Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Citation:

Dorsman, C. & G. Holst & H. Kamerlingh Onnes, Isothermals of di-atomic substances and their binary mixtures. XVII. Preliminary measurements concerning the isothermal of hydrogen at 20°C. from 60 to 90 atmospheres, in:

KNAW, Proceedings, 18 I, 1915, Amsterdam, 1915, pp. 458-464

This PDF was made on 24 September 2010, from the 'Digital Library' of the Dutch History of Science Web Center (www.dwc.knaw.nl) > 'Digital Library > Proceedings of the Royal Netherlands Academy of Arts and Sciences (KNAW), http://www.digitallibrary.nl'

collective name This word is generally only used when elements occur in more than one solid state; that this word should also be used for compounds is only an advantage, for there is no reason whatever to assume an essential difference for the phenomenon for elements and compounds. Besides we find allotropy used already several times for compounds; moreover we find it already applied to non-solid states; thus oxygen is often called allotropic, when the occurrence of oxygen as ozone and ordmary oxygen is referred to.

Why then should not we generally indicate the occurrence of different kinds of molecules by allotropy? In this sense it was already used by Prof. SMITS in his theoretical considerations. Rationally the occurrence of two or more solid states is then to be called *phase-allotropy*, the occurrence of more kinds of molecules *molecular-allotropy*. Phase allotropy will then in virtue of the above often, if not always, find its ground in molecular allotropy¹).

Nothing is known of structure and size of the molecules in solid state for ammonium chloride. In connection with the above this sufficiently justifies the choice of the title of this paper in my opinion.

> Anorganic Chemical Laboratory of the University of Amsterdam.

Physics. — "Isothermals of di-atomic substances and their binary mixtures. XVII. Preliminary measurements concerning the isothermal of hydrogen at 20° C. from 60 to 90 atmospheres". By H. KAMERLINGH ONNES, C. DORSMAN and G. HOLST. (Comm. 146a from the Physical Laboratory at Leiden).

(Communicated in the meeting of June 26, 1915)

1. Introduction. For a long time it has been the intention to extend the determination of isothermals of gases at low temperatures to pressures beyond the limit of 60 atmospheres, which had been fixed in the tirst stage of the Leiden investigations. In Communication 106 (April 1908) mention was made of a first step taken towards the realisation of that project.

On the basis of the data concerning the tensile strength of glass, published on that occasion, (about) fifteen manometer-tubes had been constructed, by which the divided open manometer (Comm. 44) could be extended in such a manner, that the entire height of mercury would correspond to a pressure of 120 atmospheres. These

¹) SMITS Zeitschr. f. physik. Chemie. 89 257 (1915).

high-pressure tubes with the boards to which they are attached were fitted to a wall of the working room, which also contains the standard-gauge of 60 atmospheres, in the same manner as the tubes of the latter. Originally it was intended (comp. Comm. 106) to fit up this wall with similar auxiliary apparatus as belong to the manometer-tubes of the 60 atmospheres-gauge, such as: pressureconnections to join the different manometer-tubes in series and to bring up_ the pressure, measuring rods suspended in cardanic rings beside the manometer-tubes used for measuring the height of the mercury columns, etc. It was further the intention to set up telescopes with which to take the readings on the new tubes in the same manner as with the standard-gauge of 60 atmospheres and finally to connect together all the tubes to one gauge of 120 atmospheres.

Want of room in the laboratory, however, prevented the execution of this plan; it would have been necessary to reserve the workingroom completely for the gauges, which it was impossible to do. For this reason it was resolved in the measurements above 60 atmospheres to proceed by an indirect method.

For measurements in the pressure-range in question a standarddifferential-manometer was constructed consisting of as many tubes for pressures above 60 atmospheres as would be necessary to supplement a pressure of about 60 atmospheres to the highest pressure to be measured. To obtain this differential gauge use is made of the same auxiliary apparatus, as serves for the measurements below 60 atmospheres, pressure-connections, taps, measuring-rods, telescopes, etc. but the tubes used for measuring pressures below 60 atmospheres are replaced by the desired number of high-pressure tubes, which are mounted in the place of the former. The highpressure tubes are joined to the system of pressure-connections and connected up in series in the same manner as with the divided open gauge and the pressures are regulated in such a manner, that in the upper space of the first tube of the series the pressure is about 60 atmospheres, and that the mercury-surface in the lower space of the last tube is subjected to the pressure to be measured. The pressure of about 60 atmospheres in the upper space of the first tube of the series is measured with a subsidiary manometer, which only serves as a pressure-indicator, the readings of which give the pressure in absolute measure by a calibration with the open standard gauge of 60 atmospheres.

If a pressure-indicator is available of sufficient accuracy for pressures of about 60 atmospheres, this method has the advantage, that the number of mercury-surfaces which have to be read becomes

30

Proceedings Royal Acad. Amsterdam. Vol. XVIII.

459

۶.

much smaller and that thereby the time required for a complete measurement is considerably shortened, which will as a rule increase the accuracy of a measurement, specially in view of the constancy of the room-temperature. The indicator used by us was the closed working manometer going from 20 to 60 atmospheres which was referred to in Comm. 78 and 97*a* and which we shall call $M_{\rm so}$. Its accuracy at 60 atmospheres can be put at about $\frac{1}{4000}$. At the time when Comm. 106 was published some progress had

been made beyond the condition described in Comm. 100, not only with the pressure-measurement, but also with the arrangement of the further apparatus required for the higher pressures. This progress especially concerns a new auxiliary manometer, a closed hydrogenmanometer of very nearly the same model as M_{60} , but arranged for the pressure-nange of 60—120 atmospheres. This manometer which we shall call M_{120} is represented diagrammatically in Plate I of communication 146c. M_{60} will similarly be found represented as C in Pl. I of Commi 97*a* fig. 1. Both are constructed according to the system described in communication 50. M_{120} has a vessel twice as large a M_{60} .

When the pressure-cylinders in the apparatus of Comm. 50 were made, the MANNESMANN-process was not yet available. It was utilized, however, in the construction of M_{120} and the pressure-cylinder can thus stand a much higher pressure. There is moreover an improvement in the mounting of the manometer, which consists principally in the mercury entering the cylinder from below, as in the closed manometers described in Comm. 50. The mounting is for the rest in every respect similar to that of the pressure-cylinder, represented in fig. 3 Plate I Comm. 97a.

The measuring tube of the manometer had been calibrated with great care by Dr. C. BRAAK. We completed the manometer and filled it with distilled hydrogen (Comm. 94 f, XIV). For its further arrangement and the method of using it in the experiments we may refer to previous communications.

By means of the completed apparatus it was possible to carry out the calibration of M_{120} with the standard manometer and obtain data in connection with the question which interested us more particularly as to whether AMAGAT's observations which only start at 100 atmospheres would join on properly to accurate measurements with the open gauge. SCHALKWIJK's measurements with the aid of the same open gauge and the accurate piezometers of Comm. 50 had given rise to some doubt on this point (comp. Comm. 70 cont. towards the end). But as those measurements had not gone beyond

- 4 -

60 atmospheres, it was quite possible, that the extrapolation on which the above conclusion was based would turn out to be impermissible.

It had been our intention to carry the calibration of a workingmanometer for pressures above 60 atmospheres and the determination of the isothermals of hydrogen at 20° C. up to 100 atmospheres. But when we had reached 90 atmospheres the connections in the pressure-system turned out less perfectly tight as was desirable. The mercury-surfaces were not completely still and to attain this it appeared necessary to affect certain improvements. But it was not till 1915 that these were carried out (comp. next Comm. 146b). Soon after the measurements mentioned above which were made in 1911, our work was interrupted by the departure of one of us and remained thus confined to a few preliminary determinations which do not extend beyond 90 atmospheres.

2. Arrangement of the divided open gauge for measurements from 60 to 100 atmospheres. The connections of the apparatus, already roughly indicated in section 1, are shown in the Plate belonging to Comm. 146c (these Proceedings below p. 472).

The figure differs from the earlier representation of the gauge by the manner in which the tubes of the open gauge which had now to serve for the measurement of 60 to 100 atmospheres are joined up: the same arrangement has been used in the measurements of the next communication. As will be seen, the first five tubes have been left intact, while the remaining tubes were replaced by tubes of greater wall-strength, destined for pressures from 60 to 100 atmospheres and tested to a pressure double of what they are intended to be used at.

This arrangement has the advantage that the first five tubes which go up to 20 atmospheres remain available as a separate open gauge, and this is necessary, because they are not only used as a standard-manometer, but also regularly as working-manometer for the range below 20 atmospheres and in this respect supplement the manometer which we have described in previous communications, going from 20 to 60 atmospheres, which above we called M_{60} . In the open gauge up to 20 atmospheres, M_{60} and M_{120} we thus possess a set of three manometers which embrace the whole range of pressure, through which the isothermals at low temperatures are measured in the Leiden-Laboratory at the present time.

The steel capillary on the left of tube B_s which normally is coupled to the T-piece T_s is now connected to a tube which through 30^*

461

A 4

the stop-cock K_{18} puts B_5 into communication with the manometer M_{60} . To begin with, when the pressure is first admitted, the stopcocks $K_6 - K_{19}$, K_{22} , K_{23} , K_{27} , K_{28} , K_{32} , K_{34} — K_{37} are all open and the pressure is raised to about 60 atmospheres, when the mercury in M_{60} will rise very nearly to the top, whereas the mercury surfaces in the open gauge will remain where they are. K_{36} is then closed and the pressure is further raised, whereby the mercury in the manometer-tubes goes up in the usual way and thus indicates the excess of the pressure above the pressure of about 60 atmospheres, which is read on M_{60} . In this manner the tubes B_5 etc. are put in series behind M_{60} as indicated in section 1. Further details of the arrangement will be sufficiently clear from an inspection of the Plate without any further description.

If it is desirable to be able to use the two parts of the open gauge simultaneously, viz. the first five tubes as open gauge up to 20 atmospheres and the next ten as differential manometer from 60 to 100, or also to connect them up into a single open gauge from 0-60 atmospheres, this is easily attained by means of a side connection to the pressure-cylinder with T-piece and two stop-cocks at the branching-point, as was actually the case in our experiments.

With the above arrangement of the manometer it was impossible to go beyond 100 atmospheres. In order to continue the measurement in a similar way, the open gauge of 20 atmospheres remaining available, it will be necessary to have a new index-manometer on which 100 atmospheres may be read to replace $M_{\rm so}$, with the addition of five suitable tubes to be joined up as a differential manometer for the difference between 100 and 120 atmospheres.

3. The normal volume. As mentioned above, the reading-tube of the manometer had been carefully calibrated. The comparison with the open standard-gauge could therefore serve at the same time as a determination of the isothermal of hydrogen at 20° C.

It was even possible to determine accurately the normal volume before and after the compression, because the vessel of the manometer (of the pattern of Comm. 50) is provided at its lower end with a small U-tube, also calibrated and containing the mercury which closes the tube, when it is not immersed in the mercury of the pressure-cylinder.

At the same time in our experiments this was not done. In a first determination of the isothermal of hydrogen from 60 to 100 atmospheres we thought ourselves justified in using an indirect determination of the normal volume, obtained by calculation from

- 6 -

a reading of M_{110} at a pressure which was also read on M_{60} and therefore accurately known through the direct comparison with the open standard-gauge. For this calculation the formula is available which represents SCHALKWIJK'S observations within the limits of their accuracy (Comm. 70).

Three measurements were made yielding the following data. The deviations from the mean are not higher than $\frac{1}{3300}$. The result may certainly be called satisfactory, considering that M_{60} gives the pressure

Date		$ u_{20}$		Þ		Normal vol.		
13	Febr.	1911	1.76969	c.M ³	62.504	atm.	99.568	c.M ³
21	n	n	1.76633	n	62.802))	99.601	"
22	n	17	1.76017	n	63.039	ູກ	99.618	n

TABLE I.

Mean 99 596

in this case with an accuracy of $\frac{1}{4000}$, as was confirmed moreover by a special comparison with the open gauge of 0—60, and that the reading of the volume in M_{120} was not more accurate than to about 1 part in 10000. The mean was therefore taken as the normal volume.

4. Results. Only one series of measurements was made. The calculation for M_{60} and for the open gauge were exactly as formerly. The only point to be mentioned is, that the corrections for the weight of the air-columns of the open gauge were calculated using the densities as given in the tables which BRINKMAN deduced from AMAGAT's observations. (Comp. also Comm. 146c). Table II (p. 468) gives the results of the measurements.

The deviations from the values which would follow from SCHALK-WIJK's formula are all with the exception of the first in the same direction. Except in the doubtful observation corresponding to the density 80, the deviation is only about 1 in 1500, the mean positive deviation (leaving out of account the observation at $d_A = 80$) 0.0003 falls on the limit of what may be considered as established, considering the degree of accuracy of the observations. The fifth column of Table II contains for the highest pressures the values according to the formula which was calculated from the series in Comm. 70 derived from Amagar's observations and given by SCHALKWIJK at

463

64

TABLE II.Isothermals of hydrogen at 20° C.								
d _A	Þ	pv _A (W)	^{pu} A.Schalkwijk	¢v _{A.} Амадат				
60.120	67.101	1.11610	1.11625					
64.059	71.729	1.11966	1.11936					
67.507	75.797	1.12281	1.12211					
70.531	79.344	1.12494	1.12454					
73.853	83,266	1,12746	1.12723	~ *				
77.470 ·	87.580	1.13043	1.13017	1.13227				
[79.852	90.509	1,13349	1.13213	1.13425]				

the end of Comm. 70. No great value can be ascribed to the extrapolation by means of this formula, which is valid for pressures above 100 atmospheres from 100 down to 60 atmospheres, but in the neighbourhood of 90 atmospheres the formula probably represents correctly to one or two parts in a thousand what would follow from AMAGAT'S observations.

Leaving out of account the observation at 90 atmospheres on the ground of a priori doubt as to its accuracy, although from the next communication it will appear, that it is really affected by a much smaller error than the others and that it would lead to a different conclusion, our results would seem to show, that an extrapolation above 60 atmospheres with SCHALKWIJK's formula calculated for 4 to 60 atmospheres, although not giving the same accuracy in that region, is still sufficiently accurate to support the suggestion, that AMAGAT's value at 100 atmospheres is too high. The error would however be less than $\frac{1}{500}$, the amount deduced from SCHALK-WIJK's formula.

464