

point without any deposition of the salt, until all at once precipitation begins, and the thermometer falls several degrees.

The steam emitted by saline solutions consists of pure water, and it is frequently asserted to have the same temperature as the steam of pure water boiling under the same pressure; but the experiments of Magnus and others have shown that this is not the case. Magnus, for example,¹ found that when a solution of chloride of calcium was boiling at 107°, a thermometer in the steam indicated 105¼°, and when by concentration the boiling-point had risen to 116°, the thermometer in the steam indicated 111.2°.

These and other observations seem to indicate that the steam emitted by a saline solution when boiling, is in the condition in which the steam of pure boiling water would be, if heated, under atmospheric pressure, to the temperature of the boiling solution. It can therefore be cooled down to the boiling-point of pure water without undergoing any liquefaction. When cooled to this point, it becomes saturated,² and precisely resembles the steam of pure water boiling under the same pressure. When saturated steam loses heat, it does not cool, but undergoes partial liquefaction, and it does not become completely liquefied till it has lost as much heat as would have cooled more than a thousand times its weight of superheated steam one degree Centigrade.

115. **Boiling-point of Liquid Mixtures.**—A mixture of two liquids which have an attraction for each other, and will dissolve each other freely in all proportions—for example, water and alcohol—has a boiling-point intermediate between those of its constituents. But a mechanical mixture of two liquids between which no solvent action takes place—for example, water and sulphide of carbon—has a boiling-point lower than either of its constituents. If steam of water is passed into liquid sulphide of carbon, or if sulphide of carbon vapour is passed into water, a mixture is obtained which boils at 42.6° C., being four degrees lower than the boiling-point of sulphide of carbon alone. This apparent anomaly is a direct consequence of the laws of vapours stated in § 95; for the boiling-point of such a mixture is the temperature at which the sum of the pressures of the two independent vapours is equal to one atmosphere.

116. **Difficulty of Boiling without Air.**—The presence of air in the

¹ Poggendorff's *Annalen*, cxii. p. 415.

² *Saturated steam* is the ordinary designation of steam at the maximum density and pressure for its actual temperature. The term *superheated* has been explained in § 94.

midst of the liquid mass is a necessary condition of regularity of ebullition, and of its production at the normal temperature; this is shown by several convincing experiments.

1. *Donny's Experiment.*—We take a glass tube bent twice, and terminated at one of its extremities by a series of bulbs. The first step is to wash it carefully with alcohol and ether, finally leaving in it some diluted sulphuric acid. These operations are for the purpose of removing the solid particles adhering to the sides, which always detain portions of air. Water is then introduced and boiled long enough to expel the air dissolved in it, and while ebullition is proceeding, the end of the apparatus is hermetically sealed. The other

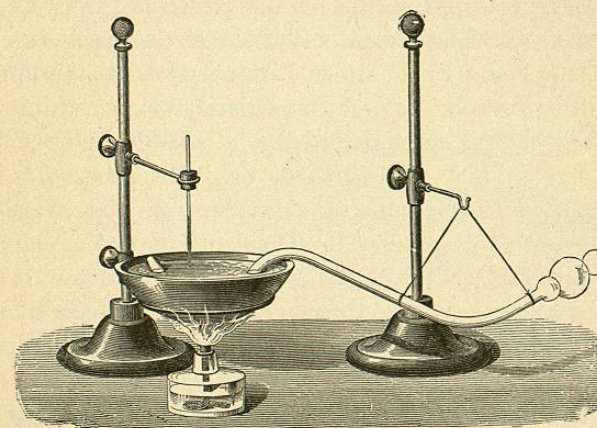


Fig. 74.—Donny's Experiment.

extremity is now plunged in a strong solution of chloride of calcium, which has a very high boiling-point, and the tube is so placed that all the water shall lie in this extremity; it will then be found that the temperature may be raised to 135° without producing ebullition. At about this temperature bubbles of steam are seen to be formed, and the entire liquid mass is thrown forward with great violence. The bulbs at the end of the tube are intended to diminish the shock thus produced.

2. *Dufour's Experiment.*—This experiment is still more decisive. A mixture of linseed-oil and oil of cloves, whose respective densities are about .93 and 1.01, is so prepared that, for temperatures near 100°, the density of the whole is nearly that of water. This mixture is placed in a cubical box of sheet-iron, with two holes opposite each other, which are filled with glass, so as to enable the observer to

perceive what is passing within. The box is placed in a metallic envelope, which permits of its being heated laterally. When the temperature of 120° has been reached, a large drop of water is allowed to fall into the mixture, which, on reaching the bottom of the box, is partially converted into vapour, and breaks up into a number of smaller drops, some of which take up a position between the two windows, so as to be visible to the observer. The temperature may then be raised to 140° , 150° , or even 180° , without producing evaporation of any of these drops. Now the maximum tension of steam at 180° is equal to 10 atmospheres, and yet we have the remarkable phenomenon of a drop of water remaining liquid at this temperature under no other pressure than that of the external air increased by an inch or two of oil. The reason is that the air necessary to evaporation is not supplied. If the drops be touched with a rod of metal, or, better still, of wood, they are immediately converted into vapour with great violence, accompanied by a peculiar noise. This is explained by the fact that the rods used always carry a certain quantity of condensed air upon their surface, and by means of this air the evaporation is produced. The truth of this explanation is proved by the fact, that when the rods have been used a certain number of times, they lose their power of provoking ebullition, owing, no doubt, to the exhaustion of the air which was adhering to their surfaces.

3. *Production of Ebullition by the formation of Bubbles of Gas in the midst of a Liquid.*—A retort is carefully washed with sulphuric acid, and then charged with water slightly acidulated, from which the air has been expelled by repeated boiling. The retort communicates with a manometer and with an air-pump. The air is exhausted until a pressure of only 150 millimetres is attained, corresponding to 60° as boiling-point. Dufour has shown that under these conditions the temperature may be gradually raised to 75° without producing ebullition. But if, while things are in this condition, a current of electricity is sent through the liquid by means of two platinum wires previously immersed in it, the bubbles of oxygen and hydrogen which are evolved at the wires immediately produce violent ebullition, and a portion of the liquid is projected explosively, as in Donny's experiment.

From these experiments we may conclude that liquid, when not in contact with gas, has a difficulty in *making a beginning* of vaporization, and may hence remain in the liquid state even at tempera-

tures at which vaporization would upon the whole involve a fall of potential energy.

That vapour (as well as air) can furnish the means of overcoming this difficulty, is established by the fact noted by Professor G. C. Foster,¹ that when a liquid has been boiling for some time in a retort, it sometimes ceases to exhibit the movements characteristic of ebullition, although the amount of vapour evolved at the surface, as measured by the amount of liquid condensed in the receiver, continues undiminished. In these circumstances, it would appear that the superficial layer of liquid, which is in contact with its own vapour, is the only part that is free to vaporize.

The preceding remarks explain the reluctance of water to boil in glass vessels carefully washed, and the peculiar formation, in these circumstances, of large bubbles of steam, causing what is called *boiling by bumping*. In the case of sulphuric acid, the phenomenon is much more marked; if this liquid be boiled in a glass vessel, enormous bubbles are formed at the sides, which, on account of the viscous nature of the liquid, raise the mass of the liquid above them, and then let it fall back with such violence as sometimes to break the vessel. This inconvenience may be avoided by using an annular brazier (Fig. 75), by means of which the upper part only of the liquid is heated.

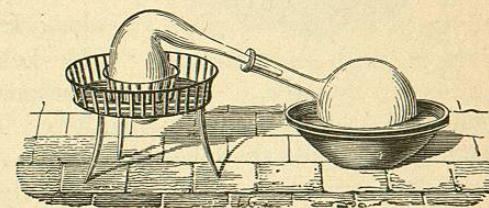


Fig. 75.—Apparatus for Boiling Sulphuric Acid.

The ebullition of ether and alcohol presents some similar features, probably because these liquids dissolve the fatty particles on the surface of the glass, and thus adhere to the sides very strongly.

117. *Spheroidal State.*—This is the name given to a peculiar condition which is assumed by liquids when exposed to the action of very hot metals.

If we take a smooth metal plate, and let fall a drop of water upon it, the drop will evaporate more rapidly as the temperature of the plate is increased up to a certain point. When the temperature of the plate exceeds this limit, which, for water, appears to be about

¹ Watts's *Dictionary of Chemistry*, art. "Heat," p. 88.

150°, the drop assumes a spheroidal form, rolls about like a ball or spins on its axis, and frequently exhibits a beautiful rippling, as represented in the figure. While in this condition, it evaporates much more slowly than when the plate was at a lower temperature.

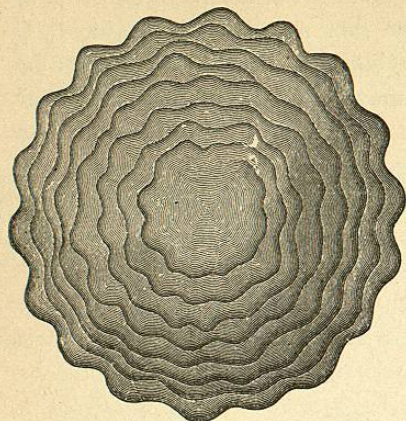


Fig. 76.—Globule in the Spheroidal State.

This latter circumstance is important, and is easily verified by experiment. If the plate be allowed to cool, a moment arrives when the globule of water flattens out, and boils rapidly away with a hissing noise. These phenomena have been long known, and were studied by Leidenfrost and Klapproth; but more complete and searching investigations were made by Boutigny. All liquids are probably capable of assuming the spheroidal state. Among those which have been tested are alcohol, ether, liquid sulphurous acid, and liquid nitrous oxide. When in this state they do not boil. Sometimes bubbles of steam are seen to rise and burst at the top of the globule, but these are always owing to some roughness of the surface, which prevents the steam from escaping in any other way; when the surface is smooth, no bubbles are observed.

If the temperature of the liquid be measured by means of a thermometer with a very small bulb, or a thermo-electric junction, it is always found to be below the boiling-point.

118. Freezing of Water and Mercury in a Red-hot Crucible.—This latter property enables us to obtain some very striking and paradoxical results. The boiling-point of liquid sulphurous acid is -10° C., and that of liquid nitrous oxide is about -70° C. If a silver or platinum crucible be heated to redness by a powerful lamp, and some liquid sulphurous acid be then poured into it, this latter assumes the spheroidal state; and drops of water let fall upon it are immediately frozen. Mercury can in like manner be frozen in a red-hot crucible by employing liquid nitrous oxide in the spheroidal state.

These experiments are due to Boutigny, who called attention to them as remarkable exceptions to the usual tendency of bodies to

equilibrium of temperature. The exception is of the same kind as that presented by a vessel of water boiling at a constant temperature of 100° over a hot fire, the heat received by the liquid being in both cases expended in producing evaporation.

119. The Metal not in Contact with the Liquid.—The basis of the entire theory of liquids in the spheroidal state is the fact that the liquid and the metal plate do not come into contact. This fact can be proved by direct observation.

The plate used must be quite smooth and accurately levelled. When the plate is heated, a little water is poured upon it, and assumes the spheroidal state. By means of a fine platinum wire which passes into the globule, the liquid is kept at the centre of the metal plate. It is then very easy, by placing a light behind the globule, to see distinctly the space between the liquid and the plate. The appearance thus presented may be easily thrown on a screen by means of the electric light.

The interruption of contact can also be proved by connecting (through a galvanometer) one pole of a battery with the hot plate, while a wire from the other pole is dipped in the liquid. The cur-

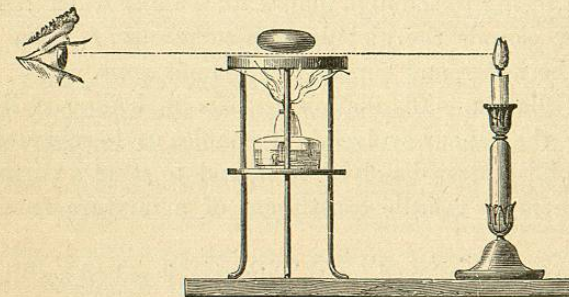


Fig. 77.—Separation between Globule and Plate.

rent refuses to circulate if the liquid is in the spheroidal state, but is immediately established when, on cooling the plate, the liquid begins to boil.

Various attempts have been made to account for the absence of contact between the liquid and the metal, but the true explanation is as yet uncertain.

In consequence of the separation, heat can only pass to the globule by radiation, and hence its comparatively low temperature is accounted for.

The absence of contact between a liquid and a metal at a high

temperature may be shown by several experiments. If, for instance, a ball of platinum be heated to bright redness, and plunged (Fig. 78) into water, the liquid is seen to recede on all sides, leaving an envelope of vapour round the ball. This latter remains red for several seconds, and contact does not take place till its temperature has fallen to about 150° . An active ebullition then takes place, and an abundance of steam is evolved.

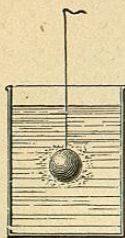


Fig. 78.—Red-hot Ball in Water.

Professor Barrett has obtained a more striking effect of the same kind by lowering a red-hot ball of iron into the soapy liquid known as "Plateau's solution."

If drops of melted sugar be let fall on water, they will float for a short time, though their density is greater than that of water, contact being prevented by their high temperature. A similar phenomenon is observed when a fragment of potassium is thrown on water. The water is decomposed; its hydrogen takes fire and burns with a red flame; its oxygen combines with the potassium to form potash; and the globule of potash floats upon the surface without touching it, owing to the high temperature under which it is formed. After a few seconds the globule cools sufficiently to come into contact with the water, and bursts with a slight noise.

120. **Distillation.**—Distillation consists in boiling a liquid and condensing the vapour evolved. It enables us to separate a liquid from the solid matter dissolved in it, and to effect a partial separation of the more volatile constituent of a mixture from the less volatile.

The apparatus employed for this purpose is called a still. One of the simpler forms, suitable for distilling water, is shown in Fig. 79.

It consists of a retort *a*, the neck of which *c* communicates with a spiral tube *d d* called the *worm*, placed in the vessel *e*, which contains cold water. The water in the retort is raised to ebullition, the steam given off is condensed in the worm, and the *distilled water* is collected in the vessel *g*.

As the condensation of the steam proceeds, the water of the cooler becomes heated, and must be renewed; for this purpose a tube descending to the bottom of the cooler is supplied with a continuous stream of cold water from above, while the superfluous water flows out by the tube *i* at the upper part of the cooler. In this way the warm water, which rises to the top, is continually removed. The

boiler is filled about three-quarters full, and the water in it can from time to time be renewed by the opening *f*; but it is advisable not to

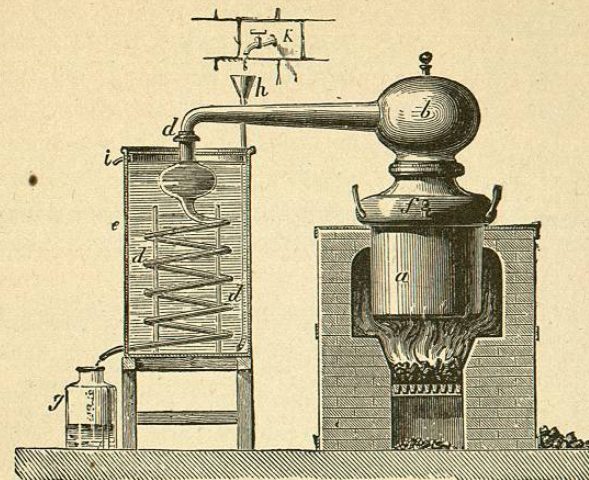


Fig. 79.—Still.

carry the process of distillation too far, and to throw away the liquid remaining in the boiler when its volume has been reduced to a fourth or a fifth of what it was originally. By exceeding this limit we run the risk of impairing the purity of the water by the carrying over of some of the solid matter contained in the liquid in the boiler.

121. **Circumstances which Influence Rapidity of Evaporation.**—In the case of a liquid exposed to the air, and at atmospheric temperature, the rapidity of evaporation increases with the extent of free surface, the dryness of the air, and the rapidity of renewal of the air immediately above the surface.

In the case of a liquid evaporated by boiling, the quantity evaporated in a given time is proportional to the heat received. This depends upon the intensity of the source of heat, the facility with which heat passes through the sides of the vessel, and the area of *heating surface*, that is to say, of surface (or more properly lamina) which is in contact with the liquid on one side, and with the source of heat on the other.