American Mineralogist, Volume 78, pages 558–564, 1993

Molecular dynamics simulations of the properties of CO_2-H_2O mixtures at high pressures and temperatures

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ABSTRACT

Molecular dynamics simulations of CO_2-H_2O mixtures have been made at X_{CO_2} of 0.25, 0.5, and 0.75 using the TIP4P and MSM3 intermolecular potentials. At approximately 400 °C and at pressures between 2 and 5 kbar the predicted excess volumes of about 1–2 cm^3/mol agree very well with the available experimental data. Although excess volumes rapidly decrease with pressure, at both 400 and 1200 °C the simulations predict that significant excess volumes of about 0.5 cm^3/mol persist to pressures of over 20 kbar. In addition, the MD simulations predict only a small decrease in excess volumes as temperature is increased from 400 to 1200 °C.

INTRODUCTION

The thermodynamic properties of fluids such as CO_2 and H_2O are of fundamental importance to Earth scientists. These fluids profoundly influence melting temperatures, melt compositions, and the rheological properties of minerals and melts. Despite their obvious geological importance, however, the thermodynamic properties of H_2O and CO_2 are known only to pressures of <10 kbar. This reflects the experimental difficulties inherent in obtaining reliable high-pressure data and forces Earth scientists to extrapolate empirical equations of state when fluid properties are required at higher pressures. Unfortunately, although such equations faithfully reproduce the experimental data, their accuracy when extrapolated outside the range of the data is impossible to assess, since they have little theoretical basis. In addition, different equations of state for the same fluid rarely predict the same volume when extrapolated by more than a few kilobars.

In order to attempt to predict fluid phase *PVT* properties in a manner that has a firmer theoretical grounding, we have undertaken a molecular dynamics (MD) study. This is done in the belief that if the forces between molecules are known, and that if these forces do not change significantly over the range of densities considered, then we can use the methods of MD to calculate thermodynamic properties at conditions that are hard or impossible to achieve experimentally. So far we have successfully applied the TIP4P intermolecular potential for H_2O (Jorgensen et al., 1983) to develop an equation of state that can be used to pressures of 300 kbar and temperatures of 2000 K (Brodholt and Wood, 1990, 1993). For CO_2 we have tested similarly many of the available intermolecular potentials and found three that reproduce much of the available low-pressure data (Brodholt and Wood, unpublished manuscript). In this paper we use these intermolecular potentials to investigate CO_2-H_2O mixtures to delineate the *P-T* conditions under which the properties of mixtures of CO_2 and H_2O deviate from ideality.

INTERMOLECULAR POTENTIALS FOR CO_2 AND H_2O

For H_2O we have used the TIP4P intermolecular potential developed by Jorgensen et al. (1983). This potential has been remarkably successful at predicting H_2O properties over a wide range of conditions in both the fluid and solid phases (Jorgensen and Madura, 1985; Madura et al., 1988; Tse and Klein, 1987). It also has been extensively tested at high pressures and temperatures by Brodholt and Wood (1993) and shown to reproduce accurately many of the available experimentally measured volumes, especially at higher pressures and temperatures. The worst agreement between the simulated H_2O volumes and the experimental data occurs at relatively low pressures (<2 kbar) and temperatures around 600 °C, where the simulated volumes are more than 6 cm^3/mol larger than the data. TIP4P has a rigid geometry, with an HOH bond angle of 104.52° and an OH bond length of 0.09752 nm, values that are consistent with the measured values of the gas phase. It contains four interaction sites consisting of a Lennard-Jones term between the O atoms and three partial Coulomb charges. Two of the three partial charges, q_H, are situated on the H atoms, with the third, q_M, situated on a site M that is close to the O atom but displaced 0.015 nm along the HOH bisector toward the H atoms. The values for the Lennard-Jones and Coulomb parameters are given below.

Of the many CO_2 intermolecular potentials tested by Brodholt and Wood (unpublished manuscript), we have chosen to use the MSM potential developed by Murthy et al. (1983). It accurately reproduces the volumes at 25 °C and 1–7 kbar, a pressure range that encompasses volumes from 63 down to 31 cm^3/mol. At higher temperatures it accurately reproduces volumes below pressures of 6 kbar. Only at high pressures and temperatures (>6 kbar

0003–004X/93/0506–0558$02.00

and >400 °C) do the simulated volumes diverge from the available experimental data, where, at these conditions, the simulated volumes are larger than the experimental volumes. This is a general feature of all the CO_2 potentials we have tested. The reason that we used the MSM potential is that it is the best potential that employs a Lennard-Jones form for the dispersion and short-range repulsive forces, and we know of no way to combine the LJ potential of TIP4P with the exp-6 forms used in many other CO_2 potentials. The original MSM potential has three Lennard-Jones sites, one on each atom of the CO_2 molecule, and five Coulomb partial charges. The five charges are used to account for higher order electrostatic moments, in addition to the quadrupole moment. Although these higher order moments make a small contribution to lattice frequencies in solid CO_2 (Murthy et al., 1983), we have found that with regard to *PVT* properties, they are not important in fluids. This means that the five partial charges can be replaced with three, with the charge size chosen so as to reproduce the quadrupole moment of the original five-site model. This results in significant savings in computer time, especially if the Ewald sum or an equivalent is used. We have called the three-site model MSM3. As with TIP4P, the MSM3 potential maintains a rigid geometry with a C-O bond length of 0.1162 nm.

The form of the Lennard-Jones potential is

$$V_{\mathrm{ab}} = 4\epsilon_{\mathrm{ab}}\left[\frac{\sigma_{\mathrm{ab}}^{12}}{r^{12}} - \frac{\sigma_{\mathrm{ab}}^{6}}{r^{6}}\right]$$

together with the Lorentz-Berthelot mixing rules for combining dissimilar atoms:

$$\sigma_{\mathrm{ab}} = \frac{\sigma_{\mathrm{aa}} + \sigma_{\mathrm{bb}}}{2}$$

$$\epsilon_{\mathrm{ab}} = \sqrt{\epsilon_{\mathrm{aa}}\epsilon_{\mathrm{bb}}}\,.$$

The so-called Lorentz-Berthelot mixing rules have little theoretical justification and are rather ad hoc. However, they are normally used as a first approximation, and additional cross-interaction energy parameters can be added later, if these combining rules fail to yield reasonable results (De Pablo and Prausnitz, 1989).

For TIP4P the potential parameter values are

$$\sigma_{\mathrm{O}} = 0.315363\ \mathrm{nm}$$
$$\epsilon_{\mathrm{O}} = 0.64857\ \mathrm{kJ/mol}$$
$$q_{\mathrm{H}} = 0.52e \qquad q_{\mathrm{M}} = -2q_{\mathrm{H}} = -1.04e$$

where e is the charge on an electron. For MSM3 the parameters are

$$\sigma_{\mathrm{O}} = 0.3014\ \mathrm{nm} \qquad \sigma_{\mathrm{C}} = 0.2785\ \mathrm{nm}$$
$$\epsilon_{\mathrm{O}} = 0.69092\ \mathrm{kJ/mol} \qquad \epsilon_{\mathrm{C}} = 0.24112\ \mathrm{kJ/mol}$$
$$q_{\mathrm{O}} = -0.297e \qquad q_{\mathrm{C}} = -2q_{\mathrm{O}} = 0.594e.$$

Both of these intermolecular potentials incorporate some of the most important aspects of a molecule, such as charge distribution and correct geometry. Obviously a truly realistic potential would have to include intramolecular forces, polarizability, and multibody interactions; however, even if such potentials for CO_2 and H_2O were not still in their infancy, it is still necessary to characterize the properties of the simpler potentials first to understand fully the effect of incorporating these additional degrees of freedom.

METHOD

We have used constant *NVE* (number of molecules, volumes, and total energy) molecular dynamics with normal cubic periodic boundary conditions (see Allen and Tildesley, 1987, for a review). All simulations used 108 molecules and a time step of between 1×10^{-15} and 7×10^{-16} s. The equations of motion were solved using a fifth-order predictor-corrector routine (Gear, 1971) and a quarternion representation for the angular motion (Evans and Murad, 1977). The long-range Coulomb forces were handled using the method of Adams and Dubey (1987), rather than the traditional Ewald sum. The eighth-order expansion was found to be sufficient. The Lennard-Jones interactions were truncated at a distance of one-half the box length, and long-range corrections caused by this have been added to the pressures. This correction is based on the assumption that the radial distribution function becomes equal to one at the edge of the box (Allen and Tildesley, 1987, p. 65). The program uses real units of kilojoules and ångströms.

Initially, starting configurations were taken from well-equilibrated configurations of either pure MSM3 or TIP4P, and the molecules were arbitrarily assigned as being either a CO_2 or H_2O molecule. Velocities were scaled for the first 500 steps to obtain roughly the desired temperature, and the configuration was then allowed to re-equilibrate for at least 500 more steps to remove any effect from the velocity scaling before thermodynamic averaging began. Averages were then taken over 5000 steps. Considerable care was taken to ensure that there were no residual effects due to the initial configuration. This was done in two ways. First, the results of simulations started from an MSM3 configuration were compared with simulations started from a TIP4P configuration. Secondly, four consecutive simulations were made, including the initial temperature scaling as described above, with each simulation starting from the final configuration of the previous simulation. The results of these tests convinced us that there were no residual effects due to the initial starting configuration.

VOLUMES OF PURE TIP4P H_2O AND MSM3 CO_2

To evaluate V^{ex} it is necessary to know the volumes of pure TIP4P and MSM3 at the same temperature and pressure as the simulation of the mixture. This can be done very accurately by interpolating between the constant *NVE* simulations of MSM3 and TIP4P. First, each

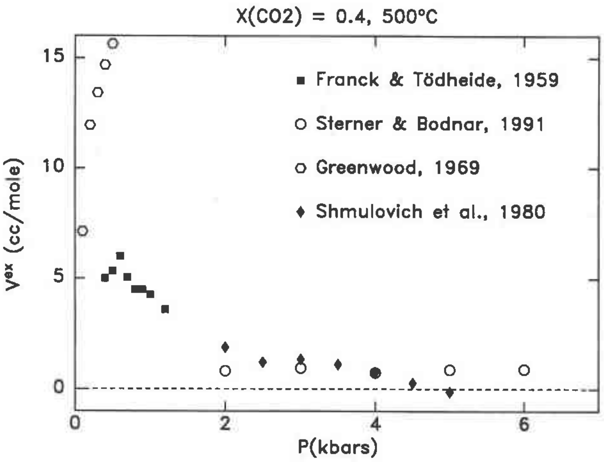

Fig. 1. A comparison of the experimental excess volumes of mixing (V^{ex}) at 500 °C and $X_{CO_2} = 0.4$. Greenwood (1969) predicted excess volumes that are 10 cc/mol greater than those of Franck and Tödheide (1959) under the same conditions. The experiments of Shmulovich et al. (1980) and Sterner and Bodnar (1991) are in reasonable agreement with each other, although the excess volumes of Sterner and Bodnar (1991) remain more or less constant over this pressure range, whereas those of Shmulovich et al. (1980) decrease.

isochore was individually fitted to a quadratic function:

$$P(T) = a + bT + cT^2.$$

An isotherm was then constructed by evaluating the pressure on each isochore at the required temperature. The isotherm was then fitted to a function:

$$V(P) = a + bP + c\sqrt{P} + d/P$$

allowing the volume at the required P and T to be calculated. To estimate the error in V, each volume (V_i) used in the fit was weighted, assuming that the error in P and T (σ_P and σ_T) from the simulations propagated into V_i, as in an ideal gas. That is

$$\sigma^2_{V_i} = \sigma^2_P\left(\frac{\partial V}{\partial P}\right)^2 + \sigma^2_T\left(\frac{\partial V}{\partial T}\right)^2$$

$$\sigma^2_{V_i} = \sigma^2_P\frac{\mathrm{R}^2T^2}{P^4} + \sigma^2_T\frac{\mathrm{R}^2}{P^2}.$$

For all simulations, σ_P and σ_T were given the values of 100 bars and 4°, respectively. To test the volumes found by interpolation, four *NVT* Monte Carlo simulations were made at the interpolated volume and temperature with pure MSM3 and TIP4P. The pressures resulting from these MC simulations agreed with the pressures used in the interpolation by 40–150 bars, indicating that the interpolated volumes are very accurate.

DATA

There are four sets of experimental data on CO_2-H_2O mixing relevant to this study. Earliest is that of Franck and Tödheide (1959), in which experiments were made in a constant-volume pressure vessel at conditions of 0.3–2.0 kbar and 400–750 °C and at mole fractions of CO_2 of 0.2, 0.4, 0.6, and 0.8. Greenwood (1969) used a similar apparatus to make measurements on CO_2-H_2O volumes; however, these were restricted to pressures <500 bars. Later, Shmulovich et al. (1980) used a displacement-type piezometer to make measurements along the isotherms at 400 and 500 °C at pressures between 1 and 5 kbar, although over a fairly restricted compositional range. Most recently Sterner and Bodnar (1991) used synthetic fluid inclusions to measure molar volumes of CO_2-H_2O mixtures at pressures from 1 to 6 kbar and temperatures of 400–700 °C. They encompassed the widest and most comprehensive compositional range, with X_{CO_2} spanning from 0.1234 to 0.8736 at each P and T.

In Sterner and Bodnar (1991) and Shmulovich et al. (1980) V^{ex} is explicitly given, whereas for Greenwood (1969) and Franck and Tödheide (1959) it has to be evaluated using the volumes of the pure phases. To do this, we used the NBS equation of state for H_2O from Haar et al. (1984), and for CO_2 we used the equation of state from Shmonov and Shmulovich (1974). This is consistent with Sterner and Bodnar (1991), who also used these two equations of state to evaluate the excess volumes from their experiments.

Figure 1 is a plot of V^{ex} as a function of pressure for the four experimental data sets at 500 °C and X_{CO_2} of 0.4. This temperature and composition allows for comparison over the largest range in pressure. The plot shows the standard behavior of V^{ex} with pressure for a homogeneous fluid mixture. At the lowest pressures H_2O and CO_2 mix ideally. When pressure increases, excess volumes rapidly increase as intermolecular interactions become important. At some pressure V^{ex} reaches a maximum, after which excess volumes decrease with pressure. Some significant differences in excess volumes exist, however, among the experimental studies. The data of Greenwood (1969) have very high excess volumes that are up to 10 cm³/mol greater than those found by Franck and Tödheide (1959) at the same pressure. This difference is much larger than the quoted experimental errors, which are about 1 cm³/mol for both studies. In addition, the excess volumes of Franck and Tödheide (1959) reach a maximum by 600 bars, whereas those of Greenwood (1969) appear to be still increasing with increasing pressure. Similar apparatus were used in both studies, and they both reproduce the end-member pure phase volumes, so it is hard to identify the source of error. Unfortunately, the MD simulations of this study cannot help to resolve these discrepancies, as the errors in volume are too large at low pressures and high temperatures, when the fluid behaves as a nearly ideal gas. The errors in pressure and temperature in the simulation are about 50 bars and 3°, which, if we propagate the errors as for an ideal gas, lead to errors of >12 cm³/mol at low pressures. However, in a recent review of H_2O-CO_2 mixtures, Mäder

TABLE 1. Summary of mixing simulations

X_{CO_2}	T (K)	P (kbar)	V (cm³/mol)	V(MSM3) (cm³/mol)	σ	V(TIP4P) (cm³/mol)	σ	V(ideal) (cm³/mol)	V^{ex}	σ
0.75	667	26.67	24	27.04	0.02	14.11	0.02	23.81	0.19	0.02
	665	13.25	28	31.34	0.03	16.28	0.03	27.58	0.32	0.03
	663	7.54	32	35.70	0.06	18.25	0.08	31.34	0.64	0.08
	662	5.00	36	39.98	0.12	19.90	0.13	34.96	1.04	0.13
	670	3.43	40	44.95	0.25	21.85	0.27	39.18	0.82	0.27
	680	2.78	44	48.91	0.37	23.34	0.39	42.52	1.48	0.39
	683	2.25	48	53.37	0.52	24.89	0.58	46.25	1.75	0.58
0.75	1426	17.18	32	35.70	0.03	20.03	0.03	31.78	0.22	0.03
	1539	12.94	36	40.01	0.04	23.21	0.04	35.81	0.19	0.04
	1541	10.03	40	43.82	0.07	25.96	0.06	39.36	0.64	0.07
	1470	7.58	44	47.97	0.12	28.77	0.11	43.17	0.83	0.11
	1466	6.03	48	52.95	0.19	32.45	0.18	47.83	0.17	0.19
	1498	5.37	52	56.20	0.23	35.00	0.22	50.90	1.10	0.22
0.5	682	32.03	20	26.11	0.03	13.66	0.03	19.89	0.11	0.01
	694	13.82	24	31.37	0.03	16.32	0.03	23.85	0.15	0.03
	693	7.47	28	36.30	0.06	18.61	0.07	27.46	0.54	0.07
	675	4.62	32	41.05	0.13	20.47	0.15	30.76	1.24	0.14
	702	3.30	36	46.72	0.28	22.86	0.28	34.79	1.21	0.28
	690	2.34	40	52.86	0.49	24.89	0.52	38.88	1.12	0.51
	693	1.94	44	57.55	0.70	26.41	0.70	41.98	2.02	0.70
0.5	1429	29.17	24	30.66	0.01	16.80	0.01	23.73	0.27	0.01
	1580	19.70	28	35.21	0.03	19.93	0.03	27.57	0.43	0.03
	1469	12.51	32	39.86	0.04	22.96	0.04	31.41	0.59	0.04
	1547	9.88	36	44.13	0.07	26.22	0.06	35.18	0.82	0.07
	1493	7.58	40	48.28	0.11	29.08	0.12	38.68	1.32	0.12
	1474	5.87	44	53.55	0.18	32.89	0.18	43.22	0.78	0.18
	1508	5.22	48	57.14	0.24	35.76	0.23	46.45	1.55	0.23
0.25	638	38.59	16	24.91	0.01	13.10	0.10	16.05	−0.05	0.10
	683	14.59	20	30.89	0.02	16.07	0.03	19.78	0.22	0.03
	671	6.38	24	37.41	0.08	19.01	0.09	23.61	0.39	0.09
	649	3.44	28	44.28	0.25	21.37	0.26	27.10	0.90	0.26
	699	2.51	32	51.76	0.45	24.61	0.47	31.39	0.61	0.46
	687	1.82	36	59.61	0.75	26.80	0.81	35.00	1.00	0.81
0.25	1539	19.32	24	35.17	0.03	19.85	0.03	23.68	0.32	0.03
	1500	12.34	28	40.32	0.04	23.35	0.04	27.59	0.41	0.04
	1542	9.42	32	44.92	0.08	26.77	0.07	31.31	0.69	0.08
	1469	6.89	36	49.88	0.13	30.16	0.13	35.09	0.91	0.13
	1496	5.78	40	54.28	0.20	33.55	0.20	38.73	1.27	0.20

Note: T, P, and V are the temperature, pressure, and molar volume of the simulation at the mole fraction of CO_2 given in the first column. The columns labeled V(MSM3) and V(TIP4P) are the volumes of the pure phases at T and P. Also given are the ideal molar volume and the excess volume. See text for an explanation of σ.

(1991) also noted that the data of Franck and Tödheide (1959) are inconsistent with other data and with equations of state that satisfy phase equilibria constraints, and he concluded that it is the data of Franck and Tödheide (1959) that are most likely to be in error.

Better agreement is found between the higher pressure data of Shmulovich et al. (1980) and Sterner and Bodnar (1991), with excess volumes of between 2 and 0 cm³/mol (Fig. 1). V^{ex} of Shmulovich et al. (1980) decreases from 1.88 cm³/mol at 2 kbar to −0.13 cm³/mol at 5 kbar, whereas Sterner and Bodnar (1991), on the other hand, reported a more-or-less constant excess volume (within error) of about 0.8 cm³/mol over this pressure range. We do not attribute much importance to these small differences.

It is worth emphasizing at this point that the observed decrease of excess volumes with increasing pressure does not equate with decreasing activity. The activity of a component in a mixture is an integrated property (with respect to pressure), and the only way that it can start to decrease is if the excess volumes become negative.

RESULTS

Simulations have been made at CO_2 mole fractions of 0.25, 0.5, and 0.75 and at temperatures close to 400 and 1200 °C. Molar volumes ranged from 16 to 52 cm³/mol, and pressures from 1.82 to 39 kbar. The results are summarized in Table 1. Since we are using the constant *NVE* ensemble, it is difficult to arrive at exactly the desired temperature. It should be noted, therefore, that when the 400 or 1200 °C isotherms are referred to in some figures, the simulated temperatures may actually differ by 20 or 30°. A similar consideration should be made for pressure. The exact pressures and temperatures are given in Table 1.

To evaluate the MD simulations, we have chosen to compare the MD results with the data of Sterner and Bodnar (1991) rather than with those of Shmulovich et al. (1980). This is not because we believe that Sterner and Bodnar's data are better, but because the compositional coverage is more extensive. Although there are some differences between the two data sets, they are generally small.

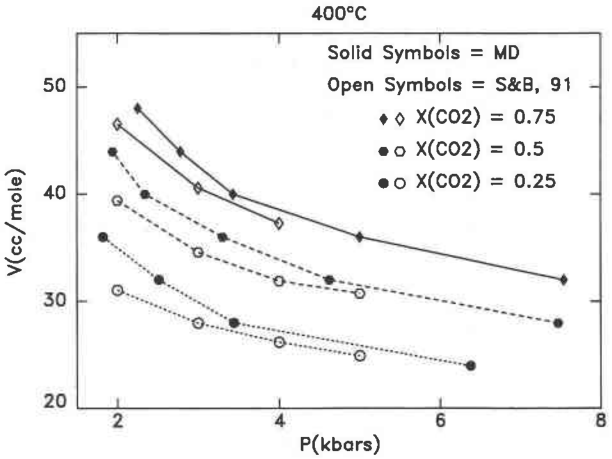

Fig. 2. The molar volumes at 400 °C obtained from the MD simulations (solid symbols) are compared with the experimental data (open symbols) of Sterner and Bodnar (1991). At low pressures the simulated volumes are always larger than the data, which is because TIP4P overestimates the volumes of H_2O at low pressures. At higher pressures TIP4P more accurately predicts H_2O volumes, and therefore the volumes of the CO_2-H_2O mixtures are more accurately reproduced.

Figure 2 compares the simulated molar volumes with the experimental data of Sterner and Bodnar (1991) along the 400 °C isotherm. Most noticeable is that the simulated volumes are substantially higher than the experimental data, especially at low pressures. This was expected, since at pressures below 5 kbar the TIP4P potential overestimates H_2O volumes by up to 6 cm^3/mol (10%) (Brodholt and Wood, 1993). However, it can be seen that as pressures approach 5 kbar, the difference between the experimental and calculated volumes becomes small (<1.0 cm^3/mol). This is a reflection of the fact that both TIP4P and MSM3 accurately predict H_2O and CO_2 volumes at these conditions. We therefore expect that at pressures exceeding 5 kbar, the volumes of CO_2-H_2O mixtures can be accurately predicted with the MSM3 and TIP4P potentials.

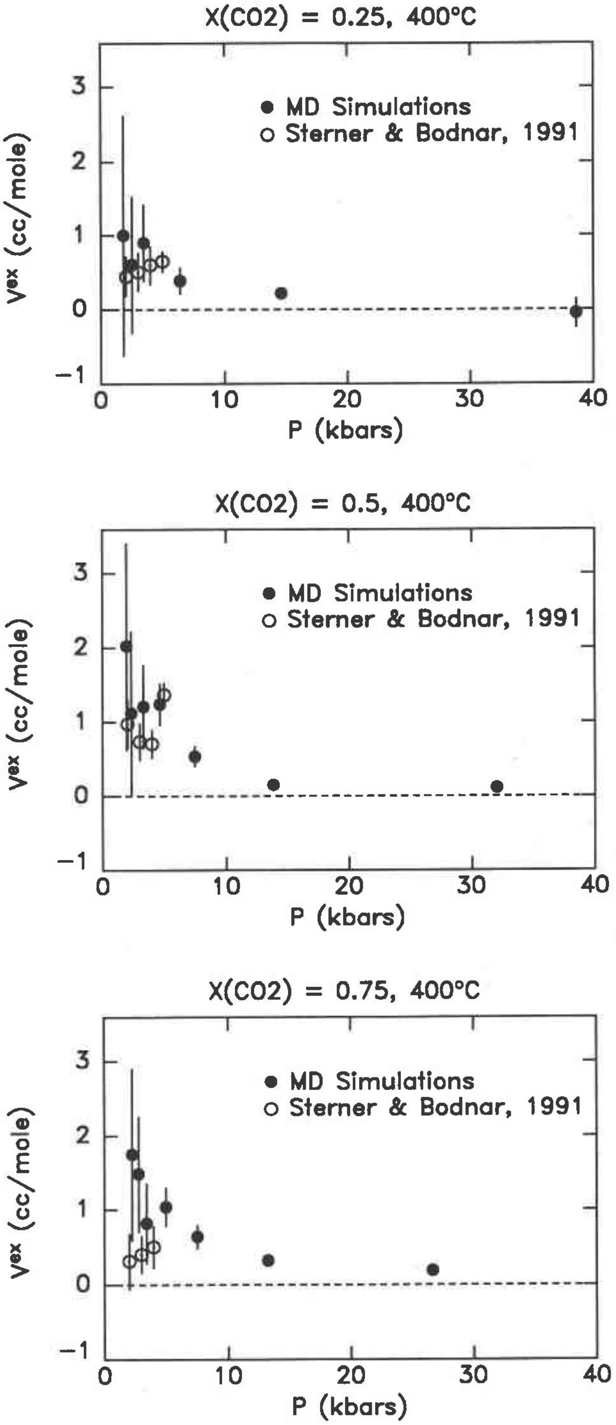

Fig. 3. A comparison of the simulated excess volumes as a function of pressure with the experimental data. The error bars are 2σ. At high pressures the predicted excess volumes fall to low values (<0.5 cc/mol).

Despite the large differences between the predicted and experimental volumes at low pressure, the excess volumes of mixing agree remarkably well with the experimental data. Plotted in Figure 3 are the experimental and simulated excess volumes at 400 °C as a function of pressure at the three compositions. The error bars shown are 2σ. In accord with theoretical expectations, the simulated excess volumes decrease from about 2.0 cm^3/mol at 2 kbar to small values at pressures exceeding 10 kbar. At X_{CO_2} of 0.25 and 0.5, the agreement between the data and the simulations is very good, whereas at X_{CO_2} of 0.75 the simulated excess volumes are somewhat larger than the data. Unfortunately Shmulovich et al. (1980) did not do experiments at X_{CO_2} of 0.75, and so we cannot directly compare with their data. However, at X_{CO_2} of 0.6 and 3.0 kbar, V^{ex} of Shmulovich et al. (1980) is about 0.4 cm^3/mol greater than that of Sterner and Bodnar (1991), which suggests that, at $X_{CO_2} = 0.6$, the data of Shmulovich et al. are in better agreement with the simulated volumes. At X_{CO_2} of 0.25 and 0.75, V^{ex} of Sterner and Bodnar (1991) appears to be increasing with pressure. If the error bars

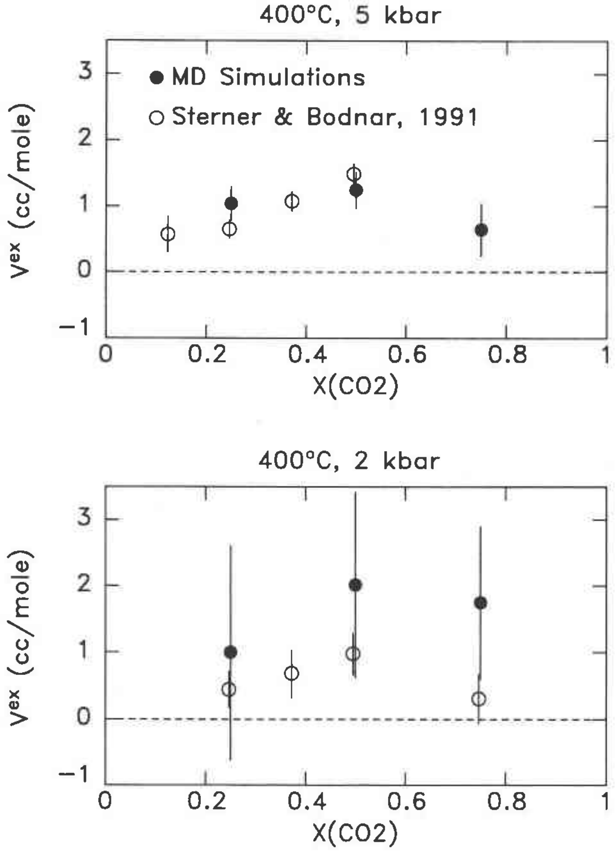

Fig. 4. Standard plots of excess volumes as a function of composition at 2 and 5 kbar. The agreement between the simulated excess volumes and the experimental data is very good. At low pressures the error in the simulated volumes is quite large. Error bars are shown as 2σ.

are taken into account, however, the trend cannot be proved. Also, the highest pressure excess volume of Sterner and Bodnar (1991), at $X_{CO_2} = 0.5$, is inconsistent with the other data.

The good agreement between the simulations and experimental data can also be seen in a plot of V^{ex} vs. X_{CO_2} (Fig. 4). Both simulations and data predict that the maximum in V^{ex} is at about X_{CO_2} of 0.5 at 2 and 5 kbar. At 2 kbar the agreement between the simulations and data is not quite as good as at 5 kbar, although at low pressures the uncertainties in the simulated excess volumes are quite large.

Temperature effects on excess volumes can be seen in Figure 5, which is a plot of V^{ex} vs. P at 400 and 1200 °C. At both temperatures V^{ex} decreases strongly with pressure. The surprising thing is that temperature does not have such a strong effect; excess volumes at 400 and 1200 °C are very similar at all three compositions. However, although we would expect mixtures to approach ideality at high temperatures, there is little experimental evidence for such an effect in CO_2-H_2O at high pressures. This can be seen in the data of Sterner and Bodnar (1991). If we

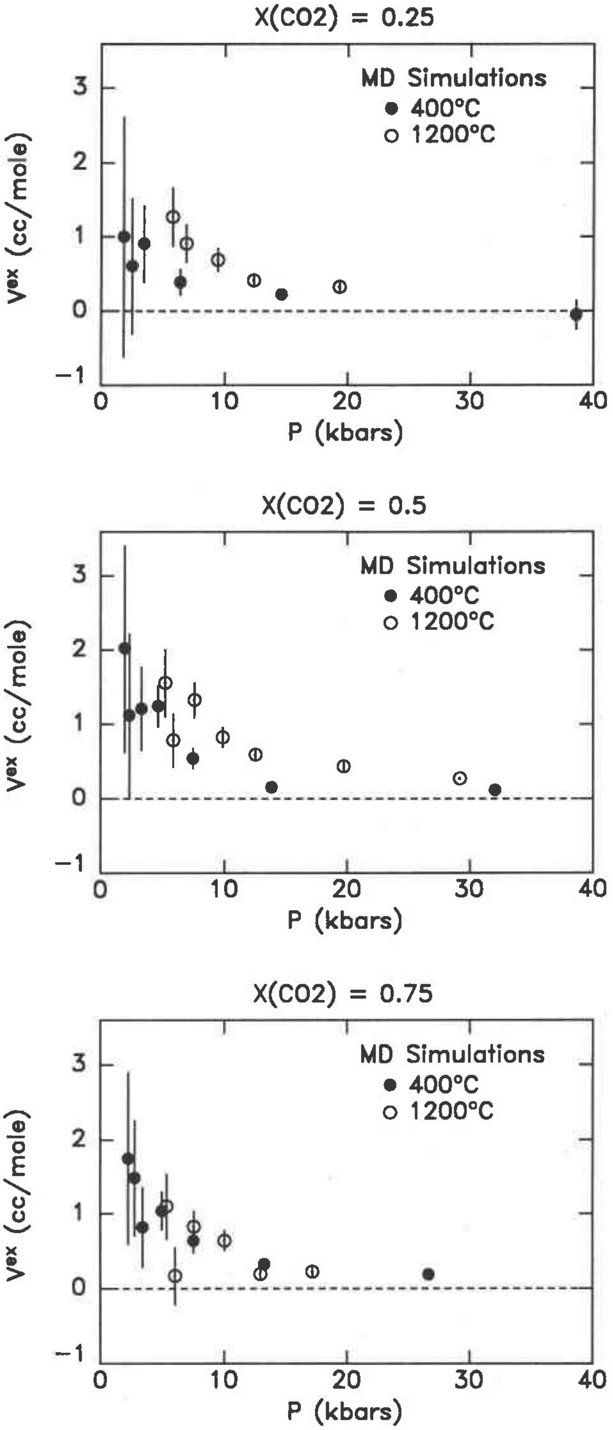

Fig. 5. The simulations at 400 °C are compared with the simulations at 1200 °C, showing that the effect of temperature on excess volumes is quite small.

look at their 5-kbar data, we see that the maximum excess volume at 400 °C is 1.20 cm³/mol at X_{CO_2} of 0.5, whereas at 700 °C the maximum excess volume is 1.18 cm³/mol at X_{CO_2} of 0.6. The only effect of temperature between 400 and 700 °C is to move the maximum excess

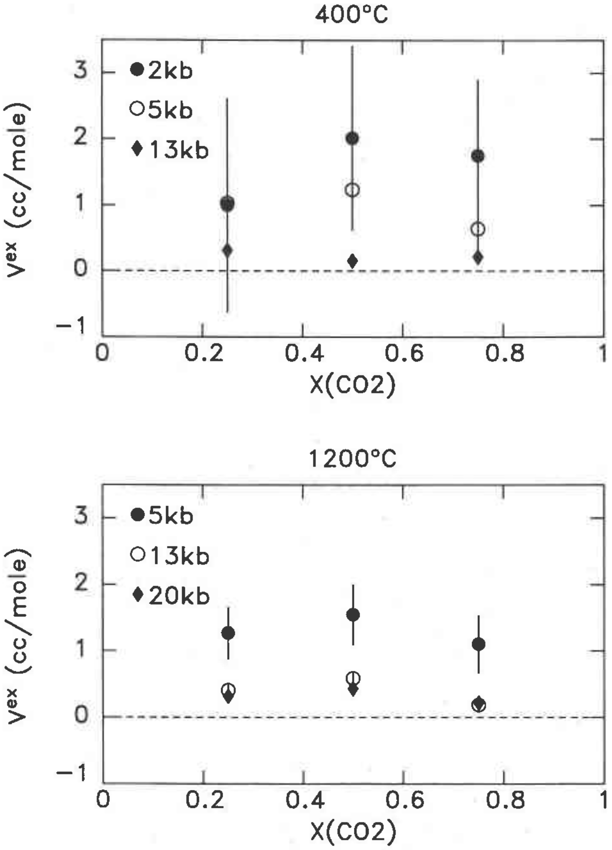

Fig. 6. Simulated excess volumes are plotted as a function of composition for 400 and 1200 °C. The excess volumes decrease quite strongly with pressure while maintaining an approximately symmetrical shape.

volume slightly, from X_{CO_2} of 0.5 to 0.6, with no decrease in its magnitude. This is consistent with the MD prediction that excess volumes decrease very little between 400 and 1200 °C.

The small effect of temperature on excess volumes predicted by the MD simulations is in contrast to the large decrease predicted by the equation of state of Kerrick and Jacobs (1981). At 1200 °C and $X_{CO_2} = 0.5$, this equation of state predicts very small excess volumes of 0.03 cm^3/mol at 5 kbar and -0.1 cm^3/mol at 13 kbar.

The combined effect of temperature and pressure on the excess volumes are illustrated in Figure 6. By 13 kbar, V^{ex} has fallen to <0.5 cm^3/mol at both temperatures, although at 1200 °C excess volumes of about 0.4 cm^3/mol persist to pressures greater than 20 kbar.

ACKNOWLEDGMENTS

This work was supported by the Natural Environmental Research Council. We thank Mike Carroll, Dave Price, and Christine Destrigneville for their advice and discussion. We also thank A. Belonoshko, S.K. Saxena, R. Cohen, and an anonymous reviewer for their reviews and suggestions.

REFERENCES CITED

Adams, D.J., and Dubey, G.S. (1987) Taming the Ewald sum in the computer simulation of charged systems. Journal of Computational Physics, 72, 156–176.

Allan, N.L., Braithwaite, M., Cooper, D.L., Mackrodt, W.C., and Wright, S.C. (1991) Ionic solids at high pressures and elevated temperatures: MgO (periclase). Journal of Chemical Physics, 95, 6792–6799.

Allen, M.P., and Tildesley, D.J. (1987) Computer simulation of liquids, 385 p. Oxford University Press, New York.

Brodholt, J.P., and Wood, B.J. (1990) Molecular dynamics of water at high temperatures and pressures. Geochimica et Cosmochimica Acta, 54, 2611–2616.

——— (1993) Simulations of the structure and thermodynamic properties of water at high pressures and temperatures. Journal of Geophysical Research, 98, 519–536.

De Pablo, J.J., and Prausnitz, J.M. (1989) Phase equilibria for fluid mixtures from Monte-Carlo simulation. Fluid Phase Equilibria, 53, 177–189.

Evans, D.J., and Murad, S. (1977) Singularity-free algorithm for molecular dynamics simulation of rigid polyatomics. Molecular Physics, 34, 327–331.

Franck, E.U., and Tödheide, K. (1959) Thermische Eigenschaften überkritischer Mischungen von Kohlendioxyd und Wasser bis zu 750 und 2000 Atm. Zeitschrift für physikalische Chemie, neue Folge, 22, 232–245.

Gear, C.W. (1971) Numerical initial value problems in ordinary differential equations, 253 p. Prentice-Hall, Englewood Cliffs, New Jersey.

Greenwood, H.J. (1969) The compressibility of gaseous mixtures of carbon dioxide and water between 0 and 500 bars pressure and 450° and 800° Centigrade. American Journal of Science, 267-A, 191–208.

Haar, L., Gallagher, J.S., and Kell, G.S. (1984) NBS/NRC steam tables, 320 p. Hemisphere, New York.

Jorgensen, W.A., and Madura, J.D. (1985) Temperature and size dependence for Monte Carlo simulations of TIP4P water. Molecular Physics, 56, 1381–1392.

Jorgensen, W.A., Chandrasekhar, J., Madura, J.D., Impey, R.W., and Klein, M.L. (1983) Comparison of simple potential functions for simulating liquid water. Journal of Chemical Physics, 79, 926–935.

Kerrick, D.M., and Jacobs, G.K. (1981) A modified Redlich-Kwong equation for H_2O, CO_2 and H_2O-CO_2 mixtures at elevated pressures and temperatures. American Journal of Science, 281, 735–767.

Mäder, U.K. (1991) H_2O-CO_2 mixtures: A review of *P-V-T-X* data and an assessment from a phase equilibrium point of view. Canadian Mineralogist, 29, 767–790.

Madura, J.D., Pettitt, B.M., and Calef, D.F. (1988) Water under high pressure. Molecular Physics, 64, 325–336.

Murthy, C.S., Singer, K., and McDonald, I.R. (1981) Interaction site models for carbon dioxide. Molecular Physics, 44, 135–143.

——— (1983) Electrostatic interactions in molecular crystals: Lattice dynamics of solid nitrogen and carbon dioxide. Molecular Physics, 50, 531–541.

Shmonov, V.M., and Shmulovich, K.I. (1974) Molar volumes and equation of state of CO_2 at temperatures from 100 to 1000°C and pressures from 2000 to 10000 bars. Døklady Akademie Nauk SSSR, 217, 206–209.

Shmulovich, V.M., Shmonov, V.M., Mazur, V.A., and Kalinichev, A.G. (1980) *P-V-T* and activity concentrations in the H_2O-CO_2 system (homogeneous solutions). Geokhimiya, 12, 1807–1824.

Sterner, S.M., and Bodnar, R.J. (1991) Synthetic fluid inclusions. X. Experimental determination of *P-V-T-X* properties in the CO_2-H_2O system to 6 kb and 700°C. American Journal of Science, 291, 1–54.

Tse, J.S., and Klein, M.L. (1987) Pressure-induced phase transformations in ice. Physical Review Letters, 58, 1672–1675.

MANUSCRIPT RECEIVED JUNE 22, 1992
MANUSCRIPT ACCEPTED DECEMBER 21, 1992