

PHYSICS

From Gas to Liquid

"A Classic of Science"

Andrews Found No Sharp Division Between Gas and Liquid; The Liquid-Solid Critical State Has Since Been Studied

ON THE CONTINUITY OF THE GASEOUS AND LIQUID STATES OF MATTER. By Thomas Andrews. In Philosophical Transactions of the Royal Society. Vol. 159 London: MDCCCLXX (1870).

IN 1861 a brief notice appeared of some of my early experiments in this direction. Oxygen, hydrogen, nitrogen, carbonic oxide, and nitric oxide were submitted to greater pressures than had previously been attained in glass tubes, and while under these pressures they were exposed to the cold of the carbonic acid and ether-bath. None of the gases exhibited any appearance of liquefaction, although reduced to less than 1/500 of their ordinary volume by the combined action of cold and pressure. In the third edition of Miller's "Chemical Physics", published in 1863, a short account, derived from a private letter addressed by me to Dr. Miller, appeared of some new results I had obtained, under certain fixed conditions of pressure and temperature, with carbonic acid. As these results constitute the foundation of the present investigation and have never been published in a separate form, I may perhaps be permitted to make the following extract from my original communication to Dr. Miller. "On partially liquefying carbonic acid by pressure alone, and gradually raising at the same time the temperature to 88° Fahr., the surface of demarcation between the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striae throughout its entire mass. At temperatures above 88° no apparent liquefaction of carbonic acid, or separation into two distinct forms of matter, could be effected, even

when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results. . . .

A New Condition of Matter?

What is the condition of carbonic acid when it passes, at temperatures above 31°, from the gaseous state down to the volume of the liquid, without giving evidence at any part of the process of liquefaction having occurred? Does it continue in the gaseous state, or does it liquefy, or have we to deal with a new condition of matter? If the experiment were made at 100°, or at a higher temperature, when all indications of a fall had disappeared, the probable answer which would be given to this question is that the gas preserves its gaseous condition during the compression; and few would hesitate to declare this statement to be true, if the pressure, as in Natterer's experiments, were applied to such gases as hydrogen or nitrogen. On the other hand, when the experiment is made with carbonic acid at temperatures a little above 31°, the great fall which occurs at one period of the process would lead to the conjecture that liquefaction had actually taken place, although optical tests carefully applied failed at any time to discover the presence of a liquid in contact with a gas. But against this view it may be urged with great force, that the fact of additional pressure being always required for a further diminution of volume, is opposed to the known laws which hold in the change of bodies from the gaseous to the liquid state. Besides, the higher the temperature at which the gas is compressed, the less the fall becomes, and at last it disappears.

The answer to the foregoing question, according to what appears to me to be the true interpretation of the experiment already described, is to be found in the close and intimate relations which subsist between the gaseous

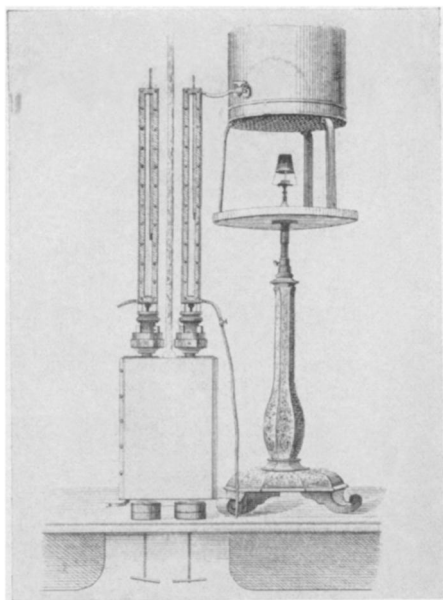
and liquid states of matter. The ordinary gaseous and ordinary liquid states are, in short, only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity. From carbonic acid as a perfect gas to carbonic acid as a perfect liquid, the transition we have seen may be accompanied by a continuous process, and the gas and liquid are only distant stages of a long series of continuous physical changes. Under certain conditions of temperature and pressure, carbonic acid finds itself, it is true, in what may be described as a state of instability, and suddenly passes, with the evolution of heat, and without the application of additional pressure or change of temperature, to the volume, which by the continuous process can only be reached through a long and circuitous route. In the abrupt change which here occurs, a marked difference is exhibited, while the process is going on, in the optical and other physical properties of the carbonic acid which has collapsed into the smaller volume, and of the carbonic acid not yet altered. There is no difficulty here, therefore, in distinguishing between the liquid and the gas. But in other cases the distinction cannot be made; and under many of the conditions I have described it would be vain to attempt to assign carbonic acid to the liquid rather than the gaseous state. Carbonic acid, at the temperature of 35°.5, and under a pressure of 108 atmospheres, is reduced to 1/430 of the volume it occupied under a pressure of one atmosphere; but if any one ask whether it is now in the gaseous or

What is a Plant's Favorite Color?

JULIUS VON SACHS

born a century ago, explains which light waves plants use in building up carbon dioxide into complex starch

IN THE NEXT CLASSIC OF SCIENCE



CRITICAL POINT APPARATUS

With these capillary tubes Andrews found the point where gases are liquids and liquids are gases.

liquid state, the question does not, I believe, admit of a positive reply. Carbonic acid at $35^{\circ}.5$, and under 108 atmospheres of pressure, stands nearly midway between the gas and the liquid; and we have no valid grounds for assigning it to the one form of matter any more than to the other. The same observation would apply with even greater force to the state in which carbonic acid exists at higher temperatures and under greater pressures than those just mentioned. In the original experiment of Cagniard de la Tour, that distinguished physicist inferred that the liquid had disappeared, and had changed into a gas. A slight modification of the conditions of his experiment would have led him to the opposite conclusion, that what had been before a gas was changed into a liquid. These conditions are, in short, the intermediate states which matter assumes in passing, without sudden change of volume, or abrupt evolution of heat, from the ordinary liquid to the ordinary gaseous state.

In the foregoing observations I have avoided all reference to the molecular forces brought into play in these experiments. The resistance of liquids and gases to external pressure tending to produce a diminution of volume, proves the existence of an internal force of an expansive or resisting character. On the other hand, the sudden diminution of volume, without the application of additional pressure externally, which occurs when a gas is compressed, at any

temperature below the critical point, to the volume at which liquefaction begins, can scarcely be explained without assuming that a molecular force of great attractive power comes here into operation, and overcomes the resistance to diminution of volume, which commonly requires the application of external force. When the passage from the gaseous to the liquid state is effected by the continuous process described in the foregoing pages, these molecular forces are so modified as to be unable at any stage of the process to overcome alone the resistance of the fluid to change of volume.

Properties are General

The properties described in this communication, as exhibited by carbonic acid, are not peculiar to it, but are generally true of all bodies which can be obtained as gases and liquids. Nitrous oxide, hydrochloric acid, ammonia, sulphuric ether, and sulphuret of carbon, all exhibited, at fixed pressures and temperatures, critical points, and rapid changes of volume with flickering movements when the temperature or pressure was changed in the neighborhood of those points. The critical points of some of these bodies were above 100° ; and in order to make the observations, it was necessary to bend the capillary tube before the commencement of the experiment, and to heat it in a bath of paraffin or oil of vitriol.

The distinction between a gas and vapour has hitherto been founded on principles which are altogether arbitrary. Ether in the state of gas is called a vapour, while sulphurous acid in the same state is called a gas; yet they are both vapours, the one derived from a liquid boiling at 35° , the other from a liquid boiling at -10° . The distinction is thus determined by the trivial condition of the boiling point of the liquid, under the ordinary pressure of the atmosphere, being higher or lower than the ordinary temperature of the atmosphere. Such a distinction may have some advantages for practical reference, but it has no scientific value. The critical point of temperature affords a criterion for distinguishing a vapour from a gas, if it be considered important to maintain the distinction at all. Many of the properties of vapours depend on the gas and liquid being present in contact with one another; and this, we have seen, can only occur at temperatures below the critical point. We may accordingly define a vapour to be a gas at any temperature under its critical point. According to this definition, a vapour may,

by pressure alone, be changed into a liquid, and may therefore exist in presence of its own liquid; while a gas cannot be liquefied by pressure—that is, so changed by pressure as to become a visible liquid distinguished by a surface of demarcation from the gas. If this definition be accepted, carbonic acid will be a vapour below 31° , a gas above that temperature; ether a vapour below 200° , a gas above that temperature.

We have seen that the gaseous and liquid states are only distant stages of the same condition of matter, and are capable of passing into one another by a process of continuous change. A problem of far greater difficulty yet remains to be solved, the possible continuity of the liquid and solid states of matter. The fine discovery made some years ago by James Thomson, of the influence of pressure on the temperature at which liquefaction occurs, and verified experimentally by Sir W. Thomson, points, as it appears to me, to the direction this inquiry must take; and in the case at least of those bodies which expand in liquefying, and whose melting-points are raised by pressure, the transition may possibly be effected. But this must be a subject for future investigation; and for the present I will not venture to go beyond the conclusion I have already drawn from direct experiment, that the gaseous and liquid forms of matter may be transformed into one another by a series of continuous and unbroken changes.

Science News Letter, May 28, 1932

ARCHAEOLOGY

Explorer of Calakmul Finds Second Ruined Maya City

A SECOND ruined Maya city, much smaller than Calakmul, has been reported by C. L. Lundell, Dallas, Texas, botanist, upon his return from Yucatan bringing details of his finds.

The second ruined city reported by Mr. Lundell is called Nohoxna and it is located fifteen miles from the Guatemalan border in the Mexican state of Petan about half way between Calakmul, the other city he reported, and Uaxactun, a ruin where Carnegie Institution archaeologists have been working. It contains nine monuments.

Mr. Lundell stopped off in New Orleans on his way home, and conferred with Dr. Frans Blom of Tulane University. The finding of Calakmul was declared by Dr. Blom to be of the greatest importance. He predicted that the