On the absorption of gases by water and other liquids

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ON THE

ABSORPTION

OF

GASES

BY

WATER AND OTHER LIQUIDS.

BY

JOHN DALTON.

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OXFORD

ABSORPTION

of
carbohydrates, water and other

liquids.

JOHN DALTON

1801.
ON THE

ABSORPTION

OF

GASES

BY

WATER AND OTHER LIQUIDS.

1. If a quantity of pure water be boiled rapidly for a short time in a vessel with a narrow aperture, or if it be subjected to the air-pump, the air exhausted from the receiver containing the water, and then be briskly agitated for some time, very nearly the whole of any gas the water may contain, will be extricated from it.

2. If a quantity of water thus freed from air be agitated in any kind of gas, not chemically uniting with water, it will absorb its bulk of the gas, or otherwise a part of it equal to some one of the following fractions, namely, $\frac{1}{3}$, $\frac{1}{7}$, $\frac{1}{23}$, $\frac{1}{23}$, &c. these being the cubes of the reciprocals of the natural numbers 1, 2, 3, &c. or $\frac{1}{1^3}$, $\frac{1}{2^3}$, $\frac{1}{3^3}$, $\frac{1}{4^3}$, &c. the same gas always being absorbed in the same proportion,
On the Absorption of Gases

as exhibited in the following table:—It must be understood that the quantity of gas is to be measured at the pressure and temperature with which the impregnation is effected.

<table>
<thead>
<tr>
<th>Bulk absorbed, the bulk of water being unity.</th>
<th>Carbonic acid gas, sulphurated hydrogen, nitrous oxide.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{4}{13} = 1 )</td>
<td></td>
</tr>
<tr>
<td>( \frac{1}{23} = \frac{1}{9} )</td>
<td>Olefiant gas, of the Dutch chemists.</td>
</tr>
<tr>
<td>( \frac{1}{33} = \frac{4}{7} )</td>
<td>Oxygenous gas, nitrous gas, carburetted hydrogen gas, from stagnant water.</td>
</tr>
<tr>
<td>( \frac{1}{43} = \frac{1}{64} )</td>
<td>Azotic gas, hydrogenous gas, carbonic oxide.</td>
</tr>
<tr>
<td>( \frac{4}{53} = \frac{1}{12} )</td>
<td>None discovered.</td>
</tr>
</tbody>
</table>

3. The gas thus absorbed may be recovered from the water the same in quantity and qua-

* According to Mr. William Henry's experiments, water does not imbibe quite its bulk of nitrous oxide; in one or two instances with me it has come very near it: The apparent deviation of this gas, may be owing to the difficulty of ascertaining the exact degree of its impurity.

† About \( \frac{1}{10} \) of nitrous gas is usually absorbed; and \( \frac{1}{7} \) is recoverable: This difference is owing to the residuum of oxygen in the water, each measure of which takes \( \frac{3}{4} \) of nitrous gas to saturate it, when in water. Perhaps it may be found that nitrous gas usually contains a small portion of nitrous oxide.
by Water and other Liquids.

lity as it entered, by the means pointed out in the 1st article.

4. If a quantity of water free from air be agitated with a mixture of two or more gases (such as atmospheric air) the water will absorb portions of each gas the same as if they were presented to it separately in their proper density.

Ex. gr. Atmospheric air, consisting of 79 parts azotic gas, and 21 parts oxygenous gas, per cent.

Water absorbs \( \frac{\frac{1}{64}}{\frac{79}{100}} \) of \( \frac{79}{100} \), azotic gas = 1.234

\[ \frac{\frac{1}{27}}{\frac{21}{100}} \] of \( \frac{21}{100} \), oxygen gas = .778

Sum, per cent. 2.012

5. If water impregnated with any one gas (as hydrogenous) be agitated with another gas equally absorbable (as azotic) there will apparently be no absorption of the latter gas; just as much gas being found after agitation as was introduced to the water; but upon examination the residuary gas will be found a mixture of the two, and the parts of each, in the water, will be exactly proportional to those out of the water.

6. If water impregnated with any one gas be agitated with another gas less or more absorbable; there will apparently be an increase
or diminution of the latter; but upon examination the residuary gas will be found a mixture of the two, and the proportions agreeable to article 4.

7. If a quantity of water in a phial having a ground stopper very accurately adapted, be agitated with any gas, or mixture of gases, till the due share has entered the water; then, if the stopper be secured, the phial may be exposed to any variation of temperature, without disturbing the equilibrium: That is, the quantity of gas in the water will remain the same whether it be exposed to heat or cold, if the stopper be air-tight.

N. B. The phial ought not to be near full of water, and the temperature should be between 32° and 212°.

8. If water be impregnated with one gas (as oxygenous), and another gas, having an affinity for the former (as nitrous), be agitated along with it; the absorption of the latter gas will be greater, by the quantity necessary to saturate the former, than it would have been if the water had been free from gas.

* One part of oxygenous gas requires \( \frac{3.4}{3} \) of nitrous gas to saturate it in water. It is agreeable to this that the rapid mixture of oxygenous and nitrous gas over a broad surface of water, occasions a greater diminution than otherwise. In fact, the nitrous acid is formed this way; whereas when
9. Most liquids free from viscosity, such as acids, alcohol, liquid sulphurets, and saline solutions in water, absorb the same quantity of gases as pure water; except they have an affinity for the gas, such as the sulphurets for oxygen, &c.

The preceding articles contain the principal facts necessary to establish the theory of absorption: Those that follow are of a subordinate nature, and partly deducible as corollaries to them.

10. Pure distilled water, rain and spring water usually contain nearly their due share of atmospheric air: if not, they quickly acquire that share by agitation in it, and lose any other gas they may be impregnated with. It is remarkable however that water by stagnation, in certain circumstances, loses part or all of its oxygen, notwithstanding its constant exposition to the atmosphere. This I have uniformly found to be the case in my large wooden pneumatic trough, containing about 8 gallons, or 1 1/2 cubic foot of water. Whenever this is replenished with tolerably pure rain water, it contains its share of atmospheric air; but in process of time it becomes deficient of oxygen: water is not present the nitric acid is formed which requires just half the quantity of nitrous gas, as I have lately ascertained.
In three months the whole surface has been covered with a pellicle, and no oxygenous gas whatever was found in the water. It was grown offensive, but not extremely so; it had not been contaminated with any material portion of metallic or sulphureous mixtures, or any other article to which the effect could be ascribed.* The quantity of azotic gas is not materially diminished by stagnation, if at all.—These circumstances, not being duly noticed, have been the source of great diversity in the results of different philosophers upon the quantity and quality of atmospheric air in water. By article 4, it appears that atmospheric air expelled from water ought to have 38 per cent. oxygen; whereas by this article air may be expelled from water that shall contain from 38 to 0 per cent. of oxygen.—The disappearance of oxygenous gas in water, I presume, must be owing to some impurities in the water which combine with the oxygen. Pure rain water that had stood more than a year in an earthenware bottle had lost none of its oxygen.

11. If water free from air be agitated with a small portion of atmospheric air (as of its bulk) the residuum of such air will have proportionally less oxygen than the original: If

* It was drawn from a leaden cistern.
we take \( \frac{1}{17} \), as above, then the residuum will have only 17 per cent. oxygen; agreeably to the principle established in article 4. This circumstance accounts for the observations made by Dr. Priestley, and Mr. William Henry, that water absorbs oxygen in preference to azot.

12. If a tall glass vessel, containing a small portion of gas be inverted into a deep trough of water and the gas thus confined by the glass and the water be briskly agitated, it will gradually disappear.

It is a wonder that Dr. Priestley, who seems to have been the first to notice this fact, should have made any difficulty of it;—the loss of gas has evidently a mechanical cause; the agitation divides the air into an infinite number of minute bubbles which may be seen pervading the whole water; these are successively driven out from under the margin of the glass into the trough, and so escape.

13. If old stagnant water be in the trough, in the last experiment, and atmospheric air be the subject, the oxygenous gas will very soon be almost wholly extracted and leave a residuum of azotic gas; but if the water be fully impregnated with atmospheric air at the beginning, the residuary gas examined at any time will be pure atmospheric air.
14. If any gas not containing either azotic or oxygenous gas, be agitated over water containing atmospheric air, the residuum will be found to contain both azotic and oxygenous gas.

15. Let a quantity of water contain equal portions of any two or more unequally absorbable gases: For instance, azotic gas, oxygenous gas and carbonic acid gas; then, let the water be boiled or subjected to the air-pump, and it will be found that unequal portions of the gases will be expelled. The azotic will be the greatest part, the oxygenous next, and the carbonic acid will be the least.—For, the previous impregnation being such as is due to atmospheres of the following relative forces nearly;

Azotic —— 21 inch. of mercury
Oxygenous — 9 ———
Carbonic acid \( \frac{1}{3} \) ———

consequently, when those forces are removed, the resiliency of the azotic gas will be the greatest, and that of the carbonic acid the least; the last will even be so small as not to overcome the cohesion of the water without violent agitation.
Remarks on the Authority of the preceding Facts.

In order to give the chain of facts as distinct as possible, I have not hitherto mentioned by whom or in what manner they were ascertained.

The fact mentioned in the first article has been long known; a doubt, however, remained respecting the quantity of air still left in water after ebullition and the operation of the air-pump. The subsequent articles will, I apprehend, have placed this in a clearer point of view.

In determining the quantity of gases absorbed, I had the result of Mr. William Henry's experience on the subject before me, an account of which has been published in the Philosophical Transactions for 1803. By the reciprocal communications since, we have been enabled to bring the results of our Experiments to a near agreement; as the quantities he has given in his appendix to that paper nearly accord with those I have stated in the second article. In my Experiments with the less absorbable gases, or those of the 2d, 3d, and 4th classes, I used a phial holding 2700 grains of water, having a very accurately
ground-stopper; in those with the more absorbable of the first class, I used an Eudiometer tube properly graduated and of aperture so as to be covered with the end of a finger. This was filled with the gas and a small portion expelled by introducing a solid body under water; the quantity being noticed by the quantity of water that entered on withdrawing the solid body, the finger was applied to the end and the water within agitated; then removing the finger for a moment under water, an additional quantity of water entered, and the agitation was repeated till no more water would enter, when the quantity and quality of the residuary gas was examined. In fact water could never be made to take its bulk of any gas by this procedure; but if it took \(\frac{9}{10}\), or any other part, and the residuary gas was \(\frac{9}{10}\) pure, then it was inferred that water would take its bulk of that gas. The principle was the same in using the phial; only a small quantity of the gas was admitted, and the agitation was longer.

There are two very important facts contained in the second article. The first is, that the quantity of gas absorbed is as the density or pressure.—This was discovered by Mr. Wm. Henry, before either he or I had formed any theory on the subject.
The other is, that the density of the gas in the water has a special relation to that out of the water, the distance of the particles within being always some multiple of that without:—Thus, in the case of carbonic acid, &c. the distance within and without is the same, or the gas within the water is of the same density as without; in olefiant gas the distance of the particles in the water is twice that without; in oxygenous gas, &c. the distance is just three times as great within as without; and in azotic, &c. it is four times. This fact was the result of my own enquiry. The former of these, I think, decides the effect to be mechanical; and the latter seems to point to the principle on which the equilibrium is adjusted.

The facts noticed in the 4th, 5th and 6th articles, were investigated à priori from the mechanical hypothesis, and the notion of the distinct agency of elastic fluids when mixed together. The results were found entirely to agree with both, or as nearly as could be expected from experiments of such nature.

The facts mentioned in the 7th article, are of great importance in a theoretic view; for, if the quantity of gas absorbed depend upon mechanical principles, it cannot be affected by temperature in confined air, as the mecha-
On the Absorption of Gases

nical effect of the external and internal air are alike increased by heat, and the density not at all affected in those circumstances. I have tried the experiments in a considerable variety of temperature without perceiving any deviation from the principle. It deserves further attention.

If water be, as pointed out by this essay, a mere receptacle of gases, it cannot affect their affinities: hence what is observed in the 8th article is too obvious to need explanation.—And if we find the absorption of gases to arise not from a chemical but a mechanical cause, it may be expected that all liquids having an equal fluidity with water, will absorb like portions of gas. In several liquids I have tried no perceptible difference has been found; but this deserves further investigation.

After what has been observed, it seems unnecessary to add any explanation of the 10th and following articles.

Theory of the Absorption of Gases by Water, &c.

From the facts developed in the preceding articles, the following theory of the absorption of gases by water seems deducible.
by Water and other Liquids.

1. All gases that enter into water and other liquids by means of pressure, and are wholly disengaged again by the removal of that pressure, are *mechanically* mixed with the liquid, and not *chemically* combined with it.

2. Gases so mixed with water, &c. retain their elasticity or repulsive power amongst their own particles, just the same in the water as out of it, the intervening water having no other influence in this respect than a mere vacuum.

3. Each gas is retained in water by the pressure of gas of its own kind incumbent on its surface abstractedly considered, no other gas with which it may be mixed having any permanent influence in this respect.

4. When water has absorbed its bulk of carbonic acid gas, &c. the gas does not press on the water at all, but presses on the containing vessel just as if no water were in.—When water has absorbed its proper quantity of oxygenous gas, &c. that is, \( \frac{1}{7} \) of its bulk, the exterior gas presses on the surface of the water with \( \frac{3}{7} \) of its force, and on the internal gas with \( \frac{4}{7} \) of its force, which force presses upon the containing vessel and not on the water. With azotic and hydrogenous gas the proportions are \( \frac{6}{7} \) and \( \frac{1}{7} \) respectively. When water contains no gas, its surface must support
the whole pressure of any gas admitted to it, till the gas has, in part, forced its way into the water.

5. A particle of gas pressing on the surface of water is analogous to a single shot pressing upon the summit of a square pile of them. As the shot distributes its pressure equally amongst all the individuals forming the lowest stratum of the pile, so the particle of gas distributes its pressure equally amongst every successive horizontal stratum of particles of water downwards till it reaches the sphere of influence of another particle of gas. For instance; let any gas press with a given force on the surface of water, and let the distance of the particles of gas from each other be to those of water as 10 to 1; then each particle of gas must divide its force equally amongst 100 particles of water, as follows:—It exerts its immediate force upon 4 particles of water; those 4 press upon 9, the 9 upon 16, and so on according to the order of square numbers, till 100 particles of water have the force distributed amongst them; and in the same stratum each square of 100, having its incumbent particle of gas, the water below this stratum is uniformly pressed by the gas, and consequently has not its equilibrium disturbed by that pressure.

When water has absorbed \( \frac{3}{7} \) of its bulk of
VIEW of a SQUARE PILE of SHOT &c.

The lower globes are to represent particles of water; the top globe represents a particle of air resting on 4 particles of water.
HORIZONTAL VIEW of AIR in WATER.

Incumbent stratum of Atmosphere, particles marked thus.

A Stratum of Air in the Water, particles marked thus.

Distance of particles 4 to 1

Air & Hydrogenous gas.

Distance of particles 3 to 1

Oxygenous, Nitrous & Carbonated Hydrogen gas.
PROFILE VIEW OF AIR IN WATER

Air

Surface

Water

Azotic & Hydrogenous gas

Density

Oxygenous, Nitrous, Carburetted

Hydrogen gas

Density
any gas, the stratum of gas on the surface of the water presses with \( \frac{3}{4} \) of its force on the water, in the manner pointed out in the last article, and with \( \frac{1}{7} \) of its force on the uppermost stratum of gas in the water: The distance of the two strata of gas must be nearly 27 times the distance of the particles in the incumbent atmosphere and 9 times the distance of the particles in the water. This comparatively great distance of the inner and outer atmosphere arises from the great repulsive power of the latter, on account of its superior density, or its presenting 9 particles of surface to the other 1. When \( \frac{1}{24} \) is absorbed the distance of the atmospheres becomes 64 times the distance of two particles in the outer, or 16 times that of the inner. The annexed views of perpendicular and horizontal strata of gas in and out of water, will sufficiently illustrate these positions.

7. An equilibrium between the outer and inner atmospheres can be established in no other circumstance than that of the distance of the particles of one atmosphere being the same or some multiple of that of the other; and it is probable the multiple cannot be more than 4. For in this case the distance of the inner and outer atmospheres is such as to make the perpendicular force of each particle of the former...
on those particles of the latter that are immediately subject to its influence, physically speaking, equal; and the same may be observed of the small lateral force.

8. The greatest difficulty attending the mechanical hypothesis, arises from different gases observing different laws. Why does water not admit its bulk of every kind of gas alike?—This question I have duly considered, and though I am not yet able to satisfy myself completely, I am nearly persuaded that the circumstance depends upon the weight and number of the ultimate particles of the several gases: Those whose particles are lightest and single being least absorbable and the others more according as they increase in weight and complexity.* An enquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new: I have lately been prosecuting this enquiry with remarkable success. The principle cannot be entered upon in this paper; but I shall just subjoin the results, as far as they appear to be ascertained by my experiments.

* Subsequent experience renders this conjecture less probable.


TABLE

of the relative weights of the ultimate particles of gaseous and other bodies.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1</td>
</tr>
<tr>
<td>Azot</td>
<td>4.2</td>
</tr>
<tr>
<td>Carbone</td>
<td>4.3</td>
</tr>
<tr>
<td>Ammonia</td>
<td>5.2</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5.5</td>
</tr>
<tr>
<td>Water</td>
<td>6.5</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>7.2</td>
</tr>
<tr>
<td>Phosphuretted hydrogen</td>
<td>8.2</td>
</tr>
<tr>
<td>Nitrous gas</td>
<td>9.3</td>
</tr>
<tr>
<td>Ether</td>
<td>9.6</td>
</tr>
<tr>
<td>Gaseous oxide of carbone</td>
<td>9.8</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>13.7</td>
</tr>
<tr>
<td>Sulphur</td>
<td>14.4</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>15.2</td>
</tr>
<tr>
<td>Sulphuretted hydrogen</td>
<td>15.4</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>15.8</td>
</tr>
<tr>
<td>Alcohol</td>
<td>15.1</td>
</tr>
<tr>
<td>Sulphurous acid</td>
<td>19.9</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>25.4</td>
</tr>
<tr>
<td>Carburetted hydrogen from stag. water</td>
<td>6.3</td>
</tr>
<tr>
<td>Olefiant gas</td>
<td>5.3</td>
</tr>
</tbody>
</table>