

sulphuric acid. At one extremity is a vertical tube, the end of which is bent over and connected with a flask containing water. The other extremity of the reservoir communicates with an air-pump, to the

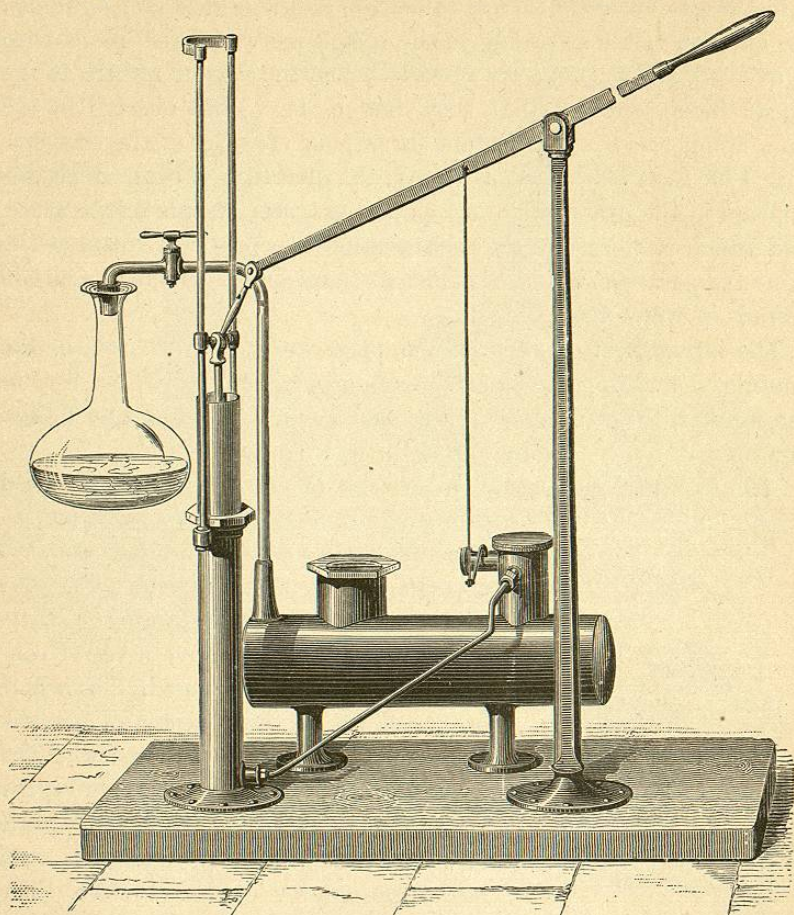


Fig. 61.—Carré's Apparatus for freezing by Sulphuric Acid.

handle of which is fitted a metallic rod, which drives an agitator immersed in the acid. By this means the surface of the acid is continually renewed, absorption takes place with regularity, and the water is rapidly frozen.

100. **Cryophorus.**—Wollaston's cryophorus (Fig. 62) consists of a bent tube with a bulb at each end. It is partly filled with water, and hermetically sealed while the liquid is in ebullition, thus expelling the air.

When an experiment is to be made, all the liquid is passed into the bulb B, and the bulb A is plunged into a freezing-mixture, or into pounded ice. The cold condenses the vapour in A, and thus produces rapid evaporation of the water in B. In a short time needles of ice appear on the surface of the liquid.

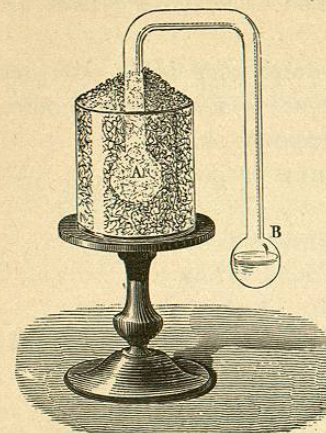


Fig. 62.—Cryophorus.

101. **Freezing of Water by the Evaporation of Ether.**—Water is poured into a glass tube dipped into ether, which is contained in a glass vessel for the purpose (Fig. 63) By means of a pair of bellows a current of air is made to pass through the ether; evaporation is quickly produced, and at the end of a few minutes the water in the tube is frozen.

If, instead of promoting evaporation of the ether by means of a

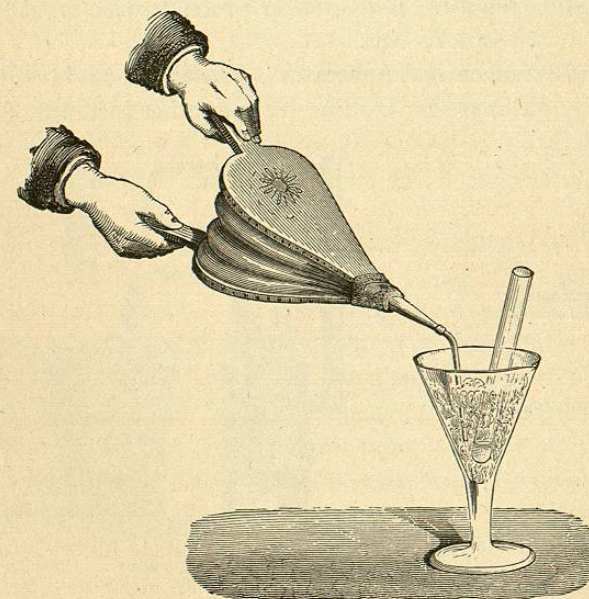


Fig. 63.—Freezing of Water by Evaporation of Ether.

current of air, the vessel were placed under the exhausted receiver of an air-pump, a much greater fall of temperature would be ob-

tained, and even mercury might easily be frozen. This experiment, however, is injurious to the pump, owing to the solvent action of the ether on the oil with which the valves and other moving parts are lubricated.

102. **Freezing of Mercury by means of Sulphurous Acid.**—Mercury may be frozen by means of liquid sulphurous acid, which is much more volatile than ether. In order to escape the suffocating action of the gas, the experiment is performed in the following manner:—

Into a glass vessel (Fig. 64) are poured successively mercury and liquid sulphurous acid. The vessel is closed by an india-rubber stopper, in which two glass tubes are fitted. One of these dips to the bottom of the sulphurous acid, and is connected at its outer end with a bladder full of air. Air is passed through the liquid by compressing the bladder, and escapes, charged with vapour, through the second opening, which is fitted with an india-rubber tube leading to the open air. Evaporation proceeds with great rapidity, and the mercury soon freezes.

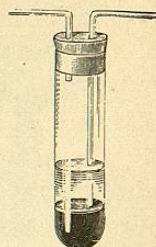


Fig. 64.  
Freezing of Mercury  
by Evaporation of  
Sulphurous Acid.

103. **Carré's Ammoniacal Apparatus.**—The apparatus invented some years ago by M. Carré for making ice is another instance of the ap-

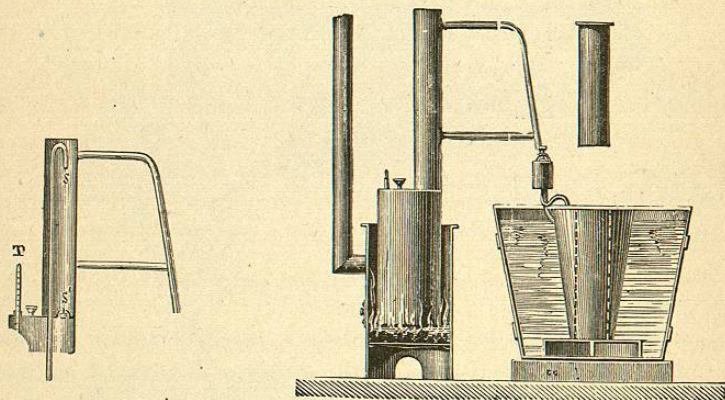


Fig. 65.

Carré's Apparatus for Freezing by Ammonia.

Fig. 66.

plication of cold produced by evaporation. It consists (Figs. 65 and 66) of two parts, a boiler and a cooler. The boiler is of wrought iron, and is so constructed as to give a very large heating surface. It is three-quarters filled with a saturated solution of ammonia.

which contains from six to seven hundred times its volume of gas. The cooler is of an annular form, and in the central space is placed a vessel containing the water to be frozen. In the sides of the cooler are a number of small cells, the object of which is to increase its surface of contact with the water in which it is immersed.

In the first part of the experiment, which is represented in the figure, the boiler is placed upon a fire, and the temperature raised to  $130^{\circ}$ , while the cooler is surrounded with cold water. Ammoniacal gas is given off, passes into the cooler by the valve *s*' opening upwards, and is condensed in the numerous cells above mentioned. This first part of the operation, in the small machines for domestic use, occupies about three-quarters of an hour. In the second part of the operation, the cylindrical vessel containing the water to be frozen is placed in the central space; the cooler is surrounded with an envelope of felt, which is a very bad conductor of heat, and the boiler is immersed in cold water. The water in the boiler, as it cools, is able again to receive and dissolve the gas, which enters by the valve *s* of the bent siphon-shaped tube. The liquid ammonia in the cooler accordingly evaporates with great rapidity, producing a fall of temperature which freezes the water in the inclosed vessel.

104. **Solidification of Carbonic Acid.**—When a small orifice is opened in a vessel containing liquid carbonic acid, evaporation proceeds so rapidly that the cold resulting from it freezes a portion of the vapour, which takes the form of fine snow, and may be collected in considerable quantity.

This carbonic acid snow, which was first obtained by Thilorier, is readily dissolved by ether, and forms with it one of the most intense freezing-mixtures known. By immersing tubes containing liquefied gases in this mixture, Faraday succeeded in reducing several of them, including carbonic acid, cyanogen, and nitrous oxide, to the form of clear transparent ice, the fall of temperature being aided, in some of his experiments, by employing an air-pump to promote more rapid evaporation of carbonic acid from the mixture. By the latter process he was enabled to obtain a temperature of  $-166^{\circ}$  F. ( $-110^{\circ}$  C.) as indicated by an alcohol thermometer, the alcohol itself being reduced to the consistence of oil. Despretz, by means of the cold produced by a mixture of solid carbonic acid, liquid nitrous oxide, and ether, rendered alcohol so viscid that it did not run out when the vessel which contained it was inverted.

105. **Continuity of the Liquid and Gaseous States. Critical Tem-**

perature.—Remarkable results were obtained by Cagniard de la Tour<sup>1</sup> by heating volatile liquids (alcohol, petroleum, and sulphuric ether) in closed tubes of great strength, and of capacity about double the volume of the inclosed liquid. At certain temperatures (36° C. for alcohol, and 42° for ether) the liquid suddenly disappeared, becoming apparently converted into vapour.

Drion,<sup>2</sup> by similar experiments upon hydrochloric ether, hyponitric acid, and sulphurous acid, showed—

1. That the coefficients of apparent expansion of these liquids increase rapidly with the temperature.

2. That they become equal to the coefficient of expansion of air, at temperatures much lower than those at which total conversion into vapour occurs.

3. That they may even become double and more than double the coefficient of expansion of air; for example, at 130° C. the coefficient of expansion of sulphurous acid was .009571.

Thilorier had previously shown that the expansion of liquid carbonic acid between the temperatures 0° and 30° C. is four times as great as that of air.

Drion further observed, that when the temperature was raised very gradually to the point of total vaporization, the free surface lost its definition, and was replaced by a nebulous zone without definite edges and destitute of reflecting power. This zone increased in size both upwards and downwards, but at the same time became less visible, until the tube appeared completely empty. The same appearances were reproduced in inverse order on gradually cooling the tube.

When the liquid was contained in a capillary tube, or when a capillary tube was partly immersed in it, the curvature of the meniscus and the capillary elevation decreased as the temperature rose, until at length, just before the occurrence of total vaporization, the surface became plane, and the level was the same within as without the tube.

Dr. Andrews, by a series of elaborate experiments on carbonic acid, with the aid of an apparatus which permitted the pressure and temperature to be altered independently of each other, showed that at temperatures above 31° C. this gas cannot be liquefied, but, when subjected to intense pressure, becomes reduced to a condition

<sup>1</sup> *Ann. de Chim.* II. xxi.

<sup>2</sup> *Ann. de Chim.* III. lvi.

in which, though homogeneous, it is neither a liquid nor a gas. When in this condition, lowering of temperature under constant pressure will reduce it to a liquid, and diminution of pressure at constant temperature will reduce it to a gas; but in neither case can any breach of continuity be detected in the transition.

On the other hand, at temperatures below 31°, the substance remains completely gaseous until the pressure reaches a certain limit depending on the temperature, and any pressure exceeding this limit causes liquefaction to commence and to continue till the whole of the gas is liquefied, the boundary between the liquefied and unliquefied portions being always sharply defined.

The temperature 31° C., or more exactly 30.92° C. (87.7° F.), may therefore be called the *critical temperature* for carbonic acid; and it is probable that every other substance, whether usually occurring in the gaseous or in the liquid form, has in like manner its own critical temperature. Dr. Andrews found that nitrous oxide, hydrochloric acid, ammonia, sulphuric ether, and sulphuret of carbon, all exhibited critical temperatures, which, in the case of some of these substances, were above 100° C.

It is probable that, in the experiments of Cagniard de la Tour and Drion, the so-called total conversion into vapour was really conversion into the intermediate condition.

The continuous conversion of a gas into a liquid may be effected by first compressing it at a temperature above its critical temperature, until it is reduced to the volume which it will occupy when liquefied, and then cooling it below the critical point.

The continuous conversion of a liquid into a gas may be obtained by first raising it above the critical temperature while kept under pressure sufficient to prevent ebullition, and afterwards allowing it to expand.

When a substance is a little above its critical temperature, and occupies a volume which would, at a lower temperature, be compatible with partial liquefaction, very great changes of volume are produced by very slight changes of pressure.

On the other hand, when a substance is at a temperature a little below its critical point, and is partially liquefied, a slight increase of temperature leads to a gradual obliteration of the surface of demarcation between the liquid and the gas; and when the whole has thus been reduced to a homogeneous fluid, it can be made to exhibit an appearance of moving or flickering striæ throughout its entire mass

by slightly lowering the temperature, or suddenly diminishing the pressure.

The apparatus employed in these remarkable experiments, which are described in the Bakerian Lecture (*Phil. Trans.* 1869), is shown in Fig. 67, where *cc* are two capillary glass tubes of great strength, one of them containing the carbonic acid or other gas to be experimented on, the other containing air to serve as a manometer. These are connected with strong copper tubes *dd*, of larger diameter, containing water, and communicating with each other through *ab*, the water being separated from the gases by a column of mercury occupying the lower portion of each capillary tube. The steel screws *ss* are the instruments for applying pressure. By screwing either of them forward into the water, the contents of both tubes are compressed, and the only use of having two is to give a wider range of compression. A rectangular brass case (not shown in the figure), closed before and behind with plate-glass, surrounds each capillary tube, and allows it to be maintained at any required temperature by the flow of a stream of water.

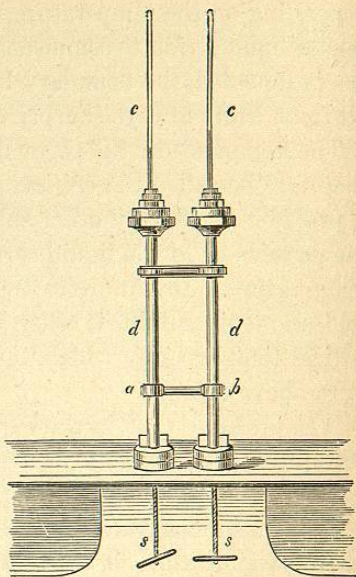


Fig. 67.—Andrews' Apparatus.

**106. Liquefaction and Solidification of Oxygen and Hydrogen.**—Up to quite recent times, air, oxygen, hydrogen, nitrogen, nitric oxide, and marsh-gas had defied all attempts to liquefy them, and were therefore called “permanent gases.” But in the latter part of the year 1877 and the beginning of 1878 they were liquefied by two investigators independently.

M. Cailletet, a French engineer, employed an apparatus similar in principle to that of Dr. Andrews described in the preceding section; the gas being compressed in a strong capillary tube by screwing a plunger into water, which transmitted the pressure to mercury in contact with the gas. When the gas had had time to lose its heat of compression, and to attain the low temperature of the inclosure by

which it was surrounded, it was suddenly allowed to expand by unscrewing a second screw plunger provided for the purpose; and under the influence of the intense cold produced by this expansion, the gas in the tube assumed the form of a cloud, showing that drops of liquid were present in it. For thus liquefying oxygen, he employed a pressure of 300 atmospheres, and, before allowing the gas to expand, cooled it to the temperature  $-29^{\circ}$  C. by means of the evaporation of sulphurous acid. For nitrogen he employed a pressure of 200, and for hydrogen of 280 atmospheres.

M. Raoul Pictet, of Geneva, who has devoted much attention to the artificial production of ice, cooled the gas under pressure, by surrounding it with two tubes one within the other, the outer one containing liquid sulphurous acid, which was rapidly evaporated by pumping away its vapour, while the inner one contained solid carbonic acid, which was also evaporated by means of a pump. The temperature of the outer tube was  $-65^{\circ}$  or  $-70^{\circ}$ ; that of the inner about  $-140^{\circ}$ ; and this inner tube immediately surrounded the tube containing the gas which it was desired to liquefy. The pressure was produced, as in Faraday's earlier experiments, by the chemical action which evolved the gas. When time had been given for the compressed gas to take the low temperature of its surroundings, a cock was opened which allowed it to escape through a small orifice into the external air, and the issuing jet was seen to be liquid. In the case of oxygen, the pressure before the escape of the jet was 320 atmospheres, in the case of hydrogen it was 650. The jet of liquid hydrogen was of a steel-blue colour, and after a short time it was changed into a hail of solid particles, showing that hydrogen had not only been liquefied but solidified. In a later experiment the jet of oxygen was submitted to optical tests (by polarized light) which showed that it contained solid particles.

**106A. Dewar's Experiments.**—More recently (1892) Professor Dewar, at the Royal Institution, has liquefied oxygen and some other gases by intense cold at atmospheric pressure. The gas to be liquefied was cooled by the continued evaporation of ethylene and of nitrous oxide, the temperature being sometimes as low as  $-200^{\circ}$  C. Liquid oxygen, in quantities of a pint, was exhibited in an open vessel, its boiling point under atmospheric pressure being  $-180^{\circ}$  C., and its latent heat of evaporation  $80^{\circ}$  C. After filtration it was a clear transparent liquid with a slight blueish tinge.

It was found to be a non-conductor of electricity, and to be so

strongly magnetic that, when placed in the spheroidal state in a cup of rock-salt beneath the poles of an electro-magnet, it leaped up as soon as the magnetizing current was turned on, and formed a bridge of hour-glass shape between the poles, as shown in Fig. 67A.<sup>1</sup> At

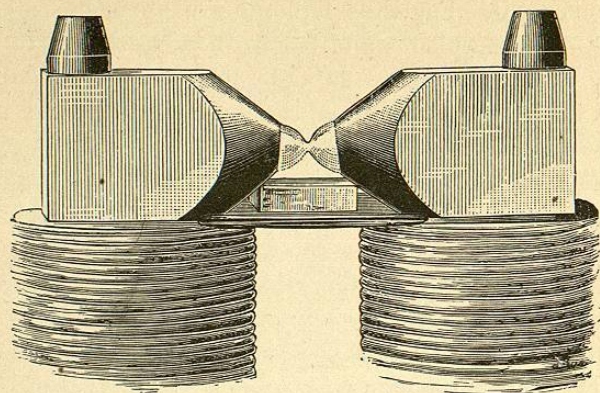


Fig. 67A.—Dewar's Experiment.

the temperature  $-200^{\circ}$  C., it was chemically inert, exhibiting no action on phosphorus or potassium dropped into it.

Air was liquefied in a similar manner, its two constituents going down together into one liquid; and when tested by the electro-magnet all the liquid went to the poles. When it was allowed to evaporate, its nitrogen boiled off before its oxygen. When surrounded by a jacket of liquid oxygen, and subjected to rapid and sustained evaporation of its nitrogen by means of a powerful pump, it was reduced to a solid block of transparent ice. The boiling point of liquid nitrogen was found to be  $-190^{\circ}$  C.

<sup>1</sup>For this figure, which is copied from a photograph, we are indebted to Professor Dewar and the publishers of the *Engineer*.

## CHAPTER IX.

### EBULLITION.

107. **Ebullition.**—When an open vessel containing a liquid is placed upon a fire or held over the flame of a lamp, evaporation at first goes on quietly and the liquid steadily rises in temperature; but after a time the liquid becomes agitated, gives off vapour much faster, and remains nearly constant in temperature. The liquid is now said to *boil* or to be in a state of *ebullition*.

If we observe the gradual progress of the phenomena—as we can easily do in a glass vessel containing water, we shall perceive that, after a time, very minute bubbles are given off; these are bubbles of dissolved air. Soon after, at the bottom of the vessel, and at those parts of the sides which are most immediately exposed to the action of the fire, larger bubbles of vapour are formed, which decrease in volume as they ascend, and disappear before reaching the surface. This stage is accompanied by a peculiar sound, indicative of approaching ebullition, and the liquid is said to be *singing*. The sound is probably caused by the collapsing of the bubbles as they are condensed by the colder water through which they pass. Finally, the bubbles increase in number, growing larger as they ascend, until they burst at the surface, which is thus kept in a state of agitation; and the liquid boils.

108. **Laws of Ebullition.**—The following are the ordinary laws of ebullition.

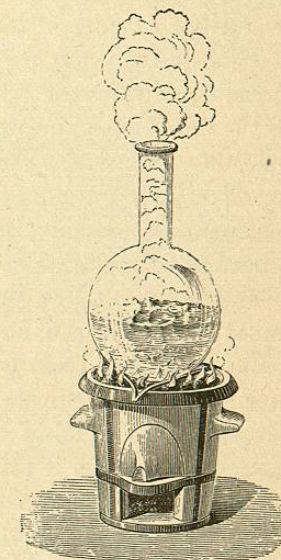


Fig. 68.—Ebullition.