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Article IX.

An Account of some Results obtained by the combined Action of Heat and Compression upon certain Fluids, such as Water, Alcohol, Sulphuric Ether, and the rectified Oil of Petroleum. By M. le Baron Cagniard de la Tour.*

It is well known that by means of a Papin's digester, the temperature of fluids may be raised much above their usual boiling point; and we are led to suppose that the internal pressure which increases with the temperature would be an obstacle to the total evaporation of the fluid, especially if the space left above the fluid be not considerable.

In reflecting on this subject, it occured to me that the expansion of a volatile fluid had necessarily some limit, beyond which the liquid, notwithstanding the pressure, must be converted into vapour, little as the capacity of the apparatus allows the fluid to extend beyond its maximum of dilatation.

In order to verify this opinion, I put some alcohol of specific gravity 0·837, and a ball or sphere of quartz, into a small Papin's digester made of the end of a very thick gun barrel; the fluid occupied nearly one of the apparatus. Having noticed the kind of noise which the ball occasioned while rolling in the cold gun barrel, and afterwards when it was slightly heated, I arrived at a point in which the ball seemed to rebound at each percussion, as if it was no longer surrounded by a fluid in the gun barrel. This effect was best observed by applying the ear to the end of the handle, which served to support the machine; it ceased upon cooling, and was reproduced when the necessary degree of heat was again applied.

The same experiment was repeated with water, but with imperfect success; for on account of the high temperature which it was necessary to employ, the apparatus could not be perfectly closed. With sulphuric ether and oil of petroleum, the case was different; they presented the same phenomena as alcohol.

In order to observe these effects of heat and compression with greater facility, I put the same liquids into small glass tubes closed at one end, and afterwards at the other, by means of the blowpipe. A small piece of glass was fastened to each tube to serve as a handle.

One of the tubes into which alcohol was introduced so as to occupy nearly two-fifths of it, was heated with the precautions requisite to prevent its being broken; in proportion as the fluid expanded, its mobility became greater; the fluid after having attained

* From the Annales de Chimie et de Physique, tom. xxi. p. 127.

nearly double its original volume, disappeared completely, and was converted into so transparent a vapour that the tube seemed suddenly empty; but on suffering it to cool for a moment, a very thick cloud was formed, after which the fluid reappeared in its original state. A second tube, nearly half full of the same fluid, gave a similar result; but a third, of which the fluid occupied more than half, was broken.

Similar experiments made with oil of petroleum, of specific gravity about 0·807, and with ether, presented analogous results, excepting that the ether appeared to require less space than the oil of petroleum to be converted into vapour without breaking the tubes, and the latter less than alcohol, which seems to indicate that the more a fluid is naturally dilated, the less volume it takes to attain its maximum of expansion.

All the tubes in these trials were exhausted of air before they were closed; the experiments when repeated with tubes in which the air was left, gave similar results; the progressive expansion of the fluid was even more easily estimated in the latter case, there being no inconvenient ebullition as in the former.

The last experiment was made with a glass tube about one-third full of water; this tube lost its transparency, and broke a few seconds afterwards. It appears that at a high temperature water is capable of decomposing glass by combining with its alkali; this suggests the idea that some other result interesting to chemistry may, perhaps, be obtained by increasing the applications of this process of decomposition.

By carefully observing the experimental tubes in which the air had been left, it was remarked that those in which the fluid matter had not quite space enough to acquire the dilatation preceding its conversion to vapour, did not always break immediately after the fluid appeared to have completely filled this space, and the explosion was slower as the excess of fluid was less apparent.

May it not be concluded that fluids which are usually but slightly compressible at a low temperature, become more so at a higher temperature? and still more strongly in the present case, in which the liquid is ready to become an elastic fluid under a pressure, which, according to theoretical calculations, would appear to be equal to several hundred atmospheres?

With respect to this, there will probably be some difficulty in admitting, that a small glass tube scarcely three millimetres in diameter, and scarcely one millimetre thick, should resist so considerable an expansive force; it will, perhaps, be thought preferable to suppose that the molecules of an elastic fluid, and particularly of a fluid vapour, are susceptible at a certain degree of compression and heat, of assuming a change of state similar to semifusion, and capable of facilitating a greater reduction of volume than that derived from the absolute pressure.

Until these doubts are removed by new experiments, it appears that we may recapitulate what has been stated in the following conclusions:

1. That alcohol of specific gravity 0·817, oil of petroleum of specific gravity 0·807, and sulphuric ether, submitted to the action of heat and compression, are susceptible of being completely reduced to vapour under a volume rather exceeding twice that of each fluid.

2. That an increase of pressure occasioned by the presence of air in several of the experiments which have been described, occasioned no obstacle to the evaporation of the fluid in the same space, that it merely rendered its expansion more quiet and more easy of observation until the moment in which the fluid suddenly disappeared.

3. That water, although undoubtedly susceptible of being reduced to very compressed vapour, could not be subjected to complete experiments for want of sufficient means to close the compressing instrument perfectly, as well as that it alters the transparency of glass tubes by combining with the alkali which enters into their composition.

I have presumed that this notice would particularly interest those who are concerned in the use of steam-engines, and also probably furnish some slight indications for the solution of the question relating to the compressibility of fluids, lately proposed as a prize subject by the Institute; it is this which determined me to present it to the class, my chief ambition being to prove, that I desire to render myself more and more worthy of the favourable reception which it has bestowed upon my former labours.

Supplement to the preceding Memoir.

I have attempted to determine the pressure which ether and alcohol exert at the moment in which these fluids are suddenly reduced to vapour. The method I adopted was the following:

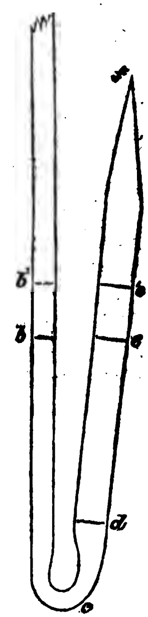
Exper. 1.—I took a tube, *a b c* (see fig. next page), of the most even bore I could obtain, the interior diameter of which was one millimetre; I united it to the tube *d e f*; the internal diameter of which was about 4¼ millimetres. The apparatus then resembled a syphon barometer. The two ends, *a* and *f*, remaining open, mercury was first introduced, and afterwards sulphuric ether. The mercury occupied the space *b c d e*, and the ether the space *e f*; by inclining the apparatus, it was easy to alter the level of the mercury so as to fill the space *b a*; by these means it was ascertained that a variation of one millimetre in the large tube, caused a variation of 20 millimetres in the smaller one; a proportion which was judged sufficient for the graduation required. The space *b a* is that which the mercury may occupy, when its level *e* in the large tube is sunk to the point *d*, the length *a b* is

528 millimetres; the space *d f* double *e f*, is that supposed to be occupied by the ether when it is entirely reduced to vapour.

The 528 millimetres were graduated on a separate scale, which was applied when required to the tube, as it was graduated towards the upper part.

The apparatus, prepared as above described, being closed at the extremities *a*, *f*, was heated with the requisite precautions. At the moment in which the ether was completely reduced to vapour, the level *b* of the mercury rose to the point *g*, the distance of which from the point *a* is 14 millimetres; *thus the column of air, which was 528 millimetres long, was reduced to 14 millimetres: this indicates a pressure of 37 or 38 atmospheres. This experiment three times repeated gave each time the same result.*

Ether is, therefore, susceptible of being reduced to vapour in a space less than double that of its original volume, and in this state of vapour, it exerts a pressure of 37 or 38 atmospheres in the tube which contains it.



Exper. 2.—Alcohol of specific gravity 0·817 was substituted for ether in the apparatus above described by opening the ends *f* and *a*; the alcohol occupied the space *f e*, that is to say, one-third of that supposed to be necessary for the total conversion of the alcohol into vapour. The mercury occupied the space *b′ b c d e′*, and filled the small tube, when, by inclining the apparatus, the level *e′* was sunk to *d*. The length of the column of air *a b′* was 476 millimetres. After the extremities *a* and *f* were closed by the blowpipe, the apparatus was exposed to heat with the same precautions as observed with respect to the ether. At the moment in which the alcohol was totally reduced to vapour, the level *b′* of the mercury rose to the point *g′*, that is to say, to four millimetres from the point *a*. Thus the column of air, of 476 millimetres in length, was reduced to four millimetres, which indicates a pressure of 119 atmospheres.

Alcohol may, therefore, be totally reduced to vapour in a space rather less than three times that of its original volume; and at this degree of expansion, it exerts a pressure of 119 atmospheres on the tube which contains it.

The extremities *a* and *f* were a little drawn out, in order that they might be more readily closed by the blowpipe; and the capacity of these parts of the tube was ascertained by introduc-

ing a little mercury, which was afterwards passed into the cylindrical part of the tube as a method of measuring it. By this precaution, it was determined, for example, that the length *a a′* of 10 millimetres ought only to be reckoned as two, &c.; the results which have been stated were obtained in this mode.

When the apparatus was cold, a small bubble of gas was observed to have been formed above the alcohol, but it produced a difference of only two millimetres in the level of the mercury in the small tube above *b′*.

In order to determine the degree of heat at which the ether and alcohol are reduced to vapour in these experiments, the tubes containing these fluids were heated in oil, in which a thermometer was placed. A cylindrical glass vessel was employed to contain the oil; by these means it was easy to determine the moment at which the liquids in the tubes were reduced to vapour; it was found that ether required 160°, and the alcohol 207° of Reaumur.

The apparatus above described for determining the pressure exerted by ether and by alcohol, was also subjected to the heat of the oil bath; but a refrigerator was previously adjusted to the upper part of the small tube containing the column of air, by which the temperature of the column was constantly kept at 18°. The results, as to the degree of vaporization and to the pressure exerted, agreed with those which have been described.

When my memoir was read to the Academy, I announced that water heated in glass tubes altered their transparency, so as to prevent any observation of what took place; since that period I have found that by adding a small quantity of carbonate of soda to the water, the transparency of the glass was much less injured. By this method, I ascertained, although with some difficulty, on account of the frequent breaking of the tubes, that at about the temperature of melting zinc, water may be completely reduced to vapour in a space equal to nearly four times that of its original volume.

Article X.

Analyses of Books.

Transactions of the Royal Geological Society of Cornwall, Vol. II. 1822.

We are happy to introduce to our readers' attention this second volume of the labours of our scientific brethren in Cornwall; the papers it contains are replete with facts that are of much importance, not only in their applicability to practical pur-