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A molecular dynamics study of the pressure-volume-temperature properties of supercritical fluids: II. CO₂, CH₄, CO, O₂, and H₂

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Abstract—The method of molecular dynamics (MD) has been used to simulate the pressure-volume-temperature (PVT) properties of CO₂, CH₄, CO, O₂, and H₂. For the MD simulation, the exponential-6 form of the intermolecular potential has been adopted. The parameters of the potential are calculated from the available experimental PVT data. The MD-simulated results fit the experimental (static) PVT data well and are in reasonable agreement with the shock-wave P - V data. Based on both the experimental PVT and the MD-simulated data, equations of the type:

$$P = a/V + b/V^2 + c/V^n$$

have been formulated for each of the five fluids in the pressure range of 5 Kbar to 1 Mbar at temperatures from 400 to 4000 K. The calculated fugacity of CO₂ has been used to show the consistency of the modeled data with the experimental phase equilibrium data on the reactions involving magnesite.

INTRODUCTION

THE PVT DATA on the C-H-O fluids are necessary in phase equilibrium calculations relevant to the earth's mantle. Many attempts have been made to model the PVT relations from the existing data (e.g., HOLLOWAY, 1977; BOTTINGA and RICHEL, 1981; KERRICK and JACOBS, 1981; DELANY and HELGESON, 1978; ROSS et al., 1983; HALBACH and CHATTERJEE, 1982). The theoretical basis of the various models used for such studies differs considerably and may be classified into groups depending on the assumptions involved. Class A models are based on the experimentally observed variations of the PVT relations, e.g., the linearity of the isochors (DELANY and HELGESON, 1978) or the constancy of the heat capacity (SHMONOV and SHMULOVICH, 1974). Class B models take into account the behavior of the attractive and repulsive forces (e.g., in the VAN DER WAALS method (1881) and its various modifications; HOLLOWAY, 1977; HALBACH and CHATTERJEE, 1982). Class C models are based on the theory of perturbation of liquid (e.g., WEEKS et al., 1971). Finally, there are class D models with computer simulation of the molecular interactions (e.g., BRODHOLT and WOOD, 1990; BELONOSHO and SAXENA, 1991; KALINICHEV, 1986). Computer simulation of molecular interactions in a dense fluid is the subject of this study.

In the low P and T ranges (below 10 Kbar and 1000 K) the precision attained in fitting the PVT relations by using class A and B models surpasses those attained by the class C and D models. This is understandable because the equations of state (EOS) using A and B are parameterized from experimental data, while the EOS based on class C and D models use the concept of intermolecular interaction potential (IP). Therefore, at moderate to high P and T , the latter should yield more precise representation and prediction of the PVT relations than those by the former. To clarify this, let us briefly consider the theory of the VAN DER WAALS (1881) EOS which has the form

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (1)$$

where R is gas constant, V volume, T temperature, and a and b adjustable parameters. The parameter b modifies the volume and the parameter a accounts for the intermolecular attraction. The REDLICH-KWONG (1949) and other modified forms follow the same form and differ mainly in the formulation of the attractive part (a/V^2). The term $RT/(V-b)$ is incorrect for describing the dense fluids because of two reasons: (a) the b parameter is a very complicated function of density and temperature, and (b) if molecules are to be treated as hard spheres, the term should be as in the CARNAHAN-STARLING (1969,1972) equation of the following form

$$P = \frac{RT}{V} \left(\frac{1+y+y^2-y^3}{(1-y)^3} \right) \quad (2)$$

where $y = b/4V$.

Therefore, the Van der Waals formulation would show an increasingly wrong asymptotic behavior with increasing density. To avoid this, many physical chemists and some geochemists (e.g., HALBACH and CHATTERJEE, 1982; KERRICK and JACOBS, 1981) have devised the parameters of the cubic EOS as complicated functions of P and T . Such EOS ensure highly reliable interpolations but, as will be discussed, we cannot rely on them for prediction of the PVT relations at high densities.

To demonstrate that the models (A) and (B) are inadequate at high T and P , we may mention the EOS for CO₂ as constructed by SHMONOV and SHMULOVICH (1974) and by BOTTINGA and RICHEL (1981). Both the equations of state are based essentially on the same experimental data. SHMONOV and SHMULOVICH (1974) used a modified form of the TAIT (1889) equation (class A); BOTTINGA and RICHEL (1981) used the modified REDLICH-KWONG (1949) equation (class B). A comparison of the extrapolated molar volumes

shows that the differences are quite large and both the data sets are inconsistent with the shock-wave data (ZUBAREV and TELEGIN, 1962) (see also discussion in SHMULOVICH et al., 1982).

The method of molecular dynamics provides an important tool to deal with this problem. We can extend the range of P and T for the applicability of such equations (e.g., that of SAXENA and FEI, 1987) by including the PVT data obtained by the MD simulation in fitting the PVT polynomials. Part 1 of this study was concerned with the MD simulation of H_2O (BELONOSHKO and SAXENA, 1991). In this paper, the PVT properties of CO_2 , CH_4 , CO , O_2 , and H_2 have been simulated following the same approach.

EFFECTIVE POTENTIAL OF INTERMOLECULAR INTERACTION

The choice of IP is critical in calculating properties of fluids with either a molecular dynamics computer simulation or with the perturbation theory. If the molecule is polyatomic, the IP should incorporate all the interatomic distances and/or orientations between two molecules. Since in this study the molecules are required to be treated as material points, the IP used here depends only on intermolecular distances; it also takes into account effectively the orientational interactions. Such an IP is referred to as *effective IP*. The studies of GORBATY and DEMJANETZ (1983) and KALINICHEV (1986) show that the model of a simple liquid (i.e., monatomic) describes structure of supercritical fluid quite adequately but the dependence of IP on distance is unclear. The nature of the long range (attractive) forces is more or less well understood. One can describe them with the Kirkwood-London expression in case of neutral particles with zero dipole moment (A/r^6 , A -constant, r -distance between interacting particles). The nature of the short range (repulsive) forces has not been studied so well. In this regard, the two most widely used potentials are the Lennard-Jones (LJ) potential

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3)$$

where U is the IP, and $2\frac{1}{6}\sigma$ and ϵ are respectively the location and the depth of the minimum and the exp-6 potential

$$U(r) = \epsilon \left\{ \frac{6}{\alpha - 6} \exp[\alpha(1 - r/r^*)] - \frac{\alpha}{\alpha - 6} \left(\frac{r^*}{r} \right)^6 \right\}, \quad (4)$$

where r^* refers to the position of the minimum and α is the stiffness parameter.

The two potentials differ in stiffness (the LJ is more stiff; we define stiffness as a force of repulsion between two particles) and in the long range tail of interaction. The long range interactions are not important for calculating the high pressure properties (CARNAHAN and STARLING, 1969, 1972; WEEKS et al., 1971). Both the LJ and the exp-6 potentials have been widely used to calculate the PVT properties of fluids at very high pressures (NELLIS et al., 1983, ROSS, 1987, SHMULOVICH et al., 1982).

Although one may choose other potentials (e.g., the TIP4P used by BRODHOLT and WOOD, 1990), for reasons discussed previously (BELONOSHKO and SAXENA, 1991), the exp-6 potential (4) was adopted in this work. Let us mention why we choose effective potential rather than the "precise" one. The present use of the effective potential rather than a rigorously calculated potential may be justified by considering the results of KATAOKA (1987) and others. Kataoka's results show that it was possible to simulate the PVT with 'real' water-water IP (i.e., quantum chemical IP with real structure of the H_2O molecule) over a wide range of density and temperature but with significant errors of pressure. Similarly, when VAN WAVEREN et al. (1986) used the 5-centered LJ potential to calculate isothermal pressures for methane at room temperature and high densities, they found that their calculated pressure at a density of $32 \text{ mol} \cdot \text{dm}^{-3}$ was about 60% too high. The same PVT data could be modeled by SAAGER et al. (1990) and SAAGER and FISCHER (1990) using an effective potential within the experimental errors. It is clear that even small error (about 2-3%) in the determination of the size parameters can lead to a large error in MD calculation of PVT properties in the high density range; for an IP determined *ab initio* for polyatomic molecules one should incorporate large number of parameters. If each parameter is known with a precision about 2-3%, the final error could be quite large. Therefore, we conclude that quantum-chemical calculation of the real potentials is not realistic at present.

We also compare our calculations of PVT properties of H_2O (BELONOSHKO and SAXENA, 1991) and those by BRODHOLT and WOOD (1990), who used the TIP4P potential. Comparison with the experimental data of LYSENGA et al. (1982) at very high P and T shows that these data are in better agreement with our computed results than with that of BRODHOLT and WOOD (1990). It seems that rigid geometry of H_2O as used by those authors does not allow them to calculate PVT precisely enough in high density range.

Parameters of the potential (3) were calculated by using the parameterization of WCA theory (WEEKS et al., 1971;

Table 1. Anchor points to calculate parameter α of potential (4).

	T, K	v , cm^3/mole	P, bar	Ref.
CO_2	1000	38.15	8000	Shmonov and Shmulovich, 1978
CH_4	673	34.17	8106	Tziklis, 1977
CO	573	29.09	10000	Babb et al., 1968
O_2	673	25.75	10132	Tziklis and Koulikova, 1965
H_2	300	10.0	30200	Mills et al., 1977

Table 2. Calculated parameters of effective IP* (4)

	$\epsilon/k^{**}, K$	$\sigma, \text{\AA}$	α
CO ₂	198.634	3.6963	13.9
CH ₄	140.941	3.7165	14.05
CO	90.805	3.6531	14.48
O ₂	99.495	3.3688	14.45
H ₂	25.144	2.9780	13.34

* Parameter $r^* = 2^{1/6} \sigma$; k - Boltzman constant.

SHMULOVICH et al., 1982) with the experimental PVT data (BABB et al., 1968; JUSA et al., 1965; KORTBEEK et al., 1986; MEL'NIK, 1978; PRESNALL, 1969; ROBERTSON and BABB, 1970; SHMULOVICH and SHMONOV, 1978; TZIKLIS, 1977; TZIKLIS and KOULIKOVA, 1965; TZIKLIS et al., 1975; VAN

THIEL and WASLEY, 1964) at pressure above 2 Kbar and temperatures above critical by minimizing

$$\sum_{i=1}^K [1 - Z_{WCA}(T, P, \epsilon, r^*)/Z_{exp}(T, P)]^2 \quad (5)$$

where Z is compressibility of the fluid and K the number of experimental points. If influence of change in structure, density and temperature on parameters of effective IP is not very large (one can check it a posteriori on basis of PVT shock-wave data), the IP calculated from the low PVT data would allow us to calculate the properties to very high pressures and temperatures. However, it is important to calculate the IP from the PVT data at temperatures sufficiently high such that the influence of the coordination forces on the thermodynamic properties is negligible. This approach was successfully applied in part 1 of this study (BELONOSHKO and SAXENA, 1991).

Table 3. Potential minima location divided $2^{1/6}(\sigma)$ and depth of well ϵ/k calculated earlier.

	$\epsilon/k, K$	$\sigma, \text{\AA}$	Potential	Ref.
CO ₂	195.2	3.941	LJ	Svehla, 1962
	245.6	3.716	exp6	Nellis et al., 1981 ¹
	211.3	3.6963	LJ	Shmulovich et al., 1982 ²
	338.3	3.6468	exp6	Johnson and Shaw, 1985 ³
	247.	3.69	LJ	Ben-Amotz and Herschbach, 1990
CH ₄	136.5	3.882	LJ	Lennard-Jones and Ingham, 1925
	148.6	3.758	LJ	Svehla, 1962
	149.1	3.743	LJ	McDonald and Singer, 1972
	154.1	3.761	exp6	Ross and Ree, 1980 ¹
	139.571	3.725	LJ	Shmulovich et al., 1982
	149.92	3.7327	LJ	Fischer et al., 1984
	147.8	3.73	LJ	Jorgensen et al., 1988
142.	3.73	LJ	Ben-Amotz and Herschbach, 1990	
CO	91.7	3.690	LJ	Svehla, 1962
	108.3	3.645	exp6	Nellis et al., 1981 ¹
	90.38	3.6534	LJ	Shmulovich et al., 1982 ²
	98.	3.69	LJ	Ben-Amotz and Herschbach, 1990
O ₂	106.7	3.467	LJ	Svehla, 1962
	125.0	3.422	exp6	Nellis et al., 1981 ¹
H ₂	33.3	2.968	LJ	Lennard-Jones and Ingham, 1925
	59.7	2.827	LJ	Svehla, 1962
	25.8457	2.9568	LJ	Shmulovich et al., 1982 ²
	36.4	3.0558	exp6	Ross et al., 1983 ⁴

¹ - parameter α of exponential-6 potential equals 13.0

² - parameters are temperature dependent in the model; values are given at 500 K.

³ - parameter α of exponential-6 potential equals 14.4

⁴ - parameter α of exponential-6 potential equals 11.1

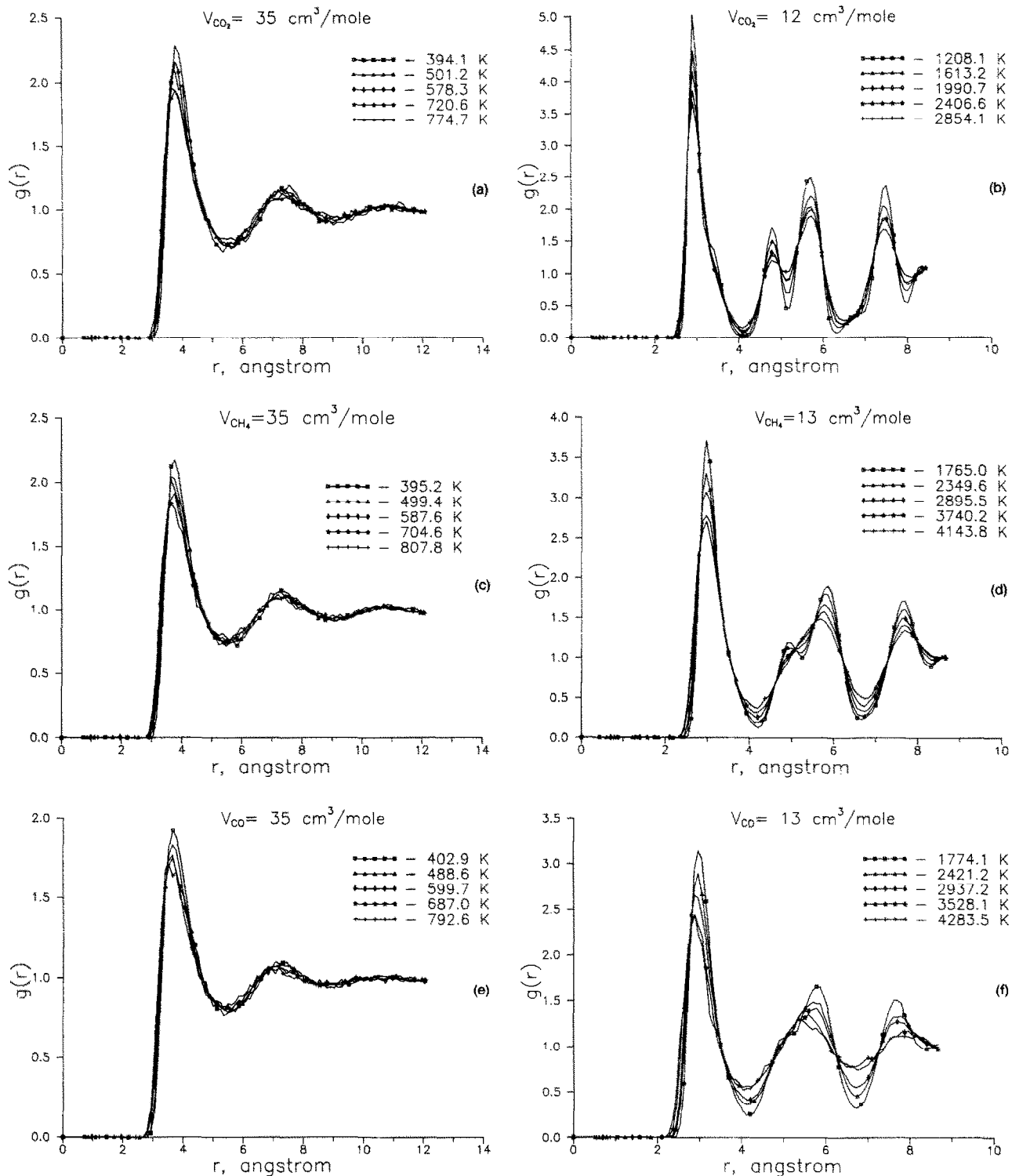


FIG. 1. Radial distribution function (RDF) of CO_2 (a,b), CH_4 (c,d), CO (e,f), O_2 (g,h), and H_2 (i,j). RDFs are shown for two values of density and five values of temperature.

With these parameters, the experimental PVT data can be fitted within 2 or 3% errors in volume; therefore, we obtain a two-parameter EOS for supercritical fluids in the C-H-O system above 2 Kbar over the ranges of experimental P and T (we can say we have got an EOS as soon as we have any

connection between PVT and some parameters). The parameters of the EOS σ and ϵ are listed in Table 2. This equation cannot be used at high densities, because (a) over some density range the LJ fluids become solid (GRACE and KENNEDY, 1967; STISHOV, 1974) and (b) calculated pressure is

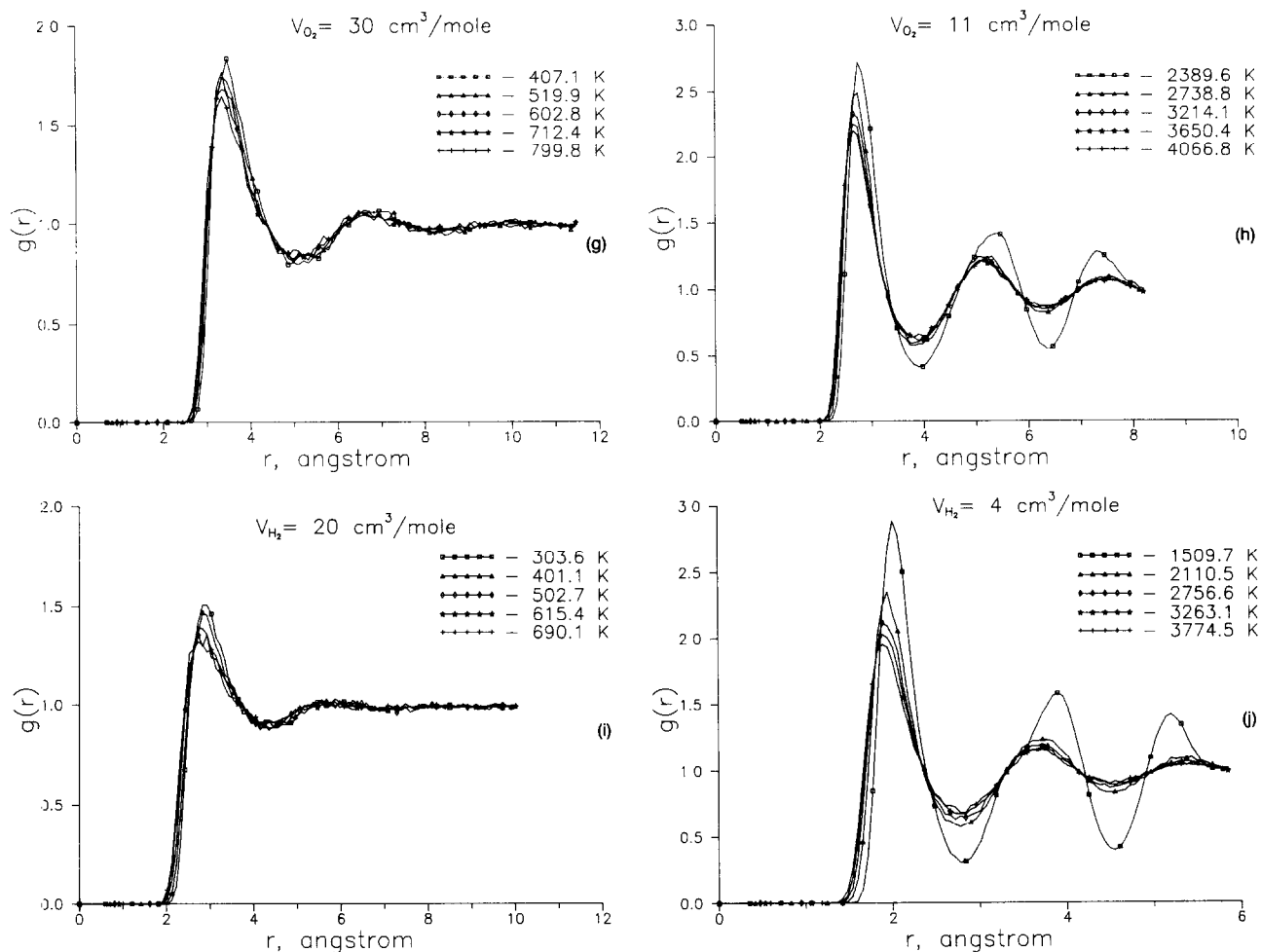


FIG. 1. (Continued)

too high in comparison to the observed or computed data (DICK, 1972,1976; FIORESE, 1980; JOHNSON and SHAW, 1985; MILLS et al., 1977; NELLIS and MITCHELL, 1980; NELLIS et al., 1981,1983; ROSS et al., 1983; WALSH and RICE, 1957; ZUBAREV and TELEGIN, 1962). The parameters of IP (4) were adopted as follows:

$$r_{\text{exp-6}}^* = 2^{1/6} \sigma_{\text{LJ}} \quad (6a)$$

$$\epsilon_{\text{exp-6}} = \epsilon_{\text{LJ}} \quad (6b)$$

The third IP (4) parameter α was calculated with the MD method simulating the experimental pressure (Table 1). The calculated parameters of potential (4) are shown in Table 2. Our parameters of effective IP (4) and parameters of effective IP (3) and (4) as calculated by others are compared in Table 3 which shows a reasonable similarity among all calculations.

It should be pointed out that parameters of effective IP may change with the structure of fluid, temperature, and density. The only way to check the possible influence of these changes is to calculate PVT properties of fluid with given IP and compare them to experimentally determined PVT. Unfortunately, we have very limited shock-wave data on PVT

properties (only for water and methane). Therefore, we must rely on the comparison of calculated and experimental data (see below) for error estimate.

THE METHOD OF SIMULATION

All computed results were obtained with the MD method for the NVE-ensemble (N , number of molecules; V , volume; E , total energy). Pressure has been calculated at constant V and N . Details of the method are described in ALLEN and TILDESLEY (1987) and in BELONOSHO and SAXENA (1991). Formulas for calculation of pressure and temperature are given in Appendix A. Some details specific to the present work are described below.

N was equal to 250 in all simulations. Initial configuration of molecules was body-centered cubic lattice structure. First PVT point on each isochor for every species has been calculated with time of equilibration about 10 psec (1 psec = 10^{-12} sec). Every other point on the isochor (at higher T) was calculated starting from the configuration obtained for the previous PVT point with time of equilibration of about 6 psec. The time step was chosen to satisfy the conservation of total energy E and was equal to a few femtoseconds (1 femtosecond = 10^{-15} sec) depending on molar weight of the species. The cut-off radius was chosen to be equal to $2.5r^*$ where it was possible. It was slightly less (about $2.3r^*$ - $2.4r^*$) under the highest density. The calculated P and T data with the appropriate errors are given in Appendix B. More detailed information including tables of E , U and $g(r)$ may be obtained from the authors.

Table 4. Parameters of equation of state (7) in C-O-H system.

	CO ₂	CH ₄	CO	O ₂	H ₂
a ₁	18.3050	21.7694	8.4373	23.5710	5.1381
a ₂	-3.2756	0.4731	5.6585	-7.3095	5.7896
b ₁	-10.9876	-13.2852	-5.7048	-8.6234	-1.0837
b ₂	12.5299	9.7013	7.0165	8.1585	1.9852
c ₁	85.3964	18.4128	13.0116	6.3861	0.1385
c ₂	-6.4540	-0.8874	-0.4606	-0.3475	-0.0066
n	4.6877	4.1674	4.2415	4.2187	3.6637
N points	151	79	84	94	74
Av. err., %	4.57	3.72	3.27	5.53	3.49
Max. err., %	22.82	11.41	12.79	16.10	10.76

Table 5. Coefficients of equation (8).

	CO ₂	CH ₄	CO	O ₂	H ₂
f ₁	-40.468	-19.293	-3.382	-10.370	6.803
f ₂	0.0670	0.0673	0.0696	0.0689	0.0701
f ₃	8.348	5.407	2.779	3.450	0.177

Note: CO₂ coefficients from Saxena and Fei (1987)

RESULTS AND DISCUSSION

Error Estimate in Simulation

An MD simulation allows us to calculate P and T within some uncertainties. Fortunately at high densities, errors of pressure are not high (ALLEN and TILDESLEY, 1987; BELONOSHKO and SAXENA, 1991). We found the deviation of temperature to be consistent with theoretical estimates (HILL, 1962). The errors of simulated volume or pressure for the

individual species cannot be compared directly with the experimental data because the simulation is a computer 'experiment' with P and T being unknown in advance. Therefore, we compare with the experimental data by first refitting the MD-simulated data to PVT equations as discussed below and then calculate the P and T corresponding to an experiment. We note that the fitted equations (see below) reproduce the MD-simulated data with a maximum average error of 3% in volume.

Structure of Fluid

We calculated $g(r)$ – radial distribution function (RDF) in all runs. An RDF can be determined as ratio of the microscopic density $\rho(r)$ to bulk density ρ

$$g(r) = \rho(r)/\rho$$

Table 6. Experimental volumes of CO₂, compared with calculated from eq. (7).

P, bar	T, K	V, cm ³ /mole		Error, %	Ref.
		exp.	calc.		
5066	473	35.10	35.68	1.65	1
6586	473	32.40	33.15	2.30	1
5066	673	39.25	39.59	1.05	1
6586	673	35.10	36.03	2.65	1
5000	473	35.09	35.82	2.08	2
8000	473	31.48	31.51	0.10	2
5000	673	39.50	39.78	0.71	2
8000	673	34.01	33.86	0.44	2
5000	973	46.13	46.56	0.93	2
8000	973	37.81	37.85	0.11	2

1-Tziklis, 1977; 2-Shmulovich and Shmonov, 1978

Table 7. Experimental volumes of CO, compared with calculated from eq. (7).

P, bar	T, K	V, cm ³ /mole		Error, %	Ref.
		exp.	calc.		
5000	473	34.32	34.63	0.90	1
7500	473	30.41	30.57	0.53	1
10000	473	28.05	28.18	0.46	1
5000	573	36.28	36.36	0.22	1
7500	573	31.79	31.68	0.28	1
10000	573	29.09	29.02	0.24	1

1 - Babb et al., 1968

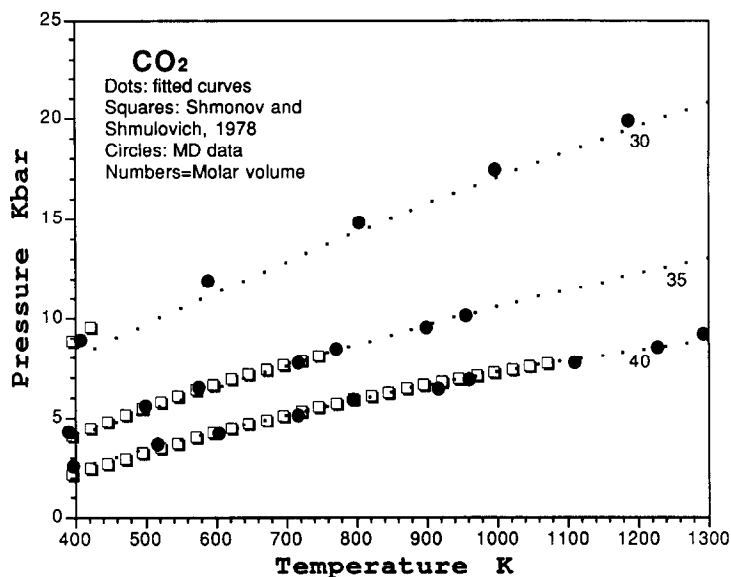


FIG. 2. A comparison of the MD-simulated data (circles) for CO_2 with experimental (squares) and data fitted from Eq. 7 (dots). Volume in cm^3/mol .

Figure 1 shows the structure of the species at several temperatures and volumes. Figs. 1 a, c, e, g, and i show structure of CO_2 , CH_4 , CO , O_2 , and H_2 in the V - T range corresponding to the experimentally investigated one. The IP parameters have been adjusted in this V - T range. Such a structure of a species in this range is typical for liquid state. Figs. 1 b, f, h, and j show structures at the highest T and density. Fig. 1d presents RDF of methane in the experimentally studied V - T range (RADOUSKY et al., 1990; see also Table 11). The RDF for methane is close to a body-centered cubic lattice structure and is similar to those in the high P - T range. If there is any influence of structural changes on IP parameters, this influence should not be much greater for CO_2 , CO , O_2 ,

Table 8. Experimental volumes of CH_4 , compared with calculated from eq. (7).

P, bar	T, K	V, cm^3/mole		Error, %	Ref.
		exp.	calc.		
5066	473	35.75	36.46	1.99	1
7093	473	32.80	33.04	0.73	1
8613	473	31.20	31.36	0.51	1
5066	573	37.72	38.14	1.11	1
7093	573	34.20	34.19	0.03	1
8613	573	32.50	32.30	0.62	1
5066	673	39.70	39.96	0.65	1
7093	673	35.57	35.40	0.48	1
8613	673	33.70	33.28	1.25	1
5000	473	36.02	36.61	1.64	2
7500	473	32.41	32.55	0.41	2
10000	473	30.16	30.18	0.07	2

1-Tziklis,1977; 2-Babb et al., 1968.

or H_2 than for CH_4 . Therefore, we have assumed that the error in volume for other species is also about the same as for methane which is about 6%.

The New PVT Equation of State

SAXENA and FEI (1987) used virial-type polynomial to fit the available experimental PVT data (both static and shock-wave). These equations may be distinguished as being Hugoniot-based as opposed to the MD-based equations which are presented below. The use of the Saxena-Fei equations is restricted to interpolation within the P - T range as originally discussed by the authors (SAXENA and FEI, 1987). It is now possible to extend the P - T range of application by basing the equations both on the MD-simulated and the experimental data. This is the only possible way the MD simulated data can be used for phase equilibrium calculations. We treat the MD data as if they are experimentally determined PVT data.

Table 9. Experimental volumes of O_2 , compared with calculated from eq. (7).

P, bar	T, K	V, cm^3/mole		Error, %	Ref.
		exp.	calc.		
5066	473	29.26	29.98	2.46	1
6079	473	27.83	27.84	0.04	1
7092	473	26.78	26.34	1.58	1
5066	573	31.04	31.69	2.09	1
7092	573	27.42	27.46	0.15	1
9119	573	24.89	25.14	1.00	1
5066	673	32.64	33.42	2.39	1
7092	673	28.76	28.63	0.45	1
10132	673	25.75	25.09	2.56	1

1 - Tziklis and Koulikova, 1965

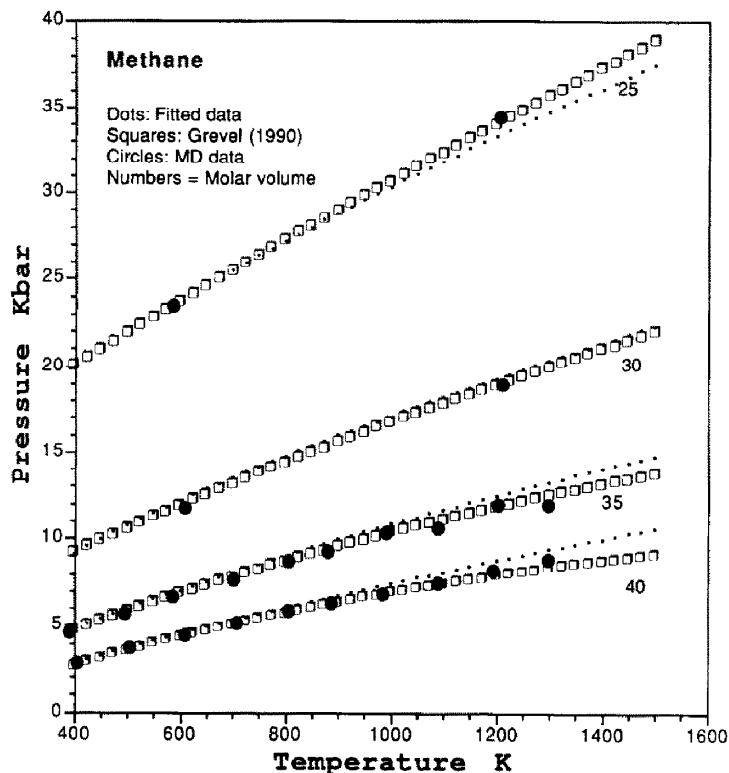


FIG. 3. A comparison of the MD-simulated data (circles) for methane with the Grevel (1990) data (squares) and the data fitted from Eqn. 7 (dots). Volume in cm^3/mol .

Note that in estimating the whole set of the IP parameters we used the experimental data only at the highest P and T , and all other data to the lowest P and T were not used. The calculated PVT data together with the experimental PVT data (above 5 Kbar) are fitted with the following polynomial in T and V :

$$P = a/V + b/V^2 + c/V^n \quad (7)$$

where

$$a = (a_1 + a_2 T/1000)10^4$$

$$b = (b_1 + b_2 T/1000)10^6$$

$$c = (c_1 + c_2 T/1000)10^9$$

P in bar, T in K, and V is molar volume in cubic centimeters.

The coefficients and some other data on the fits are shown in Table 4. Average error in pressure is between 3.27 to 5.53%, which corresponds to an average error of 1 to 2% in volume. It is remarkable that we can get such low error in volume by fitting simultaneously the experimental data (most of these not used in fixing the IP) and MD-computed results. In the range of low temperature and high pressure (T about 400 K and P more than 100 Kbar), i.e., in the range of high compressibility (Z ca. 100), the maximum error of fitting in pressure is about 15–20%. Therefore, the error in volume in these points is of the same magnitude, i.e., 1 to 2%. The fugacities of the fluids at T and at $P > 5$ Kbar may be accomplished by using the following equation for the experimentally determined fugacities as reviewed by MEL'NIK (1978):

$$RT \ln f(5 \text{ Kbar}, T) = 1000(f_1 + f_2 T + f_3 \ln T) \quad (8)$$

where R is gas constant ($\text{J}/\text{mol}/\text{deg}$), T temperature in K, f fugacity, f_i coefficients of polynomials. The coefficients are listed in Table 5.

Comparison with Static Experiments

The calculated PVT data on the fluids has been compared with the available experimental data as shown in various tables and figures that follow and are to be found in good agreement. All errors quoted in the text and in the tables are for the volume with

$$\text{Error} = 100*(V_{\text{exp}} - V_{\text{MD}})/V_{\text{exp}} \quad (9)$$

Table 10. Experimental volumes of H_2 , compared with calculated from eq. (7).

P , bar	T , K	V , cm^3/mole exp.	V , cm^3/mole calc.	Error, %	Ref.
5000	373	20.21	20.24	0.15	1
6000	373	18.75	18.55	1.07	1
7000	373	17.62	17.32	1.70	1
5000	423	21.01	21.02	0.05	1
6000	423	19.70	19.18	2.59	1
7000	423	18.17	17.85	1.76	1

1 - Tziklis et al., 1975

Table 11. Experimental and calculated densities of methane at shock-wave experimental PVT.

P, GPa	T, K	V, cm ³ /mole		Ref.
		exp.	calc.	
33.5	3700 (200)	13.76	14.51	2
42.0	4330 (200)	12.98	13.80	2

2 - Radousky et al., 1990

where V_{exp} is experimentally measured molar volume, V_{MD} is molar volume computed from Eqn. (7).

CO_2 : In the temperature and pressure range of interest in this study, the available experimental data are from SHMONOV and SHMULOVICH (1978) and TZIKLIS et al. (1975). Some representative data from both the authors are compared with the MD

data in Table 6, and Fig. 2 shows a comparison of all experimental data of former authors with our calculated data. The maximum error is 2.65%.

CO : Table 7 shows a comparison of the experimental data at representative pressures and temperatures with the MD data. The fit is generally good with a maximum error of 0.90%.

CH_4 : Two sets of the data available for methane

Table 12. Thermochemical data used for Fig.5.

Phase	Enthalpy (J/mol)				
Entropy (J/mole K)					
Heat capacity ($a+bT^{-2}+dT^2+eT^{-3}+fT^{-0.5}+gT^{-1}$)					
Volume (cm ³ /mole)	Thermal expn. ($a_1*10^4+a_2*10^8T+a_3*T^{-2}$)				
Isot. bulk mod. (Mbar), P deriv., T deriv.					
Magnesite MgCO ₃	-1112480				Holland and Powell, 1990
65.100					Holland and Powell, 1990
194.7	-0.006081	287400.0	0.0		
0.0	-2073.8	0.0			Holland and Powell, 1990
28.03	0.37817	0.0	0.0		Holland and Powell, 1990
0.93433	4.0	0.0			Holland and Powell, 1990
Orthoenstatite MgSiO ₃	-1546290				Brousse et al., 1984
66.270					Krupka et al., 1985
144.45	0.001882	-1350000.0	0.0		
461200000.0	0.0	-19380.0			Haselton, 1979
31.276	0.20303	1.28049	0.001		Saxena and Eriksson, 1983
1.07	4.2	-0.2			Fei et al., 1990
Forsterite 1/2[Mg ₂ SiO ₄]	-1087180				Saxena and Chatterjee, 1986
47.060					Robie et al., 1982
96.731003	0.001278	1890000.0	0.0		
-431200000.0	0.0	-13090.0			Watanabe, 1982
21.836	0.3052	0.8504	-0.5824		Suzuki, 1975
1.2793	5.37	-0.224			Fei et al., 1990
Periclase MgO	-601490				Robie et al., 1978
26.940					Robie et al., 1978
49.654	0.003841	-1389800.0	0.0		
127200000.0	0.0	-792.0			Robie et al., 1978
11.25	0.3681	0.9283	-0.7445		Suzuki, 1975
1.603	4.13	-0.272			Fei et al., 1990

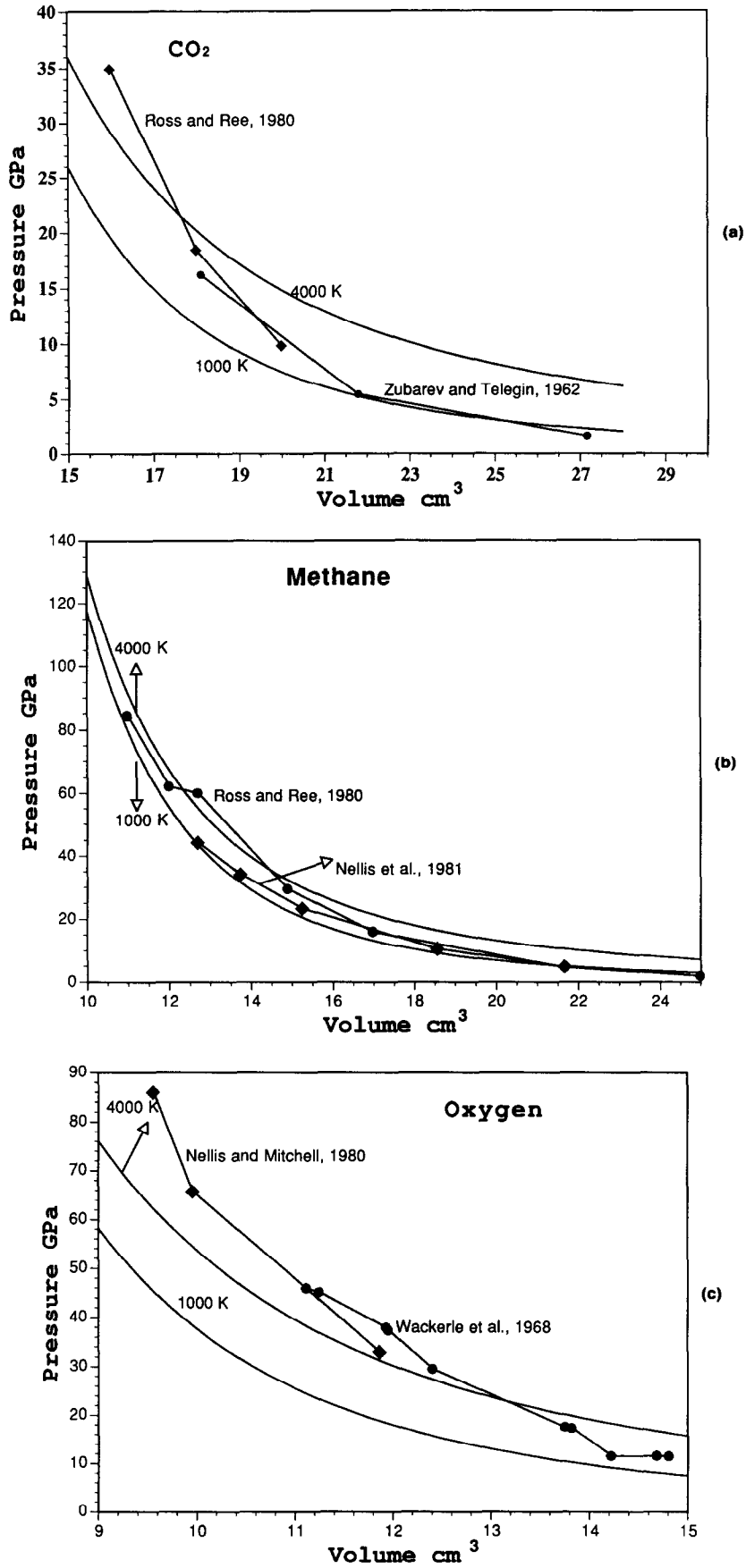


FIG. 4. A comparison of the simulated PVT data with the Hugoniot from the shock-wave data. Two isotherms calculated from Eqn. 7 are shown for comparison. See text for further discussion. a. CO₂; b. CH₄; c. O₂; d. H₂; e. CO.

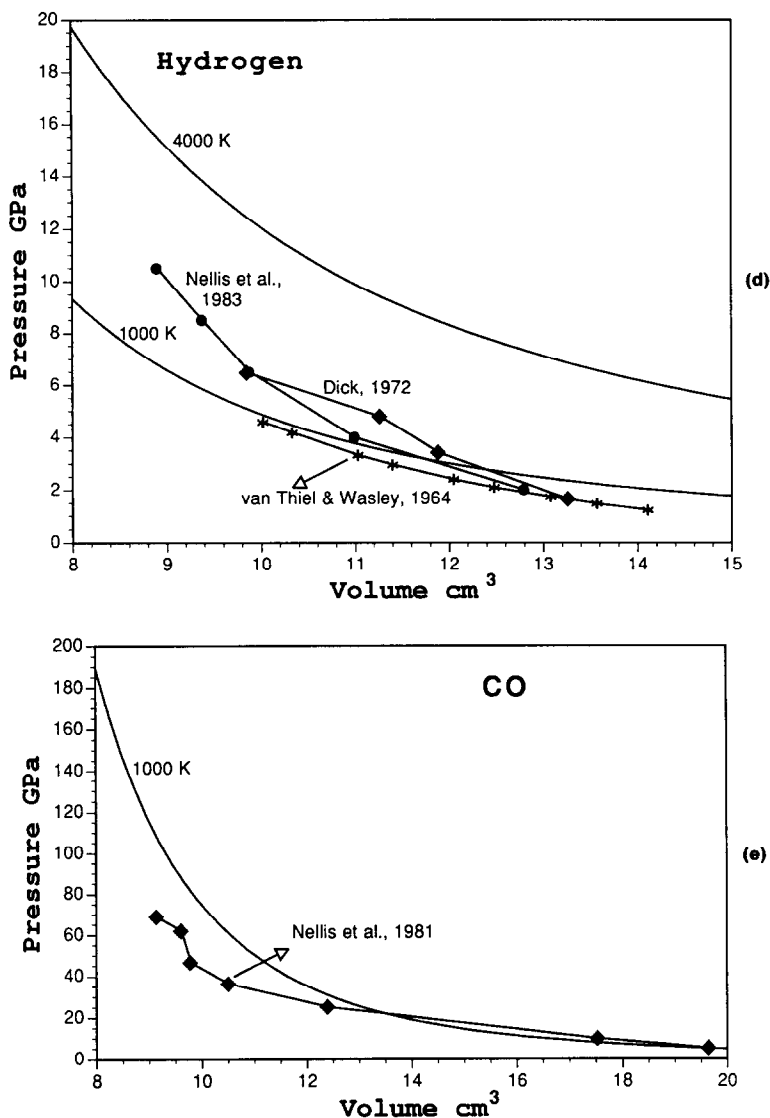


FIG. 4. (Continued)

(TZIKLIS, 1975 and BABB et al., 1968) are compared in Table 8. Maximum error noted is 1.99%. Recently GREVEL (1990) has modeled all the available PVT data on methane. According to Grevel, the errors in fitting the experimental data are less than 1%. Therefore, it is useful to compare the MD data with the model data of Grevel as shown in Fig. 3. The agreement between the two data sets is quite good.

O₂ and H₂: Comparison with the available experimental (TZIKLIS and KOULIKOVA, 1965; TZIKLIS et al., 1975) and the MD-generated data are shown in Tables 9 and 10 for O₂ and H₂ respectively. Note that the PRESNALL (1969) data are below 1800 bars and cannot be used here. The highest errors in volume reach close to 2.5% for these gases.

Comparison with the Shock-wave Data

The temperatures of the shock-wave compressed fluids are generally not known and are modeled through the use of

Hugoniot relations (e.g., ROSS and REE, 1980). It is still interesting to compare our results with the data from shock-wave experiments. Fig. 4 shows the Hugoniot shock-wave adiabats for the five gases. We have plotted the isotherms at 1000 and 4000 K for each of the five gases for comparison. The trends of the two data sets, i.e., the variation of volume with pressure, are comparable for all the gases; but the variation of volume with temperature is not easily compared. Fig. 4a shows that the low-pressure part of the Hugoniot for CO₂ is consistent in temperature with the MD data but the high-pressure part is not. As shown in Fig. 4b, the uncertainty in temperature estimates of the experiments could be quite large. The figure shows two sets of Hugoniots for methane differing by 18.6 GPa at the highest pressure. The Hugoniots calculated by ROSS and REE (1980) would be quite consistent with the MD data but not the other.

There are two experimental PVT points for methane, measured with shock-wave experiment (Table 11). Comparison with our MD-simulated results gives an error of about 6% in volume. This value could be adopted as a degree of

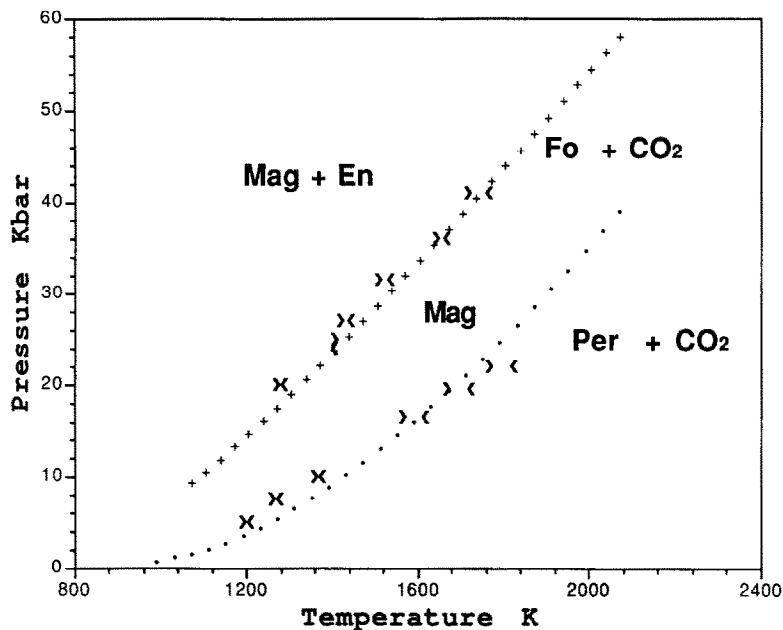
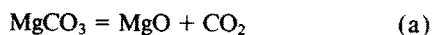


FIG. 5. The data from the PVT Eqn. (7) is used to calculate the equilibrium P and T of the reactions involving CO_2 . The experimental data on dissociation of magnesite are from IRVING and WYLLIE (1975) and GOLDSMITH and HEARD (1961). For the second reaction, the data are from NEWTON and SHARP (1975). Mag = magnesite, Per = periclase, En = enstatite and Fo = forsterite.

validity of our equations. Similarly, for the most part the plots shown in Figs. 4c and 4d for O_2 and H_2 respectively attest a general qualitative compatibility of the Hugoniot with the MD-generated data. The results on CO require discussion. NELLIS et al. (1981) found that up to about 230 Kbar the product of shock-wave experiments remains a homogeneous CO fluid with which our data are consistent (Fig. 4e). Above 230 Kbar, the precipitation of solid carbon was noted which would decrease the total pressure drastically.

Compatibility with the Phase Equilibrium Experiments

The phase equilibrium calculations for reactions involving fluids are not quite sensitive to errors in the fugacity data of the fluid and therefore cannot be used to constrain PVT equation parameters. It is still important to show that the calculated fugacity is consistent with the phase equilibrium data when calculated by using the commonly accepted thermochemical data on the solids. There are few experimental phase equilibrium data available on high pressure (> 10 Kbar) reactions involving fluids. We discussed the breakdown of brucite in the first part of the study (BELONOSHKO and SAXENA, 1991). Two other reactions involve CO_2 and are



and



Figure 5 shows the calculated and experimental equilibrium P and T of the two reactions. The thermodynamic data on the solids are listed in Table 12. The need for the reassessment of the data on magnesite has been pointed out by CONNOLLY (1991). However, the data in Table 12 are internally consistent. The data on enstatite, forsterite and periclase are

somewhat different from those of HOLLAND and POWELL (1990) but they do reproduce the experimental phase equilibrium relations with the same accuracy as do the Holland-Powell data. As the figure shows, the new data based on the MD calculations is quite consistent with the experimental data in the high P - T range.

CONCLUSIONS

The calculated data on the C-H-O fluids by the MD method employing the intermolecular potentials obtained from modeling the experimental data in the low to moderate P and T ranges satisfies the available constraints from the phase equilibrium experiments and the shock-wave data. It is, of course, difficult to define the exact limits in P and T of the application of the MD equations of state for the molecular fluid species. The fluid could be intrinsically unstable (i.e., dissociate into other molecular or ionic species) or undergo a phase transformation. In such a case one cannot treat molecules as material points and the model should incorporate a possibility to consider dissociation of a molecule. If species undergo phase transformation, parameters of interaction potential calculated in this paper could be wrong due to significant structural changes. Our EOS are valid in the range of liquid state at supercritical temperature at pressures higher than 5 Kbar. The possible error in volume due to inadequate IP adopted in this work and actual IP could be estimated as 5–6% by comparison with experimental shock-wave PVT measurements of water (BELONOSHKO and SAXENA, 1991; LYSENGA et al., 1982) and methane (RADOUSKY et al., 1990).

In case of dissociation or phase transition the data presented here will represent metastable or a 'fictive' standard state necessary in phase equilibrium computations. A theoretical and experimental study pertaining to the dissociation and

phase transformation of the fluids in the high pressure environment is now under way.

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APPENDIX A

The aim of this part is not to review methods of MD. It has been done many times before (e.g., ALLEN and TILDSELEY, 1987; BOUBLIK, 1977; KUBICKI and LASAGA, 1990). Many of the really important details will be omitted in the following description for clarity and to emphasize the central idea of the molecular dynamics approach.

We can imagine fluid (as well as solid, glass, melt, plasma, and so on) as a set of N particles (atoms, ions, molecules). If the initial coordinates and velocities are known, we can solve Newtonian equations of motion

$$m \frac{d^2 r_i}{dt^2} = f_i(r_1, r_2, \dots, r_N), \quad i = 1, 2, \dots, N \quad (1)$$

where $r_i = \{r_{xi}(t), r_{yi}(t), r_{zi}(t)\}$ is vector of i th particle, t is time, f_i is force acting on i th particle. In this way it is possible to get as long a history of the set of N particles as is needed, if f_i at all i are known. The expression for f_i is

$$f_i = - \sum_{j \neq i}^N \frac{du_{ij}}{dr_{ij}} \quad (2)$$

where u_{ij} is potential energy of interaction between particles i and j , or IP, r_{ij} is interparticle distance.

In *Principia Philosophiae* RENÉ DESCARTES (1983) claimed that if he could know coordinates and velocities of all bodies in the universe, he could calculate the future of the universe in any coming time. It is exactly the idea of molecular dynamic approach.

As soon as computers appeared, the MD approach became useful. Still the initial velocities and coordinates are not known. It appears that

- 1) For fluid the initial velocities and coordinates almost do not matter (only the time of "equilibration" is affected)
- 2) Comparably restricted number of N particles (at least in relation to the number of bodies in the universe) is sufficient

A number of techniques permit us to solve equations (1) numerically and to avoid surface effect, etc. We refer the interested reader again to the above-mentioned reviews.

From a knowledge of the velocities and coordinates (and IP, of course) of N particles enfolded in volume V , the statistical mechanics allow us to calculate P and T as follows

$$T = \frac{1}{3Nk} \sum_{i=1}^N mv_i^2 \quad (3)$$

$$P = \frac{NkT}{V} - \frac{1}{3V} \sum_{i=1}^{N-1} \sum_{j>i}^N \frac{du_{ij}}{dr_{ij}} r_{ij} \quad (4)$$

where v_i is velocity of i th particle, m is mass of particle, k is Boltzman constant.

Appendix B

Table 1. The MD simulated data. The errors in T (K) (ΔT) and P (bar) (ΔP) are shown in following columns. Molar volume in cm^3 . The data on T (column 2) and P (column 4) are simulated for a given volume (column 1). The experimental molar volume from Mel'nik (1978) corresponding to such P and T are given in column 6 for comparison.

V	T	ΔT	P	ΔP	V_{exp}
CO₂					
40.00000	400.5	11.6	2570.7	182.6	38.09
40.00000	519.5	14.2	3603.7	198.5	39.08
40.00000	607.2	14.6	4204.4	203.0	39.87
40.00000	718.8	20.3	5115.7	264.3	40.03
40.00000	798.8	20.1	5828.6	221.4	39.86
40.00000	920.2	18.4	6395.9	226.8	40.59
40.00000	963.9	30.6	6834.8	325.9	40.29
40.00000	1112.6	21.5	7731.6	225.0	40.44
40.00000	1229.6	22.1	8459.9	183.9	
40.00000	1295.5	25.2	9208.2	186.0	
35.00175	394.3	11.7	4276.1	169.9	34.30
35.00175	501.2	14.6	5586.3	199.8	34.74
35.00175	578.3	17.5	6492.1	251.9	34.87
35.00175	720.6	22.5	7744.7	293.6	35.33
35.00175	774.7	26.8	8446.4	365.3	35.15
35.00175	902.0	22.0	9464.4	285.1	
35.00175	958.4	25.5	10076.8	317.3	
30.00030	411.3	13.1	8896.1	205.4	30.14
30.00030	590.8	22.2	11921.0	336.3	
30.00030	805.7	24.8	14803.2	354.1	
30.00030	999.4	27.4	17426.9	366.4	
30.00030	1189.7	36.1	19911.6	461.7	
30.00030	1509.2	51.1	22897.7	665.1	
30.00030	1675.3	61.9	24394.5	831.0	
30.00030	1806.7	57.3	26681.1	622.7	
30.00030	1945.2	53.1	28315.3	611.3	
27.15989	408.5	14.7	11783.8	250.6	
27.15989	479.6	14.2	13525.9	238.7	
27.15989	598.3	22.3	18433.9	344.2	
27.15989	689.1	23.0	20144.6	354.3	
27.15989	773.8	24.8	21678.5	368.4	

Appendix B (Continued)

V	T	ΔT	P	ΔP	V_{exp}
27.15989	887.3	21.6	23618.7	325.9	
27.15989	1015.6	39.4	24882.9	588.1	
25.00000	410.0	16.0	17948.8	281.8	
25.00000	411.2	16.4	17936.1	285.8	
25.00000	1167.6	40.0	36991.2	601.1	
25.00000	1982.9	56.2	49523.3	787.0	
25.00000	2718.7	81.4	60668.6	1135.8	
25.00000	3637.0	66.0	70653.8	919.5	
25.00000	4418.8	181.0	79140.8	2033.2	
25.00000	5060.0	184.9	80816.4	997.2	
21.78175	399.2	14.2	37681.4	244.5	
21.78175	503.4	13.1	40265.7	228.9	
21.78175	580.5	19.5	42114.6	346.8	
21.78175	700.8	33.9	44819.3	571.5	
21.78175	812.9	17.4	47209.1	300.3	
21.78175	913.4	19.6	49552.5	348.7	
21.78175	1023.9	18.6	52902.1	320.8	
20.00000	391.2	15.1	58697.6	279.6	
20.00000	1218.1	42.5	79303.2	742.2	
20.00000	1864.2	64.9	105203.7	1053.2	
20.00000	2627.8	65.6	121785.0	975.0	
20.00000	3440.8	111.5	138943.3	1632.8	
20.00000	4321.0	62.2	150500.8	872.3	
20.00000	4978.3	113.0	163587.2	1630.9	
18.00018	395.2	15.1	102654.6	286.4	
18.00018	803.2	26.4	113487.2	488.8	
18.00018	1228.1	42.9	124668.2	787.7	
18.00018	1641.1	50.6	135561.2	873.4	
18.00018	1977.1	76.9	145216.3	1336.8	
18.00018	2413.6	55.5	156389.8	958.5	
18.00018	2755.9	132.8	167443.9	2154.3	
18.00018	3160.5	145.9	175632.4	2587.6	
18.00018	3469.0	167.2	182442.5	3056.2	
16.00000	377.9	14.6	183050.3	294.4	
16.00000	783.0	26.3	194741.0	522.6	
16.00000	1186.0	43.3	206238.6	843.0	
16.00000	1644.6	59.6	219246.8	1123.6	
16.00000	2005.9	76.0	229400.0	1406.5	
16.00000	2318.3	79.5	241055.4	1445.0	
16.00000	2769.7	131.3	250658.7	2397.5	
16.00000	3071.5	69.2	263194.4	1269.6	
16.00000	3384.0	120.6	270433.6	2184.1	
16.00000	3956.2	125.1	279938.6	2479.5	
14.99925	398.5	14.2	249942.0	298.6	
14.99925	803.7	28.2	262188.8	563.6	
14.99925	1194.5	46.5	273866.4	917.1	
14.99925	1607.5	60.2	286251.9	1185.7	
14.99925	2069.4	57.3	299692.0	1078.6	
14.99925	2399.9	74.9	309213.1	1422.2	
14.99925	2711.3	79.8	319512.7	1531.5	
14.99925	3074.7	63.6	328917.2	1124.7	
14.99925	3401.0	119.3	336723.2	2236.1	
14.99925	3938.4	135.2	347441.8	2629.2	
14.00000	397.5	13.6	344410.5	295.8	
14.00000	787.2	28.2	356684.8	583.2	
14.00000	1218.7	43.3	370190.6	886.8	
14.00000	1659.0	63.1	383602.5	1271.2	

Appendix B (Continued)

V	T	ΔT	P	ΔP	V_{exp}
14.00000	2050.2	64.8	395761.6	1301.1	
14.00000	2339.5	67.0	405031.4	1343.7	
14.00000	2792.9	110.0	419675.0	2248.8	
14.00000	3190.3	75.2	426837.6	1447.5	
14.00000	3400.7	94.1	441834.3	1915.7	
13.00000	396.3	13.8	481572.4	301.8	
13.00000	789.6	28.0	494493.8	600.9	
13.00000	1191.5	43.5	507702.1	919.5	
13.00000	1593.5	56.8	520651.3	1184.4	
13.00000	1983.7	70.7	533189.8	1469.5	
13.00000	2313.4	91.2	543831.0	1874.8	
13.00000	2885.6	95.5	562108.8	1907.5	
13.00000	3079.2	136.7	574345.8	2950.0	
13.00000	3550.5	151.9	579979.4	3866.6	
13.00000	3955.9	126.0	587123.9	3512.1	
12.00000	390.8	15.5	684108.7	360.4	
12.00000	782.0	27.7	697708.8	618.2	
12.00000	1208.1	40.8	712441.3	883.3	
12.00000	1613.2	62.5	726372.8	1374.5	
12.00000	1990.7	71.3	739817.1	1530.4	
12.00000	2406.6	60.6	753702.0	1321.4	
12.00000	2854.1	104.7	769025.8	2109.5	
12.00000	3237.6	99.9	782390.5	2248.6	
12.00000	3498.0	137.4	791571.8	2737.4	
11.00000	406.1	14.2	992109.4	362.2	
11.00000	807.0	30.4	1006906.0	716.2	
11.00000	1209.2	43.2	1021656.0	979.8	
11.00000	1599.0	52.3	1035864.0	1179.6	
11.00000	1971.0	60.6	1049204.0	1329.8	
11.00000	2415.6	81.5	1065630.0	1781.3	
11.00000	2866.2	75.8	1080554.0	1720.5	
11.00000	3012.2	62.3	1091733.0	1305.1	
11.00000	3325.8	179.8	1095738.0	3829.5	
11.00000	3959.1	124.3	1110778.0	2539.7	
		CH₄			
40.00000	408.5	10.0	2884.5	134.5	39.87
40.00000	507.7	13.5	3746.3	166.9	39.71
40.00000	610.4	15.3	4451.0	190.2	39.96
40.00000	710.7	18.6	5172.1	213.2	39.95
40.00000	807.6	20.5	5853.4	227.5	39.90
40.00000	890.2	22.0	6313.7	243.0	
40.00000	989.0	24.2	6806.8	269.5	
40.00000	1091.4	27.2	7500.6	294.0	
40.00000	1196.8	24.2	8155.6	230.1	
40.00000	1301.2	26.1	8830.0	278.7	
35.00003	395.2	12.2	4604.5	169.0	34.98
35.00003	499.4	14.2	5687.2	195.2	35.10
35.00003	587.6	18.3	6629.4	249.0	35.03
35.00003	704.6	18.4	7681.6	221.9	
35.00003	807.8	24.9	8675.6	301.1	
35.00003	884.3	23.1	9266.2	303.5	
35.00003	995.0	24.6	10339.6	302.3	
35.00003	1093.2	31.3	10600.6	350.8	
35.00003	1204.3	26.3	11943.6	280.9	
35.00003	1300.3	25.1	11938.0	289.4	

Appendix B (Continued)

V	T	ΔT	P	ΔP	V_{exp}
30.00003	612.9	19.9	11769.9	285.5	
30.00003	1214.4	39.4	18934.9	514.1	
30.00003	1741.7	45.7	24214.6	577.7	
30.00003	2372.1	67.7	29537.9	806.9	
30.00003	2952.1	79.5	34919.3	827.1	
30.00003	3523.8	105.8	38982.3	1129.6	
30.00003	4210.3	155.0	43779.2	2673.7	
25.00000	589.3	23.5	23436.0	373.0	
25.00000	1208.8	41.5	34401.5	620.5	
25.00000	1840.0	54.1	43292.0	783.4	
25.00000	2368.2	70.3	50132.4	955.6	
25.00000	3035.8	96.1	57981.1	1249.9	
25.00000	3563.1	121.4	64384.4	1517.7	
25.00000	4232.7	151.2	70983.9	1976.7	
20.00000	591.5	21.9	53862.3	393.1	
20.00000	1121.7	48.3	74929.6	830.0	
20.00000	1885.7	63.8	92553.9	1043.4	
20.00000	2426.4	76.0	103829.8	1170.8	
20.00000	3030.2	100.3	114731.3	1527.9	
20.00000	3678.9	135.6	126365.9	2038.5	
20.00000	4209.8	147.2	134066.3	2154.9	
14.99999	570.2	21.3	204348.2	434.7	
14.99999	1173.4	41.4	222417.7	833.5	
14.99999	1777.0	63.2	240441.8	1215.3	
14.99999	2488.9	99.1	261674.6	1869.9	
14.99999	3042.9	104.7	280655.4	1980.3	
14.99999	3492.7	130.2	306225.3	2497.1	
14.99999	4369.3	113.0	339830.3	2070.8	
13.00390	606.0	23.2	387631.5	498.7	
13.00390	1236.8	45.1	408257.6	950.1	
13.00390	1765.0	62.3	425522.3	1303.1	
13.00390	2349.6	80.3	444776.5	1647.6	
13.00390	2895.5	106.1	462077.2	2154.0	
13.00390	3740.2	127.5	489166.4	2489.3	
13.00390	4143.8	152.5	504988.0	3091.0	
11.00000	595.5	20.1	789467.1	471.4	
11.00000	1232.5	40.7	812729.6	936.3	
11.00000	1748.0	61.3	831603.4	1391.4	
11.00000	2455.9	94.4	857286.9	2030.4	
11.00000	2966.7	110.4	875878.6	2411.1	
11.00000	3535.9	166.6	895964.1	3649.6	
11.00000	4292.7	152.8	924208.1	3306.6	
9.000001	610.3	22.0	1771436.0	588.2	
9.000001	1192.1	45.0	1795714.0	1135.2	
9.000001	1781.2	64.8	1820239.0	1587.0	
9.000001	2304.4	91.5	1841866.0	2215.0	
9.000001	3045.8	113.8	1872648.0	2672.4	
		O			
40.00000	392.9	11.3	2686.9	149.3	39.43
40.00000	496.9	12.7	3414.2	153.1	39.52
40.00000	604.4	15.1	4014.8	179.5	39.97
40.00000	685.6	16.2	4498.4	180.7	
40.00000	828.6	19.3	5415.7	222.3	
40.00000	889.2	22.5	5813.7	239.9	
40.00000	983.9	22.4	6094.7	249.9	

Appendix B (Continued)

V	T	ΔT	P	ΔP	V_{exp}
40.00000	1080.4	30.6	6793.1	323.2	
40.00000	1152.2	28.3	6910.4	265.2	
35.00003	402.9	11.5	4220.0	157.2	34.50
35.00003	488.6	11.0	4941.8	153.5	34.73
35.00003	599.7	17.0	5857.1	223.2	34.89
35.00003	687.0	18.2	6493.7	235.5	
35.00003	792.6	19.0	7327.6	246.9	
35.00003	864.6	24.7	7942.7	285.9	
35.00003	995.6	21.2	8901.8	271.0	
35.00003	1121.9	24.8	9755.1	274.0	
35.00003	1186.7	28.6	9874.9	299.8	
30.00000	393.8	13.3	6928.6	198.6	29.86
30.00000	502.6	14.8	8237.5	215.8	30.01
30.00000	596.6	18.2	9317.0	257.8	30.10
30.00000	725.1	21.5	10779.8	289.4	
30.00000	794.2	22.9	11524.4	307.3	
30.00000	927.9	23.0	12660.7	317.0	
30.00000	996.4	25.1	13615.1	356.0	
30.00000	1076.8	32.5	14581.8	418.5	
30.00000	1232.0	33.2	15566.5	403.6	
25.00000	599.0	19.5	17687.8	306.7	
25.00000	1190.3	35.6	26325.0	529.3	
25.00000	1839.1	53.6	34202.9	755.5	
25.00000	2370.5	67.2	40023.2	915.4	
25.00000	2939.6	68.0	45934.4	837.1	
25.00000	3602.8	92.2	52045.5	1180.2	
25.00000	4134.4	82.2	55910.3	1040.6	
20.00000	620.9	24.7	37264.7	459.6	
20.00000	1205.4	42.4	55943.6	733.2	
20.00000	1797.0	58.9	67333.6	989.1	
20.00000	2339.8	85.1	76601.4	1385.9	
20.00000	2955.9	95.0	85958.2	1517.6	
20.00000	3632.4	125.5	96966.6	2058.6	
20.00000	4285.7	127.7	105943.3	2081.8	
15.00000	591.4	21.5	127699.9	462.1	
15.00000	1217.5	46.4	146999.2	958.1	
15.00000	1736.7	63.5	163546.6	1288.8	
15.00000	2448.2	73.1	201807.3	1419.2	
15.00000	3009.8	121.5	216431.8	2378.2	
15.00000	3651.0	96.7	233879.4	1770.0	
15.00000	4233.0	112.3	244036.9	1838.5	
13.00390	591.5	23.3	241601.7	538.4	
13.00390	1206.8	43.6	262646.1	966.9	
13.00390	1774.1	53.7	281770.3	1189.9	
13.00390	2421.2	88.6	304796.4	1925.6	
13.00390	2937.2	95.2	323619.1	2062.2	
13.00390	3528.1	142.1	355701.9	2963.2	
13.00390	4283.5	168.5	379676.4	3062.2	
11.00000	610.4	23.2	499216.5	580.8	
11.00000	1227.0	48.7	522751.3	1164.4	
11.00000	1805.6	57.7	544821.9	1396.3	
11.00000	2397.3	92.1	566765.7	2129.6	
11.00000	2968.8	101.6	589305.5	2427.6	
11.00000	3822.8	127.6	621915.4	2953.2	
9.000001	606.6	21.6	1143904.0	579.6	
9.000001	1231.8	49.1	1171382.0	1294.1	
9.000001	1768.7	61.5	1194530.0	1618.8	

Appendix B (Continued)

V	T	ΔT	P	ΔP	V_{exp}
9.000001	2289.9	83.3	1217317.0	2149.7	
9.000001	3021.6	102.1	1248526.0	2512.1	
9.000001	3587.1	130.4	1273226.0	3350.7	
9.000001	4099.2	145.0	1301806.0	3588.9	
O_2					
40.00000	394.3	8.0	1801.7	112.8	38.74
40.00000	503.4	9.8	2319.0	128.7	39.75
40.00000	602.0	11.5	2797.0	142.8	40.21
40.00000	707.7	13.8	3289.7	165.6	40.62
40.00000	804.1	15.6	3845.4	186.9	40.36
40.00000	896.1	17.8	4229.9	198.3	
40.00000	975.9	19.1	4576.6	217.8	
40.00000	1090.1	22.6	5151.5	247.4	
40.00000	1208.1	23.0	5698.1	250.2	
40.00000	1295.9	25.4	6027.6	287.3	
30.00000	407.1	10.8	4049.2	181.6	29.42
30.00000	519.9	13.3	5069.7	223.0	29.87
30.00000	602.8	15.3	5900.8	242.1	29.92
30.00000	712.4	15.9	6777.0	242.3	30.29
30.00000	799.8	20.3	7411.2	302.1	
30.00000	898.7	20.3	8161.1	304.5	
30.00000	979.2	25.8	8895.0	368.0	
30.00000	1106.6	22.4	9988.8	276.3	
25.00000	399.8	12.3	7208.2	240.0	24.73
25.00000	785.2	21.1	12284.3	352.9	
25.00000	1193.0	31.9	17037.9	522.4	
25.00000	1622.1	42.6	21016.7	657.0	
25.00000	1988.2	44.7	24307.5	644.2	
25.00000	2434.7	73.9	27842.6	1192.5	
25.00000	2860.2	42.7	31191.3	539.6	
25.00000	3293.6	64.3	32823.0	865.3	
25.00000	3551.2	37.6	32981.7	508.1	
25.00000	3977.3	43.2	36454.0	587.6	
20.00000	400.1	13.7	17139.0	295.0	
20.00000	781.9	22.8	25451.0	452.1	
20.00000	1158.5	31.9	32071.0	596.0	
20.00000	1634.5	44.9	39503.7	806.2	
20.00000	2030.0	59.8	45547.6	1034.7	
20.00000	2515.4	68.3	51385.8	1199.7	
20.00000	2888.3	64.5	55957.3	1025.2	
20.00000	3304.2	33.2	58201.5	613.9	
20.00000	3526.2	32.5	63053.4	447.2	
20.00000	4024.0	41.3	63520.6	769.6	
15.00000	388.4	14.8	51893.3	364.9	
15.00000	796.9	30.0	65767.5	721.5	
15.00000	1182.3	42.0	86985.9	948.8	
15.00000	1572.2	57.1	98482.5	1293.8	
15.00000	2018.7	73.0	109408.4	1615.0	
15.00000	2488.2	71.0	118869.5	1460.8	
15.00000	2862.2	84.1	132287.0	1581.8	
15.00000	3218.9	75.1	138728.9	1365.1	
15.00000	388.9	14.0	51879.1	349.4	
15.00000	803.2	28.1	66009.2	677.0	
15.00000	1228.8	42.5	88372.2	960.5	
15.00000	1550.8	54.6	97744.5	1224.9	
15.00000	1975.0	69.1	108491.7	1492.2	
15.00000	2336.8	72.0	117050.3	1528.5	

Appendix B (Continued)

V	T	ΔT	P	ΔP	V_{exp}
15.00000	2792.8	86.5	128009.7	1808.0	
15.00000	3253.6	105.1	137289.4	2165.1	
15.00000	3593.2	103.5	143951.1	2159.2	
15.00000	3910.1	111.2	150515.9	2300.8	
13.00390	392.1	14.7	103645.6	387.8	
13.00390	809.5	31.6	119088.5	815.8	
11.00000	404.9	13.7	229155.9	394.8	
11.00000	824.9	28.5	246599.0	793.6	
11.00000	1166.8	41.1	260570.5	1120.9	
11.00000	1594.1	61.4	278022.3	1664.1	
11.00000	1940.2	66.6	292409.5	1792.1	
11.00000	2389.6	94.9	314243.2	2534.0	
11.00000	2738.8	100.2	355424.8	2570.8	
11.00000	3214.1	118.0	374231.1	2973.4	
11.00000	3650.4	135.2	389602.1	3399.5	
11.00000	4066.8	134.2	403192.1	3342.9	
9.000001	404.6	14.7	564594.3	463.7	
9.000001	813.9	29.6	584001.1	901.9	
9.000001	1191.1	45.4	601650.5	1372.7	
9.000001	1609.4	51.9	621473.9	1538.9	
9.000001	1952.2	71.3	637601.3	2131.7	
9.000001	2453.6	81.9	661137.8	2428.7	
9.000001	2742.6	96.5	674768.2	2826.8	
9.000001	3207.6	117.6	696848.3	3451.1	
9.000001	3583.9	139.8	714492.3	4055.6	
9.000001	3881.9	136.9	730577.1	3959.6	
8.000000	391.0	14.2	934494.9	480.7	
8.000000	829.0	28.7	957026.7	939.2	
8.000000	1274.2	46.9	979935.0	1490.3	
8.000000	1585.0	58.5	995585.0	1851.9	
8.000000	2059.0	73.3	1019720.0	2308.9	
8.000000	2394.6	88.7	1036642.0	2770.0	
8.000000	2850.3	98.5	1059827.0	3039.2	
8.000000	3225.9	121.8	1078813.0	3739.3	
8.000000	3649.2	130.5	1100504.0	4009.4	
8.000000	3932.9	154.7	1114876.0	4724.2	
H₂					
25.000000	295.5	6.0	2359.5	96.5	25.70
25.000000	381.8	8.4	2964.6	132.4	25.68
25.000000	507.3	10.2	3785.8	152.4	25.52
25.000000	609.6	11.8	4428.3	168.9	
25.000000	704.1	14.4	5025.1	208.2	
20.000000	303.6	7.1	3877.5	131.8	20.73
20.000000	401.1	10.1	4828.0	176.3	20.96
20.000000	502.7	10.8	5817.8	183.5	20.86
20.000000	615.4	14.0	6762.2	236.5	
20.000000	690.1	13.3	7433.3	219.1	
20.000000	805.8	18.7	8397.1	294.5	
20.000000	882.1	17.8	9057.1	278.1	

Appendix B (Continued)

V	T	ΔT	P	ΔP	V_{exp}
20.000000	996.5	22.3	10027.8	339.7	
20.000000	1083.1	22.1	10630.4	334.0	
20.000000	1218.0	25.2	11617.5	372.8	
15.000000	305.8	9.0	8294.1	206.5	
15.000000	398.5	10.8	9876.6	240.5	
15.000000	494.0	13.2	11341.6	279.0	
15.000000	595.8	15.9	12973.9	336.1	
15.000000	679.4	18.3	14108.4	369.9	
15.000000	808.3	20.1	15833.4	397.6	
15.000000	889.6	22.1	16993.7	443.1	
15.000000	981.7	23.9	18258.3	471.0	
15.000000	1082.6	27.8	19341.2	539.1	
15.000000	1214.1	28.4	21051.9	528.6	
10.000000	296.2	10.6	29761.0	312.6	
10.000000	898.9	28.8	48773.8	752.8	
10.000000	1493.2	42.7	63266.7	1076.4	
10.000000	2126.3	54.5	76654.8	1293.7	
10.000000	2634.1	67.8	86119.6	1567.4	
10.000000	3280.8	78.0	98137.1	1670.8	
10.000000	3833.7	93.9	108286.2	1996.5	
7.000000	300.9	10.6	101436.5	386.8	
7.000000	913.9	31.5	145147.3	1055.8	
7.000000	1525.0	50.0	172236.6	1550.9	
7.000000	2157.1	65.4	196270.5	1954.2	
7.000000	2614.9	77.0	212067.8	2285.4	
7.000000	3367.8	97.7	236631.2	2802.2	
7.000000	3822.4	114.4	250213.5	3243.6	
6.000000	289.1	10.4	183178.8	404.2	
6.000000	920.5	32.2	239609.1	1163.2	
6.000000	1576.8	50.3	276690.4	1729.2	
6.000000	2107.2	66.7	303350.3	2191.3	
6.000000	2731.9	89.7	331082.4	2927.4	
6.000000	3171.4	102.6	348379.3	3232.8	
6.000000	3994.7	120.3	380218.8	3723.5	
5.000000	302.7	11.3	367516.9	474.8	
5.000000	901.2	34.2	411747.9	1355.1	
5.000000	1512.7	54.7	482203.8	2038.0	
5.000000	2146.7	75.0	522420.5	2721.0	
5.000000	2823.3	96.9	562062.9	3415.5	
5.000000	3335.1	108.2	589237.1	3742.6	
5.000000	3772.3	122.8	611037.9	4210.8	
4.000000	305.2	11.0	828256.6	522.6	
4.000000	895.3	34.0	878036.8	1479.4	
4.000000	1509.7	55.9	931062.5	2314.9	
4.000000	2110.5	77.1	1028511.0	3069.2	
4.000000	2756.6	93.6	1079791.0	3631.9	
4.000000	3263.1	114.2	1117625.0	4430.9	
4.000000	3774.5	131.6	1154604.0	5002.6	
3.000000	308.8	10.9	2213999.0	618.5	
3.000000	884.3	34.2	2271771.0	1631.3	