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Experimental determination of the refractivity virial coefficients of atomic gases

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Values of the second refractivity virial coefficients B_R of the atomic gases He, Ne, Ar, Kr, and Xe have been measured with a recently improved differential-interferometric technique to a high degree of accuracy. This device basically consists of two coupled grating interferometers. One interferometer, with two similar cells in series, measures differentially the higher-order effects of density while the second interferometer, with two similar cells in parallel, simultaneously measures the absolute value of the refractive index. In the range of pressure investigated (up to 40 MPa), the third refractivity virial coefficient C_R becomes significant for the gases Ar, Kr, and Xe and the fourth refractivity virial coefficient D_R becomes significant for Xe. The agreement between our experimental B_R and the theoretical prediction based on the classical dipole–induced-dipole model is fairly good for Ar, Kr, and Xe but poor for He and Ne. For He and Ne, however, good agreement is obtained when a semiclassical approach is used. Accurate values of the first refractivity virial coefficients A_R were determined independently by making absolute measurements of the refractive index as a function of pressure.

I. INTRODUCTION

The purpose of this paper is to investigate the density dependence of the refractivity of atomic gases in order to obtain accurate values of the refractivity virial coefficients. The molar refraction R_m is defined as

$$R_m = (n^2 - 1)/(n^2 + 2)\rho \tag{1}$$

and can be expanded as a power series in the density ρ (in moles per unit volume[1,2]):

$$R_m = A_R + B_R\rho + C_R\rho^2 + D_R\rho^3 + \cdots, \tag{2}$$

where A_R, B_R, C_R, D_R,... are, respectively, the first, second, third, fourth, etc. refractivity virial coefficients.

Measurements of A_R yield values for atomic polarizabilities, while B_R, C_R, and higher terms give (in principle) information on atomic interactions.

A_R, the limiting value of R_m in the case of a very dilute gas ($\rho \rightarrow 0$), can be determined from isothermal measurements of the refractive index as a function of pressure.[3-14]

B_R, C_R,..., which depend directly on the effects of molecular interactions on the refractivity of gases, are determined with the use of a differential-interferometric technique first proposed by Buckingham, Cole, and Sutter,[2] and subsequently used by Buckingham and Graham[7] and St-Arnaud and Bose.[8] The method involves a differential measurement of the total optical path when a gas is decompressed from one cell into a similar evacuated cell. To obtain precise values of B_R, C_R,..., the overflow experiments must be carried out up to the highest pressures practicable.[7,12-14]

Much progress has been made in recent times in the development of the differential-interferometric technique for measurements at high pressures.[10-12] This was accomplished by means of the design of a device basically consisting of two coupled interferometers. The new optical apparatus was used for the direct measurement of the excess contribution to R_m of the atomic gases up to 40 MPa.

In this paper we present our experimental results of B_R for He, Ne, Ar, Kr, and Xe. For Ar, Kr, and Xe, C_R is significant in the range of pressure investigated. A novel feature of the measurements on Xe is the significant contribution of the fourth term $D_R\rho^3$ [see Eq. (2)]. Separate measurements of the refractive index as a function of pressure were made and accurate values of the first refractivity virial coefficient A_R were determined from this. Calculations of B_R based on simple theoretical models are presented. Comparison of our results with experimental and theoretical coefficients from the literature are also presented.

II. EXPERIMENTAL PROCEDURE

The independent determination of B_R, C_R,..., is based on the measurement of the excess contribution of the function $(n-1)\rho^{-1}$, which is directly related to the refractive index virial coefficients B_n, C_n, etc., defined by

$$(n-1)\rho^{-1} = A_n + B_n\rho + C_n\rho^2 + \cdots. \tag{3}$$

If one compares the coefficients of ρ^i in Eq. (3) with those in Eq. (2) it is readily shown that

$$A_R = 2A_n/3, \tag{4}$$

$$B_R = 2B_n/3 - A_n^2/9, \tag{5}$$

$$C_R = 2C_n/3 - 2A_nB_n/9 - 4A_n^3/27. \tag{6}$$

The direct determination of B_n, C_n,..., consists of measuring the change in the sum of optical path lengths of two

identical sample cells during an overflow experiment. Initially, one cell is filled with the gaseous sample at density ρ_1 and the other is evacuated. Then, by opening the expansion valve between the two cells, the sample is shared with the previously evacuated cell, and at the end of the expansion procedure the initial density ρ_1 is halved. Due to the halving of the density ($\rho_2 = \rho_1/2$) and the doubling of the length of the cell filled with the sample ($l_2 = 2l_1$), the linear term in density ($lA_n\rho$) remains the same before and after the overflow experiment. If $n-1$ were proportional to the density, the change of optical path lengths given by Eq. (7) would be zero, but departures from proportionality arising from molecular interactions and bulk polarization effects produce a change of the optical path lengths that is directly related to B_n, C_n,... .

For perfectly matched cells we thus obtain

$$\lambda_0(K_1 - K_2) = l[(n_1-1) - 2(n_2-1)]$$
$$= l(\tfrac{1}{2}B_n\rho_1^2 + \tfrac{3}{4}C_n\rho_1^3 + \cdots), \quad (7)$$

when n_1 and n_2 are the initial and final values of the refractive index, $\lambda_0 K_1$ and $\lambda_0 K_2$ are the initial and final values of the measured change of the optical path lengths referred to vacuum, λ_0 is the vacuum wavelength of the laser light, and l is the length of each cell. Because the density dependence of $(n-1)\rho^{-1}$ is very small, the number of fringes K_1 and K_2 are nearly equal. To reduce the errors resulting from taking the difference between two numbers, K_1 and K_2, of nearly equal magnitude, the following more accurate procedure is employed. One measures the change in the optical path lengths directly during the actual expansion procedure by counting the change $\Delta K = (K_1 - K_2)$ of the interference fringes instead of measuring K_1 during the filling procedure and K_2 after the expansion procedure while venting the sample to vacuum. Nevertheless, one still has to measure K_1, the independent variable of $\Delta K = \Delta K(K,T)$.

In practice, it is not possible to construct identical cells. The unavoidable mismatch in cell lengths and volumes lead to systematic errors in the fringe count ΔK. These mismatch effects are eliminated by carrying out two successive expansions in opposite directions.[3,7-14]

The expansion from cell A to cell B gives the relation $\Delta K_{AB}(K_A,T)$. The initial state of cell A filled with the sample gas is determined by the variable $K_A(\rho,T)$ or $K_A(P,T)$. Similarly, if cell B contains gas and cell A is evacuated, the expansion from cell B to cell A gives the relation $\Delta K_{BA}(K_B,T)$.

When the two relations are added, the systematic errors due to the mismatch in cell lengths and volumes in ΔK_{AB} and ΔK_{BA} are cancelled. One then obtains the relation between the measured variables and the refractive index virial coefficients B_n, C_n,..., which is given by

$$F = \Delta K_{AB}/K_A + \Delta K_{BA}/K_B$$
$$= B_n(2A_n^2)^{-1}[(n_A-1) + (n_B-1)] + (3A_nC_n - 4B_n^2)$$
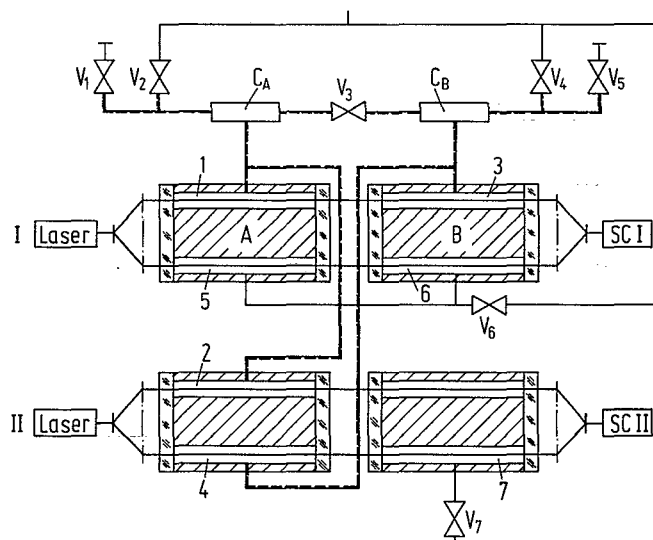$$\times (4A_n^4)^{-1}[(n_A-1)^2 + (n_B-1)^2] + \cdots. \quad (8)$$

FIG. 1. Schematic drawing of the two coupled interferometers I and II for isothermal differential measurements of the refractive index function F and for isothermal absolute measurements of the refractive index $n(P,T)$. Cells 1, 2, 3, and 4 are used for the measurements of F, and cells 5, 6, and 7 for the $n(P,T)$ measurements. V_1 to V_7 represent different valves, C_A and C_B two compensating chambers, and SC I and SC II two signal converters (optic-electric).

Here, F is the so-called refractive index function, $n_A - 1 = K_A\lambda_0/l$ and $n_B - 1 = K_B\lambda_0/l$.

The measurements are carried out in such a way that K_A is nearly equal to K_B. This increases the efficiency of the error compensation, because the systematic errors in ΔK_{AB} and ΔK_{BA} approach each other when K_A is equal to K_B. The quantity $(n_A-1)^2 + (n_B-1)^2$ in the second term of Eq. (8) can then be approximated by $[(n_A-1) + (n_B-1)]^2/2$. By making a least-squares fit of Eq. (8) to a polynomial in $[(n_A-1) + (n_B-1)]$, one can determine B_n from its slope and the significant succeeding coefficients C_n, D_n,... from its curvature.

The measurement of the refractive index function F at high pressures (40 MPa) is very difficult and time consuming because refractivity virial effects are very small and as such are unsuitable for a satisfactory adjustment of the allowable flow rate in the expansion valve during the overflow procedure. If the flow rate is exceeded by a small amount, a collapse of the interference fringe count will occur.

To overcome these difficulties, Achtermann and co-workers[10,12] have improved the differential-interferometric technique by developing a device consisting of two coupled grating interferometers. The experimental apparatus which was developed and constructed at the Institut für Thermodynamik, Universität Hannover has been previously described in detail.[12-14] Both the differential measurements of $\Delta K(K,T)$ to determine B_R, C_R,..., and the separate measurements of the refractive index $n(P,T)$ to determine A_R have been carried out with the same interferometer system (Fig. 1).

The differential measurements to obtain ΔK take place

in interferometer I with the two cells 1 and 3 in series. Interferometer II is used to measure K, the independent variable of ΔK, which determines the initial state of the overflow experiment. To provide the total fringe count K, the two cells 2 and 4 of interferometer II are in parallel. The correlated cells are connected with each other (Fig. 1). The coupled interferometers make it possible to obtain ΔK and K simultaneously during the overflow experiment.

Each cell system (A and B) contains a compensation chamber (C_A and C_B) which facilitates the controlled overflow experiment because the volume of each cell, less than 1 cm^3, is very small. The volume of each compensation chamber is approximately 350 cm^3.

In the following we consider the expansion procedure from the cell system A with the cells 1 and 2 to the cell system B with the cells 3 and 4.

The changes of the index of refraction during the overflow process are identical in the expansion cells 1 and 2, as well as in the compression cells 3 and 4. The change of the fringe count in the individual cells 1 and 2 is given by

$$\Delta K_1 = \Delta K_2$$
$$= l\lambda_0^{-1}[(n_1-1)-(n_2-1)]$$
$$= l\lambda_0^{-1}[\tfrac{1}{2}A_n\rho_1 + \tfrac{3}{4}B_n\rho_1^2 + \tfrac{7}{8}C_n\rho_1^3 + \cdots], \qquad (9)$$

and, equivalently, in the initially evacuated cells 3 and 4 with $n_1 = 1$

$$\Delta K_3 = \Delta K_4$$
$$= l\lambda_0^{-1}[-(n_2-1)]$$
$$= l\lambda_0^{-1}[-(\tfrac{1}{2}A_n\rho_1 + \tfrac{1}{4}B_n\rho_1^2 + \tfrac{1}{8}C_n\rho_1^3 + \cdots)]. \qquad (10)$$

In interferometer I the changes of the index of refraction take place in the same beam. In this case we obtain the resultant change of the fringe count $\Delta K_{AB,I}$ by adding the individual values of ΔK_1 and ΔK_3,

$$\Delta K_{AB,I} = \Delta K_1 + \Delta K_3 = l\lambda_0^{-1}(\tfrac{1}{2}B_n\rho_1^2 + \tfrac{3}{4}C_n\rho_1^3 + \cdots).$$
$$(11)$$

Due to the partial compensation between ΔK_1 and ΔK_3, the resultant change of the fringe count, $\Delta K_{AB,I}$, is only related to terms with the higher-order refractive index virial coefficients B_n, C_n,... .

In interferometer II the changes of the index of refraction take place in the two different beams (see Fig. 1) and hence the effect of compensation is avoided. In this case we obtain the resultant change of the fringe count $\Delta K_{AB,II}$ on subtraction of the individual values of ΔK_2 and ΔK_4,

$$\Delta K_{AB,II} = \Delta K_2 - \Delta K_4$$
$$= l\lambda_0^{-1}(A_n\rho_1 + B_n\rho_1^2 + C_n\rho_1^3 + \cdots) = K_1 = K.$$
$$(12)$$

Due to the lack of compensation between ΔK_2 and ΔK_4, the cumulative change of fringes in interferometer II, $\Delta K_{AB,II}$, is not only related to terms containing the higher-order refractive index virial coefficients B_n, C_n,..., but also

to the linear term containing the first refractive index virial coefficient A_n. The value of $\Delta K_{AB,II}$ is thus equal to an absolute refractive index measurement, which corresponds to a change of density between zero (initially evacuated cell) and the density ρ_1 (initially filled cell). The integrated fringe count is equal to an absolute fringe count, K, the independent variable of the differentially measured value of ΔK.

The fringe count K is about a hundredfold of the fringe count ΔK. Interferometer II therefore acts as a guiding instrument for the accurate control of decompression during the overflow experiment. The changes in fringes are indicated by the rotating electric fields produced from the optical signals of the grating interferometers. The flow rate of the expansion valve (V_3) placed between C_A and C_B is indicated exactly by the sensitive rotating electric field of interferometer II which is about 100 times faster than that of interferometer I.

It is worth noting that interferometer II is mainly designed for adjusting the maximum flow rate in the expansion valve in order to optimize the direct fringe count of ΔK and for making direct differential measurements of ΔK possible in high-pressure regions.[12]

The isothermal measurement of the refractive index as a function of pressure, $n(P,T)$, to determine A_R is carried out with the same two interferometers I and II as are used for the $\Delta K(K,T)$ measurements. For the determination of the refractive index of the sample, interferometer I with cells 5 and 6 is used (see Fig. 1). Interferometer II with cell 7 is used to determine the pressure from the refractive index of nitrogen measured at a fixed temperature. The relation between the pressure and the refractive index of nitrogen has been previously established with the use of a precision piston gauge.[15] The coupled interferometers make it possible to obtain the refractive index and the pressure simultaneously during the expansion run. The apparatus and the procedure for the absolute measurement of the refractive index as a function of pressure have recently been described.[10–13]

III. EXPERIMENTAL RESULTS

Determination of the first and the higher-order refractivity virial coefficients have been made for the atomic gases He, Ne, Ar, Kr, and Xe with the use of the Hannover apparatus. All the gases investigated were obtained commercially, and were used without further purification. The supplier and purity specification of our gas samples are given in Table I.

A. Measurement of $n(P,T)$ and determination of A_R

The absolute refractive index is obtained by counting the changes in the interference fringes while venting the gas under examination to vacuum. This reference with respect to vacuum is necessary because interferometric measurements record only changes in the refractive index. Absolute refractive indices $n(P,T)$ are calculated from the interference fringe count by means of the data reduction formula,

TABLE I. Supplier and minimum stated purity of the gases used.

Gas	Supplier	Stated minimum purity (%)	Nature of main impurities
He	Linde	99.996	$O_2 < 5$ ppm, $N_2 < 20$ ppm, $H_2O < 5$ ppm, $C_nH_m < 1$ ppm, Ne < 10 ppm
Ne	Linde	99.995	$O_2 < 2$ ppm, $N_2 < 5$ ppm, $H_2O < 3$ ppm, $C_nH_m < 0.2$ ppm, He < 40 ppm
Ar	Linde	99.998	$O_2 < 3$ ppm, $N_2 < 10$ ppm, $H_2O < 5$ ppm, $C_nH_m < 0.2$ ppm
Kr	Linde	99.99	$O_2 < 2$ ppm, $N_2 < 20$ ppm, $H_2O < 5$ ppm, $C_nH_m < 1$ ppm, $H2 < 2$ ppm, Xe < 50 ppm, Ar < 10 ppm
Xe	Linde	99.99	$O_2 < 2$ ppm, $N_2 < 10$ ppm, $H_2O < 5$ ppm, $C_nH_m < 1$ ppm, Kr < 60 ppm, Ar < 10 ppm

FIG. 2. Experimental values of RTL_n/P for He, Ne, Ar, and Kr at 303.15 K and Xe at 303.15 and 348.15 K. The intercept gives A_R the zero density (or L_n) limit. To avoid the overlapping of experimental points, we plotted only a reduced number of measured values. The best least-square fit of the experimental values of RTL_n/P are also plotted.

$$n(P,T) = K(P,T)\lambda_0/l_n + 1, \tag{13}$$

where $K(P,T)$ is the total fringe count while isothermally venting the gaseous sample at pressure P to vacuum and l_n is the length of the cell (filled with the sample) at the temperature T of the fluid.

The first refractivity virial coefficient A_R can be determined directly by means of an independent method in which only isothermal (P,n,T) measurements are involved. The density ρ in Eqs. (1) and (2) can be replaced with the use of the thermodynamic virial equation of state

$$Z = P/\rho RT = 1 + B(T)\rho + C(T)\rho^2 + \cdots, \tag{14}$$

where $B(T), C(T),\ldots$ are the virial coefficients of the expansion of the compressibility factor Z as a power series in density, and R is the molar gas constant. Dividing Eqs. (1) and (2) by Eq. (14) and substituting ρ by the inverse function of

$$L_n = A_R\rho + B_R\rho^2 + C_R\rho^3 + \cdots,$$

given by

$$\rho = L_n/A_R - (L_n/A_R)^2 B_R/A_R + \cdots,$$

we obtain

$$RTL_n/P = A_R + [B_R - B(T)A_R]L_n/A_R + \cdots, \tag{15}$$

or, equivalently,

$$RTL_n/P = A_R + [B_R - B(T)A_R]P/RT + \cdots. \tag{16}$$

For convenience, the symbol L_n is used for the term $(n^2 - 1)/(n^2 + 2)$. When one plots experimental values of RTL_n/P vs L_n [see Eq. (15)] or RTL_n/P vs P [see Eq. (16)], one can determine A_R from the intercept with an accuracy of a few parts in 10^4.

In Fig. 2 we plotted the experimental values of RTL_n/P as a function of L_n for the five gases investigated. To avoid the overlapping of experimental points we plotted only a reduced number of the values measured. For the purpose of comparison, our observed values of A_R with
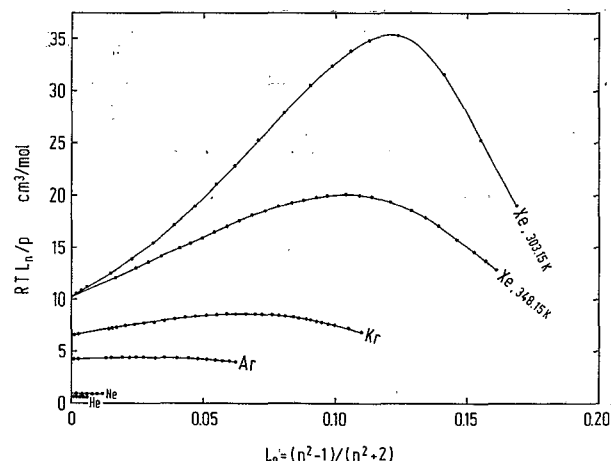
their uncertainty are summarized in Table II together with the experimental literature values.

B. Measurements of $\Delta K(K,T)$ and determination of B_R, C_R, and D_R

The differential measurements were made on the 303.15 K isotherm and at pressures up to 40 MPa. The value of the critical isotherm of Xe (289.73 K) which was close to the measurement isotherm of 303.15 K forced us to carry out the differential measurements of Xe on the 348.15 K isotherm.

The contribution to the fringe count ΔK_{AB} and ΔK_{BA} arising from the distortion of cells and compensation chambers under pressure is rather significant. This effect not only depends on the geometry of the cells and compensation chambers but also on the type of sample gas used. Since in our case the volume of the cells (2 cm^3) is negligible compared to the volume of the compensation chambers (700 cm^3), only the cylindrical pipe of the compensation chamber with external and internal radii R_e(7 mm) and R_i(4 mm) at a given initial pressure P_1 determines the systematic error in ΔK_{expt} due to distortion. If we also take into account the real gas behavior expressed by Z_1 and Z_2, the compressibility factor values before and after the expansion, the correction to the fringe count, ΔK_{expt}, due to distortion of the compensation chamber is

$$\Delta K_{\Delta V} = RT\lambda_0 K_1^2(\Delta R_i/R_i + \Delta L/2L)$$
$$\times (2Z_1 - Z_2)/lA_nP_1. \tag{17}$$

According to Landau and Lifshitz,[16] the apparatus constant of the compensation chamber $\Delta R_i/R_iP$ is given as

$$\Delta R_i/R_iP = [R_e^2(1+\sigma) + R_i^2(1+\sigma)(1-2\sigma)]/(R_e^2 - R_i^2)E], \tag{18}$$

TABLE II. Summary of the present experimental and literature values for A_R, B_R, and C_R. Experimental values for the refractivity virial coefficients have been determined at the vacuum wavelength of $\lambda_0 = 632.99$ nm. The values of A_ϵ and B_ϵ are given for comparison purposes.

Gas	T (K)	A_R (cm³/mol)	B_R (cm⁶/mol²)	C_R (cm⁹/mol³)	A_ϵ (cm³/mol)	B_ϵ (cm⁶/mol²)	Reference
He	303	0.5213±0.0002	−0.068±0.010				This work
	323	0.5213±0.0001	−0.068±0.010				Achtermann et al.[a]
	294		−0.062				Dacre[b] (calculated)
	303		−0.059				This work (calculated)
	323				0.519±0.001	−0.06±0.04	Orcutt and Cole[c]
	303				0.5210±0.0002	−0.059±0.009[d]	Kirouac and Bose[e]
	323				0.5196±0.0002	−0.07±0.01	Huot and Bose[f]
	323					−0.070	Huot and Bose[f] (calculated)
Ne	303	1.0012±0.0002	−0.11±0.02				This work
	298	0.9992	−0.14±0.14				Burns et al.[g]
	299	1.0032	−0.06±0.14				Buckingham and Graham[h]
	303		−0.157				This work (calculated)
	323				0.9969±0.0003	−0.12±0.06	Huot and Bose[f]
	323					−0.15	Huot and Bose[f] (calculated)
Ar	303	4.1955±0.0003	1.75±0.05	−85.4±2.0			This work
	323	4.196±0.0002	1.76±0.05	−86.6±2.0			Achtermann et al.[a]
	298	4.1973±0.0005	1.49±0.15	−79.0±10.0			Coulon et al.[i]
	299	4.207	2.16±0.34				Buckingham and Graham[h]
	298	4.194	1.57±0.58				Burns et al.[g]
	298		2.55				Burns et al.[g] (calculated)
	303		2.26				This work (calculated)
	303					1.22±0.09	Huot and Bose[f]
	322				4.142±0.002	0.39±0.20	Orcutt and Cole[c]
	323				4.1397±0.0006	0.72±0.12	Bose and Cole[j]
	322					0.48	Dacre[k] (calculated)
Kr	303	6.414±0.001	5.96±0.06	−275.0±10.0			This work
	298	6.362	6.23±1.55				Burns et al.[g]
	298		8.11				Burns et al.[g] (calculated)
	303		7.06				This work (calculated)
	322				6.267±0.003	5.6±0.3	Orcutt and Cole[c]
	323				6.273±0.002	4.3±0.7	Huot and Bose[f]
	322					4.68	Dacre[l] (calculated)
Xe	303	10.345±0.002					This work
	348	10.344±0.002	28.5±0.5	−1802.0±50.0			This work
	298	10.359	25.50±2.85				Burns et al.[g]
	298		25.8				Burns et al.[g] (calculated)
	348		25.23				This work (calculated)
	323					22.0±0.25	Bose[m]
	323				10.122±0.002	32±2	Huot and Bose[f]
	322					21.6	Dacre[l] (calculated)

[a]Reference 14.
[b]Reference 31.
[c]Reference 17.
[d]The uncertainty in the paper by Kirouac and Bose (Ref. 18) given as ±0.0009 is changed to ±0.009 because of a printing error in the earlier paper.
[e]Reference 18.
[f]Reference 21.
[g]Reference 3.
[h]Reference 7.
[i]Reference 22.
[j]Reference 39.
[k]Reference 35.
[l]Reference 36.
[m]Reference 40.

where ΔR_i is the change in radius due to the pressure P, E is the Young's modulus (2×10^{11} Pa), and σ is the Poisson ratio (0.3).

The apparatus constant of the compensation chamber due to the axial distortion $\Delta L/2LP$ is given as

$$\Delta L/2LP = R_i^2/(R_e^2 - R_i^2)2E, \qquad (19)$$

where ΔL is the change in length L ($L = 6962$ mm) of the compensation chamber due to the pressure P.

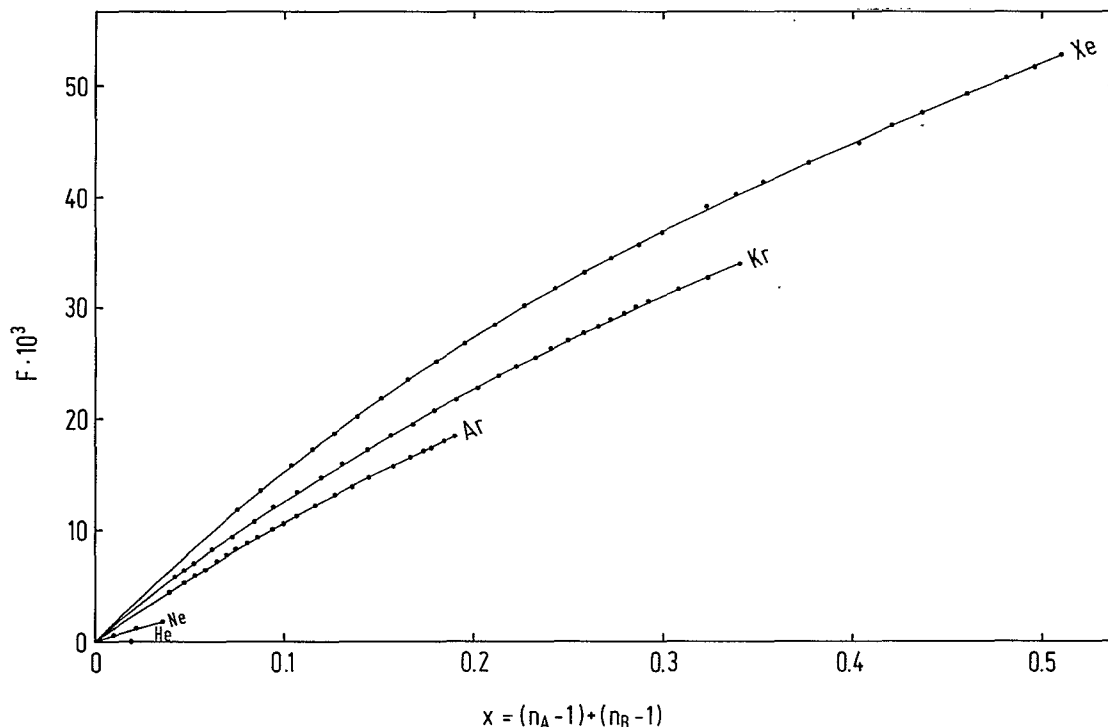Assuming linearity between pressure and density, the

FIG. 3. Experimental values of the refractive index functon F at 303.15 K for He, Ne, Ar, and Kr and at 348.15 K for Xe. The best least-squares fit of the experimental values of F are also plotted. For convenience, the symbol x is used for the independent variable $[(n_A-1)+(n_B-1)]$.

expansion volume due to distortion of the two compensation chambers remains the same before and after the overflow experiment $(\Delta V_1 = \Delta V_2 = \Delta V)$ but, due to the halving of the density $(\rho_2 = \rho_1/2)$, additional gas $(\Delta V \rho_1/2)$ is forced into the optical path of the cells which decreases the observed fringe count ΔK_{expt}.

The corrected value ΔK is given by

$$\Delta K = \Delta K_{\text{expt}} + \Delta K_{\Delta V}. \tag{20}$$

Since the form of the compensation chambers is nearly ideal (long pipes), the calculation of its distortion under pressure is very satisfactory. The effect of error correction, $\Delta K_{\Delta V}/\Delta K$, is largest at the highest pressure.

The significant values for B_n, C_n, and D_n can be obtained from the best least-squares fit of the error-corrected experimental values of the refractive index function F in a polynomial of the form

$$F = a_1 x + a_2 x^2 + \cdots, \tag{21}$$

where $x = [(n_A - 1) + (n_B - 1)]$, $a_1 = B_n/2A_n^2$, $a_2 = (3A_n C_n - 4B_n^2)/8A_n^4$, etc.

We found that, in the range of $[(n_A - 1) + (n_B - 1)]$ investigated, the best least-squares fit of F for Ne is given by a polynomial of the first degree, for Ar, Kr by a polynomial of the second degree, and Xe by a polynomial of the third degree. Using the polynomial of the form $F = a_0 + a_1 x + \cdots$, we found that the intercept a_0 was practically zero within experimental error for all gases investigated.

In contrast with gases Ne, Ar, Kr, and Xe, our measurements of $\Delta K(K,T)$ for He at 303.15 K and pressures

up to 35 MPa give for the function $F(x,T)$ a straight-line relationship along the x axis. We measured $\Delta K(K,T)$ for He at 35 MPa, and repeated the experiments ten times. The measured mean value of the fringe count for He with a cell length of $l = (47.519 \pm 0.002)$ mm yielded $(\Delta K_{\text{expt},AB} + \Delta K_{\text{expt},BA})/2 = -0.33 \pm 0.05$. (For the absolute fringe count, the value of $K = 714$ was measured.) At 35 MPa, the systematic error for $\Delta K_{\Delta V}$, Eq. (17), was calculated to be 0.31. For He, the corrected value of the fringe count, ΔK, is practically zero when these values for ΔK_{expt} and $\Delta K_{\Delta V}$ are substituted into Eq. (20). Consequently, each of the terms of the series F, Eq. (8), must also be zero within the experimental error. Therefore, the value of $B_R = -0.068$ cm^6/mol^2 was only due to the contribution of the term $-A_n^2/9$, Eq. (5). For most of the gases investigated in this paper and in our previous work,[14] we obtained positive values for B_R due to the fact that $2B_n/3 > A_n^2/9$ [see Eq. (5)]. However, in the case of He where the term $2B_n/3$ is zero and in the case of Ne where $2B_n/3 < A_n^2/9$, B_R is found to be negative.

Our values for B_R and C_R are summarized in Table II together with literature values. The third refractivity virial coefficients C_R of Kr and Xe, and the fourth refractivity virial coefficient D_R of Xe (see Sec. IV) are presented for the first time. The quoted uncertainties for B_R, C_R, and D_R are obtained by taking three standard deviations from the least-squares fit in addition to errors due to cell distortion and adsorption.[12]

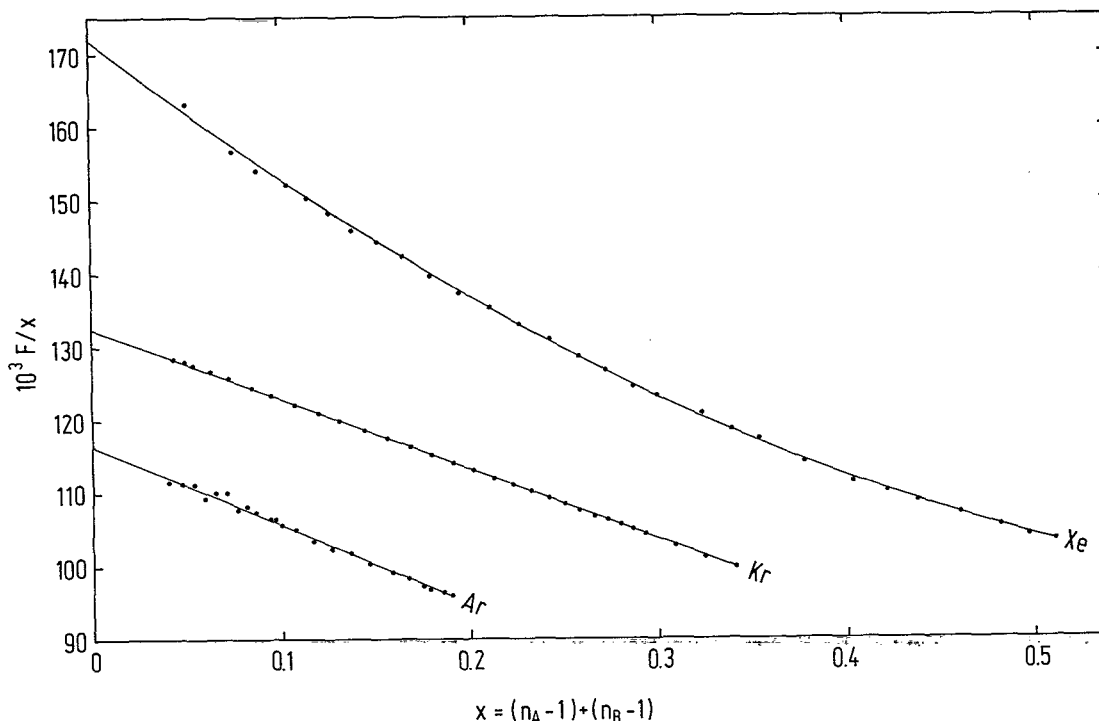In Fig. 3 we plotted the functions F for the atomic

FIG. 4. Plots of F/x for Ar and Kr at 303.15 K and for Xe at 348.15 K. For convenience, the symbol x is used for the independent variable $[(n_A-1)+(n_B-1)]$. Points are experimental and the curves are the least-squares fit.

gases. The method generally used to fit the data properly consists of fitting the data to successively higher-order polynomials, and the polynomial giving the lowest standard deviation is chosen.

We also determined the coefficients B_n and C_n for Ar, Kr, and Xe by graphical techniques based on interrelated plots of the residual quantities of the refractive index function $F=a_1x+a_2x^2+\cdots$ in the relation

$$F/x=a_1+a_2x+\cdots. \tag{22}$$

To determine which of the coefficients a_1, a_2,... are significant, we plotted successive experimental values of F and F/x vs x. The intercept as well as the slope of the functions are unique to only one of the coefficients in the above relations, whereas the curvature can be influenced by more than one coefficient. In the graph F vs x, B_n is determined from the slope $a_1=B_n/2A_n^2$. The succeeding terms a_2, a_3,... determine the curvature. In the graph F/x vs x, B_n is determined from the intercept a_1. The next term a_2, which is the first term containing C_n, is the slope. Any curvature in F/x results from the succeeding terms a_3, a_4,... containing D_n, E_n, etc. Lack of curvature in F/x indicates that the contribution due to terms containing D_n and higher are not significant in the range of x investigated.

In Fig. 4 we plotted the experimental points of F/x vs x for Ar, Kr, and Xe. The results of Ar and Kr indicate no evidence of curvature even at higher values of x, whereas the values of Xe indicate obvious curvature.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

We believe that our experimental results of B_R and C_R for the atomic gases are very accurate because we measured the expansion function F up to high values of pressure. However, errors due to distortion under pressure increase with increasing pressure. Significant contributions to the observed fringe count due to distortion have been taken into account even for cells and compensation chambers with extremely thick walls. We have therefore corrected the effects of distortion in all the observed values of the refractive index function F of the gases investigated by means of Eq. (17). This comprehensive relation contains the expressions for the radial and axial distortion as well as the factor $(2Z_1-Z_2)$ which takes into account the real-gas behavior of the sample. The distortion effect leads to a spurius decrease of the measured differential fringe count ΔK_{expt}.

We will now compare our results of A_R, B_R, and C_R with other experimental values. Buckingham and Graham[7] have previously investigated the atomic gases Ne and Ar, and Burns, Graham, and Weller[3] the gases Ne, Ar, Kr, and Xe, but they carried out the differential measurements only in the small range of pressure of approximately 0.5 MPa. The contribution of the C_n term in F is practically nonexistent in this very small range of pressure. Even for Xe the contribution of the C_n term is only about -0.7% of F at 0.5 MPa, and therefore within its experimental error. Nevertheless, if we consider the small range of pressure exam-

ined, the agreement between the experimental values of B_R published by Buckingham and Graham[7] and Burns, Graham, and Weller[3] and our B_R values is quite good; see Table II.

In the absence of a permanent dipole for gases such as He, Ne, Ar, Kr, and Xe, the refractivity and dielectric virial coefficients are essentially equal provided the optical measurements for the refractive index are carried out in the frequency region long before the commencement of dispersion due to electronic polarization.[7] Therefore, values of A_ϵ and B_ϵ are included in our work for comparison purposes.

Our experimental A_R values are slightly higher than the A_ϵ values given in Table II. This is corroborated by the reported wavelength dependence of A_R observed by Burns, Graham, and Weller[3] which indicates that A_R decreases with increasing wavelength.

The agreement between B_R und B_ϵ is very good for He and Ne, but not as good for the larger systems Ar, Kr, and Xe, for which various literature values of B_ϵ are in disagreement with one another.

We will now discuss each system in more detail.

A. The lighter systems (helium and neon)

1. Helium

A novel feature in the case of He is that the observed fringe count ΔK_{expt}, in contrast with the other gases investigated, is negative in sign. This is only due to the fact that, for this system, the excess contribution of the function $\lambda_0(K_1 - K_2)$, Eq. (7), is zero (within experimental error) in the range of pressure investigated. Therefore, the observed change of phase $\lambda_0 \Delta K_{\text{expt}}$ is equal in magnitude to the phase change $\lambda_0 \Delta K_{\Delta V}$ due to distortion of the compensation chamber under pressure but opposite in sign. Neglecting the correction $\Delta K_{\Delta V}$ would lead to a large relative error in the B_R value of He.

To the best of our knowledge, values of B_R for He have been measured only in our laboratory. Our negative value of B_R for He is corroborated by the negative dielectric constant B_ϵ values observed by Orcutt and Cole[17] and Kirouac and Bose,[18] who used differential techniques, and by Gugan and Michel[19] and Gugan,[20] who made absolute B_ϵ measurements at low temperatures (2.6 to 27.1 K). Very recently Huot and Bose[21] published a B_ϵ value of (-0.07 ± 0.01) cm^6/mol^2 at 323 K which agrees very well with our B_R value of (-0.068 ± 0.010) cm^6/mol^2 at 303.15 K.

Although the measurements for He (and Ne) of Huot and Bose[21] and our experiments cover the same density range, our results show no significant contribution from the term containing the third refractivity virial coefficient.

2. Neon

In the case of Ne, the influence of distortion is also quite considerable. The corrected fringe count ΔK, Eq. (20), was 1.15 for Ne at 35 MPa. This value is determined from the observed value ΔK_{expt} of 0.58 and the calculated value $\Delta K_{\Delta V}$ of 0.57.

The B_R value measured by Burns, Graham, and Weller[3] agrees quite well with our experimental B_R. The measurement of Buckingham and Graham[7] is higher than

the one we have measured but ours is well within their much larger error bars. As in the case of He, the negative value of B_R that we determine is corroborated by the negative B_ϵ value observed by using differential dielectric constant measurements.[21] Our value of B_R at 303.15 K of (-0.11 ± 0.02) cm^6/mol^2 agrees very well with the B_ϵ value of Huot and Bose[21] at 323.15 K $(-0.12 \pm 0.06$ cm^6/mol$^2)$.

B. The larger systems (argon, krypton, and xenon)

In the range of pressure investigated (up to 40 MPa), the third refractivity virial coefficient C_R becomes significant for the gases Ar, Kr, and Xe and, as a result, the contribution of the B_R and C_R terms could be separated completely. For the larger systems, the effect of error correction is much smaller. The maximum values of $100\Delta K_{\Delta V}/\Delta K$ at 40 MPa for Ar, Kr, and Xe are 5%, 3.5%, and 2%, respectively.

1. Argon

Our experimental values of B_R and C_R for Ar measured at 303.15 K are practically the same as the values of Achtermann, Magnus, and Bose[14] measured at 323.15 K (see Table II). The B_R values of Ar measured by Buckingham and Graham,[7] Burns, Graham, and Weller,[3] and Coulon, Montixi, and Occelli[22] agree within the experimental error with our B_R value, which is (1.75 ± 0.05) cm^6/mol^2.

2. Krypton

For Kr we have measured at 303.15 K a B_R value of (5.96 ± 0.06) cm^6/mol^2 which is comparable to that of Burns, Graham, and Weller[3] of (6.23 ± 1.55) cm^6/mol^2 measured at 298.2 K.

To the best of our knowledge, our measurement is the first determination of C_R for Kr. This value is (-275 ± 10) cm^9/mol^3.

3. Xenon

For Xe we have measured at 348.15 K a B_R value of (28.5 ± 0.5) cm^6/mol^2 which is higher than the experimental value of Burns, Graham, and Weller[3] of (25.50 ± 2.85) cm^6/mol^2 measured at 298.2 K. The C_R value of Xe, which is presented here for the first time, is (-1802 ± 50) cm^9/mol^3.

A novel feature of the measurements on Xe is the significant contribution of the fourth term $D_R \rho^3$ [see Eq. (2)] in the range of pressure investigated. For D_R, we have determined a value of (3500 ± 500) cm^{12}/mol^4. Neglecting a significant D_R causes a reduction in the value of B_R and an enlargement of C_R. If we neglect the D_R term, we then obtain a value for B_R of 23.3 cm^6/mol^2 and a value for C_R of -1194 cm^9/mol^3. The mathematical relationship for the determination of D_R is given in previous papers.[13,14]

V. THEORETICAL BACKGROUND

The first refractivity virial coefficient A_R is the value of R_m, Eq. (2), in the limit $\rho \to 0$. For atomic gases, which possess no permanent dipole moment, A_R is given by

$$A_R = \frac{4\pi N_A \alpha_0}{3}, \qquad (23)$$

where α_0 is the atomic polarizability and N_A is Avogadro's number.

The second refractivity virial coefficient B_R, which describes the initial deviation of R_m from ideal behavior, is due to two-body interactions. The usual analytical expression for B_R of a spherical molecule is[1]

$$B_R = (4\pi N_A^2/3\epsilon_0) \int_0^\infty [\tfrac{1}{2}\alpha_{12}(r) - \alpha_0]$$
$$\times \exp[-U_{12}(r)/kT] r^2 dr, \qquad (24)$$

where $\alpha_{12}(r)$ is the mean polarizability of a molecule when participating in a binary collision, α_0 is the polarizability of an isolated molecule, and $U_{12}(r)$ is the potential energy of molecules 1 and 2 at the relative separation r.

Now that accurate experimental values of B_R are available, it is important to use an accurate potential U_{12} when performing the calculation in Eq. (24) so that a realistic comparison can be made between theory and experiment. Some attempts[3] to calculate B_R have been hampered by use of outdated potential models and outdated values for the potential parameters. The potential chosen to represent the interaction must be realistic in mathematical form and possess sufficient flexibility to properly characterize the interaction. In addition, it must be fitted to reliable data for a number of properties over a wide temperature range. In this work, we utilize the recent accurate potentials of Aziz and co-workers[23-27] which have the Hartree–Fock-dispersion HFD-B form first presented by Aziz and Chen.[28]

At present, B_R can be determined to a good degree of accuracy experimentally, but the theoretical results are not as satisfactory. This is primarily because the determination of the incremental mean polarizability,

$$\Delta\alpha = \alpha_{12}(r) - 2\alpha_0, \qquad (25)$$

which appears (implicitly) in Eq. (24), is complicated and no completely satisfactory description of $\Delta\alpha$ has been found which applies for all systems. Our present experimental results should provide a good test of approximations used in different theoretical models.

The simplest method of calculating B_R uses a point dipole approximation, in which $\Delta\alpha(r)$ is calculated by the dipole–induced-dipole (DID) model originally due to Silberstein.[29] In this classical approach the incremental polarizability is given by $2(\alpha_0^3/r^6)$.[30] For the larger systems of Ar, Kr, and Xe, the calculation based on the DID term is in fair agreement with experiment. However, this is not the case for He and Ne. In fact, the room-temperature B_R for He and Ne is observed to be negative,[3,14] whereas the DID expression always gives a positive B_R. This discrepancy is primarily because the classical DID model for $\Delta\alpha$ is really

only valid at long range,[7] whereas ab initio quantum calculations for these systems show that $\Delta\alpha$ is negative at short range.[31-36] For the larger molecules, the positive long-range contribution to $\Delta\alpha(r)$ dominates in the calculation of B_R. For the smaller systems, the negative short-range contribution dominates. The short-range contribution must be determined by an ab initio procedure. Therefore, for the smaller systems of He and Ne, we determine B_R by adding the long-range positive DID term to the essentially short-range negative ab initio contribution. It is seen that this "semiclassical" approach results in predictions which are within the error bars of almost all experimental values for B_R for He and Ne.

Dacre[31-37] has used an ab initio approach to calculate values of the trace $a(r)$ of the polarizability tensor quantum mechanically. His values can be used to determine B_R once Eq. (24) is rewritten in terms of $a(r)$. Making use of Eq. (25) along with the relationship $\Delta\alpha = a(r)$ [obtained from the definitions of $a(r)$ (Ref. 33) and $\Delta\alpha$ (Ref. 32)] and working in atomic units (in which $4\pi\epsilon_0 = 1$), we obtain

$$B_R = (8\pi^2 N_A^2/3) \int_0^\infty a(r)\exp[-U_{12}(r)/kT] r^2 dr. \qquad (26)$$

In our semiclassical approach, the ab initio contribution to $a(r)$ is determined by a linear interpolation between the tabulated ab initio $a(r)$ values presented by Dacre.[31-36] Then, a DID term is added to give the total $a(r)$. B_R is then determined using Eq. (26). This method produces agreement with experiment for He and near agreement for Ne.

In his calculations of $a(r)$, Dacre used the self-consistent-field (SCF) method to determine the SCF contribution to $a(r)$ for the rare gases. For the smaller systems, with only a few electrons, the configuration-interaction (CI) contribution to $a(r)$ was also included. Unfortunately, the CI contribution is difficult to calculate especially for the larger systems which have many more electrons. As a result only the SCF contribution to $a(r)$ is available for these systems, so no attempt was made to determine B_R semiclassically for Ar, Kr, or Xe. However, for these systems it is seen that the single DID term is by far the major contribution to B_R.

VI. THEORETICAL RESULTS AND DISCUSSION

A. The lighter systems (helium and neon)

1. Helium

Using the trace determined by Dacre,[31] which includes both SCF and CI contributions to $a(r)$, and the DID term, we obtained the semiclassical value of -0.059 cm^6/mol^2 for B_R. Our calculation uses the Aziz and Slaman[23] (AS) helium potential. The recent AS potential of the HFD-B form is a significant improvement over the widely used Hartree–Fock-dispersion HFDHE2 potential of Aziz et al.[38] The semiclassical result is in excellent agreement with the experimental B_ϵ values[17,18,21] and of the experimental B_R of this work. [It is interesting to note that the ab

initio contribution when used alone gives a B_R of -0.070 cm^6/mol^2, indicating that, for this system, the positive long-range contribution to $a(r)$ may be sufficiently accounted for by the *ab initio* contribution. In any case, the DID contribution is quite small and both the purely quantum and semiclassical values are within the error bars of our experimental value.]

2. Neon

For He the *ab initio* trace alone gives excellent agreement with the experimental B_R. However, this is not the case for Ne. With just the *ab initio* trace[34] (including both SCF and CI contributions) we calculated $B_R = -0.212$ cm^6/mol^2. When the DID term is included, $B_R = -0.157$ cm^6/mol^2. This result is in within the error bars of Burns, Graham, and Weller,[3] Buckingham and Graham,[7] and Huot and Bose,[21] but not in complete agreement with our experimental B_R value with the small experimental error. The calculations were performed with the recent accurate AS neon potential of Aziz and Slaman.[24]

B. The larger systems (argon, krypton, and xenon)
1. Argon

Dacre[35,36] has calculated the SCF contribution to the trace for Ar, Kr, and Xe, but the CI contribution was not included. Therefore, for these systems, we calculated B_R by just taking into consideration the usual DID term. The *ab initio* contribution is expected to be much less significant for these systems since they are much larger than either He or Ne. Use of the recent HFD-B3 multiproperty potential of Aziz and Slaman[25] results in a B_R value of 2.26 cm^6/mol^2 at 303.15 K. This result is within the error bars of Burns, Graham, and Weller[3] and Buckingham and Graham[7] measured at nearly the same temperature, but not within the much smaller experimental error of the present work.

2. Krypton

Using the HFD-B2 krypton potential of Dham *et al.*[26] and the DID term, we calculated a value of 7.06 cm^6/mol^2 for B_R at 303.15 K. This result is within the error bars of Burns, Graham, and Weller[3] measured at nearly the same temperature, but not within the much smaller experimental error of the present work.

3. Xenon

Using only the classical DID term, we calculated (at 298.2 K) a B_R value of 27.08 cm^6/mol^2 which is within the error bars of Burns, Graham, and Weller[3] measured at 298.2 K. At 348.15 K, our calculated value is 25.23 cm^6/mol^2, not quite in agreement with the present experimental value at the same temperature. The present experimental value has much smaller error bars than that of Burns and co-workers.[3] The recent accurate HFD-B2 xenon potential of Dham *et al.*[27] was used in the calculations.

The theoretical results are summarized in Table II. It is interesting to note a trend which appears when our experimental values are compared to our calculated values

for the three larger systems for which we used only the DID term. For Ar, the theoretical value exceeds our experimental value by 29%. The Kr calculation exceeded the experimental value by 18%. For Xe, the theoretical determination differs from the experimental by -12%, but is actually lower. This suggests that the calculations are suffering from neglect of certain contributions to the trace. In the case of Ar and Kr, the calculation seems to suffer from neglect of the negative short-range contributions to $a(r)$. The discrepancy of -12% for the largest system, Xe, may be partly a result of neglecting higher-order positive terms in the DID expansion.

VII. CONCLUSIONS

We have measured values of the second refractivity virial coefficients B_R of the atomic gases He, Ne, Ar, Kr, and Xe with a recently improved differential-interferometric technique to a higher degree of accuracy than has been previously achieved. The agreement between our measurements and the B_R values that we have calculated are as good as can be expected considering the present state of the theory. The calculations on the basis of the DID model (valid only at long range) are in fair agreement with our measurements for Ar, Kr, and Xe. For He and Ne, the short-range contribution to B_R was also taken into consideration, and we found that the calculated value is within our experimental error in the case of He and nearly so in the case of Ne. Further theoretical work is required.

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