of copper wire to prevent them from knocking against each other. The entrance tube, by which the air to be examined passed into the pair 1 (or 2), was fixed through a small perforation in a rubber partition covering a hole in the box, so that there was no possibility of air being taken from the inside of the box. The box and its tubes were placed about 1 foot below the wet and dry bulbs. That the air in this position might be fairly compared with that in the shed containing the psychrometer is shown by experiment 6, in which pair 2 was placed in the shed close to the bulbs, and pair 1 in the usual place below.

In making a determination the following was the order of procedure. The wet and dry bulbs were first read off; the absorption-tubes, pairs 1 and 2, were then connected by two long pieces of rubber tubing with their respective aspirators, and the air was drawn through them at as equal a rate as possible. The readings of the thermometers in the aspirators were now taken. When one known volume (2900 cub. cent.) had been drawn through, the aspirators were quickly reversed and started again until 5800 cub. cent. of the air had been taken for each determination. The thermometers in the aspirators were now again read; the readings of the wet and dry bulbs entered; the apparatus disconnected; and the absorption pairs 1 and 2 stoppered. Everything was easily done in twelve minutes, whilst the actual period of aspiration was only about half this time, as shown by the Table of experiments.

How closely the two determinations agree Table I. will show, and there is no doubt that could they have been strictly simultaneous the agreement would have been still closer. This is well shown by a comparison of the first

five or six experiments with the last four, in which the determinations were almost exactly simultaneous.

To show that no practical error was introduced in the weighings by carrying the tubes about, the variation of the test pair 3 is given in Table I.

In calculating the results for the psychrometer in Table I. I have taken the mean of three readings—one at the beginning, one at the middle, and one at the end of each period of aspiration (*i. e.* one reading about every two minutes). These readings were obtained from a continuous photographic record of the wet and dry bulb taken at the Radcliffe Observatory. This record can be read off to two minutes and one tenth of a degree Fahrenheit, and its accuracy has been proved by years of use and comparison with eye-readings. The volume of air drawn through the tubes has always been corrected for temperature, aqueous vapour, and barometric height. In calculating the tension of aqueous vapour from the chemical determinations I have used the table given by Shaw in his paper on Hygrometric Methods[1].

The mean of all these gravimetric determinations compared with the mean of the amounts of moisture calculated from the psychrometric readings is ·0551 to ·0549 grm., or less than $+\frac{1}{2}$ per cent. Thus although the psychrometric result varied from the standard chemical method in the above series by +6 per cent. to −5 per cent., the mean difference is insensible.

[1] *Phil. Trans.* 1888, vol. A, pp. 78, 79.

TABLE I.

Experiment.	Date.	Time during which air was aspirated.	Corrected volume of air aspirated through each pair.	Gain in weight of pair 1, determination A.	Gain in weight of pair 2, determination B.	Weight of vapour calculated from readings of psychrometer by Glaisher's Tables, 7th ed.	Percentage difference of psychrometer over chemical method.	Dry bulb (mean of 3 readings).	Wet bulb (mean of 3 readings).	Variations of test pair 3, showing that carrying the tubes about introduced no error of weighing.
			cub. centim.	grm.	grm.	grm.	per cent.	°	°	grm.
1.	16 July 1889	11.39–11.48 A.M.	5723	·0421	·0430 [1]	·0450	$+5\frac{1}{2}$	61·6	53·0	+·0001
2.	17 ,,	11 39–11.45 A.M.	5722	·0529	·0524	·0552	+5	58·3	54·5	+·0002
3.	18 ,,	11.10–11.16 A.M.	5723	·0516	·0512	·0520	+1	61·3	54·9	—·0002
4.	19 ,,	11.6–11.12 A.M.	5780	·0502	·0508	·0519	+3	63·7	56·0	+·0002
5.	20 ,,	11.45–11.52 A.M.	5681	·0613	·0610	·0600	−2	57·9	56·0	+·0003
6.	22 ,,	12.13–12.16 P.M.	5732	·0440	·0435	·0452	+3	61·5	53·0	—·0002
7.	5 Aug. 1889	11.52–11.58 A.M.	5707	.....	·0687	·0668	−3	65·6	60·7	—·0003
8.	6 ,,	11.48–11.54 A.M.	5709	.....	·0564	·0548	−3	62·5	56·5	±·0000
9.	7 ,,	11.21–11.27 A.M.	5756	·0510	·0510	·0495	−3	63·0	55·2	+·0002
10.	8 ,,	11.0–11.7 A.M.	5776	·0575	·0572	·0552	−4	64.1	57·0	+·0001
11.	9 ,,	11.24–11.30 A.M.	5731	·0678	·0675	·0678	±0	61·0	58·9	+·0002
12.	10 ,,	11.32–11.39 A.M.	5755	·0583	·0585	·0553	−5	64·6	57·4	—·0001

[1] The rubber of one of the stoppers was found to be split on reaching the Observatory, and this accounts for the slight excess in weight of this pair of tubes.

During some experiments the psychrometer was very steady; at other times it showed considerable fluctuations. As examples may be given the readings of the wet and dry bulbs for the experiments 1 and 5.

Experiment 1.	Dry.	Wet.	Experiment 2.	Dry.	Wet.
11.39 A.M.	61·4	52·9	11.45 A.M.	57·9	55·9
11.43	61·8	53·1	11.49	57·9	56·0
11.47	61·6	52·9	11.52	58·0	56·0

It is to be noticed that a difference of two or three tenths of a degree Fahrenheit in the reading alters greatly the percentage error.

I have also calculated out the tension given by the chemical method, and have compared it with the results calculated from the psychrometer by means of Glaisher's, Haeghen's, Guyot's, and Wild's Tables.

TABLE II.

Experiment.	Chemical method.	Psychrometer.			
		Glaisher.	Haeghen.	Guyot.	Wild.
	mm.				
1	7·43	7·76	7·37	7·31	7·4
2	9·15	9·55	9·54	9·51	9·5
3	8·99	9·00	8·88	8·87	8·9
4	8·78	8·99	8·74	8·77	8·8
5	10·70	10·72	10·75	10·76	10·7
6	7·63	7·78	7·39	7·34	7·4
7	12·15	11·72	11·78	11·80	11·7
8	9·91	9·65	9·57	9·57	9·6
9	8·90	8·68	8·45	8·43	8·5
10	10·00	9·52	9·38	9·41	9·4
11	11·82	11·84	11·93	11·93	11·9
12	10·23	9·67	9·55	9·57	9·5
Mean	9·64	9·57	9·44	9·44	9·44

This Table shows that Glaisher's Tables are the most correct as far as my experiments go. These tables were

prepared by Glaisher from the Greenwich factors and Regnault's Table of pressures, and are in general use in England. Haeghen's Tables, which are used in France and Italy, Guyot's, which are almost identical with the last and are employed in America, and Wild's, which have been adopted by Germany and Russia, are all reduced from Regnault's table of pressure and psychrometric formulæ.

In conclusion may be given the results obtained by other observers, who have compared the psychrometer with the chemical method. Regnault[1], who made 106 experiments under very varied conditions, obtained for the mean percentage error 2, whilst the extreme percentage error varied from +12 to −10. In order to calculate out the results from the readings of the dry and wet bulbs, Regnault determined the values for the constant A in each series of experiments. Each experiment lasted about one hour; the readings of the psychrometer were taken every five minutes, and from the mean of these the result was calculated. M. Izarn made 34 comparative experiments in the Pyrenees. These are given by Regnault in his paper. The extreme percentage differences are + 2 and − 3 in the first series, and + 10 and − 10 in the second.

Shaw made comparisons in a room with a current of air passing over the instruments; he does not, however, consider them satisfactory. The tensions calculated from the psychrometer by Glaisher's Tables were generally higher than those given by the chemical determination, the variations ranging from + 30 per cent. to − 7 per cent.[2]."

Although the latest modification of the sulphuric acid hygrometer is very accurate and a determination can be readily made, yet it is evident that its use in Hygrometry is limited. It is not a self-recording instrument, and there are great difficulties in making it so. Its chief value would appear to be in a long series of comparative experiments with the Dry- and Wet-Bulb Psychrometer under various external conditions; data would then be obtained upon

[1] *Annales de Chimie*, t. xxxvii. pp. 264–285 (1835).

[2] *Phil. Trans.* 1888, vol. A, p. 111.

which accurate tables for the Psychrometer might be constructed.

In the investigation of the relative amounts of water present in the liquid and gazeous forms during mists this hygrometer would be invaluable; likewise it would be useful in experiments on dew.