
THE BENDER EQUATION OF STATE AND VIRIAL COEFFICIENTSAnatol MALIJEVSKÝ^{1,*} and Tomáš HUJO²*Department of Physical Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic; e-mail: ¹ anatol.malijevsky@vscht.cz, ² tomas.hujo@vscht.cz*Received May 9, 2000
Accepted July 15, 2000*Dedicated to Professor Eudovít Treindl on the occasion of his 70th birthday.*

The second and third virial coefficients calculated from the Bender equation of state (BEOS) are tested against experimental virial coefficient data. It is shown that the temperature dependences of the second and third virial coefficients as predicted by the BEOS are sufficiently accurate. We conclude that experimental second virial coefficients should be used to determine independently five of twenty constants of the Bender equation. This would improve the performance of the equation in a region of low-density gas, and also suppress correlations among the BEOS constants, which is even more important. The third virial coefficients cannot be used for the same purpose because of large uncertainties in their experimental values.

Key words: Equations of state; Bender equation; Second virial coefficient; Third virial coefficient; Thermodynamics.

The Bender equation¹ (BEOS) is one of the best empirical equations of state. It can describe accurately P–V–T behaviour of gas and liquid phases in large regions of temperature and pressure. The price for the accuracy is a large number (twenty) of adjustable constants. The constants are typically fitted to experimental volumetric data. However, reliable data in large regions of temperatures and pressures are available only for a limited number of substances.

There is another somewhat hidden shortcoming of the BEOS and other multiconstant equations. It is a mutual correlation among fitted constants which is virtually impossible to avoid. The correlations are not really harmful when the equation is used to interpolate experimental data used for fitting the constants. However, extrapolated P–V–T results and also derived thermodynamic quantities (enthalpy, entropy, heat capacities) may be rather uncertain.

Undesirable correlations of constants may be partly suppressed by adding constraints to their fits; typical examples of such constraints are conditions in the critical point. In this paper, we investigate using another constraint, an asymptotic behaviour of the BEOS at low densities. In the low density regime, any accurate equation of state should reproduce experimental second and third virial coefficients as functions of temperature. Using experimental virial coefficients, some constants of the BEOS may be fitted independently. These constants are not correlated with the constants fitted to direct P-V-T data. However, the question is whether the virial coefficients derived from the BEOS as functions of temperature can accurately describe experimental values in large ranges of temperature. There is also another question, whether independent virial coefficient fits do not deteriorate the accuracy of the BEOS at high densities.

RESULTS AND DISCUSSION

The BEOS written in terms of the compressibility factor $z \equiv pV/nRT$ as a function of temperature T and mole density $\rho \equiv n/V$ is

$$z = 1 + B\rho + C'\rho^2 + D\rho^3 + E\rho^4 + F\rho^5 + (G + H\rho^2)\rho^2 \exp(-\rho^2/a_{20}), \quad (1)$$

where

$$B = a_1 + \frac{a_2}{T} + \frac{a_3}{T^2} + \frac{a_4}{T^3} + \frac{a_5}{T^4} \quad (2)$$

$$C' = a_6 + \frac{a_7}{T} + \frac{a_8}{T^2} \quad (3)$$

$$D = a_9 + \frac{a_{10}}{T} \quad (4)$$

$$E = a_{11} + \frac{a_{12}}{T} \quad (5)$$

$$F = \frac{a_{13}}{T} \quad (6)$$

$$G = \frac{a_{14}}{T^3} + \frac{a_{15}}{T^4} + \frac{a_{16}}{T^5} \quad (7)$$

$$H = \frac{a_{17}}{T^3} + \frac{a_{18}}{T^4} + \frac{a_{19}}{T^5} \quad (8)$$

and a_1 to a_{20} are constants of the BEOS.

The second virial coefficient B is given by Eq. (2). The third virial coefficient C is

$$C = C' + G = a_6 + \frac{a_7}{T} + \frac{a_8}{T^2} + \frac{a_{14}}{T^3} + \frac{a_{15}}{T^4} + \frac{a_{16}}{T^5}. \quad (9)$$

If the BEOS constants are known for a given substance, predictions (2) and (9) may be compared with direct experimental data on the virial coefficients. We have taken constants a_1 to a_{20} from literature¹⁻⁸ and compared the results of Eq. (2) with the second virial coefficients compiled in the book of Dymond and Smith⁹. Comparisons have been done for 21 substances for which both the BEOS constants and second virial coefficients are known (argon, benzene, carbon dioxide, nitrogen, ethane, ethene, fluorine, isopentane, krypton, oxygen, methane, methanol, neon, neopentane (2,2-dimethylpropane), octane, propane, propene, propyne, sulfur hexafluoride, water, hydrogen). Here we show two representative examples.

Table I compares the second virial coefficients for argon. It can be seen that the deviations of the values calculated using Eq. (2) from the experimental values are within estimated uncertainties of experimental values for all but the lowest temperatures. We may conclude that the functional form of Eq. (2) can excellently reproduce the experimental temperature dependence in a large temperature range. We may also speculate that the experimental second virial coefficients were either explicitly or implicitly used for determination of the BEOS constants for argon. Similarly excellent results have been also found for carbon dioxide, ethane, fluorine, isopentane, oxygen, methane, neon, propane, propene, sulfur hexafluoride, and hydrogen.

The BEOS was developed to describe experimental data on dense gases and liquids, and it was carefully tested in these regions¹⁻⁸. The results in Table I show that the equation can also accurately describe the second virial coefficients without loss of accuracy at high densities. It seems, thus, that the independent determination of a_1 to a_5 does not deteriorate high

density results. This conclusion is further supported by a recent work of Cibulka *et al.*¹⁰ The authors calculated the BEOS constants using simultaneous correlation experimental P-V-T data in gaseous and liquid phases, vapour-liquid equilibrium data, conditions in the critical point, and second virial coefficients. They found for methane and pentane that all these data are accurately described by the BEOS.

However, not always the BEOS gives accurate second virial coefficients. Table II shows results for benzene with constants of the BEOS taken from ref.⁵: the mutual agreement is poor. This implies that using these constants negatively affects low-density P-V-T results. Constants a_1 to a_5 are evidently wrong and, thus, large correlations of constants a_1 to a_{20} are almost certain. Poor results have been also found for methanol and octane.

TABLE I

Comparison of experimental second virial coefficients, B_{exp} , for argon⁹ with the values calculated using Eq. (2), B_{calc} (ΔB_{exp} denotes estimates of uncertainty of the experimental values)

$T, \text{ K}$	B_{exp} $\text{cm}^3 \text{ mol}^{-1}$	ΔB_{exp} $\text{cm}^3 \text{ mol}^{-1}$	$B_{\text{calc}} - B_{\text{exp}}$ $\text{cm}^3 \text{ mol}^{-1}$
81.00	-276.0	5.0	16.0
85.00	-251.0	3.0	10.6
90.00	-225.0	3.0	6.5
95.00	-202.5	2.0	3.4
100.00	-183.5	1.0	1.4
110.00	-154.5	1.0	0.8
125.00	-123.0	1.0	1.3
150.00	-86.2	1.0	0.0
200.00	-47.4	1.0	-0.4
250.00	-27.9	1.0	0.1
300.00	-15.5	0.5	-0.1
400.00	-1.0	0.5	-0.3
500.00	7.0	0.5	-0.1
600.00	12.0	0.5	0.2
700.00	15.0	1.0	0.9
800.00	17.7	1.0	1.0
900.00	20.0	1.0	0.8
1 000.00	22.0	1.0	0.6

We also compared the third virial coefficients given by Eq. (9) with experimental data⁹. The comparisons have been performed for the same substances as with second virial coefficients. Table III compares the virial coefficients for krypton, with constants of the BEOS taken from ref.⁴: the agreement is excellent. Only at few temperatures, deviations between the calculated and experimental values are slightly larger than the estimated errors in the experimental data. This shows that the functional form of Eq. (9) excellently describes experimental temperature dependence of the third virial coefficients in a large temperature range.

However, it cannot be excluded that the excellent agreement in Table III is a lucky coincidence. For krypton, two other sets of the experimental third virial coefficients are available, but no estimates of errors are given for them. The data sets differ. At $T = 273.15$ K we have $3\,130 \pm 125$, $2\,757$, and $2\,455$ cm⁶/mol². For the other tested substances, agreement of experimental third virial coefficients is even much worse. For example, we have four different values for ethene at 273 K: $-7\,250$ (!), $7\,500$, $7\,900$, and $9\,300$.

TABLE II

Comparison of experimental second virial coefficients, B_{exp} , for benzene⁹ with the values calculated using Eq. (2), B_{calc}

$T, \text{ K}$	B_{exp} cm ³ mol ⁻¹	ΔB_{exp} cm ³ mol ⁻¹	$B_{\text{calc}} - B_{\text{exp}}$ cm ³ mol ⁻¹
290.00	-1 590.0	30.0	152.4
300.00	-1 450.0	20.0	121.8
310.00	-1 340.0	20.0	110.2
320.00	-1 230.0	20.0	88.8
340.00	-1 050.0	20.0	60.7
360.00	-920.0	20.0	54.9
380.00	-810.0	20.0	47.3
400.00	-710.0	20.0	32.3
440.00	-570.0	10.0	23.5
480.00	-470.0	10.0	18.3
520.00	-390.0	10.0	8.8
560.00	-340.0	10.0	12.8
600.00	-290.0	10.0	5.1

CONCLUSIONS

It has been shown that the temperature dependence of the second virial coefficient as predicted by the Bender equation of state is sufficiently accurate. Most sets of constants of the Bender equation given in literature excellently describe experimental second virial coefficients; however, literature constants for a few substances do not. These should be used with a great caution.

Experimental second virial coefficient should be used to determine independently five of twenty constants of the Bender equation. This would improve performance of the equation in the low-density gas region and also suppress compensations of the constants.

Temperature dependence of the third virial coefficient as predicted by the Bender equation of state seems to be also sufficiently accurate. If there were accurate experimental third virial coefficients data available, another six constants of the Bender equation could be calculated from them. However, the accuracy of experimental third virial coefficients is typically low. More accurate experimental values are highly desirable.

Several extensions of the Bender equation of state with more than twenty constants have been proposed. Using additional second virial coefficient

TABLE III

Comparison of experimental third virial coefficients, C_{exp} , for krypton⁹ with the values calculated using Eq. (9), C_{calc} (ΔC_{exp} denotes estimates of uncertainty of the experimental values)

T, K	C_{exp} $\text{cm}^6 \text{mol}^{-2}$	ΔC_{exp} $\text{cm}^6 \text{mol}^{-2}$	$C_{\text{calc}} - C_{\text{exp}}$ $\text{cm}^6 \text{mol}^{-2}$
273.15	3 130.0	125.0	481.2
323.15	3 000.0	120.0	-27.0
373.15	2 570.0	90.0	-65.7
423.15	1 960.0	85.0	190.1
473.15	1 755.0	75.0	117.9
573.15	1 355.0	115.0	109.9
673.15	1 260.0	150.0	-83.0
773.15	1 055.0	150.0	-93.1
873.15	760.0	170.0	34.7

data to calculate some of the constants is even more desirable than in the case of the Bender equation discussed in this work.

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