

XXIX. *On the existence of a limit to vaporization.* By M. FARADAY, F. R. S. *Corresponding Member of the Royal Academy of Sciences at Paris, &c. &c.* Communicated May 26, 1826.

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IT is well known that within the limits recognised by experiment, the constitution of vapour* in contact with the body from which it rises, is such, that its tension increases with increased temperature, and diminishes with diminished temperature; and, though in the latter case we can, with many substances, so far attenuate the vapour as soon to make its presence inappreciable to our tests, yet an opinion is very prevalent, and I believe general,† that still small portions are produced; the tension being correspondent to the comparatively low temperature of the substance. Upon this view, it has been supposed that every substance in vacuo or surrounded by vapour or gas, having no chemical action upon it, has an atmosphere of its own around it; and that our atmosphere must contain, diffused through it, minute portions of the vapours of all those substances with which it is in contact, even down to the earths and metals. I believe that a theory of meteorites has been formed upon this opinion.

Perhaps the point has never been distinctly considered;

* By the term vapour, I mean throughout this paper that state of a body in which it is permanently and indefinitely elastic.

† See Sir H. DAVY's paper on *Electrical Phenomena exhibited in Vacuo*. *Phil. Trans.* MCCCXXII. p. 70.

and it may therefore not be uninteresting to urge two or three reasons, in part dependant upon experimental proof, why this should not be the case. The object, therefore, which I shall hold in view in the following pages, is to show that a *limit* exists to the production of vapour of any tension by bodies placed in vacuo, or in elastic media, beneath which limit they are perfectly fixed.

Dr. WOLLASTON, by a beautiful train of argument and observation, has gone far to prove that our atmosphere is of finite extent, its boundary being dependant upon the opposing powers of elasticity and gravitation.* On passing upwards, from the earth's surface, the air becomes more and more attenuated, in consequence of the gradually diminishing pressure of the superincumbent part, and its tension or elasticity is proportionally diminished; when the diminution is such, that the elasticity is a force, not more powerful than the attraction of gravity, then a limit to the atmosphere must occur. The particles of the atmosphere there tend to separate with a certain force; but this force is not greater than the attraction of gravity, which tends to make them approach the earth and each other; and as expansion would necessarily give rise to diminished tension, the force of gravity would then be strongest, and consequently would cause contraction, until the powers were balanced as before.

Assuming this state of things as proved, the air at the limit of the atmosphere has a certain degree of elasticity or tension; and, although it cannot there exist of smaller tension, yet, if portions of it were removed to a farther distance from the earth, or if the force of gravity over it could in any other way

* Phil. Trans. MDCCCXXII. p. 89.

be diminished, then it would expand, and exist of a lower tension ; upon the renewal of the gravitating force, either by approximation to the earth's surface or otherwise, the particles would approach each other, until the elasticity of the whole was again equal to the force of gravity.

Inasmuch as gases and vapours undergo no change by mere expansion or attenuation, which can at all disturb the analogy existing between them in their permanent state under ordinary circumstances, all the phenomena which have been assumed as occurring with the air at the limit of our atmosphere may, with equal propriety, be admitted with respect to vapour in general in similar circumstances ; for we have no reason for supposing that the particles of one vapour more than another are *free* from the influence of gravity, although the force may, and without doubt does, vary, with the weight and elasticity of the particles of each particular substance.

It will be evident, also, that similar effects would be produced by the force of gravity upon air or vapour of the extreme tenuity and feeble tension referred to, whatever be the means taken to bring it into that state ; and it is not necessary to imagine the portion of air operated upon, as taken from the extremity of our atmosphere, for a portion of that at the earth's surface, if it could be expanded to the same degree by an air pump, would undergo the same changes : when of a certain rarity it would just balance the attraction of gravitation and fill the receiver with vapour ; but then, if half were taken out of the receiver, the remaining portion, in place of filling the vessel, would submit to the force of gravity, would contract into the lower half of the receiver,

until, by the approximation of their particles, the vapour there existing should have an elasticity equal to the force of gravity to which it was subject. This is a necessary consequence of Dr. WOLLASTON's argument.

There is yet another method of diminishing the elasticity of vapour, namely, by diminution of temperature. With respect to the most elastic substances, as air, and many gases, the comparatively small range which we can command beneath common temperatures, does nothing more at the earth's surface than diminish in a slight degree their elasticity, though two or three of them, as sulphurous acid and chlorine, have been in part condensed into liquids. But with respect to innumerable bodies, their tendency to form vapour is so small, that at common temperatures the vapour produced approximates in rarity to the air upon the limits of our atmosphere; and with these, the power we possess of lessening tension by diminution of temperature, may be quite sufficient to render it a smaller force than its opponent, gravity; in which case it will be easy to comprehend that the vapour would give way to the latter, and be entirely condensed. The metal, silver, for instance, when violently heated, as on charcoal urged by a jet of oxygen, or by the oxy-hydrogen, or oxy-alcohol flame, is converted into vapour; lower the temperature, and before the metal falls beneath a white heat, the tension of the vapour is so far diminished, that its existence becomes inappreciable by the most delicate tests. Suppose, however, that portions are formed, and that vapour of a certain tension is produced at that temperature; it must be astonishingly diminished by the time the metal has sunk to a mere red heat; and we can hardly conceive it possible, I think,

that the silver should have descended to common temperatures, before its accompanying vapour will, by its gradual diminution in tension, if uninfluenced by other circumstances, have had an elastic force far inferior to the force of gravity ; in which case, that moment at which the two forces had become equal, would be the last moment in which vapour could exist around it ; the metal at every lower temperature being perfectly fixed.

I have illustrated this case by silver, because, from the high temperature required to make any vapour appreciable, there can be little doubt, that the equality of the gravitating and elastic forces, must take place much above common temperatures, and therefore within the range which we can command. But there is, I think, reason to believe that the equality in these forces, at or above ordinary temperatures, may take place with bodies far more volatile than silver ; with substances indeed which boil under common circumstances at 600° or 700° F.

If, as I have formerly shown,* some clean mercury be put at the bottom of a clean dry bottle, a piece of gold leaf attached to the under part of the stopper by which it is closed, and the whole left for some months at a temperature of from 60° to 80°, the gold leaf will be found whitened by amalgamation, in consequence of the vapour which rises from the mercury beneath ; but upon making the experiment in the winter of 1824-5, I was unable to obtain the effect, however near the gold leaf was brought to the surface of the mercury ; and I am now inclined to believe, because the elastic force of any vapour which the mercury could have produced at that

* Quarterly Journal of Science, X. 354.

temperature, was less than the force of gravity upon it, and that consequently the mercury was then perfectly fixed.

Sir HUMPHRY DAVY, in his experiments on the electrical phenomena exhibited in vacuo, found, that when the temperature of the vacuum above mercury was lowered to 20° F. no further diminution, even down to -20° F. was able to effect any change, as to the power of transmitting electricity, or in the luminous appearances; and that these phenomena were then nearly of the same intensity as in the vacuum made over tin.* Hence, in conjunction with the preceding reasoning, I am led to conclude, that they were then produced independant of any vapour of the metals, and that under the circumstances described; no vapour of mercury existed at temperatures beneath 20° F.

Concentrated sulphuric acid boils at about 600° F. but as the temperature is lowered the tension of its vapour is rapidly diminished. Signor BELLANI† placed a thin plate of zinc at the upper part of a closed bottle, at the bottom of which was some concentrated sulphuric acid. No action had taken place at the end of two years, the zinc then remaining as bright as at first; and this fact is very properly adduced in illustration of the fixedness of sulphuric acid at common temperatures. Here I should again presume, that the elastic force which tended to form vapour, was surpassed by the force of gravity.

Whether it be admitted or not, that in these experiments the limit of volatilization, according to the principle of the balance of forces before stated had been obtained, I think, we can hardly doubt that such is the case at common temperatures, with respect to the silver, and with all bodies which

* Phil. Trans. MDCCCXXII. p. 71.

† Giornale di Fisica, v. 197.

bear a high temperature without appreciable loss by volatilization, as platina, gold, iron, nickel, silica, alumina, charcoal, &c. ; and, consequently that, at common temperatures, no portion of vapour rises from these bodies or surrounds them ; that they are really and truly fixed ; and that none of them can exist in the atmosphere in the state of vapour.

But there is another force, independent of that of gravity, at least of the general gravity of the earth, which appears to me sufficient to overcome a certain degree of vaporous elasticity, and, consequently, competent to the condensation of vapour of inferior tension, even though gravity should be suspended ; I mean the force of homogeneous attraction.

Into a clean glass tube, about half an inch in diameter, introduce a piece of camphor ; contract the tube at the lamp about four inches from the extremity ; then exhaust it, and seal it hermetically at the contracted part ; collect the camphor to one end of the tube ; and then, having placed the tube in a convenient position, cool the other end slightly, as by covering it with a piece of bibulous paper preserved in a moist state by a basin of water and thread of cotton ; in this way, a difference in temperature of a few degrees will be occasioned between the ends of the tube, and after some days, or a week or two, crystals of camphor will be deposited in the cooled part ; there will not, however, be more than three or four of them, and these will continue to increase in size as long as the experiment is undisturbed, without the formation of any new crystals, unless the difference of temperature be considerable.

A little consideration will, I think, satisfy us that, after the first formation of the crystals in the cooled part, they have

the power of diminishing the tension of the vapour of camphor, below that point at which it could have remained unchanged in contact with the glass, or in space : for the vapour of the camphor is of a certain tension in the cooled end of the tube, which it can retain in contact with the glass, and therefore it remains unchanged ; but which it cannot retain in contact with the crystal of camphor, for there it is condensed, and continually adds to its mass. Now, this can only be in consequence of a positive power in the crystal of camphor of attracting other particles to it ; and the phenomena of the experiment are such as to show, that the force is able to overcome a certain degree of elasticity in the surrounding vapour. There is therefore no difficulty in conceiving, that, by diminishing the temperature of a body and its atmosphere of vapour, the tension of the latter may be so far decreased, as at last to be inferior to the force with which the solid portion, by the attraction of aggregation, draws the particles to it ; in which case it would immediately cause the entire condensation of the vapour.

The preceding experiment may be made with iodine, and many other substances ; and indeed there is no case of distinct crystallization by sublimation* which does not equally afford evidence of the power of the solid matter, to overcome a positive degree of tension in the vapour from which the crystals are formed. The same power, or the force of aggregation, is also illustrated in crystallizing solutions ; where the solution has a tendency to deposit upon a crystal, when it has not the same tendency to deposit elsewhere.

It may be imagined that crystallization would scarcely go

* Calomel, corrosive sublimate, oxide of antimony, naphthaline, oxalic acid, &c. &c.

on from these attenuated vapours, as it does in the denser states of the vapours experimented upon. There is, however, no good reason for supposing any difference in the force of aggregation of a solid body, dependent upon changes in the tension of the vapour about it; and indeed, generally speaking, the method I have assumed for diminishing the tension of the vapour, namely, by diminishing temperature, would cause increase in the force of aggregation.

Such are the principal reasons which have induced me to believe in the existence of a limit to the tension of vapour. If I am correct, then there are at least two causes, each of which is sufficient to overcome and destroy vapour when reduced to a certain tension; and both of which are acting effectually with numerous substances upon the surface of the earth, and retaining them in a state of perfect fixity. I have given reasons for supposing that the two bodies named, which boil at about 600° F. are perfectly fixed within limits of low temperature which we can command; and I have no doubt, that, nearly all the present recognised metals, the earths, carbon, and many of the metallic oxides, besides the greater number of their compounds, are perfectly fixed bodies at common temperatures. The smell emitted by various metals when rubbed may be objected to these conclusions, but the circumstances under which these odours are produced, are such, as not to leave any serious objections on my mind to the opinions above advanced.

I refrain from extending these views, as might easily be done, to the atomic theory, being rather desirous that they should first obtain the sanction or correction of scientific men. I should have been glad to have quoted more experiments

upon the subject, and especially relative to such bodies as acquire their fixed point at, or somewhat below common temperatures. Captain FRANKLIN has kindly undertaken to make certain experiments for me in the cold regions to which he has gone, and probably when he returns from his arduous undertaking, he may have some contributions towards this subject.

Royal Institution,
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