

Second Virial Coefficients for Dimethyl Ether

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Dimethyl ether (DME) is a clean and economical alternative fuel. In addition, it is also an ozone-friendly refrigerant. Burnett measurements were carried out at temperatures from (344 to 393) K and at pressures from (0.055 to 4.015) MPa. A total of 138 experimental points, taken along 15 isotherms and 12 different temperatures, were obtained. The apparatus was calibrated by helium. The derived second coefficients were compared with the selected correlations and with literature data.

Introduction

Dimethyl ether (DME) is the simplest ether, with a chemical formula of CH_3OCH_3 . It is an important chemical material, and it has many engineering applications. It is generally produced in a two-step process: synthesis gas (syngas) is first converted to methanol and then DME is obtained by dehydration of methanol. The direct synthesis process technique from synthetic gas is still under development.¹ It can be made from coal, natural gas, residual oil, oil coke, and biomass, and its production cost is rather low. In addition, DME is nontoxic and noncarcinogenic.

Its physical properties are similar to those of liquefied petroleum gases (i.e., propane and butane), while burning DME, there are no emissions of SO_x , NO_x , or particulates. Its GWP is 0.3 per 100 years.²

Besides its use as an assistant solvent and an aerosol propellant, recently it was shown to be a good alternative fuel.¹ In addition, because of its favorable thermodynamic properties, it has been suggested as an alternative refrigerant (RE170). In particular, for air conditioning applications, a mixture of mass fraction of 60 % ammonia and 40 % dimethyl ether forms an interesting azeotrope (R723).

For all these reasons, its thermophysical properties were recently studied,³ and a preliminary fundamental equation of state was derived.⁴

DME vapor pressure measurements were carried out at temperatures from (219 to 361) K and at pressures from (0.022 to 2.622) MPa, and a total of 71 experimental points were obtained in previous research at our laboratory.⁵

After a literature search, a very limited number of second virial coefficients for DME were found in the open literature.^{6–11} In addition, the data are rather old, and excluding two points,¹⁰ they were derived at a reduced temperature range that spans from 0.68 to 0.82. In this work, 138 experimental points were collected in the superheated vapor region and at higher reduced temperature range, spanning from 0.86 to 0.98. Derived second virial coefficients were compared with the predicted values by the Tsoumpoulos correlating method.¹²

Experimental Apparatus and Procedures

The sample was provided by Aldrich Inc., USA. It was degassed by immersion in liquid nitrogen and evacuation. Its

purity was checked by gas chromatography using a thermal conductivity detector, and its mass fraction was found to be better than 99.8 % by analysis of the peak area.

A diagram of the apparatus since it is the same as described elsewhere¹³ is not reported here. It consisted of two pressure vessels, a measurement chamber, V_A , and an expansion chamber, V_B , with volumes of approximately (70 and 35) cm^3 , respectively, and several auxiliary systems for filling and mixing the compounds in the Burnett vessels and for controlling and measuring the pressure and temperature. The measurement vessel was connected to a diaphragm-type differential pressure transducer (Ruska model 2413) coupled to an electronic null indicator (Ruska model 2416).

The pressure was regulated by a precision pressure controller (Ruska model 3981), while a digital pressure indicator (Ruska model 7000) was used to measure the pressure. Nitrogen is used as the pressure-transmitting fluid, and the nitrogen system consists of a reservoir, expansion vessels, and pressure regulating systems.

The vessels were immersed in a thermostatic bath filled with about 45 L of silicon oil. The temperature of the bath was kept constant by means of a system with a PID device, controlled by a computer to which the temperature measurement system is also connected. The control and acquisition system relies on two platinum resistance thermometers calibrated according to ITS 90 at the Istituto Metrologico G. Colonnetti (IMGC) of Turin. In particular, for data acquisition and control measurements, a Hart Scientific Pt 25 resistance thermometer (Hart 5680) and a Tersid Pt 100 resistance thermometer were used, both connected to a digital temperature indicator (Corradi, RP 7000).

The Burnett constant, N , defined as the ratio of the volumes of cell A and the sum of the volumes of cells A and B at zero pressure, was found to be $N = 1.5220 \pm 0.0001$ for present measurements. Measurements were performed using the classical Burnett experimental procedure. Initially, the first vessel was filled with the sample, and its temperature and pressure were measured. Then, after evacuating the second vessel, the expansion valve was opened. Once the pressures between the vessels had equalized, the second vessel was isolated and evacuated again. This procedure was repeated until low pressures were achieved.

The uncertainty in the temperature measurements is due to the thermometer and any instability of the bath. The stability of the bath was found to be better than ± 0.015 K, and the

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Table 1. Second (B) and Third (C) Virial Coefficients for Helium^a

series	T K	B $\text{cm}^3 \cdot \text{mol}^{-1}$	abs (dB) $\text{cm}^3 \cdot \text{mol}^{-1}$	C $\text{cm}^6 \cdot \text{mol}^{-2}$	abs (dC) $\text{cm}^6 \cdot \text{mol}^{-2}$	$\rho(1)$ $\text{mol} \cdot \text{dm}^{-3}$	abs (dP) kPa	bias (dP) %
1	343.87	10.6	1.2	534	535	1.98072	0.239	0.051
2	343.87	9.7	2.1	905	906	1.80089	0.271	0.066
3	354.02	11.0	0.7	427	428	1.87893	0.156	0.039
4	354.12	11.5	0.2	272	273	1.87300	0.138	0.034
5	363.36	12.8	1.1	-146	145	1.90409	0.072	-0.009
6	364.36	11.9	0.2	135	136	1.88208	0.051	0.013
7	374.64	12.4	0.8	-10	9	1.85374	0.035	0.008
8	374.65	12.8	1.2	-140	139	1.85231	0.040	-0.002
AAD			0.9		321		0.125	0.033

^a $\rho(1)$ denote regressed initial densities.**Table 2. Experimental Pressures Measured during Burnett Expansions of DME**

series 1		series 2		series 3		series 4		series 5	
T/K		T/K		T/K		T/K		T/K	
343.86		343.86		343.86		348.96		354.08	
P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$
1.3265	0.5535	1.3654	0.5744	1.6973	0.7651	1.5747	0.6794	1.7013	0.7260
0.9286	0.3637	0.9589	0.3774	1.2256	0.5027	1.1211	0.4464	1.2129	0.4770
0.6340	0.2390	0.6564	0.2480	0.8510	0.3303	0.7749	0.2933	0.8392	0.3134
0.4280	0.1570	0.4427	0.1629	0.5784	0.2170	0.5261	0.1927	0.5699	0.2059
0.2857	0.1032	0.2958	0.1070	0.3890	0.1426	0.3534	0.1266	0.3827	0.1353
0.1898	0.0678	0.1966	0.0703	0.2592	0.0937	0.2358	0.0832	0.2552	0.0889
0.1257	0.0445	0.1302	0.0462	0.1718	0.0616	0.1567	0.0547	0.1694	0.0584
0.0831	0.0293	0.0861	0.0304	0.1137	0.0404	0.1039	0.0359	0.1122	0.0384
0.0550	0.0192	0.0570	0.0199	0.0751	0.0266	0.0689	0.0236	0.0743	0.0252
series 6		series 7		series 8		series 9		series 10	
T/K		T/K		T/K		T/K		T/K	
359.21		364.35		364.36		369.49		374.64	
P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$
2.0459	0.9065	2.2596	0.9953	2.4857	1.1491	1.9759	0.8077	2.7299	1.2338
1.4868	0.5956	1.6477	0.6540	1.8485	0.7550	1.4070	0.5307	2.0291	0.8107
1.0408	0.3913	1.1557	0.4297	1.3092	0.4960	0.9736	0.3487	1.4405	0.5326
0.7124	0.2571	0.7903	0.2823	0.9019	0.3259	0.6616	0.2291	0.9948	0.3500
0.4809	0.1689	0.5345	0.1855	0.6107	0.2141	0.4446	0.1505	0.6751	0.2299
0.3218	0.1110	0.3572	0.1219	0.4090	0.1407	0.2966	0.0989	0.4532	0.1511
0.2142	0.0729	0.2373	0.0801	0.2721	0.0924	0.1970	0.0650	0.3021	0.0993
0.1420	0.0479	0.1571	0.0526	0.1802	0.0607	0.1305	0.0427	0.2004	0.0652
0.0941	0.0315	0.1038	0.0346	0.1191	0.0399	0.0862	0.0281	0.1326	0.0428
series 11		series 12		series 13		series 14		series 15	
T/K		T/K		T/K		T/K		T/K	
379.80		384.95		390.14		390.15		393.24	
P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$	P/MPa	$\rho/\text{mol} \cdot \text{dm}^{-3}$
3.1183	1.4494	3.5918	1.7846	3.7219	1.7780	3.9365	2.0082	4.0152	1.9932
2.3529	0.9523	2.7910	1.1725	2.8615	1.1682	3.0949	1.3195	3.1377	1.3096
1.6872	0.6257	2.0457	0.7704	2.0770	0.7676	2.2913	0.8670	2.3023	0.8605
1.1718	0.4111	1.4294	0.5062	1.4540	0.5043	1.6144	0.5696	1.6238	0.5654
0.7979	0.2701	0.9803	0.3326	0.9952	0.3314	1.1134	0.3743	1.1169	0.3715
0.5365	0.1775	0.6622	0.2185	0.6714	0.2177	0.7554	0.2459	0.7561	0.2441
0.3579	0.1166	0.4431	0.1436	0.4489	0.1430	0.5070	0.1616	0.5067	0.1604
0.2375	0.0766	0.2946	0.0943	0.2984	0.0940	0.3380	0.1062	0.3373	0.1054
0.1571	0.0503	0.1951	0.0620	0.1975	0.0617	0.2244	0.0697	0.2235	0.0692
0.1038	0.0331	0.1289	0.0407					0.1477	0.0455

uncertainty of the thermometer was found to be better than 0.010 K in our temperature range. The total uncertainty in the temperature measurements was thus less than 0.025 K.

The uncertainty in the pressure measurements is due to the transducer and null indicator system and to the pressure gages. The digital pressure indicator (Ruska model 7000) has an uncertainty of $\pm 0.003\%$ of full scale. The total uncertainty in the pressure measurement is also influenced by temperature fluctuations due to bath instability and was found to be less than ± 1 kPa.

Results

The second and third virial coefficients obtained from the Burnett expansions of helium are reported in Table 1 together with deviations obtained from the McCarty equation of state.¹⁴ Results showed a good agreement with reference data¹⁴ in terms of the second virial coefficients (AAD = $0.9 \text{ cm}^3 \cdot \text{mol}^{-1}$) and slightly poorer in terms of the third virial coefficients (AAD = $321 \text{ cm}^6 \cdot \text{mol}^{-2}$). However, in terms of pressure, an AAD = 0.125 kPa was obtained.

Table 3. Second (B and B') and Third (C) Virial Coefficients for DME^a

Series	T	B	C	$\rho(1)$	abs (dP)	bias (dP)	B'	$\rho'(1)$	abs (dP')	bias (dP')
	K	cm ³ ·mol ⁻¹	cm ⁶ ·mol ⁻²	mol·dm ⁻³	kPa	%	cm ³ ·mol ⁻¹	mol·dm ⁻³	kPa	%
1	343.86	-301	15190	0.55367	0.232	0.128	-302	0.55355	0.234	0.100
2	343.86	-293	1770	0.57356	0.158	0.124	-303	0.57440	0.266	0.032
3	343.86	-274	-17560	0.75968	0.270	0.089	-306	0.76514	1.016	-0.224
4	348.96	-323	34880	0.68182	0.390	0.217	-308	0.67942	0.521	0.316
5	354.08	-301	24820	0.72744	0.239	0.139	-294	0.72604	0.264	0.176
6	359.21	-296	26570	0.90953	0.392	0.153	-286	0.90653	0.589	0.244
7	364.35	-267	15860	0.99792	0.284	0.042	-269	0.99531	0.287	0.000
8	364.36	-257	8430	1.14436	0.062	0.000	-269	1.14906	1.047	-0.194
9	369.49	-280	30970	0.81090	0.291	0.122	-266	0.80774	0.589	0.235
10	374.64	-260	20150	1.24000	0.300	0.077	-256	1.23379	0.496	0.131
11	379.80	-246	18010	1.45152	0.106	0.012	-244	1.44945	0.200	0.031
12	384.95	-236	15670	1.78343	1.576	-0.037	-237	1.78459	1.736	-0.110
13	390.14	-229	16790	1.77933	0.086	0.002	-229	1.77798	0.105	-0.005
14	390.15	-238	19720	2.02045	1.777	0.035	-230	2.00824	2.868	0.233
15	393.24	-228	17740	1.99930	0.207	0.047	-225	1.99319	0.976	0.137
AAD					0.420	0.080			0.750	0.140

^a $\rho(1)$ and $\rho'(1)$ denote regressed initial densities.

For DME, in total 138 experimental points were collected along 15 isotherms in a temperature range from (344 to 393) K and for pressures from (0.055 to 4.015) MPa. Adopting the critical temperature value of $T_c = 400.3$ K,¹⁵ the experimental reduced temperature range spanned from 0.86 to 0.98. The experimental data are shown in Table 2.

The experimental PVT measurements were used to derive the second, B , and third, C , virial coefficients of the virial equation

$$P = \frac{RT}{V} \left(1 + \frac{B}{V} + \frac{C}{V^2} \right) \quad (1)$$

In the regression, each run was treated separately and $(dP)^2$ was used as an objective function applying the Burnett constant from the helium calibration.

Defining the average absolute deviation in pressure as

$$\text{AAD} = \sum_{i=1}^N \text{abs}(dP)/N \quad (2)$$

we found $\text{AAD} = 0.63$ kPa, well within the estimated experimental uncertainty. The second and third virial coefficients are shown in Table 3, together with the pressure deviations from the fit.

The second virial coefficients (B) are also reported in Figure 1. This figure shows that the second virial coefficients, especially for values at $T_r < 0.92$, are rather scattered. This was probably caused from the small pressure range, limited by the saturation pressure of DME. This limitation also produced scattered values at low reduced temperatures for the third virial coefficients.

To overcome this problem, data were refitted keeping the third virial coefficients as fixed values according to the Orbey and Vera correlating method.¹⁶ The resulting values for the second virial coefficients, B' , and initial density, $\rho(1)$, are also reported in Table 3.

The B' values were plotted in Figure 1 together with second virial coefficients calculated by eq 1 as described above (B). Even if from the analysis of the deviations for reproducing the pressures by the different methods the B' values appear to have a slightly higher AAD, comparing the B' with the B values, a significant improvement was evident, especially at lower reduced temperatures, where the obtained B' values were clearly less scattered than the B values. For this reason, the B' values were

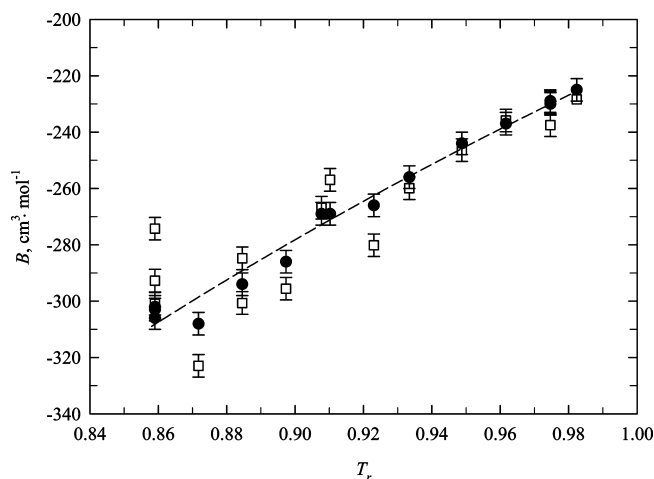


Figure 1. Second virial coefficients, $B = (\square)$ and $B' = (\bullet)$, against reduced temperature. The values fitted by eq 3 are presented by a dashed line.

taken as reference values and fitted according to the following temperature function

$$B' = b_0 + b_1/T_r \quad (3)$$

with $b_0 = 350.3812$ cm³·mol⁻¹ and $b_1 = -565.7195$ cm³·K·mol⁻¹. Equation 3 predicts the B' values with an $\text{AAD} = 3.2$ cm³·mol⁻¹. The second virial coefficients calculated by eq 3 are also reported in Figure 1 as a dashed line.

In Figure 2, the second virial coefficients (B') are plotted over a different reduced temperature scale and compared with values reported in the literature.⁶ In the figure, the values predicted by the Tsonopoulos⁷ correlating method are also shown. Considering that the literature second virial coefficients were generally obtained at very different temperatures and that only two points were obtained (by one of us), about four decades ago at our reduced temperature range (from 0.86 to 0.98), the trend of the present results can be considered satisfactory.

The uncertainties in the second virial coefficients, estimated on statistical base, are of about 4 cm³·mol⁻¹.

If the data from the Burnett expansions cover only low pressures and the number of expansions are limited, it may not be possible to tune all three parameters, namely, B , C , and $\rho(1)$, especially considering the real accuracy in the pressures measurements. Moreover, the contribution from the third virial

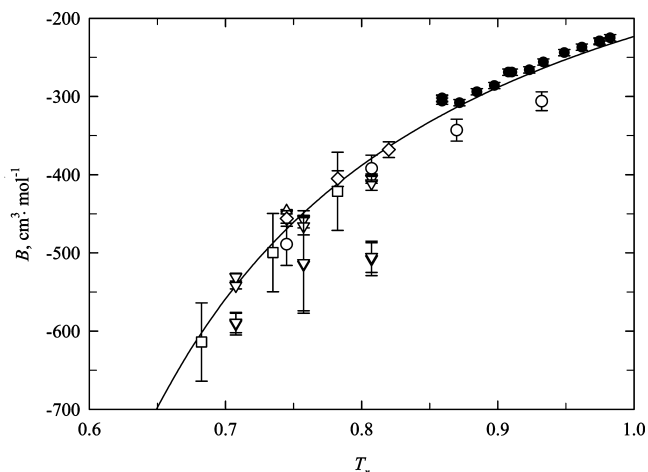


Figure 2. Second virial coefficients, B' , against reduced temperature. The values correlated by the Tsionopoulos⁷ correlating method are presented by a solid line. ●, Present work; □, ref 7; △, ref 8; ▽, ref 9; ○, ref 10; ◇, ref 11.

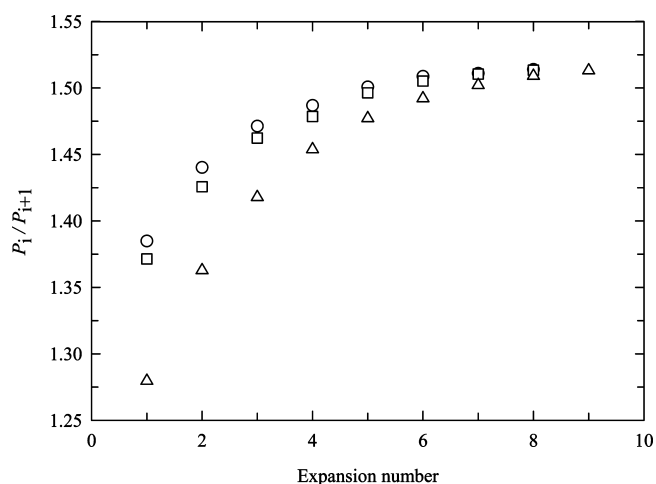


Figure 3. P_i/P_{i+1} against the expansion number for three runs. ○, $T = 343.86$ K (series 3); □, $T = 364.35$ K (series 7); △, $T = 393.24$ K (series 15).

coefficient to the values of the compressibility is much smaller than from the second virial coefficient, hence it may be better to use an alternative method for the Burnett data reduction. Keeping in mind that the contribution from the third virial coefficient is very small but not negligible, we choose the option of “a priori” estimation from one of the predictive methods of the values of the third virial coefficients, thus tuning only two parameters, namely B and $\rho(1)$. After testing, we choose the third virial coefficients from the Orbey and Vera method: in this way, B' and $\rho'(1)$ are considered as the most acceptable from our experimental data.

The eventual adsorption contribution should be detected while plotting P_i/P_{i+1} . The Burnett ratio P_i/P_{i+1} was reported in Figure 3 for three runs obtained at different temperatures and taken as

an example. The adsorption should be greater at lower temperatures, which is not evident from the graph.

Conclusions

The PVT properties of an important alternative fuel such as DME were measured at temperatures from (344 to 393) K. The second and third virial coefficients were derived and compared with empirical correlating methods and with data found in the literature. After different attempts, we decided to fix the third virial coefficients according to the Orbey and Vera correlating method. The second virial coefficients derived in this way followed approximately the same trend as the literature ones that were obtained at a different reduced temperature range.

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