

THE SECOND VIRIAL COEFFICIENT FOR GASES: A
CRITICAL COMPARISON BETWEEN THEORETICAL
AND EXPERIMENTAL RESULTS

BY HENRY MARGENAU

SLOANE PHYSICS LABORATORY, YALE UNIVERSITY

(Received November 5, 1930)

ABSTRACT

On the basis of a recent theory developed by London the second virial coefficient of the following gases is computed: He, Ne, Ar, H₂, N₂, O₂, CO₂, NH₃, H₂O. For the latter two, which have a dipole moment, the contribution of the dipole interaction is also calculated. The results are compared graphically with experimental values. Except in the case of He and H₂, where the disagreement can be accounted for by the presence of zero point energy, the accordance is as good as is compatible with the inaccuracies involved in the calculation.

IN CLASSICAL mechanics it was necessary to attribute the attractive forces between molecules, demanded by the empirical equation of state, to the action of permanent or induced electric poles. Quadrupoles of considerable moment had to be assigned to molecules such as H₂ and the rare gases, which were known to carry no permanent dipoles. On the basis of the old atomic models the required assumption of quadrupoles was entirely reasonable, but it is inconsistent with the more uniform distribution of molecular charges calculated by wave mechanics. Moreover, molecular quadrupoles are not yet accessible to measurement, so that a theory based on their presence is unsatisfactory for its lack of verification. This difficulty was very successfully removed when Eisenschitz and London¹ recognized the significance of attractive forces appearing in the second order perturbation in the interaction problem of two H atoms. They showed that Van der Waals' constant a derived from these forces had the correct order of magnitude. In a recent paper London² made a more comprehensive study of these forces (arising from what he terms the "dispersion effect") and discussed in particular their relation to two other types of attractive forces existing between molecules having electric moments (resulting from Keesom's effect of "alignment" and Debye's induction effect).³ He also calculates the contribution to the molecular interaction energy of the dispersion effect and finds that this is for many gases the dominant constituent of the interaction, resulting in a van der Waals' a which is in good agreement with the value for a computed from critical data. This is indeed a most interesting and significant observation which goes far in confirming the validity of the theory. Now it is well known that van der Waals' equation with a independent of the

¹ R. Eisenschitz and F. London, *Zeits. f. Physik* **60**, 491 (1930).

² F. London, *Zeits. f. Physik* **63**, 245 (1930).

³ Cf.² for literature.

temperature does not represent the empirical equation of state, nor does the a value computed from critical data coincide of necessity with the factor of $1/T$ in the equation of state. It is the purpose of this communication to make a closer comparison between the predictions of London's theory and experimental data, and also to include in this comparison the results of a recent paper⁴ dealing with forces between dipole molecules. We shall express the second virial coefficient, B , as a function of the temperature and examine its correspondence to the empirically known values of B for various temperatures. The results can best be shown by graphs.

It will appear that the calculation of B is of necessity very crude because idealized assumptions and lack of accurate knowledge of certain quantities involved; hence one is justified to look for qualitative agreement only. The method used is essentially the same as that employed by London to compute a and is subject to the same errors.

NON-POLAR GASES

It may be recalled that B is the coefficient of $1/V$ in an expansion of pV/RT as a power series in $1/V$. It measures the deviation from Boyle's law for small concentrations (large V) and is given analytically by:

$$B = 2\pi N \int_0^{\infty} (e^{-\epsilon/kT} - 1)r^2 dr, \quad (1)$$

where ϵ is the interaction energy of two molecules expressed as a function of r , the distance between the molecules. If N is Avogadro's number, B is in cc per mole. The result of London's⁵ investigation concerning the dispersion effect is:

$$\frac{3}{4} \frac{\alpha^2 V_a}{r^6} \leq -\epsilon \leq \frac{3}{4} \frac{\alpha^2 V_i}{r^6} \quad (2)$$

where α is the polarizability, V_a the excitation potential, and V_i the ionization potential of the substance. An accurate theoretical expression for ϵ involves the energy values and matrix elements of the molecules and is, therefore, in general difficult to evaluate. At $r < d$ the interaction energy ceases to be given by (2), ϵ merges into the rapidly rising exponential curve characteristic of the valence forces.⁶ Here the assumption will be made that

$$\epsilon = +\infty \text{ for } r < d \quad (3)$$

corresponding essentially to the supposition that the molecules have a diameter d and are impenetrable. Refinements, such as introducing a dependence of d on T , as would be necessary to take account of the finite slope of the exponential curve at $r = d$ are possible but can be omitted in view of the general lack of precision of the premises on which we are compelled to make

⁴ H. Margenau, *Zeits. f. Physik* **64**, 584 (1930).

⁵ Reference 2, p. 256.

⁶ See Fig. 1 in the paper by Eisenschitz and London.

the calculation. We shall therefore assume an empirical value for d , independent of T . Moreover we shall put

$$\epsilon = -\frac{3}{4} \frac{\alpha^2 V_i}{r^6} \quad (4)$$

introducing thereby a considerable error. (There is reason to suppose that in general ϵ is nearer the upper limit in (2).)⁷ Expanding the exponential in (1) and performing the integration using (3) and (4) we obtain

$$B = \frac{2\pi N d^3}{3} \left\{ 1 - 0.75 \frac{\theta_1}{T} - 9.4 \times 10^{-2} \left(\frac{\theta_1}{T} \right)^2 - 1.4 \times 10^{-2} \left(\frac{\theta_1}{T} \right)^3 - 1.9 \times 10^{-3} \left(\frac{\theta_1}{T} \right)^4 - 2.2 \times 10^{-4} \left(\frac{\theta_1}{T} \right)^5 - 2.2 \times 10^{-5} \left(\frac{\theta_1}{T} \right)^6 - \dots \right\}, \quad (5)$$

where

$$\theta_1 = \frac{\alpha^2}{d^6} \frac{V_i}{k}.$$

If we put

$$\frac{2\pi N d^3}{3} = B_0$$

we have

$$\theta_1 = \frac{4\pi^2 N^2}{9k} \frac{\alpha^2 V_i}{B_0^2}.$$

B_0 can be determined from the empirical B curve and is essentially the same as van der Waals' b . The values of B_0 used in the computation of B are taken from Beattie and Bridgeman's⁸ work, except for O_2 and CO_2 . For these two gases the experimental and the theoretical B obtained from the data listed by the latter authors proved to be peculiarly discrepant, more so than could be explained by the crudeness of the calculation. It may be observed, however, that while for all other gases listed here Beattie and Bridgeman's B_0 is in the neighborhood of the usual b -values (as computed from critical data), it is considerably higher for O_2 and CO_2 (46 and 105). Also, in the case of He, Ne, A, N_2 their constants are derived from isothermals up to $400^\circ C$, whereas for the two gases in question only temperatures up to $100^\circ C$ were used. If now it is remembered that B_0 is the limit of B for high temperatures one could be led to suppose that though Beattie-Bridgeman's B_0 , together with their other constants, describe the behavior of O_2 and CO_2 very well over the range of lower temperatures, it may not actually be the limit which is here required.⁹

⁷ See reference (1), action of the continuous spectrum.

⁸ Cf. for instance *Zeits. f. Physik* **62**, 95 (1930).

⁹ At 258° Beattie and Bridgeman's constants for CO_2 give a value of B which is, compared to Amagat's measurements, about 50 percent too small.

If this supposition is erroneous the discrepancy spoken of would have to be admitted as unexplained. We have in the following assumed B_0 values for O_2 and CO_2 equal to the b -values from critical data, which are in agreement with our knowledge about the size of molecules derived from other sources (viscosity). If they are chosen the experimental and the theoretical B -curves agree quite well.

Table I contains the experimental data on the basis of which the computation of B was made. The ionization potentials of some of the gases may be in considerable doubt, but in view of the other uncertainty concerning the

TABLE I.

	$\alpha \times 10^{24}$	B_0	V_i (volts)	θ_1
He	0.20	14	24.5	92
Ne	0.39	20	21.5	150
A	1.63	39	15.4	500
H_2	0.81	21	16.4	440
N_2	1.74	50	17	385
O_2	1.57	32 (46)	13	580 (280)
CO_2	2.9	42 (105)	10	880 (180)

value of V to be used (Eq. (2)) this need not disturb us particularly. It is interesting to observe the magnitude of θ_1 . The calculation of van der Waals' a^{10} neglects higher powers of θ_1/T than the first, which seems unsatisfactory, even if due consideration is given to the large errors in our assumptions. CO_2 , though having a small dipole moment ($\mu = 0.06 \times 10^{-18}$) is included in the list of non-polar gases.

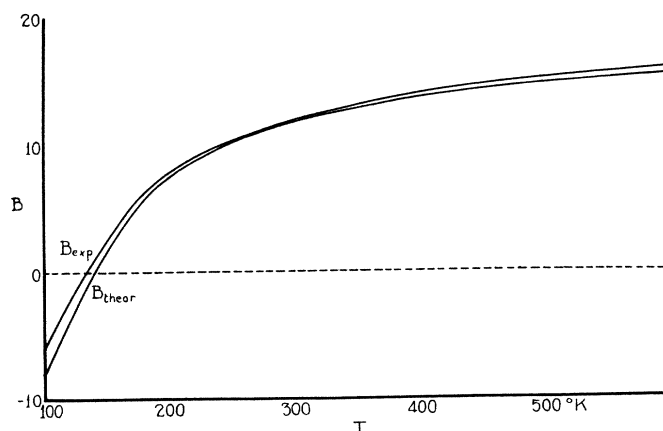


Fig. 1. Neon.

The curves in Figs. 1-7 show the results, the ordinates being in cc per mole, the abscissae in absolute degrees. Except for CO_2 (where the experimental B -values were taken from Amagat's diagram) the experimental points were computed from Beattie and Bridgeman's constants. The broken curves

¹⁰ F. London, reference 2.

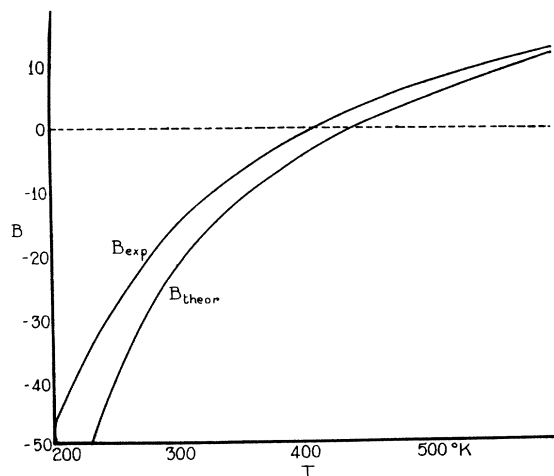


Fig. 2. Argon.

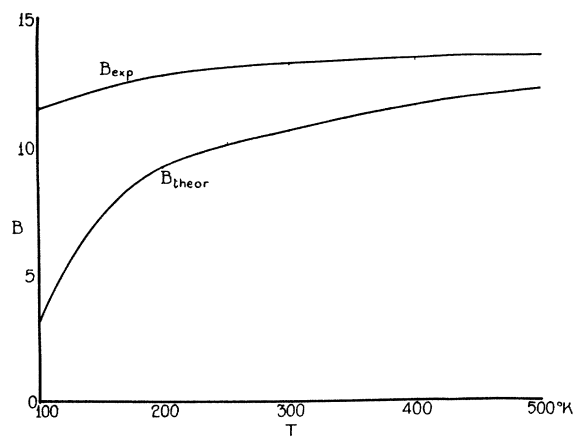


Fig. 3. Helium.

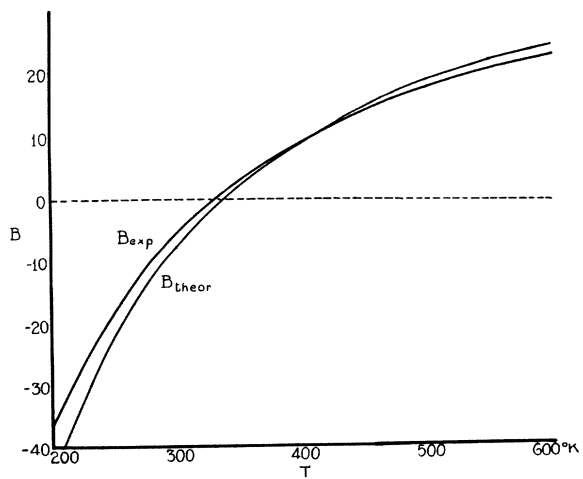


Fig. 4. Nitrogen.

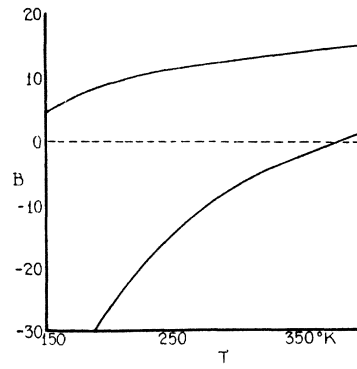


Fig. 5. Hydrogen.

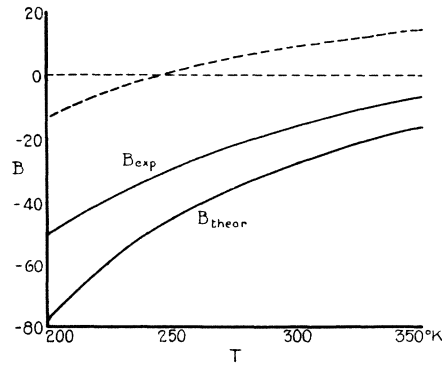


Fig. 6. Oxygen. The broken curve was computed on the assumption $B_0 = 46$.

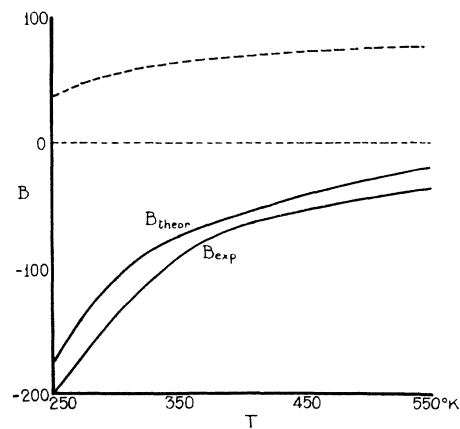


Fig. 7. Carbon dioxide. The broken curve was computed on the assumption $B = 105$.

in Figs. 6 and 7 represent the values obtained by using $B_0=46$ and 105 respectively. The agreement is seen to be good for all substances with the exception of He and H_2 , where the large deviation can be accounted for qualitatively by the zero point energy of the interacting molecules. As London has pointed out, this is negligible for molecules of larger mass, but would, in the case of He and H_2 , cause the theoretical curves to be displaced toward the experimental ones.

POLAR GASES

It has been shown¹¹ that for sufficiently high temperatures ($kT \gg h^2/8\pi^2A$) the virial coefficient of polar molecules is given by

$$B = \frac{N^2}{8\pi} \int_{\Omega} \int_0^{\infty} (e^{-V/kT} - 1) r^2 dr d\Omega \quad (6)$$

where the first integration is extended over all orientations of the two molecules and V is their classical potential energy in terms of r and the angles. For dipole molecules capable of polarization we find, if μ is the dipole moment,

$$V = \frac{\mu^2}{r^3} [-2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2)] \\ - \frac{\mu^2 \alpha}{2r^6} (3 \cos^2 \theta_1 + 3 \cos^2 \theta_2 + 2) \text{ neglecting small terms.} \quad (7)$$

The B computed from (6) will have to be added to the B resulting from the dispersion effect, but in doing so it must be remembered that the integration over r from 0 to d has already been counted, and the relevant part of (6) results from \int_d^{∞} . Expression (6) has been calculated by Falkenhagen.¹² He finds for several dipole gases, among them NH_3 and H_2O , good agreement between experimental data and the results of (6). This is very surprising from our present point of view, for it would seem to indicate that, if the dispersion effect also were taken into consideration the total B would be much too large. This difficulty, we feel, resolves itself on closer examination. It is impossible to check Falkenhagen's calculations in detail because the numerical values used in them are not all stated. (If we use the values of d derived from the B_0 of Table II, the agreement found by him is considerably disturbed.) We also note that his potential energy expression contains a polarization term (the second term in the brackets of (7)) twice as large as ours, which circumstance we are inclined to attribute to a numerical error in his G_2 . This tends to enlarge the contribution of (6) to B .

¹¹ H. Margenau, *Zeits. f. Physik* **64**, 584 (1930). In Eq. (1) of this paper a bar was omitted. It should read, of course,

$$B = 2\pi N^2 \int_0^{\infty} (e^{-V(R,\omega)/kT} - 1) R^2 dR.$$

¹² H. Falkenhagen, *Phys. Zeits.* **23**, 87 (1922).

In evaluating (6) we remember that

$$\int_{d\Omega} d\Omega = \int \int \int \int \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 d\phi_1 d\phi_2,$$

and obtain, after expanding the exponential, for the dipole contribution to the total B ,

$$\begin{aligned} B' = & -\frac{2\pi N d^3}{3} \left\{ 2z \frac{\theta_2}{T} + [0.33 + 0.73z^2] \left(\frac{\theta_2}{T}\right)^2 + [0.27z + 0.35z^3] \left(\frac{\theta_2}{T}\right)^3 \right. \\ & + [1.3 \times 10^{-2} + 0.21z^2] \left(\frac{\theta_2}{T}\right)^4 + 2.3 \times 10^{-2} z \left(\frac{\theta_2}{T}\right)^5 \\ & \left. + 5.2 \times 10^{-4} \left(\frac{\theta_2}{T}\right)^6 \right\}. \end{aligned} \quad (8)$$

Here

$$\begin{aligned} \theta_2 &= \frac{\mu^2}{k d^3} = \frac{2\pi N}{3k} \frac{\mu^2}{B_0} \\ z &= \frac{\alpha}{d^3} = \frac{2\pi N}{3B_0} \alpha. \end{aligned}$$

There is but little sense in using more terms since (1) would probably lose its validity for temperatures in which these terms become significant. The only dipole gases for which a comparison can be made at present are NH_3 and H_2O on account of the lack of experimental data for others. Table II shows the data from which the B values of these two gases were computed.

TABLE II.

	$\alpha \times 10^{24}$	B_0	V_i	$\mu \times 10^{18}$	θ_1	θ_2	z
NH_3	2.21	34	11	1.50	880	610	0.085
H_2O	1.48	34	13	1.84	470	920	0.055

B_0 for NH_3 was taken from Beattie and Bridgeman's work and the experimental B computed from their constants, while for H_2O it was necessary to take the critical data b , using for comparison experimental data by M. Jacob¹³ from which Falkenhagen¹⁴ has calculated the second virial coefficient.

In Figs. 8 and 9 the experimental curves are plotted together with values obtained from (a) (5), (b) (5) + (8). It is seen in both cases that the dipole effect is a very essential part of the interaction causing B . For NH_3 the agreement between B_{exp} and $B_{\text{disp+dipole}}$ is quite good, showing that the two effects here considered suffice to explain the molecular interaction. For H_2O , however, it is evident that they do not suffice, and that we must look, for quad-

¹³ M. Jacob, Zeits. f. Ing. 1912, p. 1980.

¹⁴ Reference 12.

rupole interaction to fill the space between the two lower curves of Fig. 9. It is plausible to assume that water molecules have a quadrupole moment, and one can without difficulty compute it from the last figure, for Keesom's

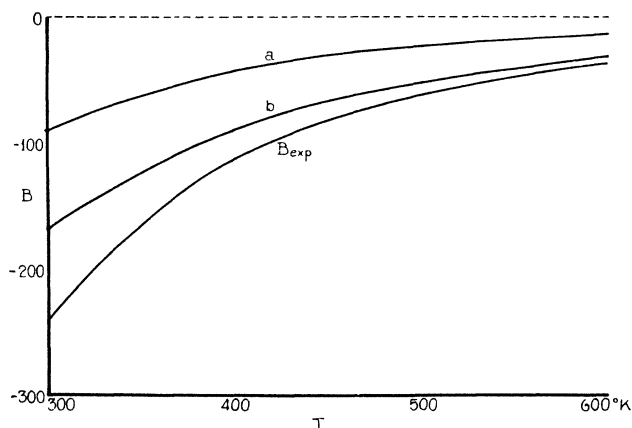


Fig. 8. Ammonia. Curve *a* represents values of *B* due to the dispersion effect, curve *b* those due to dispersion plus dipole effect.

theory, and the formulae he developed,¹⁵ have been shown to be applicable from the point of view of wave mechanics provided that the temperatures

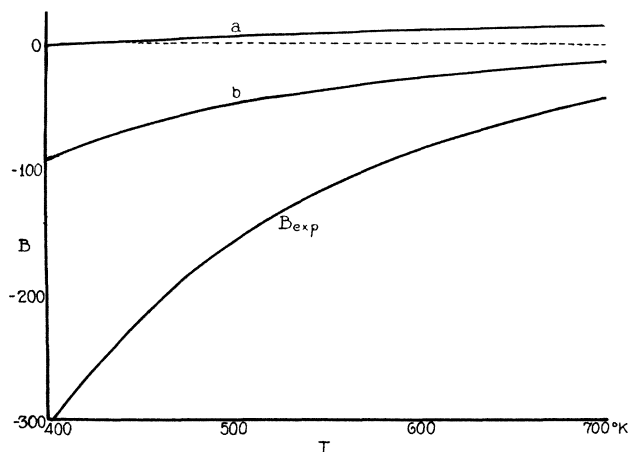


Fig. 9. H₂O. Curve *a* represents values of *B* due to the dispersion effect, curve *b* those due to dispersion plus dipole effect.

are sufficiently high.¹⁶ The result is about 5×10^{-26} for the quadrupole moment. But there appears to be no way at present of checking this value by independent experiments.

¹⁵ W. H. Keesom, *Phys. Zeits.* **22**, 129 (1921).

¹⁶ H. Margenau, reference 11.