XVIII.—*On an Improved Apparatus for the Analysis of Gases.*

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Notwithstanding the acknowledged importance of the investigation of gaseous bodies, it is only within a comparatively recent period that this branch of chemical research has received that attention which it so well deserves.

When Bunsen, in the prosecution of his admirable researches on the gases evolved from the iron-furnaces of Germany,* attempted to apply to the analysis of those gases the best methods known at that time, he found himself compelled, by the great imperfections and inaccuracies of those methods, to re-investigate and remodel the whole subject of gaseous analysis. Commencing with the construction of the eudiometers themselves, and adopting the simple plan of graduation independent of volume, with subsequent calibration or determination of the actual value of each division of this independent graduation, he attained a degree of accuracy in the measurement of volumes which left nothing to be desired in this department. He then obviated the

* Pogg. Ann. Bd. XLVI, 193; L, 81, 673.

inaccuracies inseparable from the introduction of liquid solvents into the measuring-tubes, by the employment of those solvents or absorbents in the dry state, in the form of little bullets cast upon platinum or steel wires. Thus the inner walls of the eudiometers were preserved free from adhering impurity, whilst the convexity of the internal mercury was kept uniform. By further improvements in the absorbents employed, the determination of the limits of perfect combustion in the explosion of gases with oxygen and hydrogen, and many other important points connected with the true measurement of gaseous volumes, Bunsen brought this branch of chemical analysis to a state of perfection which, as shown by numerous researches made by himself, by Playfair, Kolbe, and others, left, so far as delicacy and perfect accuracy were concerned, scarcely either room or desire for further improvement.

It was however necessary, for the successful carrying out of these methods, that a room of tolerably constant temperature should be appropriated exclusively to this object, and that an interval of from half an hour to one hour should be allowed between each determination of volume in order that the gas in the eudiometer might perfectly assume the temperature of the circumambient air. These circumstances, though of little importance in the performance of occasional gas analyses, become serious considerations when a large number of such analyses have to be made consecutively, as the expenditure of time and space becomes in such cases very great.

For the removal of this difficulty we are indebted to Regnault, who, by enclosing the eudiometer in a cylinder filled with water, renders the equalization of the temperature of the gas and the external medium, the work of a few seconds only; thus greatly reducing the time occupied by an analysis, and obviating the necessity for an apartment exclusively appropriated to gaseous investigations. This chemist has also further facilitated the various operations upon gaseous mixtures, by a more convenient division of the apparatus into two parts, the one for absorption and the other for measurement, than that employed by Bunsen; as also by adopting the admirable method of always determining the gaseous volumes when saturated with aqueous vapour. Unfortunately, these great advantages are in some respects diminished by a somewhat less amount of delicacy in the manner of determining the volumes: M. Regnault maintains the volume of the gases during an analysis, constant, and measures the amount of pressure exercised by that constant volume, over or under the pressure of the atmosphere, expressed in millimetres of mercury. This method, though unexceptionable in principle, has yet the dis-

advantage in practice, that considerable changes of volume are represented by small numerical expressions when compared with those obtained by Bunsen's method. This is more especially the case with the first determination in an analysis, great delicacy in which is usually of much greater importance than in the subsequent readings.

To illustrate more clearly what we here mean, we give the determination of a small percentage of carbonic acid, contained in a small volume of gas, by the two methods:

BY BUNSEN'S METHOD.

	Absorbed volume.	Temp.	Difference of mercury level.	Height of barometer.	Corrected vol. at 0° C. and 1 ^m pressure.
Vol. of gas used (dry)	330·2	0° C.	550·4 ^{mm}	760·0 ^{mm}	69·20
Vol. after absorption of CO ₂ (dry) . .	327·8	0° „	549·6 „	760·1 „	69·00

BY REGNAULT'S METHOD.

	Observed pressure.	Temp.	Barometer.	Corrected pressure.
Gas used (moist) . .	—686·2	0° C.	760·0 ^{mm}	69·2
After absorption of CO ₂ (moist)	—686·5	0° „	760·1 „	69·0

Percentage of carbonic acid = 0·28.

Let us now suppose that an error of $\frac{1}{10}$ of a millimetre was made in the first observation in each of the above methods, and that thus the volume of gas used was read off according to Bunsen's method 330·1 vols., and according to Regnault's method—686·3. The percentage of carbonic acid by the two methods would then be as follows:

Carbonic acid per cent (Bunsen's method) . . .	0·260
„ „ „ (Regnault's method) . . .	0·145

Thus the error in the one case would amount to only ·02 per cent, whilst in the other it would be nearly 7 times as great, and might even cause the carbonic acid to be entirely overlooked.

In endeavouring to remedy this defect, and at the same time to combine the advantages of the two methods, we proposed to ourselves the following qualifications as highly desirable in a good apparatus for the analysis of gases.

1. The determinations of the gaseous volumes should be made in a manner entirely independent of the pressure and temperature of the external atmosphere.

2. Such determinations of volume should also be self-correcting as

regards the tension of aqueous vapour and the variations in the density of mercury.

3. Each change of volume should be expressed by a numerical difference as large as possible.

4. In order to avoid the inconvenience and loss of time occasioned by tedious calculations, references to tables, &c., the numerical expression of each volume actually read off should either be the true and corrected volume, or a number from which such volume can be at once obtained by the most simple arithmetical process.

The advantage of securing the first and second of these qualifications is sufficiently obvious; for whilst we can then carry on the operations of gaseous analysis without an apartment of nearly constant temperature set apart for the purpose, the accuracy of our results is also not liable to be affected by any errors that may have been made in the determination of the expansion of gases by heat, the tension of aqueous vapour, and the expansion-coefficient of mercury. The third and fourth qualifications are also scarcely of inferior importance, the one for securing delicacy in the readings, and the other for economizing time and enabling the operator to see the corrected results of his experiments during their progress, an advantage which can be best appreciated by those who have had to make large numbers of consecutive gas analyses.

In constructing an apparatus to combine the foregoing qualifications, we have taken as a model the ingenious and very convenient arrangement of MM. Regnault and Reiset, with the mechanical arrangements of which, our apparatus, though different in principle, has much in common.

Our instrument, which is represented by the accompanying figure consists of the tripod *A* furnished with the usual levelling screws, and carrying the vertical pillar *B*, to which is attached, on the one side, the moveable mercury-trough *C*,* with its rack and pinion *a a*, and on the other the glass cylinder *D D* with its contents. This cylinder is 36 inches long and

* The mercury-trough, including its tubular well *b*, may be conveniently constructed of gutta-percha.

4 inches internal diameter; its lower extremity is firmly cemented into an iron collar *c*, the under surface of which can be screwed perfectly water-tight upon the bracket-plate *d* by the interposition of a vulcanized caoutchouc ring. The circular iron plate *d* is perforated with three apertures, into which the caps *e e e* are screwed, and which communicate below the plate with the T-piece *EE*. This latter is furnished with a double-way cock *f* and a single-way cock *g*, by means of which the tubes cemented into the sockets *e e e* can be made to communicate with each other or with the exit-pipe *h* at pleasure.

FGH are three glass tubes, which are firmly cemented into the caps *e e e*. *F* and *H*, which are only slightly shorter than the glass cylinder, are each from 15^{mm} to 20^{mm} internal diameter, and are selected of as nearly the same bore as possible, to avoid a difference of capillary action. The tube *G* is somewhat wider, and may be continued to any convenient height above the cylinder. *H* is accurately graduated with a millimetre scale, and is furnished at top with a small funnel *i*, into the neck of which a glass stopper, about 2^{mm} in diameter, is carefully ground. The tube *F* terminates at its upper extremity in the capillary-tube *k*, which is carefully cemented into the small steel stop-cock *l*. *F* has also fused into it at *m* two platinum-wires for the passage of the electric spark. After this tube has been firmly cemented into the cap *e*, its internal volume is accurately divided into ten perfectly equal parts, which is effected without difficulty by first filling it with mercury from the supply-tube *G*, up to its junction with the capillary attachment, and then allowing the mercury to run off through the nozzle *h* until the highest point of its convex surface stands at the division 10, previously made so as exactly to coincide with the zero of the millimetre scale on *H*; the weight of the mercury thus run off is carefully determined, and the tube is again filled as before and divided into ten equal parts, by allowing the mercury to run off in successive tenths of the entire weight, and marking the height of the convexity after each abstraction of metal. By using the proper precautions with regard to temperature, &c., an exceedingly accurate calibration can, in this way, be accomplished.

The absorption-tube *I* is supported by the clamp *n*, and connected with the capillary-tube *k* by the stop-cock and junction-piece *l'p* in exactly the same manner as in Regnault's apparatus.

When the instrument is thus far complete, it is requisite to ascertain the height of each of the nine upper divisions on the tube above the lowest or tenth division. This is very accurately effected

in a few minutes by carefully levelling the instrument, filling the tube *G* with mercury, opening the cock *l* and the stoppered funnel *i*, and placing the cock *f* in such a position as to cause the tubes *F H* to communicate with the supply-tube *G*. On now slightly turning the cock *g*, the mercury will slowly rise in each of the tubes *F* and *H*; when its convex surface exactly coincides with the ninth division on *F*, the influx of metal is stopped, and its height in *H* accurately observed; as the tenth division on *F* corresponds with the zero of the scale upon *H*, it is obvious that the number thus read off is the height of the ninth division above that zero-point. A similar observation for each of the other divisions upon *F* completes the instrument.

Before using the apparatus, the large cylinder *DD* is filled with water, and the internal walls of the tubes *F* and *H* are once for all moistened with distilled water by the introduction of a few drops into each, through the stop-cock *l* and the stoppered funnel *i*. The three tubes being then placed in communication with each other, mercury is poured into *G* until it rises into the cup *i*, the stopper of which is then firmly closed. When the mercury begins to flow from *l*, that cock is also closed. The tubes *F* and *H* are now apparently filled with mercury, but a minute and imperceptible film of air still exists between the metal and glass; this is effectually got rid of by connecting *F* and *H* with the exit-tube *h* and allowing the mercury to flow out until a vacuum of several inches in length has been produced in both tubes; on allowing the instrument to remain thus for an hour, the whole of the film of air above mentioned will diffuse itself into the vacuum, and will become visible as a minute bubble in each tube on allowing the vacuum to be filled up from the supply-tube *G*. These bubbles are of course easily expelled on momentarily opening the cock *l* and the stopper *i* whilst *G* is full of mercury. The absorption-tube *I* being then filled with quicksilver, and attached to *l* by the screw clamp, the instrument is ready for use.

In localities where a constant supply of water from street mains can be had, the temperature of the water in the cylinder *DD* can be maintained perfectly constant by allowing a continuous stream, direct from the main, to flow into the bottom of the cylinder and make its exit near the top. By this arrangement, it has been proved by one of us, in an extensive series of experiments, that the temperature of a cylinder supplied from the Manchester high-pressure mains does not vary more than 0.02° C. in twelve hours, a variation which scarcely requires correction in the most delicate experiments.

In illustration of the manner of using our apparatus, we will take

as an example an analysis of atmospheric air. A few cubic inches of air freed from carbonic acid having been introduced into the tube *I*, it is transferred into *F* for measurement by opening the cocks *l l'* and placing the tube *F* in communication with the exit-pipe *h*; the transference can be assisted, if needful, by elevating the trough *C*. When the air, followed by a few drops of mercury, has passed completely into *F*, the cock *l* is shut, and *f* turned so as to connect *F* and *H* with *h*. Mercury is allowed to flow out until a vacuum of 2 or 3 inches in length is formed in *H*, and the metal in *F* is just below one of the divisions: the cock *f* is then reversed, and mercury very gradually admitted from *G* until the highest point in *F* exactly corresponds with one of the divisions upon that tube; we will assume it to be the sixth division. This adjustment of mercury and the subsequent readings can be very accurately made by means of a small horizontal telescope placed at a distance of about 6 feet from the cylinder, and sliding upon a vertical rod. The height of the mercury in *H* must now be accurately determined, and if from the number thus read off, the height of the sixth division above the zero of the scale on *H*, be deducted, the remainder will express the true volume of the gas; but in order to compare this with subsequent readings made at other divisions upon *F*, the number thus obtained, which evidently represents the pressure of the gas, is reduced to what it would have been had the gas been expanded to the tenth division of *F*. Bearing in mind that the pressure of a gas is inversely as its volume, this reduction is very simply effected by multiplying the number as above obtained by $\frac{6}{10}$, or 0.6; and in all cases, any determination of pressure made at any division upon *F* may be reduced to the pressure of the same volume when expanded to the tenth division, by the use of a fractional multiplier whose denominator is 10, and numerator the number of the division at which the determination is made.

As the temperature is maintained constant during the entire analysis, no correction on that score has to be made; the atmospheric pressure being altogether excluded from exerting any influence upon the volumes or pressures, no barometrical observations are requisite, and as the tension of aqueous vapour in *F* is exactly balanced by that in *H*, the instrument is in this respect self-correcting.

Hydrogen being then introduced in the same way as the original gas, and the volume determined anew, the electric spark is passed through the mixture by means of the platinum-wires at *m*, and the determination of the contraction caused by the explosion terminates the analysis. The following are the results of an analysis of air made in this way.

VOLUME OF AIR USED.

(Determined at fifth division on *F*.)

Observed height of mercury in <i>H</i> .	.	.	673·0 ^{mm}
Height of fifth division above zero	.	.	383·0
Corrected pressure of gas	.	.	<u>290·0</u> ·5
Corrected pressure of gas at tenth division			<u>145·00</u>

VOLUME AFTER ADMISSION OF HYDROGEN.

(Determined at sixth division.)

Observed height of mercury in <i>H</i>	.	.	772·3 ^{mm}
Height of sixth division above zero	.	.	304·0
Corrected pressure of gas	.	.	<u>468·3</u> ·6
Corrected pressure of gas at tenth division			<u>280·98</u>

VOLUME AFTER EXPLOSION.

(Determined at fifth division.)

Observed height of mercury in <i>H</i> .	.	.	763·3 ^{mm}
Height of fifth division above zero	.	.	383·0
Corrected pressure of gas	.	.	<u>380·3</u> ·5
Corrected pressure of gas at tenth division			<u>190·15</u>

RESULTS.

Volume of air used	.	.	145·00
Volume of oxygen	.	.	30·276

Hence :

Nitrogen	.	.	79·120
Oxygen	.	.	<u>20·880</u>
			100·000

To show the delicacy of the indications of this instrument, we here subjoin the results of a series of analyses performed upon the same

specimen of atmospheric air, previously freed from carbonic acid by caustic potash.

	I.	II.	III.	IV.	V.	VI.
Oxygen	20·880	20·888	20·883	20·867	20·868	20·876
Nitrogen	79·120	79·112	79·117	79·133	79·132	79·124
	100·000	100·000	100·000	100·000	100·000	100·000