# IX.—*Freezing of Water and Bismuth.*

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PROFESSOR TYNDALL, in his work entitled "Heat considered as a mode of Motion," after speaking of the anomalous expansion of water prior to solidification, and the importance of this property in the economy of nature, controverts the generally received opinion that no other bodies possess the same properties in this respect, and cites bismuth as a case in point.

He says, at page 84: "The fact, however, is, that the case is not an isolated one. You see this iron bottle, rent from neck to bottom; I break it with this hammer, and you see a core of metal within. This is the metal bismuth, which, when it was in a molten condition, was poured into this bottle, the bottle being closed by a screw, exactly as in the case of the water. The metal cooled, solidified, expanded, and the force of its expansion was sufficient to burst the bottle. There are no fish here to be saved, still the molten bismuth acts exactly as the water acts."

The experiment, as above detailed, shows conclusively that molten bismuth expands either on cooling or freezing; but it affords very little or no proof of that which has been inferred from it.

The real question obviously is, not whether the fluid metal in returning to the solid condition rends an "iron bottle from neck to bottom," but whether the freezing of water and bismuth are analogous.

The results and details of the experiments which have been made with a view to answer this question form the subject of the present communication.

To ascertain the general mode of solidification, paraffin, nitrate chlorate and hydrate of potassium, and nitrate of sodium were experimented with.

The first experiments were made by simply melting bismuth, paraffin, &c., in good sized test-tubes. The solidification of the transparent molten substances, on cooling, could easily be observed to start from the bottom. The solidification of *bismuth*, likewise, was found to commence at the bottom, which was ascertained by pouring off the fluid metal, after it had somewhat cooled.

Water was observed by placing tubes about three-quarters full of the liquid in a freezing mixture—taking care to have the mixture some little distance above the surface of the water. In every experiment solidification began at the surface; but in one especially, ice was seen gradually to descend, while in the freezing mixture, to the bottom. Two or three times during the descent, the tube was removed from the freezing mixture, which instantly stopped the formation of ice.

Thinking the tubes employed favoured the solidification of bismuth, &c., at the bottom (there being comparatively a larger surface exposed to the cooling action of the air), the experiments were repeated in U-shaped tubes, but with the same results.

The experiments were likewise made in crucibles, again with the same practical results. A slight modification of this form of experiment submitted the metal to a severe, and, what was considered, conclusive test. A crucible three-quarters filled with molten bismuth was placed over a small Bunsen's gas jet, and in this way allowed to cool extremely slowly—at the same time cold air was blown upon its surface. It will be seen that this experiment decidedly favoured solidification on the surface; but the freezing of the metal commenced in every case at the bottom—the process being repeated several times.

At this stage of the inquiry the question presented itself: Have the air-currents produced by the heated tubes, &c., anything practically to do with solidification at the bottom. To ascertain this, tubes filled with melted bismuth and paraffin were placed horizontally in the centre of a cylinder, which was then immediately closed. The solidification of the paraffin—it being transparent—could be distinctly seen to start from the bottom. The bismuth was ascertained, as before, by pouring off the surface metal.

From the foregoing experiments it appears that, as a rule, substances solidify upwards—water being *the* exception. Whether water be the only exception, it is certain that bismuth follows the rule.

With regard to those bodies which commence solidifying at the bottom we are entitled to reason as follows:—

As soon as a liquid begins to cool, its temperature ceases to be uniform, some particles being more exposed to cooling influences than others. The necessary consequence of this must be, a difference in the specific gravity of the different particles, which will arrange themselves accordingly. It may be assumed, therefore, that after a short time, the denser particles will be found at the bottom, and as solidification begins there, the conclusion may be drawn that the point of greatest density coincides with that of solidification, and it stands to reason that the particles which solidify first are the coldest. It may be concluded from this that molten bismuth, on cooling, does not expand before freezing, as is the case with water, but that it continues to contract down to the solidifying point. The rapid expansion, which is well known to all chemists, is due to the act of crystallisation. The reason why the metal does not rise to the surface as soon as it becomes solid, although specifically lighter, is simply because it adheres to the bottom and sides of the vessel.

The two following experiments confirm in a great measure the above deductions: Melted paraffin and water at 100° C. were placed in tubes about six inches long, closed at both ends with corks, and then completely immersed, vertically, in cold water for a few minutes. It was found by a thermometer, that the top of each liquid was about 3° C. higher than the bottom.

Hence the analogy of bismuth with water is not perfect, but fails just in that point which causes our rivers and lakes to freeze from the surface and thus protect animal life.

The above experiments were principally, through the kindness of Dr. Gladstone, made in his laboratory, and I am much indebted to him for many valuable suggestions.