

THE LIQUEFACTION AND SOLIDIFICATION OF ARGON.<sup>1</sup>

Having been furnished, by Prof. Ramsay's kindness, with a sample of the new gas, argon, I have carried out experiments on its behaviour at a low temperature and at high pressures, in order to contribute, at least in part, to the knowledge of the properties of this interesting body.

Four series of experiments in all were carried out, two with the object of determining the critical temperature and pressure of argon, as well as measuring its vapour pressure at several other low temperatures, while two other series served to determine its boiling and freezing points under atmospheric pressure, as well as its density at its boiling point.

A detailed description of the experiments will be given in another place; I shall here give only a short description of the manner in which they were made.

For the first two experiments I made use of a Cailletet's apparatus. Its metallic manometer had been previously compared with the readings of a mercury manometer. As cooling agent I used liquid ethylene, boiling under diminished pressure. The glass tube of Cailletet's apparatus was so arranged that the portion immersed in the liquid ethylene had comparatively thin walls (not exceeding 1 mm.), so as to equalise the external and internal temperature as quickly as possible.

In both the other experiments the argon was contained in a burette, closed at both ends with glass stop-cocks. By connecting the lower end of the burette with a mercury reservoir, the argon was transferred into a narrow glass tube fused at its lower end to the upper end of the burette, and in which the argon was liquefied, and its volume in the liquid state measured. In these two series of experiments liquid oxygen, boiling under atmospheric or under diminished pressure, was employed as a cooling agent. I made use of a hydrogen thermometer in all these experiments to measure low temperatures.

*Determination of the Critical Constants of Argon.*

As soon as the temperature of liquid ethylene had been lowered to  $-128^{\circ}6$ , the argon easily condensed to a colourless liquid under a pressure of 38 atmospheres. On slowly raising the temperature of the ethylene, the meniscus of the liquid argon became less and less distinct, and finally vanished.

Seven determinations of the disappearance of the meniscus proved that the critical pressure was 50.6 atmospheres; but determinations of the critical temperature show slight differences.

quadruple walls, so as to isolate the liquid from external heat. After the liquid oxygen had been thus poured under atmospheric pressure, a great part of it evaporated, but there still remained about 70 c.c. boiling under atmospheric pressure. A calibrated tube, intended to receive the argon to be liquefied, and the hydrogen thermometer were immersed in the boiling oxygen. At this temperature ( $-182^{\circ}71$ ) on admitting argon, no appearance of liquefaction could be noticed, even when compressed by adding a quarter of an atmosphere pressure to that of the atmosphere. This shows that its boiling point lies below that of oxygen. But on diminishing the temperature of the liquid oxygen below  $-187^{\circ}$ , the liquefaction of argon became manifest. When liquefaction had taken place, I carefully equalised the pressure of the argon with that of the atmosphere, and regulated the temperature, so that the state of balance was maintained for a long time. This process gives the boiling point of argon under atmospheric pressure. Four experiments gave the numbers  $-186^{\circ}7$ ,  $-186^{\circ}8$ ,  $-187^{\circ}0$ , and  $-187^{\circ}3$ . The mean is  $-186^{\circ}9$ , which I consider to be the boiling point under atmospheric pressure (740.5 mm.).

The quantity of argon used for these experiments, reduced to normal temperature and pressure, was 99.5 c.c.; the quantity of liquid corresponding to that volume of gas was approximately 0.114 c.c. Hence the density of argon at its boiling point may be taken as approximately 1.5. Two other determinations of the density of liquid argon, for which I employed still smaller quantities of the gas, yielded rather smaller numbers. Owing to the small amount of argon used for these experiments, the numbers given cannot lay claim to great exactness; yet they prove that the density of liquid argon at its boiling point ( $-187^{\circ}$ ) is much higher than that of oxygen, which I have found, under similar conditions, to be 1.124.

By lowering the temperature of the oxygen to  $-191^{\circ}$  by slow exhaustion, the argon froze to a crystalline mass, resembling ice; on further lowering temperature it became white and opaque. When the temperature was raised it melted; four observations which I made to determine its melting point gave the numbers:  $-189^{\circ}0$ ,  $-190^{\circ}6$ ,  $-189^{\circ}6$ , and  $-189^{\circ}4$ . The mean of these numbers is  $-189^{\circ}6$ ; and this may be accepted as the melting point of argon.

In the following table I have given a comparison of physical constants, in which those of argon are compared with those of other so-called permanent gases. The data are from my previous work on the subject.

Name.	Critical temperature.	Critical pressure.	Boiling point.	Freezing point.	Freezing pressure.	Density of gas.	Density of Liquid at boiling point.	Colour of liquid.
	Below.	Atmos.			mm.			
Hydrogen (H <sub>2</sub> ) ... ..	$-220^{\circ}0$	20.0	?	?	?	1.0	?	Colourless.
Nitrogen (N <sub>2</sub> ) ... ..	$-146^{\circ}0$	35.0	$-194^{\circ}4$	$214^{\circ}0$	60	14.0	0.885	„
Carbonic oxide (CO) ... ..	$-139^{\circ}5$	35.5	$-190^{\circ}0$	$-207^{\circ}0$	100	14.0	?	„
Argon (A <sub>1</sub> ) ... ..	$-121^{\circ}0$	50.6	$-187^{\circ}0$	$-189^{\circ}6$	?	19.9	1.5	„
Oxygen (O <sub>2</sub> ) ... ..	$-118^{\circ}8$	50.8	$-182^{\circ}7$	?	?	16.0	1.124	Bluish.
Nitric oxide (NO) ... ..	$-93^{\circ}5$	71.2	$-153^{\circ}6$	$-167^{\circ}0$	138	15.0	?	Colourless.
Methane (CH <sub>4</sub> ) ... ..	$-81^{\circ}8$	54.9	$-164^{\circ}0$	$-185^{\circ}8$	80	8.0	0.415	„

The mean of the seven estimations of the critical temperature is  $-121^{\circ}$ , and this may be taken as the critical temperature of argon.

The vapour pressures at ten temperatures from  $-128^{\circ}6$  to  $139^{\circ}1$  were also determined.

*Determination of the Boiling and Freezing Points.*

Two hundred cubic centimetres of liquid oxygen, prepared in my large apparatus,<sup>2</sup> was poured into a glass vessel with

<sup>1</sup> Abstract of a paper by Dr. K. Olszewski, Professor of Chemistry in the University of Cracow.

<sup>2</sup> *Bulletin international de l'Academie de Cracovie*, June 1890; also *Wiedemann's Beiblätter*, vol. 15, p. 29.

As can be seen from the foregoing table, argon belongs to the so-called "permanent" gases, and, as regards difficulty in liquefying it, it occupies the fourth place, viz. between carbon monoxide and oxygen. Its behaviour on liquefaction places it nearest to oxygen, but it differs entirely from oxygen in being solidifiable; as is well known, oxygen has not yet been made to assume a solid state.

The high density of argon rendered it probable that its liquefaction would take place at a higher temperature than that

<sup>1</sup> I have re-determined the boiling point of oxygen, using large quantities of oxygen, and a hydrogen thermometer of much larger dimensions than previously. The registered temperature is  $1^{\circ}3$  lower than that which I previously recorded.

at which oxygen liquefies. Its unexpectedly low critical temperature and boiling point seem to have some relation to its unexpectedly simple molecular constitution.

After the reading of the three foregoing papers, a discussion followed, of which we give the most important parts.

Dr. H. E. Armstrong said that the case for the existence of the new constituent was undoubtedly a very strong one, and would, no doubt, meet with very considerable criticism throughout the world. But, apart from the facts which were brought forward, there was a portion which was of a wildly speculative character: viz. the portion dealing with the probable nature of this new element. Apparently the authors were not entirely satisfied with the evidence to be adduced from the application of the Clausius method for the determination of the atomicity of the gas. It was quite conceivable that the condition which Prof. Ramsay pointed out as being the only alternative to the one which was apparently accepted by the authors of the communication, is a conceivable condition. It was quite likely that the two atoms existed so firmly locked in each other's embrace, that there was no possibility for them to take notice of anything outside, and that they were perfectly content to roll on together without taking up any of the energy that is put into the molecule. The spectroscopic evidence was not sufficient to justify the conclusion that the new gas was a mixture. The great difficulty in accepting the conclusion that the gas was an element having a molecular weight of 40, and an atomic weight of 20, arose from the difficulty of placing an element of that kind. All these matters, however, would have to be discussed later on more fully: they were matters which could only be discussed very gradually, as more was learned about the new substance.

Prof. A. W. Rüchtersaid that the one certain fact which came out indisputably from the facts described by Prof. Ramsay was, that in spite of the doubt which may have existed on the matter for the last few weeks or months, it was certain that they had now a new constituent of the atmosphere. It seemed to him that one of the most interesting results arrived at from the physical point of view was the fact that the gas was monatomic, arguing from the determined ratio of the specific heats. The experiments carried out by Lord Rayleigh and Prof. Ramsay made it certain that the element had the particular ratio of specific heats mentioned. Well, then the question arose, What followed from this? In order that this ratio might be obtained it was necessary that the atom with which they were dealing should be regarded as spherical. In conclusion, he said that whatever the effect might be upon the great chemical generalisation of Mendeléeff, that was, after all, an empirical law based at present upon no dynamical foundation. If it held its own in this case, it would, of course, strengthen the belief in it, but, on the other hand, the law did not stand on the footing of those great mechanical generalisations which could not be upset without upsetting the whole of our fundamental notions of science.

Prof. Roberts Austen remarked that in the Bessemer process alone some ten tons of iron were put into a vessel called a converter. During the conversion no less than 100,000 cubic feet of air passed through the fluid iron. Therefore 1000 cubic feet of argon went somewhere. He had taken Bessemer-blown metal which had not been treated with ferro-manganese, and pumped out forty times its volume of gas, of which one-twentieth was nitrogen. In that nitrogen he had not been able to detect any argon that could not have come from the water which was necessarily used in the manipulation. It remained to be seen whether the argon found its way into the iron, and if it stayed there, whether certain peculiarities that made Bessemer metal different from other kinds of steel could be traced to some of this 1000 cubic feet of argon, which had either passed into the air or into the iron.

Lord Rayleigh, in the course of his remarks, referred to the argument in favour of the monatomicity of the gas. Of course, what was directly proved by the experiment was that the whole, or nearly the whole, of the energy put into the gas, when it was heated, was devoted to increasing the energy of its translatory motion, and that no margin remained over to be attributed to intermolecular or interatomic motion. At first sight it seemed rather a strange thing that there should be no rotation in the molecules of the gas. That condition was met by the suggestion which had been put forward, and which had also been communicated by Prof. Fitzgerald, in the following words: "The reason why the ratio of specific heats of 1.66 is supposed to prove monatomicity in a gas is because in a monatomic

gas there are no internal motions of any consequence. Now, if the atoms in a molecule are so bound together that hardly any internal motions exist, it would, so far as specific heat is concerned, behave like a monatomic element. That the atoms in argon may be very closely connected seems likely from its very great chemical inertness. Hence the conclusion from the ratio of its specific heats may be, not that it is monatomic, but that its atoms are so bound together in its molecule that the molecule behaves as a whole as if it was monatomic." It was difficult to conceive the possibility of such an eccentrically-shaped atom as that to move about without acquiring a considerable energy of rotation. He therefore thought that the only interpretation was that the gas was monatomic.

Lord Kelvin remarked as to the condition under which the ratio of the specific heats could be exactly 1.66, that he did not admit that a spherical atom could fulfil that condition. A spherical atom would not be absolutely smooth. In other words, it must be a Boscovitch point. In fact, the only kind of atom that could be conceived as giving, in the dynamical theory of heat, rigorously the ratio 1.66 for the specific heat, was the ideal Boscovitch mathematical point endowed with the property of inertia, and with the other property of acting upon neighbouring points with a force depending upon distance.

#### UNIVERSITY AND EDUCATIONAL INTELLIGENCE.

OXFORD.—A meeting was held on Monday last, in the rooms of the Regius Professor of Medicine, at the University Museum, and was attended by all the scientific professors and teachers of the University, with the exception of one or two, who, being unable to be present, expressed their concurrence by letter. It was unanimously resolved that a memorial connecting Sir Henry Acland's name in a permanent manner with the University Museum should be established. Sympathy was generally expressed with the scheme already before the public, but it was felt that a more distinctly personal memorial in the Museum was desirable. The future consideration of the proposal will be the subject of a second meeting to be held shortly.

Mr. A. Trevor Batty delivered a lecture before the Ashmolean Society, on Monday last, entitled "Ice-bound in Kolguev." The lecturer narrated his personal experiences, and gave an account of the manners and customs of the Samoyedi, illustrated by numerous lantern-slides and specimens, and he also described the ornithological features of the island.

The Sibthorpe Professor of Rural Economy, Mr. R. Warrington, F.R.S., gave his inaugural lecture to a large audience in the University Museum on Monday afternoon. The subject chosen was "The Present Relations of Agricultural Art and Natural Science." He deplored the want of really good agricultural and horticultural libraries.

CAMBRIDGE.—The election to the Sadlerian Professorship of Pure Mathematics, vacant by the death of Prof. Cayley, will be held on Monday, February 25, at 2.30 p.m. The names and testimonials of candidates are to be sent to the Vice-Chancellor by Monday, February 18. The electors are the Vice-Chancellor (Mr. Austen Leigh), Dr. Phear, Dr. Ferrers, Dr. Taylor, Sir G. G. Stokes, Sir R. S. Ball, and Prof. G. H. Darwin.

The Observatory Syndicate propose the appointment of a Second Assistant Observer, at a stipend of £100 a year. The appointment will be for five years, and will be made by the Director, with the consent of the Vice-Chancellor.

#### SCIENTIFIC SERIALS.

*American Meteorological Journal*, January.—Solar magnetism in meteorology, by Prof. F. H. Bigelow. This article contains some general remarks on the present state of the problems arising out of the relations that have been traced by the author's study of solar magnetism and its influences upon meteorological phenomena. Prof. Bigelow endeavours to show that the usually accepted mode of propagation of energy from the sun to the earth is not the only one that exists, and suggests that another possible mode is due to polarised solar magnetic force, such as surrounds a magnet. The progress of the investigation was made in three distinct stages: (1) the detection of the true period of the sun's rotation; (2) the determination of