A FEW FORCED EXPANSION PHENOMENA OF LIQUIDS

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If we fill a capillary tube with water at a temperature of 28 or 30 degrees and this tube is somewhat strong, one end of which is closed and the other terminating in a tapered tip; if we cool this tube to 18 degrees in order to let a certain quantity of air enter through the open tip; if we close it and heat it again until it reaches 28 degrees, and then gradually higher, the air completely dissolves after a certain period of time. If we cool it to 18 degrees, the initial temperature at which the tube contained both gas and liquid, we note that the water continues to occupy the entire inside capacity, and thereby keeps a constant density from 28 to 18 degrees. We can lower the temperature even more, by dripping ether on the tube. At this moment, the slightest shock or jolt, the slightest vibration causes the instant reappearance, with a sort of boiling, a slight noise and fairly noticeable shake, the gas dissolves in the water. It expands rapidly and in less than one second recovers the volume it initially occupied at 18 degrees.

The dissolution takes place when exposed to the heat of the hand, provided that care is exercised by shaking to displace the gaseous bubbles inside the liquid. As long as a trace of undissolved gas remains, during the cooling, it expands again continuously without producing the same phenomenon. If, among a certain number of bubbles only a few of them completely dissolve, without this happening to all of them, the cooling expansion fully affects those which remain, without anything reappearing at the tip where the bubbles dissolved. If the bubbles are left at the same point in the tapered point, we can greatly increase the pressure without being able to dissolve it: thus filled tubes, as I stated, could be brought to 75 degrees, without the gas bubble ceasing to be visible; moreover the pressure under these conditions is more than 400 atmospheres. Whereas the dissolution is complete by exposing to the sun the blown glass balls containing water and a little air, these balls obviously being incapable of much resistance.

I made the same observations with the following liquids, selected from all classes:

- Water; aqueous dissolution of soda sulfate, soda carbonate, copper sulfate, lead acetate, potassium manganate; sugar; concentrated soda; ammonium polysulfide; chorine, sulfurous acid, hydrochloric acid, ammonia gas;
- Hydrochloric dissolution of carbon oxide in copper protochloride;
- Fuming and ordinary nitric acid, monohydrated sulfuric acid, acetic acid, succinic acid, butyric acid;

- Absolute, ordinary, salted alcohol; absolute and ordinary ether; acetone; Dutch liquor;
- Turpentine; olive oil; creosote;
- Carbon sulfide; sodium protochloride and bichloride; tin bichloride; chlorchromic acid;
- Bromine.

Mercury is the only liquid with which I was not able to succeed, both in the presence of air and in a vacuum. An air bubble remains several days in the presence of mercury without dissolving, at least completely, and this was under pressures of 200 to 300 atmospheres, produced while destroying the expansion of mercury during this period for 8 to 10 degrees.

The phenomenon is especially easy to produce with very fluid liquids. Sulfuric acid offers a few problems. The gas is released sometimes as a cloud of fine bubbles, sometimes as one or two fairly voluminous bubbles. The mode of release seems to be associated with the slowness of the cooling: the longer it lasts, the more the bubbles are finer and uniformly distributed. A few liquids, especially caustic soda and sugar water can be cooled to zero without any gas reappearing.

In the observations I just described, there are two very distinct aspects:

1. An oversaturation of liquid by the gas produced under the influence of the pressure. The oversaturation is destroyed by shock or vibrations: we have numerous examples of these types of facts.
2. A forced expansion state of the liquid; the latter, in effect, one instant before the vibration, fills the volume that the gas occupies one instant after jointly with it and this volume is the same as the one the expanded liquid occupied by a temperature rise of 8 to 10 degrees and higher. This forced expansion is not an illusion resulting from a decreased capacity of the tube subjected to atmospheric pressure on its outside surface only: because the volume decrease produced by this cause is only a very small fraction of the liquid's expansion for one degree of increase in its temperature. Nor should the phenomenon be attributed to the density variation produced by the dissolution of the gas in the liquid: because the quantity of gas is very small relative to the volume of the liquid, since it corresponds to the expansion of the latter for some ten degrees, and the liquid occupies, as I stated, before the vibration, precisely the same volume occupied by the liquid and the gas combined afterward. The density variation thus produced is enormous: for water it is equal to 1/420-th (0.238%) of its volume at 18 degrees; for alcohol to 1/93-rd (1.075%), for ether to 1/59-th (1.695%), etc. A similar, opposite effect, would require a pressure of about 50 atmospheres for water, 150 for ether. This is thus a forced expansion phenonemon of liquids, a very general phenomenon, as proven by the variety of liquids I worked with. It probably accompanies all oversaturations, but to variable degrees and directions, but this cannot always be brought to light.

According to the counsel of Mr. Regnault, I tried to separate the two facts and produce the forced expansion of the liquid under vacuum. Here is the apparatus that I used to completely fill the tubes with liquids from which air was rigorously removed Pl. II. (A = test tube, B = flask where boiling takes place, C = condenser balloon).

I took a 1 liter flask, filled three-quarters of the way full of liquid. Two tubes engage in the plug, one with two curvatures whose outer end opens up in a condenser balloon under a layer of the same liquid, the other tube, straight and very short, receives the tip of a thick glass tube, closed by one end and tapered at the other end to give its tip a length of 60 to 80 centimeters, which is curved in its middle and lowers to the bottom of the liquid contained in the flask. The tank is filled with water and the capillary part expands with air, causing the liquid which entered while cooling to boil and driving out the last air bubbles by the expansion of the substance. When this is done, we place a small piece of cotton in the tube through which the tapered tip plunges in the flask and we pour watered plaster on the cotton. When the plaster has set, we heat the liquid of the flask, keep it at a boil for two to three hours, then drive out the entire liquid contained in the test tube. To produce this distillation without explosion, we fully heat the liquid in the tube until it comes close to its normal boiling point, then we overheat only the capillary part at its point of junction with the tank; and we continue the vaporization started at this point, while still heating the upper layer of the liquid. We thus only have fairly small ordinary trembling movements. We repeat this operation six to eight times, every quarter of an hour, without ever letting the boil stop in the flask. We then let the liquid in the test tube cool, and we bring the temperature below that of the atmosphere by vaporizing a few drops of ether. We then boil the liquid in one point of the tapered part, that we pull and close under a lamp while heating it as little as possible and within the narrowest limits, if the substance offers little chance of decomposition by the heat.

I thus filled the tubes with water and ether, and I saw the forced expansion phenomenon reproduce. It is not very marked with water, but extremely notable with the ether, more perhaps than in the presence of air. The water tube, when I broke its tip under mercury, showed absolutely no trace of gas; the vacuum which was found in its upper part suddenly vanished. An air bubble that I then caused to enter did not dissolve essentially in a few minutes. In the ether tube, the first air bubbles that had thus entered had disappeared almost instantly.

The phenomenon took place in the vacuum and in the air, and it is independent of the oversaturation. This continued existence of the liquid density in a fairly large temperature range, seemed to me to be due to the adhesiveness of the glass and liquid: this is a force which opposes the division of the latter and which can only be destroyed by increasing the molecular attraction of the liquid for itself, which is an increase produced under the influence of the cooling.