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LETTER

Molecular dynamics simulation of *PVT* properties of geological fluids and a general equation of state of nonpolar and weakly polar gases up to 2000 K and 20,000 bar

ZHENHAO DUAN, NANCY MØLLER, and JOHN H. WEARE
Department of Chemistry, 0340, University of California, San Diego, La Jolla, CA 92093-0340, USA

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Abstract—The *PVT* properties of CH_4 from 30–360 cm^3 mol and roughly from 273–2000 K and from 100–20,000 bar have been simulated by molecular dynamics using Lennard-Jones potentials. The simulated results compare with data within 1.5% in volume. Using these simulated values and experimental *PVT* data, an equation of state (EOS) was developed. Because of the choice of potential, a simple scaling generalizes the EOS to predict the supercritical *PVT* properties of CO_2, N_2, CO, H_2, O_2, and Cl_2 within an average error of about 1.5%.

INTRODUCTION

THE *PVT* PROPERTIES OF natural fluids, such as CH_4, CO_2, N_2, H_2O, O_2, and H_2, are very important to the understanding of physical or chemical processes in the Earth's crust and mantle. Most measurements are limited to pressures below 5000 bar because of experimental difficulties. Although it is possible for an equation of state to extrapolate beyond this data range, such extrapolations become unreliable after the database is exceeded by about 3000 bar and 300°C.

With the increasing availability of computer facilities, it is becoming possible to predict the thermodynamic properties of real systems by computer simulation. Recent examples of simulating *PVT* properties of gases are the molecular dynamics (MD) simulations for CH_4 (HANLEY and WATTS, 1975; WAVEREN et al., 1986; SAAGER and FISCHER, 1990; BELONOSHKO and SAXENA, 1991b), for CO_2 (LUCKAS and LUCAS, 1989; BELONOSHKO and SAXENA, 1991b), and for H_2O (BRODHOLT and WOOD, 1990, BELONOSHKO and SAXENA, 1991a). The most comprehensive study has been reported by BELONOSHKO and SAXENA (1991b), who simulated the *PVT* properties of CO_2, CH_4, CO, O_2, and H_2 for the molar volume range from about 6–40 cm^3/mol and for the approximate temperature range from 500–4000 K.

In this letter, we report our results of the use of computer simulation to predict the *PVT* behavior of methane with accuracy close to experimental results in the range of 30–360 cm^3/mol and roughly from 273–2000 K and from 100–20,000 bar. These simulated data, together with experimental *PVT* data, were used to establish an equation of state (EOS) of methane, which is accurate within an average deviation of 0.8% from experimental or simulated data ranging from 273–2000 K and from 0–20,000 bar. This EOS is, by a simple scaling, used for predicting the *PVT* properties of nonpolar or weakly polar species such as CO_2, N_2, CO, and Cl_2 over a large *T-P* space. Our results show that this generalized EOS is accurate for a large number of supercritical fluids within an average deviation of 1.5% from experimental data.

THE MOLECULAR DYNAMICS SIMULATION

Our MD simulations were performed at constant energy, constant volume, and constant number of particles. The interactions between molecules were assumed to be effective pairwise additive. Lennard-Jones (L-J) and exp-6 potentials have been widely used to calculate the *PVT* properties of fluids (SHMULOVICH et al., 1982; ROSS et al., 1983; BELONOSHKO and SAXENA, 1991b). BELONOSHKO and SAXENA (1991b) chose the exp-6 potential because they believed that the L-J potential is too stiff in the repulsive part and gives too large of pressures for a given temperature and volume of high-density fluids. Using both the exp-6 potential and the L-J potentials, we simulated the *PVT* properties of methane at different temperatures and volumes. The results indicated that neither L-J potential nor exp-6 potential is universally correct from low *T-P* (e.g., 273 K and 1 bar) to very high *T-P* (e.g., over 3000 K and 25 kbar), unless their parameters are dependent on *T* and *P*. However, if we use the L-J potential, the simulated results are within about 1.5% of experimental data at pressures below 8000 bar and within about 2% of the simulated results by BELONOSHKO and SAXENA (1991b) at pressures around 20,000 bar. In addition, there are certain scaling properties of the L-J potential which allow these results to be generalized to a large number of systems. Therefore, in this study, we use the L-J potential, as follows:

$$V_{ij} = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]. \tag{1}$$

The methane molecule was approximated as a united atom with only one L-J term at the center of the carbon atom. The L-J parameters were taken initially from JORGENSEN et al. (1984). However, the simulated volumes were systematically higher than experimental data, by 1.5–2.5%. The parameters were then adjusted slightly by trial and error.

The simulations were initiated either with a face-centered cubic lattice or a previous configuration of N particles in a simulating box with a specified volume. (If molar volume > 45 cm^3, we used 108 particles; otherwise, we used 256 particles.) The trajectories of particles were calculated using the Verlet algorithm (ALLEN and TILDESLEY, 1989). The minimum image criterion and periodic boundary conditions were used. The cutoff radius was taken to be half of the box length. The time step was 2.4×10^{-15} sec. At each Verlet time step, the temperature is calculated as

$$T = \frac{2E}{3Nk_B}, \tag{2}$$

Table 1. The Molecular Dynamics Simulated PVT Data of Methane

T (K)	P (bar)	V* (cm^3)	V (cm^3, MD)
258.6	50.5	364.96	360.00
293.5	60.6	360.65	360.00
382.8	86.3	355.13	360.00
557.1	131.1	361.96	360.00
790.7	193.3	359.48	360.00
1128.6	281.9	357.79	360.00
1612.4	407.4	-	360.00
2314.6	587.2	-	360.00
211.1	60.4	-	180.00
251.8	85.1	182.03	180.00
304.1	118.5	180.62	180.00
365.1	158.2	179.42	180.00
448.9	209.5	180.54	180.00
543.3	266.7	180.88	180.00
663.4	342.2	179.09	180.00
811.5	429.4	179.33	180.00
997.5	535.9	179.86	180.00
1223.1	667.6	179.37	180.00
1504.0	833.2	178.44	180.00
1840.0	1035.6	-	180.00
2250.6	1261.3	-	180.00
2761.0	1551.8	-	180.00
3376.9	1894.6	-	180.00
264.5	131.9	120.06	120.00
312.9	183.2	121.00	120.00
382.7	261.6	119.91	120.00
464.0	344.9	121.21	120.00
556.0	437.1	121.93	120.00
677.1	565.7	120.75	120.00
822.3	715.8	120.03	120.00
1001.5	880.5	121.24	120.00
1211.6	1096.4	120.03	120.00
1468.3	1367.6	-	120.00
1796.4	1692.0	-	120.00
2175.1	2073.6	-	120.00
2660.3	2503.6	-	120.00
3234.6	3071.1	-	120.00
240.2	135.0	90.75	90.00
80.8	198.6	91.83	90.00
323.5	266.4	92.50	90.00
384.5	372.2	91.33	90.00
458.1	494.9	90.97	90.00
653.7	806.7	90.67	90.00
781.5	1011.1	90.11	90.00
937.0	1245.4	90.12	90.00
1116.6	1495.3	90.79	90.00
1330.6	1838.1	89.74	90.00
1577.6	2233.2	-	90.00
244.0	739.0	44.48	45.00
274.1	971.4	44.70	45.00
329.3	1271.6	45.76	45.00
379.6	1622.2	45.55	45.00
444.5	2080.2	45.13	45.00
507.5	2422.1	45.37	45.00
579.1	2821.1	45.46	45.00
623.7	3131.0	45.16	45.00
664.3	3305.3	45.44	45.00
769.4	4002.6	44.95	45.00
862.9	4390.0	45.48	45.00
1010.1	5232.5	45.33	45.00
1128.2	5833.9	45.45	45.00
1265.7	6546.7	45.52	45.00
1474.4	7508.3	-	45.00
1700.6	8592.9	-	45.00
2003.7	9906.1	-	45.00
2329.1	11507.9	-	45.00
2768.7	13101.0	-	45.00
3229.7	15227.7	-	45.00
221.0	968.4	39.70	40.00
243.1	1149.8	40.46	40.00
275.2	1537.9	40.26	40.00
310.0	1889.4	40.23	40.00
359.4	2320.4	40.28	40.00
412.7	2791.0	40.16	40.00
481.4	3249.1	40.46	40.00
13.4	3606.4	40.06	40.00
553.1	3866.9	40.19	40.00
636.4	4447.0	40.30	40.00
725.5	5216.9	39.98	40.00
788.4	5641.1	40.07	40.00
848.5	6002.3	40.25	40.00
916.3	6434.3	40.37	40.00
978.2	6985.3	40.14	40.00
1053.8	7397.9	40.40	40.00
1127.4	8138.7	39.99	40.00
1222.3	8638.4	40.31	40.00
1880.7	2697.1	-	90.00
2266.1	3156.2	-	90.00
2698.1	3810.8	-	90.00
292.5	313.4	71.01	70.00
346.7	455.6	71.12	70.00
409.6	611.5	71.39	70.00
492.0	821.7	70.97	70.00
590.7	1050.2	71.26	70.00
714.7	1335.9	71.26	70.00
850.3	1656.5	70.89	70.00
1015.9	2053.5	70.35	70.00
1332.6	2750.8	70.43	70.00
1773.2	3723.1	-	70.00
2128.6	4464.9	-	70.00
2573.1	5412.0	-	70.00
3090.3	6419.2	-	70.00
242.1	251.1	60.08	60.00
257.6	307.3	60.33	60.00
307.0	490.3	60.38	60.00
360.3	661.7	61.19	60.00
426.1	885.4	61.14	60.00
501.6	1166.3	60.27	60.00
593.6	1432.6	60.89	60.00
702.1	1734.7	61.44	60.00
828.0	2161.8	60.68	60.00
973.3	2639.2	60.17	60.00
1140.8	3122.5	60.33	60.00
1346.1	3719.0	60.39	60.00
1605.7	4427.9	-	60.00
1913.6	5341.2	-	60.00
2278.7	6258.3	-	60.00
2718.4	7353.6	-	60.00
3223.9	8753.9	-	60.00
233.4	373.5	50.37	50.00
276.0	594.3	51.28	50.00
322.5	908.0	50.06	50.00
383.5	1148.2	51.31	50.00
450.3	1516.2	50.67	50.00
530.7	1890.0	50.71	50.00
632.4	2383.9	50.42	50.00
752.5	2927.2	50.36	50.00
894.8	3651.6	49.78	50.00
1072.1	4340.2	50.25	50.00
1268.6	5178.8	50.27	50.00
1524.3	6220.9	50.44	50.00
2193.5	8668.1	-	50.00
2626.4	10059.7	-	50.00
3130.9	11928.8	-	50.00
1310.4	9082.9	40.61	40.00
1516.7	10282.8	40.97	40.00
1794.5	11901.1	-	40.00
2104.4	13573.5	-	40.00
2448.2	15513.3	-	40.00
220.8	2060.1	34.68	35.00
250.8	2482.4	35.22	35.00
287.6	2992.7	35.40	35.00
323.5	3458.5	35.42	35.00
369.9	4017.3	35.39	35.00
425.1	4651.6	35.31	35.00
487.1	5444.8	35.03	35.00
564.6	6256.3	34.99	35.00
652.7	6977.8	35.23	35.00
743.8	8118.6	34.88	35.00
861.9	9224.6	34.97	35.00
1008.1	10372.2	35.32	35.00
1176.6	11863.6	35.48	35.00
1362.6	13543.8	35.60	35.00
1582.4	15302.5	35.90	35.00
1869.1	17317.8	-	35.00
2208.0	20099.1	-	35.00
2892.7	22438.8	-	35.00
230.5	5077.9	29.92	30.00
248.9	5549.5	30.09	30.00
271.2	6096.7	30.16	30.00
302.2	6583.8	30.36	30.00
326.4	7111.6	30.29	30.00
357.4	7705.3	30.23	30.00
393.2	8278.6	30.21	30.00
442.6	9207.3	30.03	30.00
480.3	9742.8	30.02	30.00
533.6	10655.1	29.88	30.00
594.6	11623.5	29.79	30.00
665.3	12582.3	29.80	30.00
745.7	13754.1	-	30.00
927.8	16291.4	-	30.00
1193.8	20041.0	-	30.00

* The volume calculated from the equation of state (Duan et al,1992a). This EOS is within experimental error (0.466% as compared with 1083 data points).

Table 2. parameters for Eq. (5a)

a_1	3.75504388D-02
a_2	-1.08730273D+04
a_3	1.10964861D+06
a_4	5.41589372D-04
a_5	1.12094559D+02
a_6	-5.92191393D+03
a_7	4.37200027D-06
a_8	4.95790731D-01
a_9	-1.64902948D+02
a_{10}	-7.07442825D-08
a_{11}	9.65727297D-03
a_{12}	4.87945175D-01
a_{13}	1.62257402D+04
a_{14}	8.99000000D-03

Table 3. L-J Potential Parameters

Species	ε/k (K)	σ (A)	Reference
CH_4	154.0 (147.8)	3.691 (3.73)	Jorgensen et al., 1984
CO_2	235.0 (247.0)	3.69 (3.69)	Ben-Amotz and Herschbach, 1990
CO	98.0 (98.0)	3.66 (3.69)	Ben-Amotz and Herschbach, 1990
O_2	115.7 (106.7)	3.365 (3.467)	Svehla, 1962
N_2	99.0 (95.)	3.622 (3.698)	Hirschfelder et al., 1964
H_2	34.6 (33.3)	2.91 (2.968)	Jones and Ingham, 1925
Cl_2	348.7	3.692	

The numbers in brackets are from the references

Table 4. Comparison of Experimental Data with the EOS (Eq. 5)

Species	T(K)	P(bar)	average error%	# of measurements
CH_4	250-723	1-8000	0.8	1083
CO_2	380-1273	1-8000	1.5	2560
N_2	248-1800	1-22000	0.7	903
H_2	373-873	100-7000	0.96	102
CO	308-573	1500-10000	0.66	72

The numbers in brackets are from the references

and the pressure as

$$P = \frac{Nk_BT}{V} - \frac{1}{3V}\sum_i \sum_{j>i} r_{ij}\frac{\partial V_{ij}}{\partial r_{ij}} + P_{LRC}, \tag{3}$$

where E is total kinetic energy, k_B is Botzman constant, V_{ij} is the potential energy between particles i and j, r_{ij} is the distance between i and j, and P_{LRC} is long-range correction pressure calculated from

$$P_{LRC} = \frac{\pi\epsilon\sigma^3}{V^2}\left[\frac{32}{9}\left(\frac{\sigma}{r_c}\right)^9 - \frac{16}{3}\left(\frac{\sigma}{r_c}\right)^3\right], \tag{4}$$

which is derived from Eqn. (2.137) of ALLEN and TILDESLEY (1989). r_c is the cutoff radius.

Each run was terminated after the system reached equilibrium (usually in 2000 time steps), with temperature and pressure fluctuating around an average value. In order to obtain more precise results, we used two 2000 time steps for each run. The deviations in average temperature and pressure between the two runs is about 1 and 3%, respectively. The simulated results are reported in Table 1. In order to compare the simulated results with experimental data, the calculated results of the EOS of DUAN et al. (1992a) are also listed in Table 1. This EOS represents smoothed experimental data of 1083 data points. For the high-pressure points indicated by "-" in the third and seventh columns of Table 1, there are no data for comparison. These points usually correspond to high temperatures. While there are no data for comparison, we note that the simulations for the same density but lower temperatures agree well with the experiment.

A GENERAL EQUATION OF STATE

Using the simulated results (Table 1), together with all the experimental data of methane (Table 1 of DUAN et al., 1992a), we obtain an EOS with an average deviation of 0.8%, as compared with all the 1083 experimental data points (Table 1 of DUAN et al., 1992a) and the 174 simulated data points (Table 1) roughly from 273–2000 K and from 0–20,000 bar:

$$Z = \frac{P_rV_r}{RT_r} = 1 + \frac{a_1 + a_2/T_r^2 + a_3/T_r^3}{V_r} + \frac{a_4 + a_5/T_r^2 + a_6/T_r^3}{V_r^2} + \frac{a_7 + a_8/T_r^2 + a_9/T_r^3}{V_r^4} + \frac{a_{10} + a_{11}/T_r^2 + a_{12}/T_r^3}{V_r^5} + \frac{a_{13}}{T_r^3V_r^2}\left(1 + \frac{a_{14}}{V_r^2}\right)\exp\left(-\frac{a_{14}}{V_r^2}\right). \tag{5a}$$

Here the subscript r means the reference fluid, i.e., methane. The parameters are listed in Table 2.

If interactions in the system are described by an L-J potential (but with different parameters, σ and ϵ), the reduced temperature $T^* = kT/\epsilon$ and reduced volume $V^* = V/\sigma^3$

Table 5. PTV Data for N_2,CO, and H_2

System	Authors	Temperature (K)	P(bar)	# of Measurements
N_2	Michels et al., 1936	273-423	194-3000	148
	Robertson and Babb, 1969	308-673	1500-10000	84
	Malbrunot and Vodar, 1969	473-1273	1000-4000	63
	Tsiklis and Polyakov, 1968	298-673	1500-10000	69
	Antanovich and Plotnikov, 1976	400-1773	1000-5000	44
	Bartlett et al., 1928	273-673	1-1000	53
	Biswas and Seldam, 1991	248-323	2000-10000	156
	Benedict, 1937a+1937b	150-473	1000-5800	114
	Holborn and Otto, 1922, 1924	273-673	0-100	112
	Mills et al., 1975	273-320	3000-22000	60
CO	Robertson and Babb, 1970	308-573	1000-10000	72
H_2	Presnall, 1969	373-873	1-1800	96
	Tsiklis et al., 1975	373-423	5000-7000	6

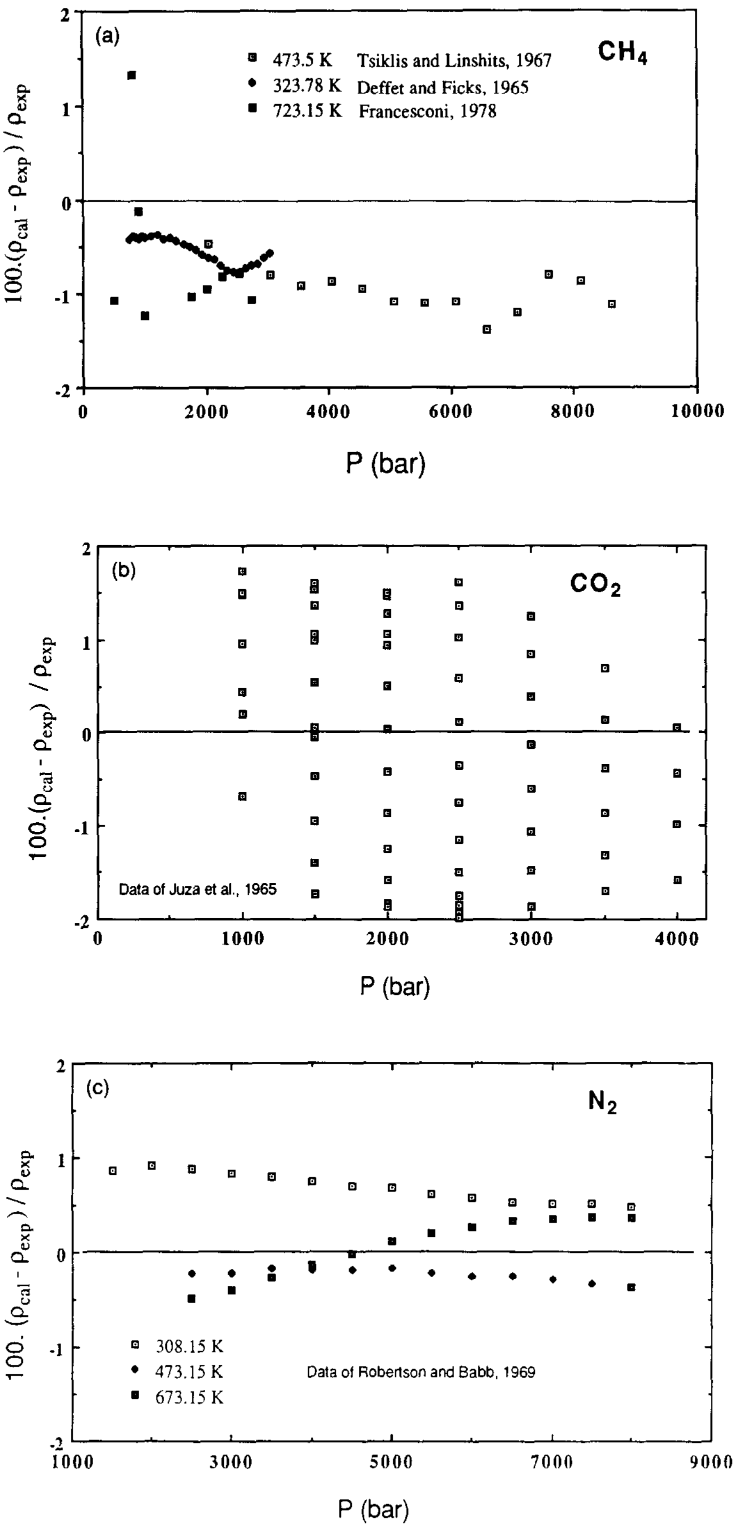

FIG. 1. Experimental density data of (a) CH_4, (b) CO_2, (c) N_2, and (d) CO compared with predictions of Eqn. (5).

will be the same for all systems (MCQUARRIE, 1976). This leads to a simple generalization of Eqn. (5a) that provides similar accuracy for a large number of gases (e.g., CO_2, CO, N_2, O_2) with the following:

$$P_r = \frac{3.0626\sigma^3 P}{\epsilon}, \tag{5b}$$

$$T_r = \frac{154T}{\epsilon}, \quad \text{and} \tag{5c}$$

$$V_r = \left(\frac{3.691}{\sigma}\right)^3 V. \tag{5d}$$

The L-J parameters for the various gases can be found in

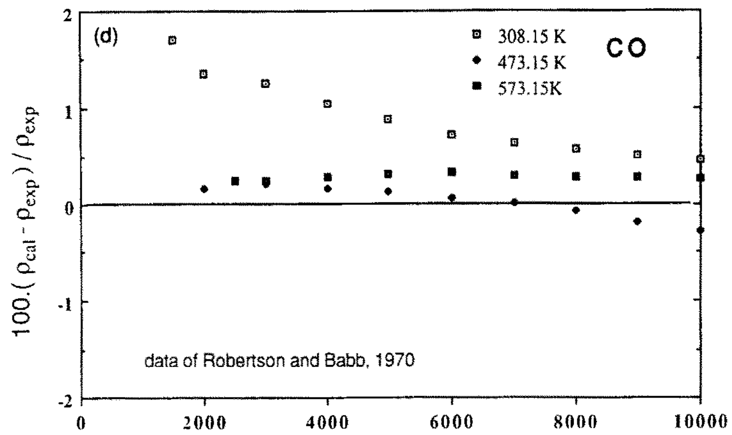

FIG. 1. (Continued)

the literature (parameters within brackets in Table 3) or evaluated from data (parameters outside brackets in Table 3). Usually only a few to tens of data points are needed in the evaluation. We have compared a large number of experimental data of CH_4, CO_2, N_2, H_2, and CO with the predictions from Eqn. (5). The results are listed in Table 4, which shows that Eqn. (5) is accurate within an average error of 0.6–1.5%. The data sources of CH_4 and CO_2 are listed in Table 1 (DUAN et al., 1992a,b). The data sets for N_2, CO, and H_2 are listed in Table 5. Some representative comparisons of data points with Eqn. (5) are shown in Fig. 1 and Table 6. They indicate that Eqn. (5) can predict the *PVT* properties of different species within an average error of less than 1.5%.

As far as we know, N_2 is the only species that has *PVT* data above 10,000 bar. It is remarkable that Eqn. (5) can predict N_2 density up to 22,000 bar (Table 7), even though it is developed based on CH_4 data alone. Although there is no CH_4 data above 8500 bar, the small error of the predictions of Eqn. (5) in N_2 up to 22,000 bar may demonstrate from another prospective that our simulation of CH_4 *PVT*

Table 6. Comparison of the Experimental Molar Volume with Eq. (5)

T(K)	P(bar)	$V_{cal.}$ (cm^3)	$V_{exp.}$ (cm^3)	Error%	Reference
CH_4					
273.2	16.4	1333.46	1333.33	0.01	Douslin et al., 1964
623.2	41.8	1253.88	1250.00	0.31	-
323.5	2026.5	40.20	40.20	-0.01	Tsiklis and Linshits, 1967
323.5	8612.6	29.01	29.30	-0.99	-
673.5	2026.5	55.29	55.80	-0.91	-
673.5	8106.0	33.76	34.20	-1.30	-
673.5	8612.6	33.16	33.40	-0.90	-
1214.0	18935.0	30.26	(30.00)	0.86	
589.0	23436.0	24.72	(25.00)	-1.14	
CO_2					
1073.15	25.00	3587.93	3607.40	-0.5397	Kennedy, 1954
373.15	100.00	238.45	234.47	1.6978	-
1073.15	100.00	911.47	909.30	0.2392	-
373.15	500.00	55.13	53.70	2.6640	-
1073.15	500.00	199.33	200.32	-0.4949	-
373.15	1000.00	45.46	44.77	1.5480	-
1073.15	1000.00	112.22	114.13	-1.6749	-
373.15	2000.00	39.11	38.70	1.0565	Juza et al., 1965
573.15	2000.00	48.51	48.93	-0.8643	-
648.15	4000.00	41.25	41.10	0.3609	-
473.15	8000.00	31.93	31.48	1.4349	Shmulovich and Shmonov, 1978
673.15	8000.00	34.49	34.01	1.4153	-
973.15	8000.00	37.97	37.81	0.4285	-
1295.50	9208.20	39.72	(40.00)	-0.7077	
1189.70	19911.3	30.34	(30.00)	1.1291	
1945.20	28315.3	30.87	(30.00)	2.9045	
773.80	21678.3	27.51	(27.16)	1.2869	
N_2					
273.15	52.91	424.20	421.00	0.7602	Michels et al.,1936
373.15	299.60	120.20	119.80	0.3362	-
373.15	1444.00	47.54	47.66	-0.2581	-
373.15	2602.60	38.54	38.65	-0.2765	-
248.15	1594.50	38.95	38.46	1.2773	Biswas and Seldam, 1991
248.15	5107.70	29.09	28.99	0.3593	-
248.15	7988.80	26.29	26.32	-0.1176	-
1800.00	1000.00	180.73	183.01	-1.2466	Antanovich and Plotnikov, 1976
1800.00	5000.00	58.51	58.82	-0.5276	-
273.30	3000.00	33.81	33.63	0.5453	Mills et al., 1975
273.30	20000.00	21.64	21.49	0.6889	-
297.40	3000.00	34.55	34.47	0.2302	-
297.40	22000.00	21.26	21.23	0.1360	-
320.80	3000.00	35.26	35.27	-0.0356	-
320.80	22000.00	21.33	21.42	-0.4222	-

Table 6. (Continued)

T(K)	P(bar)	$V_{cal.}$ (cm^3)	$V_{exp.}$ (cm^3)	Error%	Reference
H_2					
373.15	5000.00	19.98	20.21	-1.1591	Tsiklis et al., 1975
373.15	6000.00	18.64	18.75	-0.5775	-
373.15	7000.00	17.62	17.62	0.0017	-
423.15	5000.00	20.99	21.01	-0.0968	-
423.15	6000.00	19.53	19.70	-0.8380	-
423.15	7000.00	18.43	18.17	1.4215	-
Cl_2					
550.15	10.00	4504.52	4497.00	0.1672	Angus et al., 1985
550.15	100.00	384.81	379.50	1.4005	-
550.15	250.00	117.02	118.40	-1.1670	-
900.15	100.00	736.58	737.90	-0.1792	-
900.15	250.00	290.59	291.80	-0.4158	-
O_2					
473.15	5066.00	28.91	29.26	-1.1807	Tsiklis and Koulikova, 1965
473.15	7092.00	26.10	26.78	-2.5300	-
573.15	5066.00	30.76	31.04	-0.9011	-
573.15	9119.00	25.41	24.89	2.1037	-
673.15	5066.00	32.61	32.64	-0.0848	-
673.15	10132.00	25.68	25.75	-0.2611	-
394.30	1801.70	38.60	38.74	-0.3549	-
1295.90	6027.60	40.27	(40.00)	0.6733	-
407.10	4049.20	29.62	(30.00)	-1.2649	-
1193.80	17037.20	25.74	(25.00)	2.9476	-
CO					
308.15	2000.00	40.15	39.61	1.3593	Robertson and Babb, 1970
308.15	5000.00	31.11	30.84	0.8853	-
308.15	10000.00	26.20	26.08	0.4636	-
373.15	2000.00	43.00	42.65	0.8212	-
373.15	5000.00	32.38	32.27	0.3268	-
373.15	10000.00	26.86	26.90	-0.1470	-
473.15	2000.00	47.43	47.35	0.1708	-
473.15	5000.00	34.37	34.32	0.1357	-
473.15	10000.00	27.97	28.05	-0.2804	-
573.15	2500.00	47.11	47.00	0.2415	-
573.15	5000.00	36.39	36.28	0.3077	-
573.15	10000.00	29.17	29.09	0.2678	-

The number in bracket is the simulated result by Belonoshko and Saxena (1991b)

properties is reliable up to 20,000 bar or even higher. One can also calculate the thermodynamic properties of other species (e.g., C_2H_6, He, Ar, Xe, NO_2) using Eqn. (5) just by plugging in the two L-J parameters obtained from the literature. It is also relatively easy to obtain L-J parameters through Eqn. (5) using some *PVT* data, or with knowledge using other kinds of data, such as enthalpy, entropy, and the second virial coefficient.

Unlike other general EOS or corresponding state EOS, such as the equations of Lee and Kesler (1975), Eqn. (5) is accurate to very high pressure (with fewer parameters). The Lee-Kesler EOS is accurate only below 100–300 bar in the supercritical region. Compared with the EOS of Belonoshko and Saxena (1991b), Eqn. (5) needs only one pair set of parameters for each species, while the EOS of Belonoshko and Saxena (1991b) needs a complete reparameterization of parameters for every species. Equation (5) and the EOS of Belonoshko and Saxena (1991b) cover different *T-P* range. The EOS of Belonoshko and Saxena (1991b) is not suitable for pressures below 5000 bar. Therefore, in order to calculate fugacities using the EOS of Belonoshko and Saxena (1991b), another EOS is needed. Compared with our EOS published earlier (Duan et al., 1992a,b), Eqn. (5) is general for many species but cannot predict liquid vapor equilibria. The EOS of Duan et al. (1992a,b) can predict both phase equilibrium and *PVT* properties of both pure systems and mixtures but is limited to pressures below 8000 bar and needs as many sets of parameters as the number of species. It is difficult to generalize Eqn. (5) to include such polar species as H_2O and H_2S.

Table 7. Comparison of the Experimental Molar Volume of N_2 with Eq. (5)

T(K)	P(bar)	$V_{cal.}$ (cm^3)	$V_{exp.}$ (cm^3)	Error%
N_2				
247.50	3000.00	33.01	32.70	0.9355
247.50	5000.00	29.22	28.98	0.8440
247.50	10000.00	25.01	24.78	0.9253
247.50	15000.00	22.90	22.65	1.1243
273.30	3000.00	33.81	33.63	0.5453
273.30	5000.00	29.74	29.61	0.4454
273.30	10000.00	25.27	25.16	0.4486
273.30	15000.00	23.06	22.94	0.5372
273.30	20000.00	21.64	21.49	0.6889
297.40	3000.00	34.55	34.47	0.2302
297.40	5000.00	30.21	30.19	0.0678
297.40	10000.00	25.51	25.51	0.0039
297.40	15000.00	23.21	23.20	0.0272
297.40	20000.00	21.72	21.71	0.0686
297.40	22000.00	21.26	21.23	0.1360
320.80	3000.00	35.26	35.27	-0.0356
320.80	5000.00	30.66	30.74	-0.2568
320.80	10000.00	25.74	25.85	-0.4172
320.80	15000.00	23.35	23.45	-0.4387
320.80	20000.00	21.81	21.91	-0.4476
320.80	22000.00	21.33	21.42	-0.4222

The experimental data are from Mills et al. 1975

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