

Citation:

W.H. Keesom, On the second virial coefficient for monatomic gases, and for hydrogen below the Boyle-point, in:
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of germination of spores to that of disinfection. Three species were examined. With two of them development took place in accordance with the formula of the unimolecular reactions.

The reaction-(germinating) velocity of the third species however was not constant, but decreased progressively.

For the same species the orderly progress of disinfection and germination do not always agree as to their types (fig. 12).

Physics. — “*On the second virial coefficient for monatomic gases, and for hydrogen below the BOYLE-point*”. By W. H. KEESOM. Supplement N°. 26 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

§ 1. *Introduction.* In Suppl. N°. 25 (Sept. '12) a comparison was made between the experimental data at present available concerning the second virial coefficient, B , for monatomic gases, and the relations for the variation of B with temperature deduced in Suppl. N°. 24 (June '12) from certain definite assumptions concerning the structure and the mode of action of the molecules. In continuation of that investigation the present paper supplies a similar comparison for the monatomic gases, and also, in view of the correspondence obtained in § 3*d* of Suppl. No. 25 between these gases and hydrogen below the BOYLE-point, for hydrogen, too, in that region of temperature. Until such time as the theories introduced by NERNST and EINSTEIN concerning the application of the quantum hypothesis to the rotations of the molecules have been further developed, only the suppositions made in Suppl. No. 24*b* § 5 are of any account as simplified assumptions if the specific heats of those gases are taken into account; according to those assumptions the molecules behave as if they were smooth rigid spheres of central structure, attracting one another with a force which is a function of the distance between their centres and is directed along the line joining their centres. As was done towards the end of § 5 of Suppl. No. 24*b*, this function is more closely specified by assuming that the attraction potential may be put equal to $-r^{-q}$ where q is a constant¹⁾. It

¹⁾ For the present comparison is postponed with the assumption made by TANNER, Diss. Basel 1912, in which, for simplicity, the action of the attractive force is supposed to be completely localised in a thin concentric spherical shell surrounding the molecule supposed spherical.

is true that without further evidence one is rather disinclined to regard such a distance law for the attraction potential as a fundamental property of the monatomic atom, and, should agreement with experiment be obtained with any definite value of q , one would like to obtain a deeper insight into the structure of the atom which would lead to the same law of distance for the resultant of the probable electric forces originating at various points of the atom; yet it is still clear that the results eventually obtained in the present paper for the index q can give important indications of the direction in which one must look for the development of the correct atomic model.

§ 2. A comparison was first made between the experimental data and the hypothesis of rigid spheres of central structure exerting central attractive forces upon one another proportional to $r^{-(q+1)}$ where q is a constant (potential energy proportional to $-r^{-q}$). This was done, following § 2 of Suppl. No. 25, by moving the $\log B_N$, $\log T$ -diagram for the experimental substance over the \mathcal{F}_s , $\log hv$ -diagram, where, following equation (42) of Suppl. No. 24b,

$$\mathcal{F}_s = \log \left\{ 1 - \frac{3}{q-3} hv - \frac{1}{2!} \frac{3}{2q-3} (hv)^2 - \frac{1}{3!} \frac{3}{3q-3} (hv)^3 \dots \right\}. \quad (1)$$

For the meaning of h and v reference may be made to § 5 of Suppl. No. 24b. The scale was again 0.005 to the mm. and $\log hv$ was again drawn increasing in the direction opposite to that in which $\log T$ increases.

In this connection it is to be noted that when q is just slightly greater than 3, and then v must be taken small in comparison, the terms of equation (1) involving the square and higher powers of hv are small in comparison with the preceding term. The variation of B with temperature then becomes the same as in the case of the assumption of constant a_w and b_w . Hence comparison of experiment with the hypothesis of constant values of a_w and b_w can be made the same as comparison with the present assumption concerning the attraction potential with a value for q which is but slightly greater than 3.

§ 3. Argon, and hydrogen below the BOYLE-point.

a. In the case of argon ¹⁾ the deviations of the experimental points

¹⁾ As in Suppl. No. 25 § 3d the individual virial coefficients of Comm. No. 118b have been used. In Comm. No. 128, June 1912, KAMERLINGH ONNES and CROMMELIN gave values of $B_{\Lambda(71)}$ adjusted according to the temperature polynomial of the empirical equation of state; in these were included the lowest three temperatures, for which only a few points of the isotherms were observed and for which, individually, no sufficiently reliable values for the coefficients could be calculated; these, therefore, must be regarded as known with less certainty than

from the curves for q slightly greater than 3 (a_w and b_w const.), for $q=4$, and for $q=5$ were all found to be relatively small. With the experimental material at present available for this gas it is difficult to settle the question as to which of these three values gives the best agreement (cf. Fig. 1). An extension of the temperature region for which B is known for argon, particularly towards the region of lower temperatures, as is already contemplated by KAMERLINGH ONNES and CROMMELIN, will be (cf. Fig. 1) of the greatest assistance in settling the point.

b. From Fig. 1¹⁾ it is evident that the best agreement is obtained for hydrogen below the BOYLE-point (see in particular the points representing the lowest three temperatures) on putting $q=4$. (Compare fig. 1 of Suppl. N°. 25, on which may be placed fig. 3 of the same

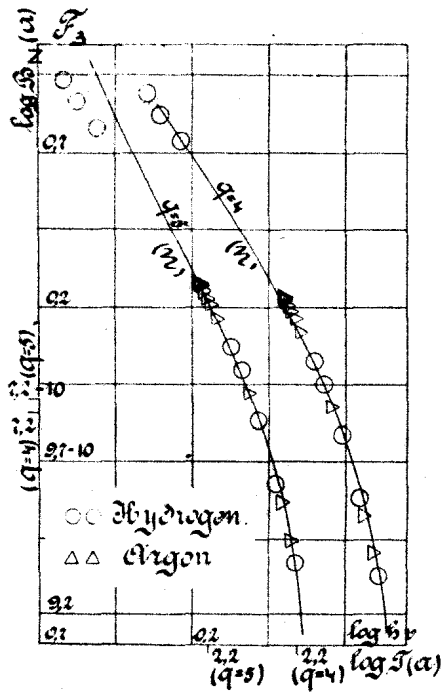


Fig. 1

paper for the argon points so as to exhibit the degree of agreement for q slightly greater than 3). Hence, as far as B is concerned, the behaviour of hydrogen below the BOYLE-point appears to be in pretty good agreement with the assumption of rigid spheres of central structure with an attraction potential²⁾ proportional to $-r^{-4}$.

If we assume that, as far as B is concerned, hydrogen behaves in a manner similar to the monatomic argon not only (as in Suppl. N°. 25 § 3d) within that region of temperature corresponding to the respective observational region for argon, but also towards lower temperatures, so that the series of argon points may be supplemented by means of

the others. As the calculations of the present paper may be regarded as another method of adjusting the virial coefficients, it seemed more reasonable to effect a direct comparison of the equation with the individual values. Comparison of the deviations occurring in this method which are independent of the adjustment to the empirical temperature polynomial, with those obtained by the latter method can then afford a basis of judging whether the deviations are greater or less than the degree of accuracy of the observations (cf. p. 646 note 1).

¹⁾ In this the point $\log T = 2,0$, $\log B_N = 6,5 - 10$ for H_2 coincides with the point $\log h_v = 9,551 - 10$, $\mathcal{F}_3 = 9,488 - 10$ when $q = 4$, and with the point $\log h_v = 9,815 - 10$, $\mathcal{F}_3 = 9,495 - 10$ when $q = 5$.

²⁾ BRAAK, Diss. Leiden 1908, p. 85, finds for H_2 at these low temperatures a

hydrogen below the BOYLE-point, then it follows from fig. 1¹⁾ that the attraction potential for argon is also proportional to $-r^{-4}$; but this conclusion must always be subject to reserve concerning the validity of the assumption just made down to the lowest temperatures, which has not yet been submitted to the test of experiment in the present case.

c. Following § 6 of Suppl. N^o. 25, the accompanying table gives the temperature variation of $\eta T^{-1/2}$ (η is the coefficient of viscosity) as given by the measurements of KOPSCH²⁾ compared with values of b_W^{-1} from

$$b_W = \frac{1}{2} n \cdot \frac{4}{3} \pi \sigma^3 \cdot e^{h\nu} \dots \dots \dots (2)$$

The latter relation appears on the separation of the attraction virial from the collision virial, as is indicated in equation (41) of Suppl. N^o. 24b. For ν the value $1.46 \cdot 10^{-14}$ is taken from the data given on p. 645 note 1 for the superposition of the diagram for H₂, A upon that for the attraction potential $-r^{-q}$ with $q=4$ (for the relative positions of the H₂ and the A diagrams see p. 425 note 3 of Suppl. N^o. 25).

t	$\frac{\eta}{\eta_{00C}} \sqrt{\frac{T_{00C}}{T}}$ argon	$\frac{b_{W00C}}{b_W}$ attraction potential $-r^{-q}$ $\nu = 1.46 \cdot 10^{-14}$
0	1.000	1.000
— 40.17	0.949	0.927
— 78.82	0.883	0.836
— 132.30	0.729	0.660
— 183.17	0.606	0.406

corresponding value for the index of r in the law of distance governing the force. From the ratio of the potential (heat of expansion) to the virial, REINGANUM, Ann. d. Phys. (4) 6 (1901), p. 546, deduces that the force is proportional to from r^{-4} to r^{-5} .

1) The deviations of the individual values of B_N from $q=4$ are of the same order of magnitude and are throughout in the same sense as their deviation from the values adjusted according to the empirical temperature polynomial.

2) W. KOPSCH. Diss. Halle 1909.

Comparison of the second and third columns would lead one to desire a smaller value for r , and this in turn would lead one to fix¹⁾ the index q more closely as lying between 3 and 4, but nearer 4 than 3²⁾. (Reference should be made, however, to the reserve of § 6 of Suppl. N^o. 25 qualifying the validity of these conclusions drawn from the influence of molecular attraction upon viscosity).

d. The $\log B$, $\log T$ -diagram for argon could not be made to coincide with the curve for constant doublets (Suppl. No. 25 § 3 *c*); this is in agreement with § 3 *d* and *c* of Suppl. No. 25 (and in particular with Figs. 2 and 3 of that paper) and also with the known caloric behaviour of this substance.

§ 4. *Helium*³⁾. Helium shows, at the higher temperatures, a deviation from all the hypotheses introduced in Suppl. No. 24 and tested in Suppl. No. 25 and in the present paper, for the maximum exhibited by B at these temperatures (cf. Figs. 15 and 16 of Suppl. No. 23, Math. Enc. V 10) is not given by any of these assumptions. It can well be that the peculiarity ascribed by KAMERLINGH ONNES to the helium atom at low temperatures is also present at these higher temperatures, so that one would have to assume the helium atom to be compressible, or to assume a relatively large increase in the attraction (cf. also note 4 on this page).

Moreover, the points for the lowest three temperatures cannot be regarded as known with the same degree of certainty as the others.

From both these circumstances it follows that the moving of the helium diagram over that for rigid spheres with an attraction potential $-r^{-q}$ ($q = \text{const.}$) can be made to take place in a manner to a very large extent quite arbitrary. Fig. 2 shows a superposition for the case $q = 4$. In this the point $\log T = 1,3$, $\log B_N = 6,5 - 10$ coincides with the point $\log hv = 9,478 - 10$, $\mathcal{F}_s = 9,688 - 10$.

With the exception of the highest temperatures⁴⁾ the coincidence is

¹⁾ The data given in note 1 p. 645 for the superposition in Fig. 1 would yield $v = 2.68.10^{-14}$ for $q = 5$.

²⁾ Cf. also C. BRAAK, loc. cit. p. 645 note 2.

³⁾ The individual virial coefficients for He are taken from Table II of Comm. No. 102a by KAMERLINGH ONNES; these are supplemented by the virial coefficients for $-252,072$ and $-258,082$ C., which have not yet been published but have kindly been placed at my disposal by Prof. KAMERLINGH ONNES (they have already been used for the construction of Figs. 15 and 16 of Suppl. No. 23) and also by the value for $4,029$ K. taken from Comm. No. 119 § 5b.

⁴⁾ At these temperatures Prof. KAMERLINGH ONNES tells me there is some uncertainty; improved values are being obtained.

not to be regarded as wholly bad, so that at the lower temperatures (below $-100^{\circ}\text{C}.$) the experimental results at present available for

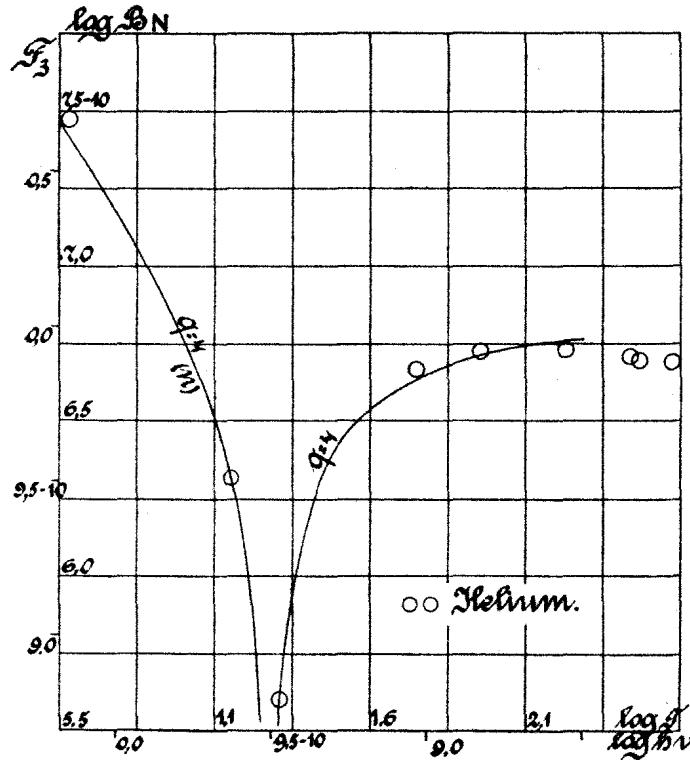


Fig. 2.

helium are, as far as B is concerned, compatible with the assumption of rigid spheres of central structure with an attraction potential proportional to $-r^{-4}$.

Having now reached the end of the considerations advanced in Suppl. N^o. 24, 25, and 26 it is my pleasant duty to thank Prof. KAMERLINGH ONNES for having invited me to participate in the investigation of the second virial coefficient for gases of low critical temperature, which he had undertaken with the object of reaching some conclusion regarding the structure and mode of action of the molecule, in particular with the help afforded by the application of BOLZMANN'S principles, and also for his kindness in leaving to me the continuation of the investigation within the particular region which I have treated in this series of papers.

Physics. — “On the HALL effect, and the change in resistance in a magnetic field at low temperatures. III. Measurements at temperatures between $+17^{\circ}$ C. and -200° C. of the HALL effect, and of the change in the resistance of metals and alloys in a magnetic field”. By BENGT BECKMAN. (Communicated by Prof. H. KAMERLINGH ONNES). Communication No. 130a from the Physical Laboratory of Leiden.

(Communicated in the meeting of September 28, 1912).

§ 1. *Introduction.* A communication was made by KAMERLINGH ONNES and the present writer to the meeting of June 29th 1912, of the results of measurements of the HALL-effect and of the increase of resistance in a magnetic field made by us at liquid hydrogen temperatures. In the present paper those results are extended to the temperatures which are obtainable with liquid ethylene and liquid oxygen, with the same experimental material and following the same experimental methods. It is of great importance that observations made with any particular substance should be distributed as uniformly as possible over the region of temperature under investigation. The measurements now completed make it possible for the results obtained at liquid hydrogen temperatures to be compared with those of former experimenters, who, without exception, proceed only to liquid air temperatures.

For a description of methods and material we may refer to the above Communication N^o. 129a. In order to complete the diagrams of the present paper the results for liquid hydrogen temperatures in the paper quoted are also indicated without making specific mention of the fact on each occasion. The present paper is confined to a discussion of the results obtained with bismuth.

I. Bismuth.

§ 2. *Change in the resistance of a wire of electrolytic bismuth.* The resistance of the bismuth wire B_{iA} was measured in eight different fields at five different temperatures: $T = 290^{\circ}$ K, 170° K, 139.5° K, 90° K, 72° K. These results are given in Table I. H is the field strength in gauss, w'_T the resistance in ohms in the magnetic field at the absolute temperature T , w_T the resistance without field at that temperature, and w_0 the resistance without field at 0° C.

Fig. 1 shows the increase of resistance as a function of the field at constant temperature (Isotherms), and fig. 2 the increase of resistance as a function of the temperature under constant field (Isopedals).