

*THE BEHAVIOUR OF LIQUIDS UNDER
HIGH PRESSURES.*

ONE of the most important generalisations which has been obtained in recent years from the study of the effect of temperature and pressure on the volume of stable liquids and gases may be expressed by the law that if the volume of a given mass of substance be kept constant, increase of pressure is proportional to increase of temperature. This relationship was proposed as early as 1878 by Lévy, who was indeed anticipated to some extent by Dupré in 1869, but was first set upon a firm experimental basis, at least for vapours, by Ramsay and Young in 1887. They represent it algebraically by the equation $p = bt - a$, in which p is the pressure, t the temperature, and b and a are constants which vary with the volume and the chemical nature of the substances employed, and the curve corresponding to this equation they term an isochor. The law may therefore be shortly expressed by stating that for stable substances the isochors are straight lines. This generalisation leads, as Fitzgerald has shown, to the significant conclusions that specific heat at constant volume must be a function of the temperature only, and internal energy and entropy must be expressible as the sum of two functions, one of which is a function of the temperature only, and the other a function of the volume only.

The experiments of Ramsay and Young extend at most over a pressure range of about 100 atmospheres, and it thus becomes a matter of considerable interest to ascertain if the linear isochor still persists under pressures which are very much higher, especially when the substances operated upon are liquids at temperatures which are well below their critical temperatures. Important data on this point may be gleaned from Nos. 92 and 96 of the *Bulletin* of the United States Geological Survey, wherein are grouped together accounts of the varied researches carried out during the last few years by Mr. Carl Barus on several of the high pressure phenomena of liquid substances.

His earlier work (*Bulletin* 92), completed in 1889, dealt with the isothermal compressibility of some fourteen liquids at temperatures and pressures having values as high as 310° and 600 atm. respectively—the pressure range being thus six times as great as that employed by the English observers.

From the data obtained, isochors¹ were eventually deduced with the result that, although below 180° they pursued a linear course, above this temperature under the high pressures employed they gave definite indication of being curved. To test by careful experiment over still wider ranges of pressure, this important question of curvature is the object of the later observations of Mr. Barus, which are detailed in No. 96 of the *Bulletin*.

The principle of the method there described consists in keeping the volume of the substance constant, and directly measuring the pressures which it supports at different temperatures, and thus obtaining immediately the data necessary for plotting the isochors. A new compression pump was devised, by means of which the enormous pressures of 2000 or 3000 atm. could be exerted. The temperature range was similar to that of the previous experiments, and the substances operated upon were ether, alcohol, thymol, para-toluidine, and diphenylamine.

The results thus obtained pointed conclusively to the fact that at high temperatures and high pressures the isochors of the liquids employed are really curved. In general the linear isochor persisted up to pressures of 1000 atm., and over temperature ranges which varied with the nature of the substance, the maximum temperature being about 115° in the case of ether, and

65° in the case of diphenylamine for the volumes used. These volumes, it may be mentioned, were not measured, so that no stress can be put upon the absolute slopes obtained for the curves. In all cases but that of thymol, the deviation from the straight curve was a marked abrupt phenomenon, and occurred generally between 1000 and 1500 atm. Thymol, however, gave no appreciable deviation.

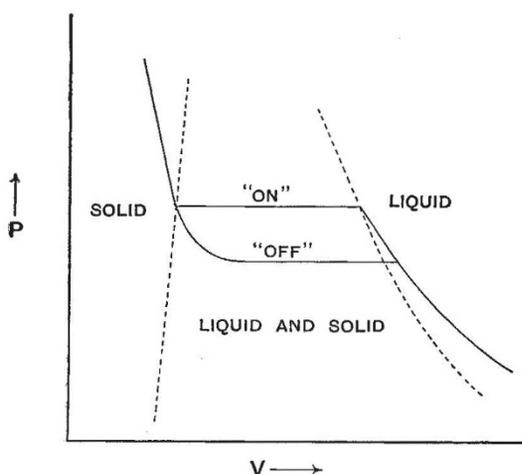
What this curvature may mean is as yet but a matter for speculation. The author inclines to the belief that it indicates a change of molecular state, and evidence into which he does not enter may be taken to point to the same conclusion. Ramsay and Young's work on dissociating gaseous substances like nitrogen peroxide and acetic acid has shown that during the progress of molecular decomposition curved isochors are obtained, which apparently bridge over the gap between the linear isochors corresponding with the simple and complex molecular states. If a like explanation applies to the liquids at present under consideration, it leads to rather a curious result, for the curvature of the isochor for alcohol is in the opposite direction to that of the isochors for all the other liquids. It would therefore follow that under increasing pressure at constant volume the alteration of the molecular state of alcohol is in the opposite sense to that of all the other liquids, and the observed direction of curvature favours the view that the liquid alcohol molecule eventually becomes simpler, while those of the other liquids become more complex. Such a condition of things may the more readily be conceived when it is borne in mind that the general physical behaviour of alcohol, and more especially its behaviour with regard to surface energy, indicate that under ordinary conditions it probably contains molecular aggregates, the complexity of which alters as the temperature alters. A liquid like ether, on the other hand, seems to contain under ordinary conditions simple gaseous molecules. The above results would thus have the interpretation that, volume remaining constant, the complex molecule of liquid alcohol corresponding with the origin of the isochor remains of the same degree of complexity over wide ranges of pressure until in the region of high pressures it becomes less complex; whereas the simple molecules of a liquid like ether, under the same conditions, eventually become associated into more complex aggregations. Of course, until more data have been accumulated, the above explanation must be regarded as but a conjecture; indeed, any definite reason why the molecular complexities of liquids like alcohol and ether should be so different, under ordinary conditions, is at present entirely wanting. Whatever happens, the significant observations here considered have definitely shown that the law of linear isochors, although it is valid throughout wide variations in the external conditions, eventually breaks down in the region of high pressures and high temperatures.

No less striking results are obtained by Mr. Barus on the effect of pressure in solidifying a liquid. Here he studies the volume changes produced by pressure during the solidification and fusion of naphthalene at various constant temperatures, and he is thus enabled to plot several of the isothermal lines for liquid-solid naphthalene between the temperatures of 60° and 130° , and between the pressures of 40 and 1700 atm.

The remarkable result arrived at in this way is, that during change of state the "on" curve obtained by increasing the pressure and passing from liquid to solid is quite distinct from the "off" curve obtained on passing from solid to liquid. At any temperature solidification always occurred at a higher pressure than that at which the solid fused. This is, of course, in harmony with the well-known fact that the temperature of the ordinary melting point of a substance is in general higher than its temperature of solidification.

¹ Instead of isochor, Mr. Barus uses throughout his papers the term isometric, originally proposed by Willard Gibbs.

The curious cyclic shape of the isothermals is diagrammatically indicated in the figure, which also brings out another difference in the processes of fusion and solidification. For when the liquid begins to solidify there is a sharp angle in the curve, solidification being an abrupt phenomenon. When the solid melts, however, there is no such sharp angle, the inclined portion of the isothermal gradually curves round and merges into the horizontal portion which represents the condition of the substance when fusion has actually set in. By repeated tests the author satisfied himself that this curvature of the isothermal was not the result of imperfect experiment, but indicated a real condition of the substance, and it may therefore be taken to correspond to a portion of the continuous curve originally proposed by Prof. James Thomson to express what actually goes on during isothermal change of state, and which is predicted for liquids and gases by the equations of van der Waals and of Ramsay and Young. From a general survey of the isothermals obtained, it appears that the volume at which solidification begins, decreases, and the volume at which it ends remains constant, or perhaps slightly increases as temperature rises. These facts are indicated by the



General shape of a Liquid-solid Isothermal.

dotted lines in the figure. We are thus enabled to map out a diagram for solid-liquid in precisely the same way as for liquid-gas, and arrive at the conclusion that at sufficiently high temperatures and pressures we shall reach the solid-liquid critical point. As far as the present experiments go, this point lies in the region of pressures above 4000 atm. and of temperatures higher than 200°. When the critical point is reached, the observations also show that the cyclic character of the isothermals will disappear. There will be no "volume lag" during fusion.

This "volume lag" the author regards as but a special case of hysteresis, having, besides its electrical and magnetic analogues, its counterpart in the phenomena of supersaturation, and the occurrence of all such phenomena he attributes to changes of molecular state. That a similar change lies at the root of the phenomena of solid-viscosity is the aim of a special series of investigations by Mr. Barus, which are collected in No. 94 of the *Bulletin*. The results obtained, however, are beyond the scope of the present article.

The main importance attaching to this work on naphthalene lies in the fact that it constitutes the beginning of a systematic study of the phenomena of solidification, which in conjunction with what is known regarding liquefaction, will ultimately permit of the entire transition from gas to liquid and from liquid to solid being repre-

sented on a single diagram. When this has been accomplished, material will be to hand for framing a comprehensive theory of what goes on during the obscure processes of change of state. Enough has already been done to give some idea of the extent to which the complexity of an equation like that of van der Waals, which involves but the third power of the volume, must be increased when attempting to express the complete passage from gas to liquid and from liquid to solid.

J. W. RODGER.

NOTES.

IT is announced that an International Electrical Exposition will be held in Paris from July 1 to October 31, 1895.

DR. W. HAVELBURG has been appointed director of a laboratory recently established at Rio de Janeiro for the study of leprosy.

THE death is announced of Dr. L. Calderon, Professor of Chemistry in Madrid University, and of Dr. Karl Schmidt, Professor of Chemistry in Dorpat University.

WITH reference to the brief notice of the death of Mr. W. Pengelly, F.R.S., in our last number, Mrs. Pengelly points out to us that "he was spoken of as Secretary, instead of Honorary Secretary, of the Torquay Natural History Society, a title of which he was naturally and reasonably jealous, seeing that his connection with the Society was always of a donative, and never of a receptive, character."

MR. F. MOCKLER'S collection of relics of Dr. Jenner, recently exhibited at Bristol, is now on view at the First Avenue Hotel, Holborn. Admission to the exhibition is free to all members of the medical profession. A movement is on foot to purchase the relics as a whole by public subscription, and to offer them to the Royal College of Surgeons.

SIR PHILIP CUNLIFFE-OWEN, whose death occurred on Friday last, at the age of sixty-six, played an important part in the development of the Department of Science and Art. In 1857 he was appointed Deputy-General Superintendent of the South Kensington Museum, and three years later he became Assistant Director. He succeeded Sir Henry Cole as Director of the Museum in 1873, and held that position until last year, when he retired. He did much to organise the collections at South Kensington, and in the Bethnal-green Museum, of which he was also a Director. His ability to organise, and great energy, led to his appointment as executive commissioner on a number of exhibitions of the works of science and the arts, and for these labours, numerous British and foreign orders were conferred upon him. Though not a man of science, he claims our esteem for the many things he did to advance scientific interests.

THE British Museum has recently acquired a section of a trunk of *Sequoia gigantea* from California, having a diameter of somewhat over 15 feet. The annual rings have been carefully counted by Mr. Carruthers, and, two years ago, when the tree was cut down, it was 1330 years old. It was then still living and vigorous. It had, therefore, already attained a considerable age when St. Augustine introduced Christianity into Great Britain. The rings indicate a remarkably symmetrical growth on all sides of the tree. For the first five or six centuries they show a considerable annual increase in the girth of the trunk, getting gradually thinner as the superficies to be covered became larger, and becoming very thin for the last three or four centuries. It is satisfactory to learn, on the authority of Mr. Carruthers, that there were, in 1884, in all the groves which he visited, trees of various ages, so that the *Sequoia* is in no danger of early extinction.