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VI. On the Liquefaction and Solidification of Bodies generally existing as Gases. By Michael Faraday, Esq., D.C.L. F.R.S., Fullerian Prof. Chem. Royal Institution, Foreign Associate of the Acad. Sciences, Paris, Corr. Memb. Royal and Imp. Acadd. of.Sciences, Petersburgh, Florence, Copenhagen, Berlin, Göttingen, Modena, Stockholm, \&c. \&c.

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THE experiments formerly made on the liquefaction of gases*, and the results which from time to time have been added to this branch of knowledge, especially by M. Thilorier $\downarrow$, have left a constant desire on my mind to renew the investigation. This, with considerations arising out of the apparent simplicity and unity of the molecular constitution of all bodies when in the gaseous or vaporous state, which may be expected, according to the indications given by the experiments of M. Cagniard de la Tour, to pass by some simple law into their liquid state, and also the hope of seeing nitrogen, oxygen, and hydrogen, either as liquid or solid bodies, and the latter probably as a metal, have lately induced me to make many experiments on the subject; and though my success has not been equal to my desire, still I hope some of the results obtained, and the ineans of obtaining them, may have an interest for the Royal Society; more especially as the application of the latter may be carried much further than I as yet have had opportunity of applying them. My object, like that of some others, was to subject the gases to considerable pressure with considerable depression of temperature. To obtain the pressure, I used mechanical force, applied by two air-pumps fixed to a table. The first pump had a piston of an inch in diameter, and the second a piston of only half an inch in diameter ; and these were so associated by a connecting pipe, that the first pump forced the gas into and through the valves of the second, and then the second could be employed to throw forward this gas, already condensed to ten, fifteen, or twenty atmospheres, into its final recipient at a much higher pressure.

The gases to be experimented with were either prepared and retained in gas holders or gas jars, or else, when the pumps were dispensed with, were evolved in strong glass vessels, and sent under pressure into the condensing tubes. When the gases were over water, or likely to contain water, they passed, in their way from the air-holder to the pump, through a coil of thin glass tube retained in a vessel filled with a good mixture of ice and salt, and therefore at the temperature of $0^{\circ}$ Fahr.; the water that was condensed here was all deposited in the first two inches of the coil.

[^0]The condensing tubes were of green bottle glass, being from $\frac{1}{6}$ th to $\frac{1}{4}$ th of an inch external diameter, and from $\frac{1}{42} \mathrm{~d}$ to $\frac{1}{30}$ th of an inch in thickness. They were chiefly of two kinds, about eleven and nine inches in length; the one, when horizontal, having a curve downward near one end to dip into a cold bath, and the other, being in form like an inverted siphon, could have the bend cooled also in the same manner when necessary. Into the straight part of the horizontal tube, and the longest leg of the siphon tube, pressure gauges were introduced when required.

Fig. 1.


Fig. 2.


Caps, stop-cocks and connecting pieces were employed to attach the glass tubes to the pumps, and these, being of brass, were of the usual character of those employed for operations with gas, except that they were small and carefully made. The caps were of such size that the ends of the glass tubes entered freely into them, and had rings or a female screw worm cut in the interior, against which the cement was to adhere. The ends of the glass tubes were roughened by a file, and when a cap was to be fastened on, both it and the end of the tube were made so warm that the cement*, when applied, was thoroughly melted in contact with these parts, before the tube and cap were brought together and finally adjusted to each other. These junctions bore a pressure of thirty, forty, and fifty atmospheres, with only one failure, in above one hundred instances; and that produced no complete separation of parts, but simply a small leak.

The caps, stop-cocks, and connectors, screwed one into the other, having one common screw thread, so as to be combined in any necessary manner. There were also screw plugs, some solid, with a male screw to close the openings or ends of caps, \&c., others with a female screw to cover and close the ends of stop-cocks. All these screw joints were made tight by leaden washers; and by having these of different thickness, equal to from $\frac{4}{8}$ th to $\frac{12}{8}$ th of the distance between one turn of the screw thread and the next, it was easy at once to select the washer which should allow a sufficient compression in screwing up to make all air-tight, and also bring every part of the apparatus into its right position.

[^1]I have often put a pressure of fifty atmospheres into these tubes, and have had no accident or failure (except the one mentioned). With the assistance of Mr . Addams I have tried their strength by a hydrostatic press, and obtained the following results:-A tube having an external diameter of 0.24 of an inch and a thickness of 0.0175 of an inch, burst with a pressure of sixty-seven atmospheres, reckoning one atmosphere as 15 lb . on the square inch. A tube which had been used, of the shape of fig. 1 , its external diameter being 0.225 of an inch, and its thickness about 0.03 of an inch, sustained a pressure of 118 atmospheres without breaking, or any failure of the caps or cement, and was then removed for further use.

A tube such as I have employed for generating gases under pressure, having an external diameter of 0.6 of an inch, and a thickness of 0.035 of an inch, burst at twenty-five atmospheres.

Having these data, it was easy to select tubes abundantly sufficient in strength to sustain any force which was likely to be exerted within them in any given experiment.

The gauge used to estimate the degree of pressure to which the gas within the condensing tube was subjected was of the same kind as those formerly described*, being a small tube of glass closed at one end with a cylinder of mercury moving in it. So the expression of ten or twenty atmospheres, means a force which is able to compress a given portion of air into $\frac{1}{10}$ th or $\frac{1}{20}$ th of its bulk at the pressure of one atmosphere of thirty inches of mercury. These gauges had their graduation marked on them with a black varnish, and also with Indian ink :-there are several of the gases which, when condensed, cause the varnish to liquefy, but then the Indian ink stood. For further precaution, an exact copy of the gauge was taken on paper, to be applied on the outside of the condensing tube. In most cases, when the experiment was over, the pressure was removed from the interior of the apparatus, to ascertain whether the mercury in the gauge would return back to its first or starting-place.

For the application of cold to these tubes a bath of Thilorier's mixture of solid carbonic acid and ether was used. An earthenware dish of the capacity of four cubic inches or more was fitted into a similar dish somewhat larger, with three or four folds of dry flannel intervening, and then the bath mixture was made in the inner dish. Such a bath will easily continue for twenty or thirty minutes, retaining solid carbonic acid the whole time ; and the glass tubes used would sustain sudden immersion in it without breaking.

But as my hopes of any success beyond that heretofore obtained depended more upon depression of temperature than on the pressure which I could employ in these tubes, I endeavoured to obtain a still greater degree of cold. There are, in fact, some results producible by cold which no pressure may be able to effect. 'Thus, solidification has not as yet been conferred on a fluid by any degree of pressure. Again, that beautiful condition which Cagniard de la Tour has made known, and

[^2]which comes on with liquids at a certain heat, may have its point of temperature for some of the bodies to be experimented with, as oxygen, hydrogen, nitrogen, \&c., below that belonging to the bath of carbonic acid and ether; and, in that case, no pressure which any apparatus could bear would be able to bring them into the liquid or solid state.

To procure this lower degree of cold, the bath of carbonic acid and ether was put into an air-pump, and the air and gaseous carbonic acid rapidly remored. In this way the temperature fell so low, that the vapour of carbonic acid given off by the bath, instead of having a pressure of one atmosphere, had only a pressure of $\frac{1}{24}$ th of an atmosphere, or $1 \cdot 2$ inch of mercury; for the air-pump barometer could be kept at $28 \cdot 2$ inches when the ordinary barometer was at $29 \cdot 4$. At this low temperature the carbonic acid mixed with the ether was not more volatile than water at the temperature of $86^{\circ}$, or alcohol at ordinary temperatures.

In order to obtain some idea of this temperature, I had an alcohol thermometer made, of which the graduation was carried below $32^{\circ} \mathbb{F}_{\text {AHr. }}$, by degrees equal in capacity to those between $32^{\circ}$ and $212^{\circ}$. When this thermometer was put into the bath of carbonic acid and ether surrounded by the air, but covered over with paper, it gave the temperature of $106^{\circ}$ below $0^{\circ}$. When it was introduced into the bath under the air-pump, it sank to the temperature of $166^{\circ}$ below $0^{\circ}$; or $60^{\circ}$ below the temperature of the same bath at the pressure of one atmosphere, i.e. in the air. In this state the ether was very fluid, and the bath could be kept in good order for a quarter of an hour at a time.

As the exhaustion proceeded I observed the temperature of the bath and the corresponding pressure, at certain other points, of which the following may be recorded:The external barometer was 29.4 inches:
inch. Fahr. when the mercury in the air-pump barometer was 1 the bath temperature was- 106 ,

but as the thermometer takes some time to acquire the temperature of the bath, and the latter was continually falling in degree; as also the alcohol thickens considerably at the lower temperature, there is no doubt that the degrees expressed are not so low as they ought to be, perhaps even by $5^{\circ}$ or $6^{\circ}$ in most cases.

With dry carbonic acid under the air-pump receiver I could raise the pump barometer to twenty-nine inches when the external barometer was at thirty inches.

The arrangement by which this cooling power was combined in its effect on gases with the pressure of the pumps, was very simple in principle. An air-pump receiver open at the top was employed; the brass plate which closed the aperture had a small brass tube about six inches long, passing through it air-tight by means of a stuffingbox, so as to move easily up and down in a vertical direction. One of the glass condensing siphon tubes, already described, fig. l, was screwed on to the lower end of the sliding tube, and the upper end of the latter was connected with a communicating tube in two lengths, reaching from it to the condensing pumps; this tube was small, of brass, and $9 \frac{1}{2}$ feet in length; it passed six inches horizontally from the condensing pumps, then rose vertically for two feet, afterwards proceeded horizontally for seven feet, and finally turned down and was immediately connected with the sliding tube. By this means the latter could be raised and lowered vertically, without any strain upon the connexions, and the condensing tube lowered into the cold bath in vacuo, or raised to have its contents examined at pleasure. The capacity of the connecting tubes beyond the last condensing pump was only two cubic inches.

When experimenting with any particular gas, the apparatus was put together fast and tight, except the solid terminal screw-plug at the short end of the condensing tube, which being the very extremity of the apparatus, was left a little loose. Then, by the condensing pumps, abundance of gas was passed through the apparatus to sweep out every portion of air, after which the terminal plug was screwed up, the cold bath arranged, and the combined effects of cold and pressure brought to unite upon the gas.

There are many gases which condense at less than the pressure of one atmosphere when submitted to the cold of a carbonic acid bath in air (which latter can upon occasions be brought considerably below - $106^{\circ}$ Fahr.). These it was easy, therefore, to reduce, by sending them through small conducting tubes into tubular receivers placed in the cold bath. When the receivers had previously been softened in a spirit lamp flame, and narrow necks formed on them, it was not difficult by a little further management, hermetically to seal up these substances in their condensed state. In this manner chlorine, cyanogen, ammonia, sulphuretted hydrogen, arseniuretted hydrogen, hydriodic acid, hydrobromic acid, and even carbonic acid, were obtained, sealed up in tubes in the liquid state; and euchlorine was also secured in a tube receiver with a cap and screw-plug. By using a carbonic acid bath, first cooled in vacuo, there is no doubt other condensed gases could be secured in the same way.

The fluid carbonic acid was supplied to me by Mr. Addams, in his perfect apparatus, in portions of about 220 cubic inches each. The solid carbonic acid, when produced from it, was preserved in a glass; itself retained in the middle of three concentric glass jars, separated from each other by dry jackets of woollen cloth. So effectual was this arrangement, that $I$ have frequently worked for a whole day of twelve and fourteen hours, having solid carbonic acid in the reservoir, and enough for all
the baths I required during the whole time, produced by one supply of 220 cubic inches*.

By the apparatus, and in the manner, now described, all the gases before condensed were very easily reduced, and some new results were obtained. When a gas was liquefied, it was easy to close the stop-cock, and then remove the condensing tube with the fluid from the rest of the apparatus. But in order to preserve the liquid from escaping as gas, a further precaution was necessary; namely, to cover over the exposed end of the stop-cock by a blank female screw-cap and leaden washer, and also to tighten perfectly the screw of the stop-cock plug. With these precautions I have kept carbonic acid, nitrous oxide, fluosilicon, \&c. for several days.

Even with gases which could be condensed by the carbonic acid bath in air, this apparatus in the air-pump had, in one respect, the advantage; for when the condensing tube was lifted out of the bath into the air, it inmediately became covered with hoar frost, obscuring the view of that which was within ; but in vacuo this was not the case, and the contents of the tube could be very well examined by the eye.

Olefiant gas.-This gas condensed into a clear, colourless, transparent fluid, but did not become solid even in the carbonic acid bath in vacuo; whether this was because the temperature was not low enough, or for other reasons referred to in the account of euchlorine, is uncertain.

The pressure of the vapour of this substance at the temperature of the carbonic acid bath in air ( $-103^{\circ} F_{\text {Ahr. }}$ ) appeared singularly uncertain, being on different occasions, and with different specimens, $3 \cdot 7,8 \cdot 7,5$ and 6 atmospheres. The Table below shows the tension of vapour for certain degrees below $0^{\circ}$ Fahr., with two different specimens obtained at different times, and it will illustrate this point.


[^3]I have not yet resolved this irregularity, but believe there are two or more substances, physically, and perhaps occasionally chemically different, in olefiant gas; and varying in proportion with the circumstances of heat, proportions of ingredients, \&c. attending the preparation.

The fluid affected the resin of the gauge graduation, and probably also the resin of the cap cement, though slowly.

Hydriodic acid.-This substance was prepared from the iodide of phosphorus by heating it with a very little water. It is easily condensable by the temperature of a carbonic acid bath : it was redistilled, and thus obtained perfectly pure.

The acid may be obtained either in the solid or liquid, or (of course) in the gaseous state. As a solid it is perfectly clear, transparent, and colourless; having fissures or cracks in it resembling those that run through ice. Its solidifying temperature is nearly $-60^{\circ}$ Fahr., and then its vapour has not the pressure of one atmosphere; at a point a little higher it becomes a clear liquid, and this point is close upon that which corresponds to a vaporous pressure of one atmosphere. The acid dissolves the cap cement and the bitumen of the gauge graduation ; and appears also to dissolve and act on fat, for it leaked by the plug of the stop-cock with remarkable facility. It acts on the brass of the apparatus, and also on the mercury in the gauge. Hence the following results as to pressures and temperatures are not to be considered more than approximations:-

At $0^{\circ}$ Fahr. pressure was $2 \cdot 9$ atmospheres.
At $32^{\circ}$ Fahr. pressure was 3.97 atmospheres.
At $60^{\circ}$ Fahr. pressure was $5 \cdot 86$ atmospheres.
Hydrobromic acid.-This acid was prepared by adding to perbromide of phosphorus* about one-third of its bulk of water in a proper distillatory apparatus formed of glass tube, and then applying heat to distil off the gaseous acid. This being sent into a very cold receiver, was condensed into a liquid, which being rectified by a second distillation, was then experimented with.

Hydrobromic acid condenses into a clear colourless liquid at $100^{\circ}$ below $0^{\circ}$, or lower, and has not the pressure of one atmosphere at the temperature of the carbonic acid bath in air. It soon obstructs and renders the motion of the mercury in the airgauge irregular, so that I did not obtain a measure of its elastic force; but it is less than that of muriatic acid. At and below the temperature of $-124^{\circ} \mathrm{FAHR}^{2}$, it is a ments of ice which formed on it in the air conducted, for when touched it preserved its electric state. Believing as yet that the account I have given of the cause of the electric state of an issuing jet of steam and water (Phil. Trans. 1843, p. 17) is the true one, I conclude that this also was a case of the production of electricity simply by friction, and unconnected with vaporization.

* The bromides of phosphorus are easily made without risk of explosion. If a glass tube be bent so as to have two depressions, phosphorus placed in one and bromine in the other; then by inclining the tube, the vapour of bromine can be made to flow gradually on to, and combine with, the phosphorus. The fluid protobromide is first formed, and this is afterwards converted into solid perbromide. The excess of bromine may be dissipated by the careful application of heat.
solid, transparent, crystalline body. It does not freeze until reduced much lower than this temperature; but being frozen by the carbonic acid bath in vacuo, it remains a solid until the temperature in rising attains to $-124^{\circ}$.

Fluosilicon.-I found that this substance in the gaseous state might be brought in contact with the oil and metal of the pumps, without causing injury to them, for a time sufficiently long to apply the joint process of condensation already described. The substance liquefied under a pressure of about nine atmospheres at the lowest temperature, or at $160^{\circ}$ below $0^{\circ}$; and was then clear, transparent, colourless, and very fluid like hot ether. It did not solidify at any temperature to which I could submit it. I was able to preserve it in the tube until the next day. Some leakage had then taken place (for it ultimately acted on the lubricating fat of the stop-cock), and there was no liquid in the tube at common temperatures; but when the bend of the tube was cooled to $32^{\circ}$ by a little ice, fluid appeared : a bath of ice and salt caused a still more abundant condensation. The pressure appeared then to. be above thirty atmospheres, but the motion of the mercury in the gauge had become obstructed through the action of the fluosilicon, and no confidence could be reposed in its indications.

Phosphuretted hydrogen.-This gas was prepared by boiling phosphorus in a strong pure solution of caustic potassa, and the gas was preserved over water in a dark room for several days to cause the deposition of any mere vapour of phosphorus which it might contain. It was then subjected to high pressure in a tube cooled by a carbonic acid bath, which had itself been cooled under the receiver of the air-pump. The gas in its way to the pumps passed through a long spiral of thin narrow glass tube immersed in a mixture of ice and salt at $0^{\circ}$, to remove as much water from it as possible.

By these means the phosphuretted hydrogen was liquefied; for a pure, clear, colourless, transparent and very limpid fluid appeared, which could not be solidified by any temperature applied, and which when the pressure was taken off immediately rose again in the form of gas. Still the whole of the gas was not condensable into this fluid. By working the pumps the pressure would rise up to twenty-five atmospheres at this very low temperature, and yet at the pressure of two or three atmospheres and the same temperature, liquid would remain. There can be no doubt that phosphuretted hydrogen condensed, but neither can there be a doubt that some other gas, not so condensable, was also present, which perhaps may be either another phosphuretted hydrogen or hydrogen itself.

Fluoboron.-This substance was prepared from fluor spar, fused boracic acid and strong sulphuric acid, in a tube generator such as that already described, and conducted into a condensing tube under the generating pressure. The ordinary carbonic acid bath did not condense it, but the application of one cooled under the airpump caused its liquefaction, and fluoboron then appeared as a very limpid, colourless, clear fluid, showing no signs of solidification, but when at the lowest temperature mobile as hot ether. When the pressure was taken off, or the temperature raised, it returned into the state of gas.

The following are some results of pressure, all that I could obtain with the liquid in my possession; for, as the liquid is light and the gas heavy, the former rapidly disappears in producing the latter. They make no pretensions to accuracy, and are given only for general information.

| Farr. | Atmospheres. | FAhr. | Atmospheres. | Farr. | Atmospheres. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $-100$ | . $4 \cdot 61$ | $-7 \times 1$ | . 9.23 | $-62$ | . $11 \cdot 54$. |
| 82 | $7 \cdot 5$ | -66 | . $10 \cdot 00$ |  |  |

The preceding are, as far as I am aware, new results of the liquefaction and solidification of gases. I will now briefly add such other information respecting solidification, pressure, \&c., as I have obtained with gaseous bodies previously condensed. As to pressure, considerable irregularity often occurred, which I cannot always refer to its true cause; sometimes a little of the compressed gas would creep by the mercury in the gauge, and increase the volume of inclosed air; and this varied with different substances, probably by some tendency which the glass had to favour the condensation of one (by something analogous to hygrometric action) more than another. But even when the mercury returned to its place in the gauge, there were anomalies which seemed to imply, that a substance, supposed to be one, might be a mixture of two or more. It is, of course, essential that the gauge be preserved at the same temperature throughout the observations.

Muriatic acid.-This substance did not freeze at the lowest temperature to which I could attain. Liquid muriatic acid dissolves bitumen; the solution, liberated from pressure, boils, giving off muriatic acid vapour, and the bitumen is left in a solid frothy state, and probably altered, in some degree, chemically. The acid unites with and softens the resinous cap cement, but leaves it when the pressure is diminished. The following are certain pressures and temperatures which, I believe, are not very far from truth; the marked numbers are from experiment.


The result formerly obtained* was forty atmospheres at the temperature of $50^{\circ}$ Fahr.

[^4]Sulphurous acid.-When liquid, it dissolves bitumen. It becomes a crystalline, transparent, colourless, solid body, at $-105^{\circ}$ Fahr.; when partly frozen the crystals are well-formed. The solid sulphurous acid is heavier than the liquid, and sinks freely in it. The following is a table of pressures in atmospheres of 30 inches mercury, of which the marked results are from many observations, the others are interpolated. They differ considerably from the results obtained by Bunsen*, but agree with my first and only result.


Sulphuretted hydrogen.-This substance solidifies at $122^{\circ}$ Fahr. below $0^{\circ}$, and is then a white crystalline translucent substance, not remaining clear and transparent in the solid state like water, carbonic acid, nitrous oxide, \&c., but forming a mass of confused crystals like common salt or nitrate of ammonia, solidified from the melted state. As it fuses at temperatures above $-122^{\circ}$, the solid part sinks freely in the fluid, indicating that it is considerably heavier. At this temperature the pressure of its vapour is less than one atmosphere, not inore, probably, than 0.8 of an atmosphere, so that the liquid allowed to evaporate in the air would not solidify as carbonic acid does.

The following is a table of the tension of its vapour, the marked numbers being close to experimental results, and the rest interpolated. The curve resulting from these numbers, though coming out nearly identical in different series of experiments, is apparently so different in its character from that of water or carbonic acid, as to leave doubts on my mind respecting it, or else of the identity of every portion of the fluid obtained, yet the crystallization and other characters of the latter seemed to show that it was a pure substance.

[^5]

Carbonic acid.-The solidification of carbonic acid by M. Thilorier is one of the most beautiful experimental results of modern times. He obtained the substance, as is well known, in the form of a concrete white mass like fine snow, aggregated. When it is melted and resolidified by a bath of low temperature, it then appears as a clear, transparent, crystalline, colourless body, like ice; so clear, indeed, that at times it was doubtful to the eye whether anything was in the tube, yet at the same time the part was filled with solid carbonic acid. It melts at the temperature of $-70^{\circ}$ or $-72^{\circ}$ Fahr., and the solid carbonic acid is heavier than the fluid bathing it. The solid or liquid carbonic acid at this temperature has a pressure of 5.33 atmospheres nearly. Hence it is easy to understand the readiness with which liquid carbonic acid, when allowed to escape into the air, exerting only a pressure of one atmosphere, freezes a part of itself by the evaporation of another part.

Thilorier gives $-100^{\circ} \mathrm{C}$. or $-148^{\circ} \mathrm{F}$ ahr, as the temperature at which carbonic acid becomes solid. This however is rather the temperature to which solid carbonic acid can sink by further evaporation in the air, and is a temperature belonging to a pressure, not only lower than that of 5.33 atmospheres, but even much below that of one atmosphere. This cooling effect to temperatures below the boiling-point often appears. A bath of carbonic acid and ether exposed to the air will cool a tube containing condensed solid carbonic acid, until the pressure within the tube is less than one atmosphere ; yet, if the same bath be covered up so as to have the pressure of one atmosphere of carbonic acid vapour over it, then the temperature is such as to produce a pressure of $2 \cdot 5$ atmospheres by the vapour of the solid carbonic acid within the tube.

The estimates of the pressure of carbonic acid vapour are sadly at variance; thus, Thilorier* says it has a pressure of 26 atmospheres at $-4^{\circ}$ Fahr., whilst Addams $\downarrow$ says that for that pressure it requires a temperature of $30^{\circ}$. Addams gives the pressure about $27 \frac{1}{2}$ atmospheres at $32^{\circ}$, but Thilorier and myself $\ddagger$ give it as 36 atmospheres at the same temperature. At $50^{\circ}$ Brunel§ estimates the pressure as 60

[^6]atmospheres, whilst Addams makes it only $34 \cdot 67$ atmospheres. At $86^{\circ}$ Thilorier finds the pressure to be 73 atmospheres; at $4^{\circ}$ more, or $90^{\circ}$, Brunel makes it 120 atmospheres; and at $10^{\circ}$ more, or $100^{\circ}$, Addams makes it less than Thilorier at $86^{\circ}$, and only 62.32 atmospheres; even at $150^{\circ}$ the pressure with him is not quite 100 atmosplieres.

I am inclined to think that at about $90^{\circ}$ Cagniard de la Tour's state comes on with carbonic acid. From Thilorier's data we may obtain the specific gravity of the liquid and the vapour over it at the temperature of $86^{\circ}$ Fahr., and the former is little more than twice that of the latter; hence a few degrees more of temperature would bring them together, and Brunel's result seems to imply that the state was then on, but in that case Addams's results could only be accounted for by supposing that there was a deficiency of carbonic acid. The following are the pressures which I have recently obtained :-


Carbonic acid is remarkable amongst bodies for the high tension of the vapour which it gives off whilst in the solid or glacial state. There is no other substance which at all comes near it in this respect, and it causes an inversion of what in all other cases is the natural order of events. Thus, if, as is the case with water, ether, mercury or any other fluid, that temperature at which carbonic acid gives off vapour equal in elastic force to one atmosphere, be called its boiling-point; or, if (to produce the actual effect of ebullition) the carbonic, acid be plunged below the surface of alcohol or ether, then we shall perceive that the freezing and boiling-points are inverted, i. e. that the freezing-point is the hotter, and the boiling-point the colder of the two, the latter being about $50^{\circ}$ below the former.

Euchlorine.-This substance was easily converted from the gaseous state into a solid crystalline body, which, by a little increase of temperature, melted into an orange-red fluid, and by diminution of temperature again congealed; the solid euchlorine had the colour and general appearance of bichromate of potassa; it was moderately hard, brittle and translucent; and the crystals were perfectly clear. It melted at the temperature of $75^{\circ}$ below $0^{\circ}$, and the solid portion was heavier than the liquid.

When in the solid state it gives off so little vapour that the eye is not sensible of its presence by any degree of colour in the air over it when looking down a tube four inches in length, at the bottom of which is the substance. Hence the pressure of its vapour at that temperature must be very small.

Some hours after, wishing to solidify the same portion of euchlorine which was then in a liquid state, I placed the tube in a bath at $-110^{\circ}$, but could not succeed either by continuance of the tube in the bath, or shaking the fluid in the tube, or opening the tube to allow the full pressure of the atmosphere; but when the liquid euchlorine was touched by a platinum wire it instantly became solid, and exhibited all the properties before described. There are many similar instances amongst ordinary substances, but the effect in this case makes me hesitate in concluding that all the gases which as yet have refused to solidify at temperatures as low as $166^{\circ}$ below $0^{\circ}$, cannot acquire the solid state at such a temperature.

Nitrous oxide.-This substance was obtained solid by the temperature of the carbonic acid bath in vacuo, and appeared as a beautiful clear crystalline colourless body. The temperature required for this effect must have been very nearly the lowest, perhaps about $150^{\circ}$ below $0^{\circ}$. The pressure of the vapour rising from the solid nitrous oxide was less than one atmosphere.

Hence it was concluded that liquid nitrous oxide could not freeze itself by evaporation at one atmosphere, as carbonic acid does; and this was found to be true, for when a tube containing much liquid was freely opened, so as to allow evaporation down to one atmosphere, the liquid boiled and cooled itself, but remained a liquid. The cold produced by the evaporation was very great, and this was shown by putting the part of the tube containing the liquid nitrous oxide, into a cold bath of carbonic acid, for the latter was like a hot bath to the former, and instantly made it boil rapidly.

I kept this substance for some weeks in a tube closed by stop-cocks and cemented caps. In that time there was no action on the bitumen of the graduation, nor on the cement of the caps; these bodies remained perfectly unaltered.

Hence it is probable that this substance may be used in certain cases, instead of carbonic acid, to produce degrees of cold far below those which the latter body can supply. Down to a certain temperature, that of its solidification, it would not even require ether to give contact, and below that temperature it could easily be used mingled with ether; its vapour would do no harm to an air-pump, and there is no doubt that the substance placed in vacuo would acquire a temperature lower than any as yet known, perhaps as far below the carbonic acid bath in vacuo as that is below the same bath in air.

This substance, like olefiant gas, gave very uncertain results at different times as to the pressure of its vapour; results which can only be accounted for by supposing that there are two different bodies present, soluble in each other, but differing in the elasticity of their vapour. Four different portions gave at the same temperature,
namely, $-106^{\circ}$ Fahr., the following great differences in pressure, $1 \cdot 66 ; 4 \cdot 4 ; 5 \cdot 0$; and 6.3 atmospheres, and this after the elastic atmosphere left in the tubes at the conclusion of the condensation had been allowed to escape, and be replaced by a portion of the respective liquids which then rose in vapour. The following Table gives certain results with a portion of liquid which exerted a pressure of six atmospheres at $-106^{\circ}$ Fahr.


The second column expresses the pressures given as the fluid was raised from low to higher temperatures. The third column shows the pressures given the next day with the same tube after it had attained to and continued at the atmospheric temperature for some hours. There is a difference of four or five atmospheres between the two, showing that in the first instance the previous low temperature had caused the solution of a more volatile part in the less volatile and liquid portion, and that the prolonged application of a higher temperature during the night had gradually raised it again in vapour. This result occurred again and again with the same specimen*.

Cyanogen.-This substance becomes a solid transparent crystalline body, as Bunsen has already stated $\downarrow$, which raised to the temperature of $-30^{\circ}$ Fatr. then liquefies. The solid and liquid appear to be nearly of the same specific gravity, but the solid is perhaps the denser of the two.

[^7]The mixed solid and liquid substance yields a vapour of rather less pressure than one atmosphere. In accordance with this result, if the liquid be exposed to the air, it does not freeze itself as carbonic acid does.

The liquid tends to distil over and condense on the cap cement and bitumen of the gauge, but only slightly. When cyanogen is made from cyanide of mercury sealed up hermetically in a glass tube, the cyanogen distils back and condenses in the paracyanic residue of the distillation, but the pressure of the vapour at common temperatures is still as great, or very nearly so, as if the cyanogen were in a clean separate liquid state.

A measured portion of liquid cyanogen was allowed to escape and expand into gas. In this way one volume of liquid at the temperature of $63^{\circ} \mathrm{F}_{\text {AHR }}$ gave 393.9 volumes of gas at the same temperature and the barometric pressure of 30.2 inches. If 100 cubic inches of the gas be admitted to weigh 55.5 grains, then a cubic inch of the liquid would weigh $218 \cdot 6$ grains. This gives its specific gravity as 0.866 . When first condensed I estimated it as nearly $0 \cdot 9$.

Cyanogen is a substance which yielded on different occasions results of vaporous tension differing much from each other, though the substance appeared always to be pure. The following are numbers in which I place some confidence, the pressures being in atmospheres of 30 inches of mercury, and the marked results experimental*.


Ammonia.-This body may be obtained as a solid, white, translucent, crystalline substance, melting at the temperature of $103^{\circ}$ below $0^{\circ}$; at which point the solid substance is heavier than the liquid. In that state the pressure of its vapour must be very small.

Liquid ammonia at $60^{\circ}$ was allowed to expand into ammoniacal gas at the same temperature; one volume of the liquid gave $1009 \cdot 8$ volumes of the gas, the barometer being at the pressure of 30.2 inches. If 100 cubic inches of ammoniacal gas be allowed to weigh 18.28 grains, it will give 184.6 grains as the weight of a cubic inch of liquid ammonia at $60^{\circ}$. Hence its specific gravity at that temperature will be 0.731 . In the old experiments I found by another kind of process that its specific gravity was 0.76 at $50^{\circ}$.

[^8]The following is a table of the pressure of ammonia vapour, the marked results, as before, being those obtained by experiment:-


Arseniuretted Hydrogen.-This body, liquefied by Dumas and Souberran, did not solidify at the lowest temperature to which I could submit it, i. e. not at $166^{\circ}$ below $0^{\circ} \mathrm{F}_{\mathrm{Ahr}}$. In the following table of the elasticity of its vapour the marked results are experimental, and the others interpolated:-


The following bodies would not freeze at the very low temperature of the carbonic acid bath in vacuo ( $-166^{\circ}$ Fанr.) :-Chlorine, ether, alcohol, sulphuret of carbon, caoutchoucine, camphine or rectified oil of turpentine. The alcohol, caoutchoucine, and camphine lost fluidity and thickened somewhat at $-106^{\circ}$, and still more at the lower temperature of $-166^{\circ}$. The alcohol then poured from side to side like an oil.

Dry yellow fluid nitrous acid when cooled below $0^{\circ}$ loses the greater part of its colour, and then fuses into a white, crystalline, brittle and but slightly translucent substance, which fuses a little above $0^{\circ} \mathrm{F}_{\text {Ahr }}$. The green and probably hydrated acid required a much lower temperature for its solidification, and then became a pale bluish solid. There were then evidently two bodies, the dry acid which froze out first, and then the hydrate, which requires at least $-30^{\circ}$ below $0^{\circ}$ before it will solidify.

The following gases showed no signs of liquefaction when cooled by the carbonic acid bath in vacuo, even at the pressures expressed:-
Hydrogen at
Oxygen at . . . . . . . .
Nitrogen at . . . . . . . .
Nitric oxide at . .

The difference in the facility of leakage was one reason of the difference in the pressure applied. I found it impossible, from this cause, to raise the pressure of hydrogen higher than twenty-seven atmospheres by an apparatus that was quite tight enough to confine nitrogen up to double that pressure.
M. Cagniard de la Tour has shown that at a certain temperature, a liquid, under sufficient pressure, becomes clear transparent vapour or gas, having the same bulk as the liquid. At this temperature, or one a little higher, it is not likely that any increase of pressure, except perhaps one exceedingly great, would convert the gas into a liquid. Now the temperature of $166^{\circ}$ below $0^{\circ}$, low as it is, is probably above this point of temperature for hydrogen, and perhaps for nitrogen and oxygen, and then no compression without the conjoint application of a degree of cold below that we have as yet obtained, can be expected to take from them their gaseous state. Further, as ether assumes this state before the pressure of its vapour has acquired thirty-eight atmospheres, it is more than probable that gases which can resist the pressure of from twenty-seven to fifty atmospheres at a temperature of $166^{\circ}$ below $0^{\circ}$ could never appear as liquids, or be made to lose their gaseous state at common temperatures. They may probably be brought into the state of very condensed gases, but not liquefied.

Some very interesting experiments on the compression of gases have been made by M. G. Aime *, in which oxygen, olefiant, nitric oxide, carbonic oxide, fluosilicon, hydrogen, and nitrogen gases were submitted to pressures, rising up to 220 atmospheres in the case of the two last; but this was in the depths of the sea where the results under pressure could not be examined. Several of them were diminished in bulk in a ratio far greater than the pressure put upon them; but both M. Cagniard de la Tour and M. Thilorier have shown that this is often the case whilst the substance retains the gaseous form. It is possible that olefiant gas and fluosilicon may have liquefied down below, but they have not yet been seen in the liquid state except in my own experiments, and in them not at temperatures above $40^{\circ}$ Fahr. The results with oxygen are so unsteady and contradictory as to cause doubt in regard to those obtained with the other gases by the same process.

Thus, though as yet I have not condensed oxygen, hydrogen, or nitrogen, the ori-

[^9]ginal objects of my pursuit, I have added six substances, usually gaseous, to the list of those that could previously be shown in the liquid state, and have reduced seven, including ammonia, nitrous oxide, and sulphuretted hydrogen, into the solid form. And though the numbers expressing tension of vapour cannot (because of the difficulties respecting the use of thermometers and the apparatus generally) be considered as exact, I am in hopes they will assist in developing some general law governing the vaporization of all bodies, and also in illustrating the physical state of gaseous bodies as they are presented to us under ordinary temperature and pressure.

## Royal Institution,

Nov. 15, 1844.

Note.-Additional remarks respecting the Condensation of Gases.
By Michael Faraday, Esq.

Received February 20,-Read February 20, 1845.

Nitrous oxide.-Suspecting the presence on former occasions of nitrogen in the nitrous oxide, and mainly because of muriate in the nitrate of ammonia used, I prepared that salt in a pure state from nitric acid and carbonate of ammonia previously proved, by nitrate of silver, to be free from muriatic acid. After the nitrous oxide prepared from this salt had remained for some days in well-closed bottles in contact with a little water, I condensed it in the manner already described, and when condensed I allowed half the fluid to escape in vapour, that as much as possible of the less condensable portion might be carried off. In this way as much gas as would fill the capacity of the vessels twenty or thirty times or more was allowed to escape. Afterwards the following series of pressures was obtained:-


These numbers may all be taken as the results of experiments. Where the temperatures are not those actually observed, they are in almost all cases within a degree of it, and proportionate to the effects really observed. The departure of the real observations from the numbers given is very small. This table I consider as far more worthy of confidence than the former, and yet it is manifest that the curve is not consistent with the idea of a pure single substance, for the pressures at the lowest temperature are too high. I believe that there are still two bodies present, and that the more volatile, as before said, is condensable in the liquid of the less volatile; but I think there is a far smaller proportion of the more volatile (nitrogen, or whatever it may be) than in the former case.

Olefiant gas.-The olefiant gas condensed in the former experiment was prepared in the ordinary way, using excellent alcohol and sulphuric acid; then washed by agitation with about half its bulk of water, and finally left for three days over a thick mixture of lime and water with occasional agitation. In this way all the sulphurous and carbonic acids were removed, and I believe all the ether, except such minute portions as could not interfere with my results. In respect of the ether, I have since found that the process is satisfactory; for when I purposely added ether vapour to air, so as to increase its bulk by one-third, treatment like that above removed it, so as to leave the air of its original volume: There was yet a slight odour of ether left, but not so much as that conferred by adding one volume of the vapour of ether to 1200 or 1500 volumes of air. I find that when air is expanded $\frac{1}{4}$ th or $\frac{1}{3}$ rd more by the addition of the vapour of ether, washing first of all with about $\frac{1}{10}$ th of its volume of water, then again with about as much water, and lastly with its volume of water, removes the ether to such a degree, that though a little smell may remain, the air is of its original volume.

As already stated, it is the presence of other and more volatile hydrocarbons than olefiant gas, which the tensions obtained seemed to indicate, both in the gas and the liquid resulting from its condensation. In a further search after these I discovered a property of olefiant gas which I am not aware is known (since I do not find it referred to in books), namely its ready solubility in strong alcohol, ether, oil of turpentine, and such like bodies*. Alcohol will take up two volumes of this gas; ether can absorb two volumes; oil of turpentine two volumes and a half; and olive oil one volume by agitation at common temperatures and pressure; consequently, when a vessel of olefiant gas is transferred to a bath of any of these liquids and agitated, absorption quickly takes place.

Examined in this way, I have found no specimen of olefiant gas that is entirely absorbed; a residue always remains, which, though I have not yet had time to examine it accurately, appears to be light carburetted hydrogen; and I have no doubt that this is the substance which has mainly interfered in my former results. This sub-

[^10]stance appears to be produced in every stage of the preparation of olefiant gas. On taking six different portions of gas at different equal intervals, from first to last, during one process of preparation, after removing the sulphurous and carbonic acid and the ether as before described, then the following was the proportion per cent. of insoluble gas in the remainder when agitated with oil of turpentine, $10.5 ; 10$; $10.1 ; 13.1 ; 28.3 ; 61.8$. Whether carbonic oxide was present in any of these undissolved portions I cannot at present say.

In reference to the part dissolved, I wish as yet to guard myself from being supposed to assume that it is one uniform substance; there is indeed little doubt that the contrary is true; for whilst a volume of oil of turpentine introduced into twenty times its volume of olefiant gas cleared from ether and the acids, absorbs $2 \frac{1}{2}$ volumes of the gas, the same volume of fresh oil of turpentine brought into similar contact with abundance of the gas which remains when one-half has been removed by solution only dissolved 1.54 part, yet there was an abundant surplus of gas which would dissolve in fresh oil of turpentine at this latter rate. When two-thirds of a portion of fresh olefiant gas were removed by solution, the most soluble portion of that which remained required its bulk of fresh oil of turpentine to dissolve it. Hence at first one volume of camphine dissolved $2 \cdot 50$, but when the richer portion of the gas was removed, one volume dissolved $1 \cdot 54$ part; and when still more of the gas was taken away by solution, one volume of camphine dissolved only one volume of the gas. This can only be accounted for by the presence of various compounds in the soluble portion of the gas.

A portion of good olefiant gas was prepared, well-agitated with its bulk of water in close vessels, left over lime and water for three days, and then condensed as before. When much liquid was condensed, a considerable proportion was allowed to escape to sweep out the uncondensed atmosphere and the more condensable vapours; and then the following pressures were observed:-


On examining the form of the curve given by these pressures, it is very evident that, as on former occasions, the pressures at low temperatures are too great to allow the condensed liquid to be considered as one uniform body, and the form of the curve at the higher pressures is quite enough to prove that no ether was present either in
this or the former fluids. On permitting the liquid in the tube to expand into gas, and treating 100 parts of that gas with oil of turpentine, eighty-nine parts were dissolved, and eleven parts remained insoluble. There can be no doubt that the presence of this latter substance, soluble as it is under pressure in the more condensable portions, is the cause of the irregularity of the curve, and the too high pressure at the lower temperatures.

The ethereal solution of olefiant gas being mixed with eight or nine times its volume of water, dissolved and gradually minute bubbles of gas appeared, the separation of which was hastened by a little beat. In this way about half the gas dissolved was re-obtained, and burnt like very rich olefiant gas. One volume of the alcoholic solution, with two volumes of water, gave very little appearance of separating gas. Even the application of heat did not at first cause the separation, but gradually about half the dissolved olefiant gas was liberated.

The separation of the dissolved gas by water, heat, or change of pressure from its solutions, will evidently supply means of procuring olefiant gas in a greater state of purity than heretofore; the power of forming these solutions will also very much assist in the correct analysis of mixtures of hydrocarbons. I find that light carburetted hydrogen is hardly sensibly soluble in alcohol or ether, and in oil of turpentine the proportion dissolved is not probably $\frac{1}{15}$ th the volume of the fluid employed; but the further development of these points I must leave for the present.

Carbonic acid.-This liquid may be retained in glass tubes furnished with cemented caps, and closed by plugs or stop-cocks, as described, but it is important to remember the softening action on the cement which, being continued, at last reduces its strength below the necessary point. A tube of this kind was arranged on the 10th of January and left ; on the 15th of February it exploded, not by any fracture of the tube, for that remained unbroken, but simply by throwing off the cap through a failure of the cement. Hence the cement joints should not be used for long experiments, but only for those enduring for a few days.

Oxygen.-Chlorate of potassa was melted and pulverized. Oxide of manganese was pulverized, heated red-hot for half an hour, mixed whilst hot with the chlorate, and the mixture put into a long strong glass generating tube with a cap cemented on, and this tube then attached to another with a gauge for condensation. The heat of a spirit lamp carefully applied produced the evolution of oxygen without any appearance of water, and the tubes, both hot and cold, sustained the force generated. In this manner the pressure of oxygen within the apparatus was raised as high as 58.5 atmospheres, whilst the temperature at the condensing place was reduced as low as $-140^{\circ} \mathrm{F}_{\text {ahr. }}$, but no condensation appeared. A little above this pressure the cement of two of the caps began to leak, and I could carry the observation no further with this apparatus.

From the former scanty and imperfect expressions of the elasticity of the vapour of the condensed gases, Dove was led to put forth a suggestion*, whether it might not ultimately appear that the same addition of heat (expressed in degrees of the thermometer) caused the same additional increase of expansive force for all gases or vapours in contact with their liquids, provided the observation began with the same pressure in all. Thus to obtain the difference between forty-four and fifty atmospheres of pressure, either with steam or nitrous oxide, nearly the same number of degrees of heat were required; to obtain the difference between twenty and twenty-five atmospheres, either with steam or muriatic acid, the same number were required. Such a law would of course make the rate of increasing expansive force the same for all bodies, and the curve laid down for steam would apply to every other vapour. This, however, does not appear to be the case. That the force of the vapour increases in a geometrical ratio for equal increments of heat is true for all bodies, but the ratio is not the same for all. As far as observations upon the following substances, namely, water, sulphurous acid, cyanogen, ammonia, arseniuretted hydrogen, sulphuretted hydrogen, muriatic acid, carbonic acid, olefiant gas, \&c., justify any conclusion respecting a general law, it would appear that the more volatile a body is, the more rapidly does the force of its vapour increase by further addition of heat, commencing at a given point of pressure for all; thus for an increase of pressure from two to six atmospheres, the following number of degrees require to be added for the different bodies named : water $69^{\circ}$, sulphurous acid $63^{\circ}$, cyanogen $64^{\circ} 5$, ammonia $60^{\circ}$, arseniuretted hydrogen $54^{\circ}$, sulphuretted hydrogen $56^{\circ} 5$, muriatic acid $43^{\circ}$, carbonic acid $32^{\circ} 5$, nitrous oxide $30^{\circ}$; and though some of these numbers are not in the exact order, and in other cases, as of olefiant gas and nitrous oxide, the curves sometimes even cross each other, these circumstances are easily accounted for by the facts already stated of irregular composition and the inevitable errors of first results. There seems every reason therefore to expect that the increasing elasticity is directly as the volatility of the substance, and that by further and more correct observation of the forces, a general law may be deduced, by the aid of which, and only a single observation of the force of any vapour in contact with its fluid, its elasticity at any other temperature may be obtained.

Whether the same law may be expected to continue when the bodies approach near to the Cagniard de la Tour state is doubtful. That state comes on sooner in reference to the pressure required, according as the liquid is lighter and more expansible by heat and its vapour heavier, hence indeed the great reason for its facile assumption by ether. But though with ether, alcohol and water, that substance which is most volatile takes up this state with the lowest pressure, it does not follow that it should always be so; and in fact we know that ether takes up this state at a pressure between thirty-seven and thirty-eight atmospheres, whereas muriatic acid, nitrous oxide, carbonic acid and olefiant gas, which are far more volatile, sustain a higher pressure

[^11]than this without assuming that peculiar state, and whilst their vapours and liquids are still considerably different from each other. Now whether the curve which expresses the elastic force of the vapour of a given fluid for increasing temperatures continues undisturbed after that fluid has passed the Cagniard de la Tour point or not is not known, and therefore it cannot well be anticipated whether the coming on of that state sooner or later with particular bodies will influence them in relation to the more general law referred to above.

The law already suggested gives great encouragement to the continuance of those efforts which are directed to the condensation of oxygen, hydrogen and nitrogen, by the attainment and application of lower temperatures than those yet applied. If to reduce carbonic acid from the pressure of two atmospheres to that of one, we require to abstract only about half the number of degrees that is necessary to produce the same effect with sulphurous acid, it is to be expected that a far less abstraction will suffice to produce the same effect with nitrogen or hydrogen, so that further diminution of temperature and improved apparatus for pressure, may very well be expected to give us these bodies in the liquid or solid state.

Royal Institution,
Feb. 19, 1845.



[^0]:    * Philosophical Transactions, 1823, pp. 160, $189 . \quad+$ Annales de Chimie, 1835, 1x. 427, 432.

[^1]:    * Five parts of resin, one part of yellow bees'-wax, and one part of red ochre, by weight, melted together.

[^2]:    * Philosophical Transactions, 1823, p. 192.

[^3]:    * On one occasion the solid carbonic acid was exceedingly electric, but I could not produce the effect again: it was probably connected with the presence of oil which was in the carbonic acid box; neither it nor the fila-

[^4]:    * Philosophical Transactions, 1823, p. 198.

[^5]:    * Bibliothèque Universelle, 1839, xxiii. p. 185.

[^6]:    * Annales de Chimie, 1835, lx. 427, 432.
    $\ddagger$ Philosophical Transactions, 1823, p. 193.
    $\dagger$ Report of British Association, 1838, p. 70.
    § Royal Institution Journal, xxi. 132.

[^7]:    * This substance is one of those which I liquefied in 1823 (see Philosophical Transactions). Since writing the above I perceive that M. Natterer has condensed it into the liquid state by the use of pumps only (see Comptes Rendus, 1844, 18 th Nov. p. 1111), and obtained the liquid in considerable quantities. The non-solidification of it by exposure to the air perfectly accords with my own results.
    $\dagger$ Bibliothèque Universelle, 1839, xxiii. p. 184.

[^8]:    * See Bunsen's results, Bibliothèque Universelle, 1839, xxiii. p. 185.

[^9]:    * Annales de Chimie, 1843, viii. 275.

[^10]:    * Water, as Berzefius and others have pointed out, dissolves about $\frac{1}{8}$ th its volume of olefiant gas, but] find that it also leaves an insoluble residue, which burns like light carburetted hydrogen.

[^11]:    * Poggendorff's Annalen, xxiii. 290 ; or Thomson on Heat and Electricity, p. 9.

