The Second and Third Density Virial Coefficients of Six Ar-Ne Mixtures at 25.0°C

Önder KORFALI

Faculty of Engineering and Technology, Galatasaray University, Ortaköy, İstanbul-TURKEY

In this paper we present a detailed experimental study of the pressure and density of six argon–neon mixtures of mole fractions, x_{Ar} = 0.0821, 0.2727, 0.3618, 0.5838, 0.7722 and 0.9049 at 25.0°C. The pressures are measured with a dead – weight tester. The densities are determined from knowledge of the precise volume and weight measurement of the mixtures. Statistical analysis of the experimental data yielded very precise values for the second and third density virial coefficients. The second virial coefficients calculated with the least squares fitting method and corresponding to above argon mole fractions are 10^6B = 11.03, 9.16, 7.65, 1.83, -4.98 and –11.00 m^3mole^{-1}. Similarly the third virial coefficients are 10^{12} C = 272, 388, 458, 648, 849 and 1013 m^6mole^{-2}.

Key Words: Ar–Ne mixtures, second virial coefficient, third virial coefficient.

Introduction

For a long time, there has been a need to know precisely the second and third virial coefficients of rare gas mixtures. After careful screening of the literature back to 1975 we could not find any reliable virial coefficient data in this field. Therefore we decided to determine experimentally the second and third virial coefficients of Ar-Ne mixtures at 25.0°C. Another literature survey carried out recently has again shown that there was no Ar–Ne mixture virial coefficient data published in the period from 1975 up to the present. The statistical analysis of two of these Ar–Ne mixtures, namely x_{Ar} = 0.2727 and x_{Ar} = 0.7722, were published[1] in 2001. In this paper we report, in addition to these two, the statistical analysis of four additional Ar – Ne mixtures.

The whole experimental part of this study was carried out at the Thermodynamics and Transport Properties Laboratory of Brown University.

Experimental Method

The Ar–Ne mixtures used in this experiment were prepared in two different cylinders by direct weighing of the masses of the components on a high precision, high capacity balance manufactured by Voland Corporation, New Rochell, N.Y. The balance and the procedure for determining the mole fractions are described in Kestin et al.[2]. The direct gravimetric method allowed us to determine the mole fractions with an uncertainty of ±0.0001.

Figure 1 shows the experimental set-up for Ar–Ne mixtures. The volume of each mixture cylinder was determined prior to the measurements. The details of this determination will be given later. The experimental procedure was as follows. First we connect the mixture cylinder to the system through flexible tubing and evacuate the whole system with the aid of a vacuum pump (to 0.02 mmHg). Then closing valve "2" and opening the small valve "1" we fill the piping connecting dead–weight tester and pressure gauge to the mixture cylinder with the mixture contained in the cylinder. After allowing enough time for the system to reach thermal equilibrium in a room where the temperature was kept constant at $25 \pm 0.1°C$, we measure the pressure with the dead–weight tester by opening valve "7". Before starting a measurement, valves "3" and "5" would be completely open while valve "1" would be only cracked open. It is clear that in this operation the only valve that can cause density differences between the mixture cylinder and the dead–weight tester is valve "1". However, since valve "1" has a very small stem diameter and is manipulated only very little, the closing of it could cause a negligible increase in the density of the mixture cylinder whose total volume is approximately two liters. After closing valve "1" we close valve "3", disconnect the flexible tubing from the adapter and carry the mixture cylinder with the adapter on it to the balance for weighing. From the knowledge of the weight of the charge of mixture cylinder and its volume we determine the density of the mixture. All the densities of Ar–Ne mixtures were determined by this method. The room in which the measurements were carried out was equipped with an air-conditioner controlled by a thermostat capable of keeping the room within $\pm 0.1°C$ of the required temperature.
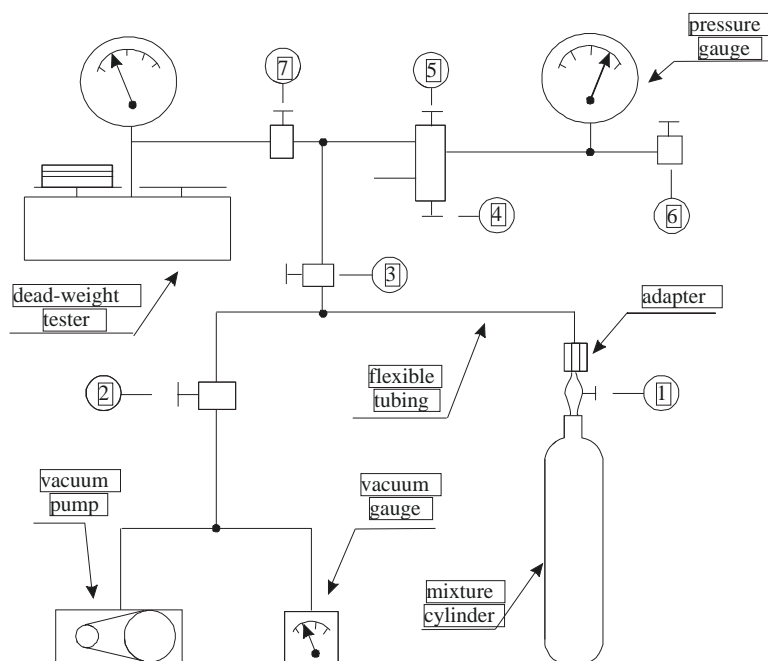

Figure 1. Experimental set-up.

Experimental Determination of the Volumes of Mixture Cylinders

The volumes of the two mixture cylinders used for Ar-Ne measurements were determined by filling each with Ar and Ne separately to a given pressure and temperature, calculating the corresponding densities with respect to the p-V-T data of Michels et al. [3,4] and weighing the charges. The measurements were carried out with the experimental set-up shown in Figure 1 in the room thermostated to $25 \pm 0.1°C$. The procedure

was as follows. First we filled the mixture cylinder with Ar and then with Ne to the desired pressure and connected it to the flexible tubing. Then closing valves "4" and "6" and opening fully "2", "3" and "5" we evacuated the piping system connecting the dead-weight tester, pressure gauge and mixture cylinder. When the vacuum was satisfactory we closed valve "2" and slightly opened small valve "1". After allowing about two hours for the system to reach thermal equilibrium we opened valve "7" slightly and measured the pressure. Then closing valve "1" and disconnecting the mixture cylinder we weighed it. Finally from a knowledge of the weight of the charge and its density we determined the internal volume of the mixture cylinder. The volumes of the two mixture cylinders calculated by the above method are listed in Table 1.

Table 1. Experimental determination of the volumes of two mixture cylinders at $25\pm0.1°$C

Cylinder Number	Gas	Pressure $p \times 10^{-5}$ (Pa)	Mass of the gas $m \times 10^3$ (kg)	Density ρ (kg/m^3)	Volume $V \times 10^6$ (m^3)
1	Ar	29.516 ± 0.0034	98.290 ± 0.006	48.4034	2030.64 ± 0.6
1	Ne	34.116 ± 0.0034	55.524 ± 0.006	27.3356	2031.20 ± 0.7
2	Ar	33.725 ± 0.0034	112.593 ± 0.006	55.4318	2031.20 ± 0.6
2	Ne	34.573 ± 0.0034	56.216 ± 0.006	27.6743	2031.34 ± 0.7

Error Analysis for Density

Error in the determination of the volume of mixture cylinders

Taking the experimental virial equation of state of Michels et al.[3] for Ar at 25°C

$$pv = A + Bd + Cd^2 \tag{4.1}$$

and converting it to the form below with the use of v = 1 / d

$$p = Ad + Bd^2 + Cd^3$$

and finally taking the derivative with respect to d we obtain

$$\Delta p/\Delta d = A + 2Bd + 3Cd^2. \tag{4.2}$$

Here p is the pressure in atm, d is the density in amagat units and A, B and C are constants. Inserting the experimental data for cylinder 1 for Ar from Table 1 into eq. (4.2) we obtain

$$\Delta p/\Delta d \cong 1.06. \tag{4.3}$$

For Δp = ±0.0034 atm $\cong \pm$ 0.0034 x 10^5 Pa, the accuracy of our pressure measurements, the use of eq. (4.3) together with the data of Table 1 for cylinder 1 with Ar gives

$$\Delta d/d = \pm0.00012.$$

The relative uncertainty of the density data of Michels et al.[3] is $\pm$ 1:10000. Thus the total relative uncertainty in the determination of the density of Ar in cylinder 1 is

$$\Delta d/d = \Delta\rho/\rho = \pm 0.00012 \pm 0.0001 = \pm 0.00022.$$

Finally the relative uncertainty in the determination of the volume of cylinder 1 with respect to Ar can be calculated from

$$\Delta V/V = \pm\Delta m/m \pm \Delta\rho/\rho. \tag{4.4}$$

The absolute error in the determination of the mass of the gas inside the cylinder being ± 0.006 g, using Table 1 one finds

$$\frac{\Delta m}{m} = \pm\frac{0.006}{100} = \pm 0.00006.$$

Consequently,

$$\Delta V/V = \pm 0.00006 \pm 0.00022 \cong \pm 0.0003.$$

It follows that the uncertainty in the volume of cylinder 1 is $\pm$ 0.6 cm^3. A similar analysis for Ne gives an uncertainty of $\pm$ 0.7 cm^3 in volume for the same cylinder. The volumes determined experimentally with respect to two different gases check very well with each other within their experimental error. Table 1 displays the results of the volume determination.

Correction for the deformation of cylinders

From accurately known volumes and heights of the mixture cylinders we derived their internal radii. First assuming an infinitely long cylinder we used the formula[5]

$$\Delta r_i = (pr_i/E)\left[(1 + r_i^2/r_0^2)/(1 - r_i^2/r_0^2) + \mu\right] \tag{4.5}$$

to determine the change Δr_i in the internal radius. Here r_i is the internal, and r_0 the external radius of the mixture cylinder. P is the pressure difference between the inside and outside of the latter. E is the modulus of elasticity and μ is Poisson's ratio of the cylinder material. Equation (4.5) can be simplified to the form

$$\Delta r_i = pK \tag{4.6}$$

where

$$K = (r_i/E)\left[(1 + r_i^2/r_0^2)/(1 - r_i^2/r_0^2) + \mu\right]. \tag{4.7}$$

Then the radial volume change, ΔV_r, is given by

$$\Delta V_r = (2\pi r_i hK)p \tag{4.8}$$

where h is the height of the cylinder. The longitudinal volume change, ΔV_l, due to the axial forces can be computed from Hooke's Law and is given as

$$\Delta V_l = \left[(\pi h r_i^4/E)/(r_0^2 - r_i^2)\right]p. \tag{4.9}$$

Superposing both volume changes and inserting numerical values into eqs. (4.8) and (4.9) we obtain

$$\Delta V_t = 1.595 \times 10^{-13}p \tag{4.10}$$

as the total volume change due to deformation. Here ΔV_t is in m^3, p is in Pa. Taking as reference the pressures and volumes of Table 1 and applying eq. (4.10) we were able to determine the correct volume at each point. At the highest pressure, 164×10^5 Pa, the correction for expansion was 2.6×10^{-6} m^3. Thus we claim a relative accuracy of $\pm 0.04\%$ in the determination of the volume of mixture cylinders.

Relative accuracy in the determination of density

Since our balance was sensitive to 2 mg a simple error analysis based on the relation

$$\Delta \rho/\rho = \Delta m / m + \Delta V / V$$

enables us to ascertain a relative accuracy of $\pm 0.1\%$ in the density range 3 kg/$m^3 < \rho < 10$ kg/m^3 and $\pm 0.05\%$ for densities higher than 10 kg/m^3.

Experimental Pressures and Densities for Six Ar-Ne Mixtures at 25°C

Measurements of the pressures and densities of six Ar-Ne mixtures were carried out at 25.0°C. The experimental set-up and method used were described previously. The pure gases Ar and Ne were supplied by the Union Carbide Corporation. The purities were guaranteed to be 99.998% or better. Experimental results are given in Table 2.

Comparison of experimentally determined virial coefficients with those calculated with the method of Brewer et al.[6]

First using the least squares method we fitted the compressibility data of Michels et al. for argon[3] and neon[4] at 25.0°C in the pressure range $0 < p < 160$ atm, corresponding to the range of our experiments, to the truncated virial equation of state limited to three terms:

$$pV/RT = 1 + B(T)/V + C(T)/V^2. \tag{6.1}$$

The second and third virial coefficients for pure Ar and Ne determined by this method are listed in Table 3. Following this and using the same least squares method we fitted the experimental pressure and density data of Table 2 for all mole fractions to the same eq. (6.1). The second and third mixture virial coefficients thus obtained are again listed in Table 3. On the other hand, for all six Ar-Ne mixtures and using the method of Brewer and Vaughn[6], we determined the respective truncated virial equations of state limited to three terms, namely eq. (6.1). In this method the second virial coefficient for binary monoatomic gas mixtures is given as

Table 2. Experimental pressures and densities for six Ar – Ne mixtures at 25.0°C

$x_{Ar} = 0.0821$		M = 21.806 kg / kmole	
Point Number n	Pressure p (MPa)	Density ρ (kg/m^3)	Density ρ (mole/m^3)
1	0.4384	3.9	179
2	0.7083	6.2	284
3	1.1257	9.9	454
4	1.5118	13.2	605
5	2.0741	18.1	830
6	2.6507	23.0	1055
7	3.1380	27.2	1247
8	4.1797	36.1	1656
9	5.2567	45.2	2073
10	6.2244	53.2	2440
11	7.3268	62.3	2857
12	8.2864	70.2	3219
13	9.3158	78.6	3605
14	10.2095	85.7	3930
15	11.1235	93.0	4265
16	12.2998	102.3	4691
17	13.3800	110.7	5077
18	14.2351	117.3	5379
19	15.3994	126.3	5792
20	16.7055	136.2	6246

Table 2. (continued)

$x_{Ar} = 0.2727$		M = 25.573 kg / kmole	
Point Number n	Pressure p (MPa)	Density ρ (kg/m^3)	Density ρ (mole/m^3)
1	0.4342	4.5	175
2	1.4650	15.0	587
3	2.1729	22.2	868
4	3.6705	37.3	1459
5	5.5303	55.8	2184
6	7.5791	75.8	2965
7	10.0930	99.9	3905
8	12.1752	119.4	4671
9	14.2949	138.8	5429
10	16.3964	157.7	6168

Table 2. (continued)

$x_{Ar} = 0.3618$		M = 27.334 kg / kmole	
Point Number n	Pressure p (MPa)	Density ρ (kg/m^3)	Density ρ (mole/m^3)
1	0.2951	3.3	121
2	0.5559	6.1	223
3	1.3699	15.0	549
4	2.2008	24.1	882
5	3.0266	33.1	1211
6	3.9193	42.7	1562
7	4.9538	53.7	1965
8	5.5921	60.5	2213
9	6.1504	66.5	2433
10	7.0826	76.2	2788
11	7.9510	85.3	3121
12	8.7251	93.3	3413
13	9.5306	101.6	3717
14	10.0008	106.4	3893
15	10.9877	116.4	4258
16	12.0982	127.6	4668
17	13.2057	138.6	5071
18	14.2767	149.2	5458
19	15.4125	160.2	5861
20	16.2728	168.5	6164

Table 2. (continued)

$x_{Ar} = 0.5838$		M = 31.722 kg / kmole	
Point Number n	Pressure p (MPa)	Density ρ (kg/m^3)	Density ρ (mole/m^3)
1	0.2539	3.3	104
2	0.5237	6.7	211
3	0.9932	12.7	400
4	2.0214	25.8	813
5	2.9202	37.3	1176
6	4.0449	51.5	1623
7	5.0379	64.1	2021
8	6.0633	77.0	2427
9	7.0309	89.1	2809
10	7.5254	95.2	3001
11	8.0209	101.4	3197
12	8.9004	112.3	3540
13	9.6380	121.3	3824
14	10.2065	128.3	4045
15	11.1934	140.3	4423
16	12.1813	152.3	4801
17	13.2057	164.6	5189
18	14.2382	176.8	5573
19	15.1167	187.2	5901
20	16.3772	201.9	6365

Table 2. (continued)

$x_{Ar} = 0.7722$		M = 35.446 kg / kmole	
Point Number n	Pressure p (MPa)	Density ρ (kg/m^3)	Density ρ (mole/m^3)
1	0.7032	10.1	352
2	1.5821	22.6	639
3	2.5737	36.9	1042
4	3.6913	53.1	1497
5	5.5313	79.7	2250
6	6.8759	99.1	2796
7	8.7089	125.5	3540
8	10.9472	157.5	4442
9	12.4458	178.9	5047
10	12.8044	183.8	5185
11	13.6961	196.1	5533

Table 2. (continued)

$x_{Ar} = 0.9049$		M = 38.068 kg / kmole	
Point Number n	Pressure p (MPa)	Density ρ (kg/m^3)	Density ρ (mole/m^3)
1	0.2575	4.0	105
2	0.5208	8.0	210
3	1.0548	16.3	428
4	1.5807	24.5	644
5	2.1197	32.9	864
6	3.1512	49.0	1287
7	4.1817	65.3	1715
8	5.1818	81.1	2130
9	6.1727	96.9	2545
10	7.0593	111.0	2916
11	7.6318	120.2	3158
12	8.2631	130.2	3423
13	9.2337	145.8	3830
14	10.1670	160.7	4221
15	11.0556	174.9	4594
16	11.6929	185.0	4860
17	12.6413	200.1	5256
18	13.6637	216.3	5682
19	14.7316	233.1	6123
20	15.9273	251.8	6614

$$B = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22} \qquad (6.2)$$

and the third virial coefficient as

$$C = x_1^3 C_{111} + 3x_1^2 x_2 C_{112} + 3x_2^2 x_1 C_{122} + x_2^3 C_{222}. \qquad (6.3)$$

Here above, B_{11} and B_{22} are the second virial coefficients of pure components and B_{12} is the interaction second virial coefficient. Similarly C_{111} and C_{222} are the third virial coefficients of pure Ar and Ne. C_{112} corresponds to interactions involving two molecules of component 1 and one molecule of component 2, and C_{122}, to one molecule of component 1 and two molecules of component 2. Finally x_1 and x_2 are the mole fractions of the components and V the molar volume of the mixture. The values of B_{11}, B_{22}, C_{111} and C_{222} are taken from Table 3. B_{12} is determined using the method developed by Brewer and Vaughn[6],

Table 3. Experimentally determined second and third virial coefficients of Ar–Ne mixtures at 25°C

x_{Ar}	B x 10^6 (m^3/mole)	C x 10^{12} (m^3/mole)	Standard Deviation %
0.0000^4	11.43	228	0.12
0.0821	11.03	272	0.09
0.2727^1	9.16	388	0.09
0.3618	7.65	458	0.08
0.5838	1.83	648	0.10
0.7722^1	-4.98	849	0.11
0.9049	-11.00	1013	0.08
1.0000^3	-15.73	1145	0.13

$$B_{12} = E + (B_{11} + B_{22})/2 \tag{6.4}$$

where E is the excess second virial coefficient at 25.0°C for Ar–Ne mixtures. C_{112} and C_{122} are calculated from the following formulae given in the same reference[6]:

$$C_{112} = \left(C_{111}^2 C_{222}\right)^{1/3}, C_{122} = \left(C_{111} C_{222}^2\right)^{1/3}. \tag{6.5}$$

Here $V = 1/\rho$ is in m^3 / mole unit and the molecular weights of the mixtures are calculated from the relation $M = x_{Ar} M_{Ar} + x_{Ne} M_{Ne}$. In the calculation of B_{12} from eq. (6.4) above the value of E is taken as $E = 13$ x 10^{-6} m^3 / mole from Brewer and Vaughn[6] and is same for all mole fractions. The values of B_{11} and B_{22} are taken from Table 3. Consequently for all mole fractions the interaction second virial coefficient is the same and equal to $B_{12} = 10.85$ x 10^{-6} m^3/mole. Inserting this value into eq. (6.2) we have for the second virial coefficients of Ar–Ne mixtures at 25.0°C the formula

$$B = -15.73x_1^2 + 21.70x_1x_2 + 11.43x_2^2 \tag{6.6}$$

where $x_1 = x_{Ar}$ and $x_2 = x_{Ne}$.

In the calculation of C, the third virial coefficient of mixtures, C_{111} and C_{222}, are again taken from Table 3. C_{112} and C_{122} are calculated using eqs. (6.5). The final expression for the third virial coefficients of Ar-Ne mixtures at 25.0°C is

$$C = 1145x_1^3 + 2005.86x_1^2x_2 + 1171.32x_1x_2^2 + 228x_2^3 \tag{6.7}$$

where again $x_1 = x_{Ar}$ and $x_2 = x_{Ne}$.

Table 4. Virial coefficients of Ar – Ne mixtures at 25.0°C calculated with the method of Brewer et al.[6]

x_{Ar}	B x 10^6 (m^3/mole)	C x 10^{12} (m^3/mole)^2
0.0000[4]	11.43	228.0
0.0821	11.16	270.4
0.2727[1]	9.18	388.4
0.3618	7.61	453.7
0.5838	1.89	647.2
0.7722[1]	-4.97	849.3
0.9049	-10.91	1014.4
1.0000[3]	-15.73	1145.0
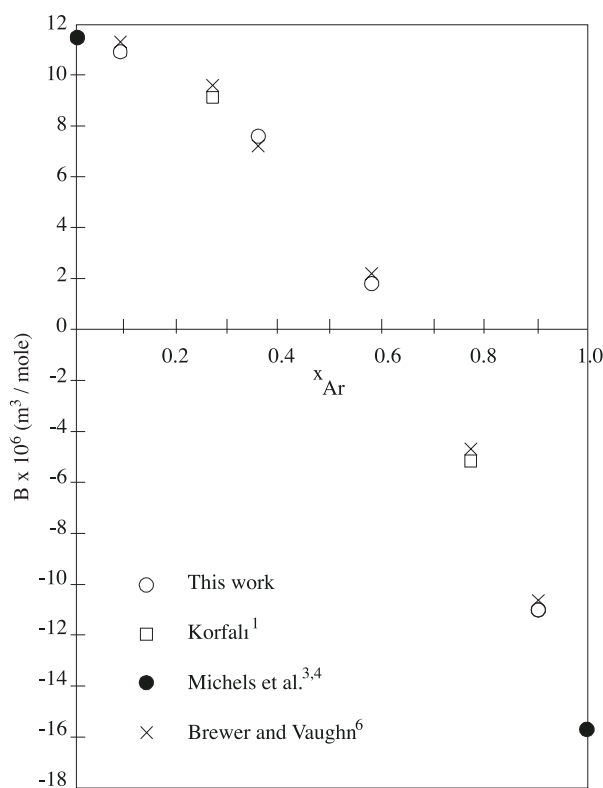
Figure 2. Second virial coefficients of Ar–Ne mixtures at 25.0°C

The second and third virial coefficients of all six Ar–Ne mixtures calculated with the use of eqs. (6.6) and (6.7) respectively are listed in Table 4. Finally the data in Tables 3 and 4 are plotted in Figures 2 and 3.

Conclusion

Statistical analysis of the experimental pressure and density data yielded very precise values for the second and third density virial coefficients of Ar-Ne mixtures. Figures 2 and 3 can be used for the accurate interpolation of these coefficients. A comparison of Tables 3 and 4 show that the maximum percentage deviation between experimental and theoretical second virial coefficients, $[(B_{exp} - B_{theo}) / B_{theo}]$ 100, is less

than 3% and that between third virial coefficients is below 1%. Overall the predictions of Brewer's method are in very good agreement with the experimental results. Furthermore, the satisfactory agreement between experimental and theoretical results show that the choice of E = 13.00 x 10^{-6} m^3/mole in the determination of Ar-Ne second virial coefficients is an excellent one. In conclusion Brewer's method is a very good tool for predicting second and third virial coefficients of monoatomic gas mixtures, and equations (6.6) and (6.7) can be used to calculate accurately those of Ar-Ne mixtures at 25.0°C.
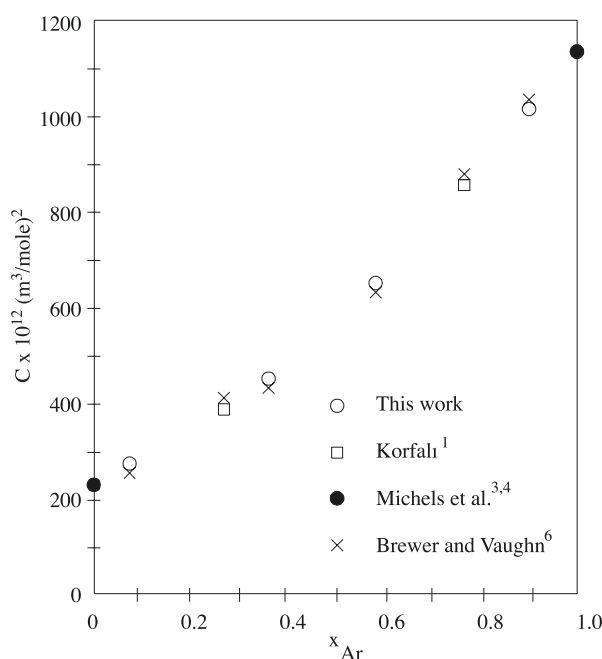

Figure 3. Third virial coefficients of Ar–Ne mixtures at 25.0°C

Symbols

B	Second virial coefficient, m^3/mole.
C	Third virial coefficient, $(m^3/mole)^2$.
ΔV_r	Radial volume change.
ΔV_l	Longitudinal volume change.
E	Excess second virial coefficient, m^3/mole.
M	Molecular weight, kg/kmole.
p	Pressure, Pascal.
r_i	Internal radius of the mixture cylinder.
r_0	External radius of the mixture cylinder.
R	Universal gas constant, R = 8.31432 m^3Pa /mole K.
ρ	Density, kg/m^3.
T	Absolute temperature, K.
V	Volume, m^3/mole.
x_{Ar}	Mole fraction of argon.
x_{Ne}	Mole fraction of neon.
Z	Compressibility factor.

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