

As, Fe, Bi, Zn, Pd, Ir, and Rd,—and the tetragonal Sn, isomorphous to Bo, may, under certain circumstances, crystallize on the regular system, while Au, Ag, Cu, Pb, &c., and also Sn, may be rhombohedralic.—*Mining Journal*.

*On Boiling Water.* By W. GROVE, Esq., Q.C., F.R.S., M.R.I.

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A paper by M. Donny ("*Mémoires de l'Académie Royale de Bruxelles*," 1843,) makes known the fact that in proportion as water is deprived of air, the character of its ebullition changes, becoming more and more abrupt, and boiling like sulphuric acid with *soubresauts*, and that between each burst of vapor the water reaches a temperature above its boiling point. To effect this, it is necessary that the water be boiled in a tube with a narrow orifice, through which the vapor issues; if it be boiled in an open vessel it continually re-absorbs air and boils in the ordinary way.

In my experiments on the decomposition of water by heat, I found that with the oxyhydrogen gas given off from ignited platinum plunged into water, there was always a greater or less quantity of nitrogen mixed; this I could never entirely get rid of, and was thus led into a more careful examination of the phenomenon of boiling water, and set before myself this problem—what will be the effect of heat on water, perfectly deprived of air or gas?

Two copper wires were placed parallel to each other through the neck of a Florence cask, so as nearly to touch the bottom; joining the lower ends of these was a fine platinum wire, about an inch and a-half long, and bent horizontally into a curve. Distilled water, which had been well boiled and cooled under the receiver of an air-pump, was poured into this flask so as to fill about one-fourth of its capacity. It was then placed under the receiver of an air pump, and one of the copper wires brought in contact with a metallic plate covering the receiver, the other bent backwards over the neck of the flask and its end made to rest on the pump-plate. By this means, when the terminal wires from a voltaic battery were made to touch the one, the upper and the other lower plate, the platinum wire would be heated, and the boiling continued indefinitely in the vacuum of a very excellent air-pump. The effect was very curious: the water did not boil in the ordinary manner, but at intervals a burst of vapor took place, dashing the water against the sides of the flask, some escaping into the receiver. (There was a projection at the central orifice of the pump-plate to prevent this overflow getting into the exhaustion tube.)

After each sudden burst of vapor, the water became perfectly tranquil, without a symptom of ebullition until the next burst took place. These sudden bursts occurred at measured intervals, so nearly equal in time that, had it not been for the escape from the flask at each burst of a certain portion of water, the apparatus might have served as a time-piece.

This experiment, though instructive, did not definitely answer the

question I had proposed, as I could not, of course, ascertain whether there was some minute residuum of gas which would form the nucleus of each ebullition; and I proceeded with others. A tube of glass, 5 ft. long and  $\frac{4}{10}$ ths inch internal diameter, was bent into a V-shape; into one end a loop of platinum wire was hermetically sealed with great care, and the portion of it in the interior of the tube was platinized. When the tube had been washed, distilled water which had been well purged of air as before, was poured into it to the depth of 8 inches, and the rest of the tube filled with olive oil; when the V was inverted, the open end of the tube was placed in a vessel of olive oil, so that there would be 8 inches of water resting on the platinum wire, separated from the external air by a column of 4 ft. 4 ins. of oil. The projecting extremities of the platinum wire were now connected with the terminals of a voltaic battery, and the water heated; some air was freed and ascended to the level of the tube—this was made to escape by carefully inverting the tube so as not to let the oil mix with the water—and the experiment continued. After a certain time the boiling assumed a uniform character, not by such sudden bursts as in the Florence flask experiment, but with larger and more distinct bursts of ebullition than in its first boiling.

The object of platinizing the wire was to present more points for the ebullition, and to prevent *soubresauts* as much as possible.

The experiment was continued for many hours, and in some repetitions of it for days. After the boiling had assumed a uniform character, the progress of the vapor was carefully watched, and as each burst of vapor condensed in the oil, which was kept cool, it left a minute bead of gas, ascended through the oil to the bend of the tube: a bubble was formed here which did not seem at all absorbed by the oil. This was analyzed by a eudiometer, which I will presently describe, and proved to be nitrogen. The beads of gas, when viewed through a lens and micrometer scale at the same height in the tube, appeared as nearly as may be of the same size. No bubble of vapor was condensed completely, or without leaving this residual bubble. The experiment was frequently repeated, and continued until the water was so nearly boiled away that the oil, when disturbed by the boiling, nearly touched the platinum wire; here it was necessarily stopped.

To avoid any question about the boiling being by electrical means, similar experiments were made with a tube, without a platinum wire, closed at its extremity, and the boiling was produced by a spirit lamp. The effects were the same, but the experiment was more difficult and imperfect, as the bursts of vapor were more sudden, and the duration of the intervals more irregular.

The beads of gas were extremely minute, just visible to the naked eye, but were made visible to the audience by means of the electric lamp.

In these experiments there was no pure boiling of water—i.e., no rupture of cohesion of the molecules of water itself, but the water was boiled, to use M. Donny's expression, by evaporation against a surface of gas.

It is hardly conceivable that air could penetrate through such a column of oil, the more so as the oil did not perceptibly absorb the nitrogen freed by the boiling water and resting in the bend of the tube; but to meet this conjectural difficulty, the following experiment was made:—A tube, 1 foot long and  $\frac{1}{10}$ ths inch internal diameter, bent into a slight angle, had a bulb  $\frac{3}{4}$ -inch diameter blown on it at the angle; this angle was about 3 inches from one end and 9 from the other; a loop of platinum wire was sealed into the shorter leg and the whole tube and bulb filled with and immersed into mercury, water distilled, and purged of air as before was allowed to fill the short leg, and by carefully adjusting the inclination, the water could be boiled so as to allow bubbles to ascend into the bulb and displace the mercury. The effect was the same as with the oil experiment,—no ebullition, without leaving a bead of gas; the gas collected in the bulb, and was cut off by what may be termed a valve of mercury, from the boiling water, then allowed to escape, and so on; the experiment was continued for many days and the bubbles analyzed from time to time; they proved, as before, to be nitrogen; and, as before, continued indefinitely.

A similar experiment was made without the platinum wire, and though, from the greater difficulties, the experiment was not so satisfactory, the result was the same.

As the mercury of the common barometer will keep air out of its vacuum for years, if not for centuries, there could be no absorption here from the external atmosphere, and I think I am fairly entitled to conclude from the above experiments—which I believe went far beyond any that have been recorded—that no one has yet seen the phenomenon of pure water boiling—*i.e.*, of the disruption of the liquid particles of the oxyhydrogen compound so as to produce vapor which will, when condensed, become water, leaving no permanent gas. Possibly, in my experiment of the decomposition of water by ignited platinum, it may be that the sudden application of intense heat, and in some quantity, so forces asunder the molecules, that not having sufficient nitrogen dissolved to supply them with a nucleus for evaporation, the integral molecules are severed, and the decomposition takes place. If this be so, and it seems to me by no means a far-fetched theory, there is probably no such thing as boiling, properly so called, and the effect of heat on liquid in which there is no dissolved gas may be to decompose them.

Considerations such as these led me to try the effect of boiling on an elementary liquid, and bromine occurred as the most promising one to work upon; as bromine could not be boiled in contact with water, oil, or mercury, the following plan was ultimately devised:—A tube, 4 feet long and  $\frac{1}{10}$ ths inch diameter, had a platinum loop sealed into one closed extremity; bromine was poured into the tube to the height of 4 inches; the open end of the tube was then drawn out to a fine point by the blow-pipe, leaving a small orifice; the bromine was then heated by a spirit-lamp and when all the air was expelled, and a jet of bromine vapor issued from the point of the tube, it was sealed by the blow-pipe. There was then, when the bromine vapor had condensed

a vacuum in the tube above the bromine. The platinum loop was now heated by a voltaic battery, and the bromine boiled: this was continued for some time, care being taken that the boiling should not be too violent. At the end of a certain period—from half-an-hour to an hour—the platinum loop gave way, being corroded by the bromine; the quantity of this had slightly decreased. On breaking off, under water, the point of the tube, the water mounted, and showed a notable quantity of permanent gas, which on analysis proved to be pure oxygen. As much as a quarter of a cubic inch was collected at one experiment. The platinum wire which had severed at the middle, was covered with a slight black crust, which, suspecting to be carbon, I ignited by a voltaic spark in oxygen in a small tube over lime-water; it seemed to give a slight opalescence to the liquid, but the quantity was so small that the experiment was not relied on. No definite change was perceptible in the bromine; it seemed to be a little darker in color and had a few black specks floating in it, which I judged to be minute portions of the same crust which had formed on the platinum wire, and which had become detached.

The experiment was repeated with chloride of iodine, and with the same result, except that the quantity of oxygen was greater: I collected as much as half a cubic inch in some experiments, from an equal quantity of chloride of iodine; the platinum wire, however, was more quickly acted on than with bromine, and the glass of the tube around it to some extent.

Melted phosphorus was exposed to the heat of the voltaic disruptive discharge by taking this between platinum points in a tube of phosphorus, similarly to an experiment of Davy's, but with better means of experimenting; a considerable quantity of phosphuretted hydrogen was given off, amounting in several experiments to more than a cubic inch.

A similar experiment was made with melted sulphur, and sulphuretted hydrogen was given off, but not in such quantities as the phosphuretted hydrogen. I tried in vain to carry on these experiments beyond a certain point; the substance became pasty, mixed with platinum from the arc, and from the difficulty of working with the same freedom as when they were fresh, the glass tubes were always broken after a certain time. Had I time for working on the subject now, I should use the discharge from the Ruhmkorf coil which had not been invented at the period of these experiments. At a subsequent period when this discharge was taken in the vacuum receiver of an air-pump from a metallic point to a metallic capsule containing phosphorus, a considerable yellow deposit lined the receiver, which, on testing, turned out to be allotropic phosphorus. No gas is however given off. I had an air-pump (described "*Phil. Trans.*," 1852, p. 101) which enabled me to detect very small quantities of gas, but I could get none. It was in making these experiments that I first detected the striæ in the electric discharge, which have since become a subject of such interesting observations, which are seen, perhaps, more beautifully in this phosphorus vapor than in any other medium, and which cease or become very feeble, where the allotropic phosphorus is not produced.

I tried also phosphorus highly heated by a burning-glass in an atmosphere of nitrogen, but could eliminate no perceptible quantity of gas, though the phosphorus was changed into the allotropic form.

It is not difficult to understand why gas is not perceptibly eliminated in the last two experiments; the effect is probably similar to that described in my paper on the "*Decomposition of Water by Heat*," where when the arc or electric spark is taken in aqueous vapor, a minute bubble of oxyhydrogen gas is freed and disseminated through the vapor, re-combination being probably prevented by this dilution; but, however long the experiment may be continued, no increased quantity of the gas is obtained, all beyond this minute quantity being re-combined. If, however, the bubble of gas be collected, by allowing the vapor to cool, and then expelled, a fresh portion is decomposed, and so on.

So with the phosphorus in the experiments in the air-pump and with the burning-glass; if any gas is liberated it is probably immediately re-combined with the phosphorus; possibly a minute residuum might escape re-combination, but the circumstances of the experiment did not admit of this being collected, as the gas was with the aqueous vapor.

When, on the other hand, the gas freed is immediately cut off from the source of heat, as when the spark is taken in liquids, an indefinite quantity can be obtained.

Decomposition and the elimination of gas may thus take place by the application of intense heat to a point in a liquid, or also in gas or vapors; but in the latter case it is more likely to be masked by the quantity of gas or vapor through which it is disseminated.

I believe there are very few gases in which some alteration does not take place by the application of the intense heat of the voltaic arc or electric spark. If the arc be taken between the platinum points in dry oxygen gas over mercury, the gas diminishes indefinitely, until the mercury rises, and by reaching the point where the arc takes place, puts an end to the experiment. I have caused as much as a cubic inch of oxygen to disappear by this means. I at one time thought this was due to the oxidation of the platinum; but the high heat renders this improbable, and the deposit formed on the interior of the glass tube in which the experiment is made has all the properties of platinum-black; so if the spark from a Ruhmkorf coil be taken in the vapor of water for several days, a portion of gas is freed which is pure hydrogen, the oxygen freed being probably changed into ozone, and dissolved by the water in this case, while in the former it combined with the mercury.

I have alluded to the eudiometer by which I analyzed the gases obtained in these experiments; it was formed simply of a tube of glass, frequently not above  $2\frac{1}{2}$  millimetres in diameter, with a loop of wire hermetically sealed into one end, the other having an open bell mouth. By a platinum wire a small bubble of the gas to be examined could be got up through water or mercury into the closed end of the tube, and by the addition of a bubble of oxygen or hydrogen gas, a very accurate analysis of very minute quantities of gas could be made: I have analyzed by this means quantities no larger than a partridge-shot.

I need hardly allude to results on the compound liquids, such as oils

and hydrocarbons, as the fact that permanent gas is given off in boiling such liquids would not be unexpected; but the above experiments seem to show that boiling is by no means necessarily the phenomenon that has generally been supposed, viz: a separation of cohesion in the molecules of a liquid from distention by heat. I believe, from the close investigation I made into the subject, that (except with the metals, on which there is no evidence) no one has seen the phenomenon of pure boiling without permanent gas being freed, and that what is ordinarily termed boiling arises from the extrication of a bubble of permanent gas either by chemical decomposition of the liquid, or by the separation of some gas associated in minute quantity with the liquid, and from which human means have hitherto failed to purge it; this bubble once extricated, the vapor of the liquid expands it, or, to use the appropriate phrase of M. Donny, the liquid evaporates against the surface of the gas.

My experiments are, in a certain sense, the complement of his. He showed that the temperature of the boiling point was raised in some proportion as water was deprived of air and that under such circumstances the boiling took place by *soubresauts*. I have, I trust, shown that when the vapor liberated by boiling is allowed to condense, it does not altogether collapse into a liquid, but leaves a residual bubble of permanent gas, and that at a certain point this evolution becomes uniform.

Boiling, then, is not the result of merely raising a liquid to a given temperature; it is something much more complex.

One might suppose that with a compound liquid the initial bubble by which evaporation is enabled to take place, might, if all foreign gas were or could be extracted, be formed by decomposition of the liquid: but this could not be the case with an elementary liquid; whence, the oxygen from bromine or the hydrogen from phosphorus and sulphur?

As with the nitrogen in water, it may be that a minute portion of oxygen, hydrogen, or of water, is inseparable from these substances, and that if boiled away to absolute dryness, a minute portion of gas would be left for each ebullition.

With water there seems a point at which the temperature of ebullition and the quantity of nitrogen yielded become uniform, though the latter is excessively minute.

The circumstances of the experiments with bromine, phosphorus, and sulphur did not permit me to push the experiment so far as was done with water; but as far as it went the result was similar.

When an intense heat, such as that from the electric spark or voltaic arc is applied to permanent gas, there are, in the greater number of cases, signs either of chemical decomposition or of molecular change; thus compound gases, such as hydrocarbons, ammonia, the oxides of nitrogen, and many others are decomposed. Phosphorus in vapor is changed to allotropic phosphorus, oxygen to ozone, which, according to present experience, may be viewed as allotropic oxygen. There may be many cases where, as with aqueous vapor, a small portion only is decomposed, and this may be so masked by the volume of undecomposed gas as to escape detection. If, for instance, the vapor of water were uncondensable, the fact that a portion of it is decom-

posed by the electric spark or ignited platinum would not have been observed.

All these facts show that the effect of intense heat applied to liquids and gases is much less simple, and presents greater interest to the chemist, than has generally been supposed. In far the greater number of cases, possibly in all, it is not mere expansion into vapor which is produced by intense heat, but there is a chemical or molecular change. Had circumstances permitted, I should have carried these experiments further, and endeavored to find *experimentum crucis* on the subject. There are difficulties with such substances as bromine, phosphorus, &c., arising from their action on the substances used to contain and heat them, which are not easy to vanquish, and those who may feel inclined to repeat my experiments will find these difficulties greater than they appear in narration; but I do not think they are insuperable, and hope that, in the hands of those who are fortunate enough to have time at their disposal, they may be overcome.

To completely isolate a substance from the surrounding air, and yet be able to experiment on it, is far more difficult than is generally supposed. The air-pump is but a rude mode for such experiments as are here detailed.

Caoutchouc joints are out of the question. Even platinum wires carefully sealed into glass, though, as far as I have been able to observe, forming a joint which will not allow gas to pass, yet it is one through which liquids will effect a passage, at all events, when the wires are repeatedly heated.

In some experiments with the ignited platinum wire hermetically sealed into a tube of glass, the end of the tube containing the platinum wire was placed in a larger tube of oil, to lessen the risk of cracking the glass. After some days experimenting, though the sealing remained perfect, a slight portion of carbon was found in the interior liquid. This does not affect the result of my experiments, as I repeated them with glass tubes closed at the end and platinum wires, and also without the oil-bath: but it shows how difficult it is to exclude sources of error. When water has been deprived of air to the greatest practicable extent it becomes very avid for air. The following experiment is an instance of this:—A single pair of the gas battery, the liquid in which was cut off from the external air by a greased glass stopper, having one tube filled with water, the other with hydrogen; the platinized platinum plates in each of these tubes were connected with a galvanometer, and a deflection took place from the reaction of the hydrogen on the air dissolved in the water. After a time the deflection abated, and the needle returned to zero, all the oxygen of the air having become combined with the hydrogen. If now the stopper were taken out, a deflection of the galvanometric needle immediately took place, showing that the air rapidly enters the water as water would a sponge. Absolute chemical purity in the ingredients is a matter, for refined experiments, almost unattainable. The more delicate the test, the more some minute residual product is detected. It would seem (to put the proposition in a somewhat exaggerated form)

that in nature everything is to be found in anything if we carefully look for it.

I have indicated the above sources of error to show the close pursuit that is necessary when looking for these minute residual phenomena. Enough has, I trust, been shown in the above experiments to lead to the conclusion that hitherto simple boiling, in the sense of a liquid being expanded by heat into its vapor, without being decomposed or having permanent gas eliminated from it, is a thing unknown. Whether such boiling *can* take place may be regarded as an open question though I incline to think it cannot; that if water, for instance, could be absolutely deprived of nitrogen, it would not boil until some portion of it was decomposed; that the physical severance of the molecules by heat is also a chemical severance. If there be anything in this theoretic view, there is great promise of important results on elementary liquids, if the difficulties to which I have alluded can be got over.

The constant appearance of nitrogen in water, when boiled off out of contact with the air almost to the last drop, is a matter well worthy of investigation. I will not speculate on what possible chemical connexion there may be between air and water. The preponderance of these two substances on the surface of our planet, and the probability that nitrogen is not the inert diluent in respiration that is generally supposed, might give rise to not irrational conjectures on some unknown bond between air and water. But it would be rash to announce any theory on such a subject; better to test any guess one may make by experiment than to mislead by theory without sufficient data, or to lessen the value of facts by connecting them with erroneous hypotheses.

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*Preservation of Meat.*

From the Journal of the Society of Arts, No. 590.

The preservation of meat, whether for the use of our sailors on board ship, or for other purposes, has long engaged the attention of scientific and practical men, and various ways of affecting this object have been from time to time devised. The methods hitherto adopted on a large scale have been the packing of cooked meat in air-tight cases, or impregnating it with salt, and keeping it in barrels immersed in brine. The first, though effectual for preserving the meat for almost any amount of time, leaves the flesh, even when the utmost care is taken in the process, more or less insipid and tasteless; the second, though also preservative for a considerable time, renders the meat not only flavorless, but absolutely extracts from it, as Liebig tells us, nearly all its nutritive properties, as well as those peculiar qualities which are necessary for keeping the body in health. It is well-known that a long continuance of such food, thus prepared, engenders scurvy. The Admiralty are now making experiments with a process devised by Dr. Morgan, an Irish gentleman; and a few weeks since some animals were slaughtered, and their carcasses subjected to this process in the presence of officers of her Majesty's Victualling Department at Deptford. A bullock having been killed in the usual way, the chest was immediately