

III. *Experiments on the Quantity of Gases absorbed by Water, at different Temperatures, and under different Pressures.* By Mr. William Henry. Communicated by the Right Hon. Sir Joseph Banks, K. B. P. R. S.

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THOUGH the solubility of an individual gas in water forms, generally, a part of its chemical history, yet this property has been overlooked, in the examination of several species of the class of aëriform substances. The carbonic acid, indeed, is the only gas whose relation to water has been an object of much attention; and, at a very early period of its history, Mr. CAVENDISH, in the course of inquiries, the results of which were the groundwork of the most important subsequent discoveries, ascertained, with peculiar care, the proportion of carbonic acid gas condensible in water, at the temperature of  $55^{\circ}$  of FAHRENHEIT. Dr. PRIESTLEY also, about the same period, directed his attention to the saturation of water with fixed air, and contrived a simple and effectual mode of obtaining this impregnation. His apparatus, afterwards, gave way to the more manageable one of Dr. NOOTH; and this, in its turn, has been superseded by the improved mode of condensing, into water, many times its bulk of various gases, invented and practised by several chemical artists, (as well as by myself,) both in this country and abroad.

The influence of pressure, in accomplishing this strong impregnation, was first, I believe, suggested by Dr. PRIESTLEY.

“In an exhausted receiver,” that most ingenious philosopher observes, “Pymont water will actually boil, by the copious discharge of its air; and I do not doubt, therefore, that by means of a condensing engine, water might be much more highly impregnated with the virtues of the Pymont spring.”\*

Before describing my experiments on the effects of additional pressure, in saturating water with gases, it will be necessary to state the results of others, that were previously expedient, to determine the quantity of each gas combinable with water, at a given temperature, and under the ordinary weight of the atmosphere. In a few instances, also, it was deemed proper to ascertain the influence of different temperatures, over the condensation of gases in water.

## SECTION I.

### ON THE QUANTITY OF GASES ABSORBED BY WATER, UNDER THE USUAL PRESSURE OF THE ATMOSPHERE.

In order to attain considerable minuteness in observing the proportion of gases absorbed by water, an apparatus was employed, of which the following is a description.

The vessel A (Plate I. Fig. 1) is of glass, about 2 inches diameter, and  $4\frac{1}{2}$  inches long. It is graduated into cubical inches, and quarter inches; and furnished at the top with a brass cap, into which a cock *a* is screwed. To the lower aperture, a copper tube C is cemented, which is bent at a right angle, the leg nearest the vessel being carried downwards, and furnished with a cock *b*. B is a glass tube, of about  $\frac{1}{4}$  inch bore,

\* Experiments on Air, arranged and methodized, Vol. I. p. 51.

bent at a right angle, and graduated, from a given point, into hundredth parts of a cubical inch. It is attached to the copper pipe, by a tube of Indian rubber D, over which is a covering of leather, forming a joint, which admits of the vessel A being briskly agitated. When the apparatus is used, it is first filled with quicksilver; a transfer bottle of elastic gum, furnished with a cock, and containing water of a known temperature, is screwed on; and a communication is opened, through the cocks, between the bottle and the glass vessel. The lower cock *b* is then opened, through which the mercury runs out, while its place is supplied by a quantity of water from above, measurable by the scale on A. This transfer is removed, and another containing gas being substituted, a measured quantity of gas is admitted in a similar manner. Strong agitation is now applied, by means of the joint D; and mercury is poured into the tube B, to supply the descent occasioned by the absorption in A; its level being exactly preserved in both legs of the syphon, both at the commencement and close of the experiment. The quantity of mercury required for this purpose, indicates precisely the amount of the gas absorbed.

The only advantage of this apparatus over a cylindrical jar, inverted in the usual way over mercury, is, that by means of the tube B, very minute degrees of absorption may be measured, which would scarcely be perceived in a wide vessel.

For the more absorbable gases, I found this instrument to answer perfectly well; but, for ascertaining the solubility of those which are taken up by water in only small proportion, I preferred one of different construction. It consisted simply of a glass vessel, of the capacity of  $57\frac{1}{2}$  cubical inches, and shaped as in Fig. 2. At *a* was cemented a cock, provided with a screw;

and the lower cock *b* was of glass, accurately ground in. The vessel was then filled with water which had been long boiled; a lifting valve was screwed on *a*, the cock being open; and the vessel was placed under the receiver of an air pump, where it was kept for some time, the pump being occasionally worked, as long as any air bubbles could be seen to arise. The gas under examination was next admitted from an elastic bottle, the cock *b* being opened, and a measured quantity of water let out. The gas and water were then violently agitated together; and the cock *b* opened under mercury, which ascended into the vessel. The agitation was still continued, observing to preserve the same level of mercury without as within the vessel; and, when it rose no higher, the ascent was noted by means of the graduated scale. The quantity of mercury that had entered the vessel, indicated the amount of absorption that had ensued.

It might, however, be objected, that the water would acquire air again, while poured into the vessel; and I therefore sometimes used large glass globes, having long necks, accurately graduated. These globes, being of very thin glass, were filled with boiling water, and inverted instantly in a trough of quicksilver. When the water became cold, the mercury was, of course, found to have risen partly into the vessel. This portion was displaced by a measured quantity of gas; and the absorption was denoted by the ascent of the mercury in the graduated neck.

The water employed in these experiments was boiled, during several hours, in a tin vessel having an aperture barely sufficient to allow the egress of the steam, and poured, while boiling hot, into glass vessels, which were corked, and tightly tied over with bladder. An equable temperature was produced in the

water, mercury, and gas, except when above  $85^{\circ}$ , by regulating that of the room in which the experiments were made; and the glass vessel, during agitation, was carefully guarded from the warmth of the hand. The agitation was continued, till it appeared, by the scale, to produce no further effect; and, in the absorption of difficultly condensable gases, was repeated at intervals, during a space of from twelve to twenty-four hours. Alterations of the barometer were always observed; and the residuary gas measured, or estimated, at a pressure of  $29\frac{1}{2}$  inches.

1. *Absorption of Carbonic Acid Gas by Water.*

That the temperature of water influences the proportion of carbonic acid which it is capable of absorbing, is already known as a general fact;\* but the exact amount of this influence has not, I believe, been hitherto ascertained. In the course of a series of experiments to determine it with precision, I was surprised by obtaining results which differed considerably from each other, at the same temperature of the gas and water; when both were, in different experiments, of like purity; and when the barometer had the same elevation. Of the cause of these variations I was not aware, till my friend Mr. DALTON suggested, that they probably depended on the variable amount of the residues; and, on repeating the experiments, with different proportions between the gas and the water, this suggestion was fully confirmed. Thus, when two measures of carbonic acid gas were agitated with one measure of water, the absorption was considerably greater than when, to the same quantity of water, a less proportion of gas was used. The cause of this diminished

\* See Mr. CAVENDISH's experiments in the *Phil. Trans.* Vol. LVI. p. 163; and FOURCROY's *Système*, 4to. Tom I. p. 215.

absorption, seems to be connected with the proportion of common air contained in the unabsorbed residuum; for, besides the unavoidable contamination of the gas employed, with a minute portion of the air of the vessel used for its extrication, a small quantity will always be liberated from the water, whatever pains have been taken to deprive it of air, by previous long boiling, exposure under the air pump, or both in succession. That this is the true explanation, appears also, from the result of adding to the gas a proportion of common air. Thus, when, at the temperature of  $55^{\circ}$ , 20 measures of carbonic acid are agitated with 10 of water, at least 10 measures of gas are taken up; but, from a mixture of 20 measures of carbonic acid with 10 of common air, 10 parts of water take only 6 of carbonic acid, or  $\frac{3}{5}$  less than in the former instance.

An analogous fact was observed by Dr. BROWNRIGG,\* who remarked that gas does not escape from the water which it impregnates, unless the water be in contact with air: for, when the Pouhon water was excluded from air, but, at the same time, liberty was given for its gas to arise into an empty bladder, the gas did not spontaneously separate from the water; but, on the contrary, remained united with it, when exposed to the greatest heat of our climate. When the impregnated water, he observes, is thus excluded from air, the gas will escape very slowly, at any temperature less than  $110^{\circ}$  of FAHRENHEIT, although such heat be sufficient for the distillation of water; nor can it be wholly expelled by a heat of  $160^{\circ}$  or  $170^{\circ}$ , continued two hours. But it is well known, that water saturated with carbonic acid gives up its gas rapidly, when freely exposed to the atmosphere.

\* See Dr. BROWNRIGG'S Paper on the Pouhon Water, Phil. Trans. Vol. LXIV.

In fixing the proportion of carbonic acid absorbed, it is therefore necessary to note the quantity of residuum, as is done in the following table.

Experiment.	Temperature.	Measures of water.	Measures of gas.	Quantity absorbed.	Residue.	Absorbed by 100 inches of water.
1	55	13	32	14	18	108
2	85	13	32	11	21	84
3	55	13	24	14	10	108
4	55	10	15	10	5	100
5	55	20	20	18	2	90
6	55	19	19	16	3	84
7	85	19	19	13	6	70
8	110	10	20	6	14	60
9	110	20	20	9	11	45

Since the above table was drawn up, I have been gratified by remarking that, in the experiments of Mr. CAVENDISH, similar variations in the quantities absorbed, were produced by the variable amount of the residua; as will appear from the following deductions from his experiments.

At the temperature of  $55^{\circ}$ .

1. When the gas absorbed was to the residue as 100 to 164,  
100 cubical inches of water took up - - - 116
2. When the absorbed gas was to the residue as 100 to 16,  
100 inches of water took up - - - 107
3. The absorbed gas being to the residue as 100 to 10,  
100 parts of water absorbed - - -  $102\frac{1}{2}$
4. The absorption being to the residue as 100 to  $1\frac{1}{2}$ ,  
100 parts of water took up - - -  $95\frac{1}{2}$

The quality of the residuum, I only ascertained in experiments 5 and 6 of the preceding table. In experiment 5, the residuary two measures contained  $7\frac{1}{2}$  per cent. of common air,

or 0.15 of a measure. But, of those, .13 existed previously in the 20 measures of carbonic acid gas; and the 20 measures of water had, therefore, only given up .02 of a measure, or about  $\frac{1}{10000}$  of its bulk. I apprehend, however, that the whole of the common air was not, even thus, extricated from the water. In experiment 6, the 3 residuary measures contained  $\frac{1}{6}$  of common air.

To judge of the influence of temperature, it is essential that the experiments compared should be on similar proportions of gas and water. Thus, from a comparison of experiment 1 and 2, it appears, that about  $\frac{1}{14}$  of the whole bulk absorbable at 55°, is the diminution of the quantity of absorption produced by each elevation of 10° of temperature; and the same inference follows from various other experiments, the results of which I have thought it needless to state.\*

### 2. *Sulphuretted Hydrogen Gas.*

One hundred parts of water, at 55° of temperature, absorb 86 parts of this gas, obtained from sulphuret of iron and dilute sulphuric acid, a residue being left, equal in bulk to the gas absorbed. At 85°, under similar circumstances, the same quantity absorbs 78.

### 3. *Nitrous Oxide.*

At 45°, 100 cubic inches of water take up 50 of nitrous oxide; and, at 70°, the same quantity takes up only 44. According to Mr. DAVY, in whose experiments, from his intimate

\* During the absorption of carbonic acid by water, the gas and water having previously the same temperature, there is an extrication of caloric, sufficient to raise the temperature of the water between  $\frac{1}{2}$  and  $\frac{3}{4}$  of a degree of FAHRENHEIT. The same effect is produced by the condensation of sulphuretted hydrogen, and nitrous oxide gases, though less apparently. To perceive this phenomenon, considerable quantities of gas and water should be used.



knowledge of this gas, and skill in its preparation, I place more confidence than in my own, 100 inches of water at  $45^{\circ}$ , take up 54 of nitrous oxide, the residuum being about one half the volume of the gas absorbed.

#### 4. *Less absorbable Gases.*

The experiments with those gases which are absorbed only in sparing proportion by water, I could not conveniently make at more than one temperature; nor, indeed, did the object appear to me worthy of the time and attention which such a repetition of them would have required. Of the accuracy of the following, however, I satisfied myself, by repeating each two or three times; and with gases of the greatest attainable purity.

100 cubic inches of water, at  $60^{\circ}$ , absorb,

Of nitrous gas	-	-	-	5	inches.
Oxygenous gas	-	-	-	2.63	
Phosphuretted hydrogen ditto	-	-	-	2.14	
Gaseous oxide of carbon	-	-	-	2.01	
Carburetted hydrogen gas	-	-	-	1.40	
Azotic gas	-	-	-	1.20	
Hydrogen gas	-	-	-	1.08	

The solubility of atmospherical air cannot easily be ascertained; for, as I shall hereafter shew, in a memoir on the expulsion of gases from water by each other, air is decomposed by agitation with boiled water, its oxygenous portion being absorbed in preference.

From the statements given by various philosophers, (the Abbé NOLLET, Drs. HALES, PRIESTLEY, and PEARSON,) of the quantity of air separable from water of different kinds, by heat or a diminished pressure, I expected that a much larger proportion of the gases constituting the atmosphere would have been absorbed by water, than the above numbers assign. It is to be

recollected, however, that no method hitherto discovered detaches from water all its air; and the unknown quantity remaining in it, after these modes of separation have been employed, is to be added to that with which a given volume of water can be artificially impregnated. Dr. PEARSON, in his enquiries into the nature of the gas obtained by passing electric discharges through water, was at great pains to purify the subject of his experiments from air, by boiling and a powerful air pump; but he always found, that after the full effect of both these methods, electricity liberated a further, and not an inconsiderable, portion of air.\*

Common spring water may, I think, be fairly taken as a specimen of water fully charged with atmospherical air; and, with the view of determining the quantity and kind of gases extricated from it, I made the following experiment. A glass globe, of the capacity of  $117\frac{1}{2}$  cubical inches, was filled with water fresh from the well. To its mouth was adapted a curved and stoppered tube, which held  $\frac{3}{4}$  of an inch; and this was also filled with water. The globe was then placed in a vessel of brine, which was kept boiling between six and seven hours; and the gases were received over mercury. Their quantity and quality were as follows.

No.	Cub. inches.	Consisted of		Proportion of Oxygen gas in the residuary air.
		Carbonic acid.	Air.	
1	1.25	0.50	0.75	0.20
2	1.25	0.85	0.40	0.16
3	1.63	1.23	0.40	0.16
4	0.50	0.49	0.01	lost by acci- dent,
	<u>4.63</u>	<u>3.07</u>	<u>1.56</u>	
Air remaining in the bent tube	<u>0.75</u>			
5.38, total gas from $117\frac{1}{2}$ inches of water.				

\* Phil. Trans. for 1797.

But,  $4\frac{1}{2}$  inches of water were expelled, owing to the expansion by heat. Therefore,  $117\frac{1}{2} - 4\frac{1}{2} = 113$  inches of water, gave 5.38 inches of gas; and 100 inches, consequently, gave 4.76, of which 3.38 were carbonic acid, and 1.38 atmospherical air. Hence, the water afforded about  $\frac{1}{70}$  its bulk of atmospherical air, and  $\frac{1}{20}$  of a mixture of gases. In this estimate, the gas remaining in the tube is reckoned as carbonic acid, which may be allowed, since the portion last obtained held only  $\frac{1}{50}$  its bulk of common air.

## SECTION II.

ON THE INFLUENCE OF PRESSURE IN PROMOTING THE ABSORPTION OF GASES; AND THE DESCRIPTION OF AN APPARATUS FOR EXHIBITING THIS PHENOMENON.

For the purpose of determining the ratio between the addition of pressure and the increased absorption of gases by water, I employed the apparatus, with some addition, which has been already described. The tube B was lengthened at pleasure, with the view of obtaining, by a column of mercury, any additional pressure that might be required. The vessel A, Fig. 1, was then filled completely with mercury, which rose to its corresponding level in the tube B. A given quantity of water, of a known temperature, and afterwards a measured volume of gas, were transferred into the vessel, in the mode already described; and, as the mercury, by opening the cock *b*, was brought to the same level in both legs of the syphon, the gas, it is evident, must have been under the ordinary weight of the atmosphere. A quantity of mercury was next poured into the leg B, sufficient to form a column 28 inches higher than the level of the mercury in A, after this addition; and the bulk of the gas was again noted. This was found to be, pretty exactly,  $\frac{1}{2}$ ,  $\frac{1}{3}$ , &c. of

the space occupied before, when one, two, or more additional atmospheres were applied. Brisk agitation was now used, as long as any absorption took place; and, into the tube B an assistant poured mercury, so as to preserve in it the excess of 28 inches above the level of the mercury in A. The degree of absorption was known by the scale on A, or, more accurately, by the quantity of mercury required to support the elevation of 28 inches in B.

By lengthening the column in B to 56 inches, the pressure of two additional atmospheres was obtained; and this was the utmost extent to which the addition of weight could be carried, without forcing the joint at D.

When the cock *b* was opened, and the column in each leg thus suddenly fell to the same level, the water, which had been previously charged with gas, under a pressure of three atmospheres, effervesced violently; but some time elapsed before the additional gas, forced in by compression, was wholly evolved. These appearances are very striking and amusing; and are well calculated for exhibition in a chemical lecture. The apparatus, however, I have no doubt, may be greatly improved; but, at the distance of nearly 200 miles from the metropolis, I was under the necessity of using such an one as could be constructed by my own hands.

A considerable improvement in the construction of the apparatus, which would obviate the expediency of the flexible tube D, would be the following. To the lower neck of the vessel A, Fig. 1, let a cap and cock, with a female screw, be cemented; and let the upper end of the pipe C be terminated by a cock with a male screw. Introduce the gas and water, in the manner already described; apply the increased pressure; and, having shut the two additional cocks, unscrew them from each other.

The vessel A will thus be detached, and agitation may be easily applied; after which, again screw it into its former place, and, on opening the two cocks, the mercury will rise in the vessel A. Supply the descent in B by fresh mercury, and proceed as before, repeating alternately the pressure and agitation, as long as any further absorption takes place.

A further amendment of the apparatus, would consist in the substitution of cocks of some other metal than brass, which, however perfect at first, are always injured by the repeated action of the mercury. If cocks of glass could be ground sufficiently tight, metal caps with screws might be cemented to them.

For observing the increased absorption of less condensable gases, I found it necessary to substitute a vessel of larger size than A, and of the capacity of at least 50 cubical inches. It is represented by the dotted lines in Fig. 1, and was furnished with a cock and screw at *c*. As it would have been troublesome to have filled so large a vessel entirely with quicksilver, it was filled with boiled water, with the exception of a quantity of quicksilver rather exceeding the bulk of the gas employed. The gas was admitted, as usual, from a transfer bottle, the mercury which it replaced escaping through the cock *b*. The increased pressure was next applied; and the experiment conducted as before, except that the agitation was much longer continued.

The results of a series of at least fifty experiments, on carbonic acid, sulphuretted hydrogen gas, nitrous oxide, oxygenous and azotic gases, with the above apparatus, establish the following general law: *that, under equal circumstances of temperature, water takes up, in all cases, the same volume of condensed gas as of gas under ordinary pressure.* But, as the spaces occupied

by every gas are inversely as the compressing force, it follows, that water takes up, of gas condensed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice, &c. the volume absorbed under the common pressure of the atmosphere. By frequent repetition of the experiments, I obtained results differing a little from the general principle above stated; but, for all practical purposes, I apprehend, the law has been announced with sufficient accuracy.\*

In place of the cock *a*, I cemented, in one experiment, a very sensible thermometer. The vessel was next filled with mercury through the cock *b*; and the tube B being also filled, the cock *b* was shut, and a bottle of carbonic acid gas screwed on. The cock *b* being then opened, the mercury descended, and a measured quantity of carbonic acid arose into the vessel A. In the same way, a measured quantity of water was introduced. When the density of the air was suddenly doubled by a column of quicksilver, the mercury in the thermometer, whose bulb was still surrounded by the condensed gas, rose about  $1\frac{1}{2}$  degree. On agitating the vessel, till the water encompassed the bulb of the thermometer, an elevation of barely  $\frac{1}{2}$  a degree ensued in the temperature of the water. This ascent would probably have been greater, if the evolved heat had not been carried off by the mercury on which the water floated.

Manchester,

Dec. 8th, 1802.

\* That the facts did not, with invariable accuracy, correspond to the law, was perhaps, in part, owing to the addition of only 28 inches of pressure; when, in strictness,  $29\frac{1}{2}$  should have been used, or twice the elevation of the mercury in the barometer, during each experiment.

