Thermodynamic modeling of the C-H-O-S fluid system

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ABSTRACT

The pressure-volume-temperature (P-V-T) relations and fugacities of pure fluid phases in the C-H-O-S system (H_2O, CO_2, CH_4, CO, O_2, H_2, S_2, SO_2, COS, H_2S) are determined from the equation of corresponding state and other empirical equations from low temperature and pressure to moderate temperature and pressure. The intermolecular potential theory is used to calculate the pressure-volume-temperature-composition (P-V-T-X) and pressure-volume-temperature-activity (P-V-T-a) relations in the C-H-O-S fluid mixture. The model is useful in calculations of phase equilibria and fluid proportions over the temperature-pressure range of the crust of the Earth.

INTRODUCTION

Knowledge of the composition of a C-H-O-S multicomponent fluid in equilibrium with carbonate + silicate + oxide + sulfide assemblages is important in understanding the origin and evolution of the heterogeneous phase equilibria involving fluids in natural geological systems and industrial processes. The main fluid species in this system are H_2O, CO_2, CH_4, CO, O_2, H_2, S_2, SO_2, COS, and H_2S.

Thermodynamic properties for the C-H-O fluid system have been successfully modeled by several versions of modified Redlich-Kwong (MRK) equation (e.g., Holloway, 1977, 1982; Flowers, 1979; Delany and Helgeson, 1978; Kerrick and Jacobs, 1981; Bottinga and Richet, 1981; Halbach and Chatterjee, 1982; Flowers and Helgeson, 1983; Connolly and Bodnar, 1983; Rimbach and Chatterjee, 1987), Ursell-Mayers virial equation (e.g., Haar et al., 1984), Levelt Sengers nonclassical equation (e.g., Levelt Sengers et al., 1983a, 1983b; Sengers and Levelt Sengers, 1984, 1986; Hill and White, 1985), Saul-Wagner equation (e.g., Saul and Wagner, 1987, 1989; Sato et al., 1989), Schmidt-Wagner equation (e.g., Friend et al., 1989), unified fundamental equation (e.g., Hill, 1990; Johnson and Norton, 1991), and some other polynomials (e.g., Grevel, 1990; Holland and Powell, 1991). The corresponding-state formulation was used by Ross and Ree (1980) and Saxena and Fei (1987a, 1987b, 1988b) to study the P-V-T relationships, and a molecular-potential mixing model was used to investigate the P-V-T-X and P-V-T-a relations in the C-H-O fluid mixtures by Saxena and Fei (1988a). The theory of perturbation of liquid (e.g., Weeks et al., 1971) and the method of molecular dynamics (e.g., Brodholt and Wood, 1990; Belonoshko and Saxena 1991a, 1991b; Fraser and Refson, 1992) are also utilized in simulating the P-V-T relations of C-H-O fluids at high temperatures and pressures. However, few studies treat the complete C-H-O-S fluid system (Ryzhenko and

Volkov, 1971; Ohmoto and Kerrick, 1977; Burruss, 1981; Ferry and Baumgartner, 1987; Poulson and Ohmoto, 1989; Hall et al., 1991).

This study extends the work of Belonoshko and Saxena (1991a, 1991b) and Saxena and Fei (1987a, 1987b, 1988a, 1988b) to include a lower pressure-temperature range from critical points up to 2000 °C and 20 kbar and the S-bearing species. We determined new equations for H_2O and the four S-bearing species and used new fits for H, completing a C-H-O-S multicomponent fluid model that is applicable over a sufficient range of geologically interesting temperatures and pressures. We used all available experimental P-V-T data on pure fluid species and P-V-T-X and P-V-T-a data on fluid mixtures (Kennedy, 1954; Takenouchi and Kennedy, 1964; Jusa et al., 1965; Tziklis and Koulikova, 1965; Babb et al., 1968; Burnham et al., 1969; Greenwood, 1969, 1973; Presnall, 1969; Robertson and Babb, 1970; Ryzhenko and Malinin, 1971; Mel'nik, 1972, 1978a, 1978b; Shmonov and Shmulovich, 1974; Tziklis et al., 1975; Angus et al., 1976; Tanishita et al., 1976; Tziklis, 1977; Schmidt, 1979; Hilbert, 1979; Shmulovich and Shmonov, 1978; Shmulovich et al., 1980, 1982; Hanafusa et al., 1983; Zakirov, 1984; Frantz, 1990; Sterner and Bodnar, 1991). To demonstrate the applicability of this complete model of multicomponent C-H-O-S fluids, we also used the experimental data from several experiments on phase equilibria (e.g., Eugster and Wones, 1962; French and Eugster, 1965; French, 1966; Craig and Scott, 1974; Chou, 1978, 1986, 1987; Chou and Cygan, 1990; Barton and Toulmin, 1964; Burt, 1971, 1972; Gamble, 1978, 1982; Burton, 1978; Haselton et al., 1978; Burton et al., 1982; Myers and Eugster, 1983; Whitney, 1984; Jakobsson and Oskarsson, 1990; Kishima, 1986, 1989; Ulmer and Luth, 1991, among others).

Applications of this model of C-H-O-S multicomponent fluid to some geological systems, including calculations of some important buffers of f_{O_2}, f_{H_2}, f_{CO_2}, f_{CH_4}, and

f_{S_2}, the phase equilibria and fluid proportions in the Fe-Si-O-H-S system, the stability of graphite under a number of buffer conditions, and the stability of hedenbergite and andradite, will be presented in other papers.

EQUATIONS OF STATE FOR PURE PHASES

The law of corresponding states

$$Z = \frac{PV}{RT} = f(P_r, T_r) \qquad (1)$$

where Z is the compressibility factor, P_r is the reduced pressure (P/P_{cr}), and T_r is the reduced temperature (T/T_{cr}), has been used in modeling the C-H-O fluid phases at moderate to high pressures and temperatures by Mel'nik (1972, 1978a), Ross and Ree (1980), and Saxena and Fei (1987a, 1987b, 1988b). The equation of Saxena and Fei (1987a, 1987b, 1988b), in terms of compressibility factor as a function of pressure and temperature, is

$$Z(P,T) = A(T) + B(T)P_r + C(T)P_r^2 + D(T)P_r^3 \quad (2)$$

for the corresponding-state gases (CO_2, CO, CH_4, and O_2) and H_2. The formulations of temperature-dependent coefficients $A(T)$, $B(T)$, $C(T)$, $D(T)$ can be generalized as follows:

$$Q(T)_{(P \geq 1 \text{ kbar})} = Q_1 + Q_2 T_r + Q_3 T_r^{-1}$$
$$+ Q_4 T_r^2 + Q_5 T_r^{-2} + Q_6 T_r^3$$
$$+ Q_7 T_r^{-3} + Q_8 \ln T_r \qquad (3a)$$

$$Q(T)_{(P < 1 \text{ kbar})} = Q_1 + Q_2 T_r^{-1} + Q_3 T_r^{-1.5}$$
$$+ Q_4 T_r^{-3} + Q_5 T_r^{-4} \qquad (3b)$$

where Q_1–Q_8 are constants listed in Table 1. This generalization is useful in organizing the coefficients in Equation 2 in tabular form, avoiding the writing of several equations. This is also computationally convenient.

Since the molar Gibbs free energy of a species requires the $\int V \, dP$ term, we use the following relations for expressing the molar volume as a function of P and T:

$$V(P,T) = \frac{RTZ(P,T)}{P} \qquad (4)$$

i.e., for CO_2, CO, CH_4, O_2, and H_2,

$$V(P,T) = RT[A(T)P^{-1} + B(T)P_{cr}^{-1} + C(T)P_{cr}^{-2}P$$
$$+ D(T)P_{cr}^{-3}P^2]. \qquad (5)$$

Table 1 gives the values for the temperature-dependent coefficients in $Z(P,T)$ and $V(P,T)$ (Eqs. 2, 3, 5) used or determined in this study. Many of these values have been adopted from previous studies. For individual pure H_2O phase, many equations are available in literature. As pointed out by Saxena and Fei (1987a), the virial-type formulations (Saxena and Fei, 1987a, 1987b; Holland and Powell, 1991) are not useful at or near critical range be-

cause, first, the specific partial derivatives of the state surface diverge to $\pm\infty$ at critical point and $V(P,T)$ changes discontinuously across the saturation curve and, second, there are substantial discrepancies between the theoretical and experimental P-V-T data. We therefore adopted the Saul-Wagner equation (Saul and Wagner, 1987, 1989), which covers the range from the melting line to 1000 °C and 25 kbar as well as the critical range. For other C-H-O phases (CO_2, CO, CH_4, O_2, and H_2), we chose the results from Saxena and Fei (1987a, 1987b, 1988b), shown in Table 1, parts a and b. Our calculated P-V-T relations for H_2O, CO_2, CH_4, and H_2 are not significantly different from those obtained from some of the other existing models (e.g., Holloway, 1977, 1982; Halbach and Chatterjee, 1982; Haar et al., 1984; Rimbach and Chatterjee, 1987; Friend et al., 1989; Hill, 1990; Holland and Powell, 1991; Johnson and Norton, 1991).

In this study, we determined the equation of state using the corresponding-state equation for H_2 and pure S-bearing species (S_2, SO_2, COS, and H_2S). In order to use the theory of corresponding state, the critical points (P_{cr}, T_{cr}) for each species must be known. These data are known for H_2, SO_2, COS, and H_2S, shown in Table 2, but had to be estimated for S_2 (see discussion below).

The values determined for the temperature-dependent coefficients for H_2 are given in Table 1, part b, which are same as those in Saxena and Fei (1987a) at pressures below 1 kbar. A reoptimization led to an improved fit of the data above 1 kbar; therefore the data are slightly different from those shown in Saxena and Fei (1988b) at pressures above 1 kbar. Figures 1a–1c show the P-V-T relations for H_2. There is excellent agreement between our theoretical curve and the data of Presnall (1969). The precision of the fit with the experimental data for H from this set of parameters, in terms of $\delta Z(P,T)$, is quite good: the maximum of $\delta Z(P,T)$ is ± 0.0186, which is much smaller than ± 0.0253 in Saxena and Fei (1988b). The error in volume is generally smaller than $\pm 2.5\%$. For a discussion of fit of the experimental P-V-T data on species CO_2, CO, CH_4, and O_2, refer to Saxena and Fei (1987a, 1987b).

The P-V-T relationships of four S-bearing species in the C-H-O-S system (S_2, SO_2, COS, and H_2S) were assessed by using the volume-explicit equation (Eqs. 5, 3a) in this study. Some experimental P-V-T data are available for SO_2 (Mel'nik, 1978b) and H_2S (Reamer et al., 1950; Mel'nik, 1978b; Rau and Mathia, 1982). Because the misfit of P-V-T data calculated directly from the corresponding-state equation derived in Saxena and Fei (1987a) is substantial for both SO_2 and H_2S, the parameters in the equation for them should be adjusted. The optimized parameters for the equation of state are presented in Table 1, parts c and d. Figure 2 shows the P-V-T relationships for SO_2 at pressures from 5 bars to 10 kbar, and Figure 3 shows the relationships for H_2S from 100 bars to 10 kbar. The theoretical curves fit the experimental points very well. The precision of the fit with the experimental data for these two species from this set of

TABLE 1. Modeling of P-V-T properties of C-H-O-S supercritical fluids

P (bar)		(1a) Corresponding-states fluid species (O_2, CO_2, CO, CH_4, S_2, COS)			
		A (T)	B (T)	C (T)	D (T)
<1000*	Q_1	1.00	0	0	
	Q_2	0	0.9827E − 01	0	
	Q_3	0	0	−0.1030E − 02	
	Q_4	0	−0.2709E + 00	0	
	Q_5	0	0	0.1427E − 01	
1000–5000*	Q_1	1.000E + 00	0	0	
	Q_2	0	0	0	
	Q_3	0	9.122E − 02	0	
	Q_4	0	0	0	
	Q_5	−5.917E − 01	0	−1.416E − 04	
	Q_6	0	0	0	
	Q_7	0	0	0	
	Q_8	0	0	−2.835E − 06	
>5000**	Q_1	2.0614E + 0	0	0	0
	Q_2	0	0	0	0
	Q_3	0	5.513E − 02	−1.894E − 06	5.053E − 11
	Q_4	0	0	0	0
	Q_5	−2.235E + 00	3.934E − 02	−1.109E − 05	0
	Q_6	0	0	0	−6.303E − 21
	Q_7	0	0	−2.189E − 05	0
	Q_8	−3.941E − 01	0	0	0

P (bar)		(1b) H_2			
		A (T)	B (T)	C (T)	D (T)
<1000*	Q_1	1.00	0	0	
	Q_2	0	0.9827E − 01	0	
	Q_3	0	0	−0.1030E − 02	
	Q_4	0	−0.2709E + 00	0	
	Q_5	0	0	0.1427E − 01	
>1000	Q_1	2.2615E + 00	−2.6707E − 04	−2.3376E − 09	−3.2606E − 15
	Q_2	0	0	0	0
	Q_3	−6.8712E + 01	2.0173E − 01	3.4091E − 07	2.4402E − 12
	Q_4	0	0	0	0
	Q_5	−1.0573E + 04	4.5759E + 00	−1.4188E − 03	−2.4027E − 09
	Q_6	0	0	0	0
	Q_7	0	0	0	0
	Q_8	−1.6936E − 01	3.1452E − 05	3.0117E − 10	0

P (bar)		(1c) SO_2		
		A (T)	B (T)	C (T)
1–10000	Q_1	0.92854E + 00	0.84866E − 03	−0.35456E − 03
	Q_2	0.43269E − 01	−0.18379E − 02	0.23316E − 04
	Q_3	−0.24671E + 00	0.66787E − 01	0.94159E − 03
	Q_4	0	0	0
	Q_5	0.24999E + 00	−0.29427E − 01	−0.81653E − 03
	Q_6	0	0	0
	Q_7	−0.53182E + 00	0.29003E − 01	0.23154E − 03
	Q_8	−0.16461E − 01	0.54808E − 02	0.55542E − 04

P (bar)		(1d) H_2S		
		A (T)	B (T)	C (T)
1–500	Q_1	0.14721E + 01	0.16066E + 00	−0.28933E + 00
	Q_2	0.11177E + 01	0.10887E + 00	−0.70522E − 01
	Q_3	0.39657E + 01	0.29014E + 00	0.39828E + 00
	Q_4	0	0	0
	Q_5	−0.10028E + 02	−0.99593E + 00	−0.50533E − 01
	Q_6	0	0	0
	Q_7	0.45484E + 01	−0.18627E + 00	0.11760E + 00
	Q_8	−0.38200E + 01	−0.45515E + 00	0.33972E + 00
500–10000	Q_1	0.59941E + 00	0.22545E − 01	0.57375E − 03
	Q_2	−0.15570E − 02	0.17473E − 02	−0.20944E − 05
	Q_3	0.45250E − 01	0.48253E − 01	−0.11894E − 02
	Q_4	0	0	0
	Q_5	0.36687E + 00	−0.19890E − 01	0.14661E − 02
	Q_6	0	0	0
	Q_7	−0.79248E + 00	0.32794E − 01	−0.75605E − 03
	Q_8	0.26058E + 00	−0.10985E − 01	−0.27985E − 03

* Data from Saxena and Fei (1987a).
** Data from Saxena and Fei (1987b).

TABLE 2. The critical data of C-H-O-S fulid phases

Phase	T_{cr} (K)	P_{cr} (bar)
H_2O	647.25	221.1925
CO_2	304.15	73.8659
CH_4	191.05	46.4069
CO	133.15	34.9571
O_2	154.75	50.7638
H_2	33.25	12.9696
S_2	208.15	72.954
SO_2	430.95	78.7295
COS	377.55	65.8612
H_2S	373.55	90.0779

Note: The critical data for H_2O, CO_2, CH_4, CO, O_2, H_2, SO_2, COS, and H_2S are from Mills (1974), JANAF (1985), Prausnitz et al. (1986), Reid (1986), Weast et al. (1988). For S_2, the critical data are assumed in this study.

parameters is $\delta Z(P,T) = \pm 0.080$ and $\delta V(P,T) = \pm 4.0\%$. There are no experimental data on S_2 and COS.

In a recent study by Poulson and Ohmoto (1989), the critical point of S_2 was assumed to be the same as that of S ($T_{cr} = 1314$ K, $P_{cr} = 209.74$ bars, taken from Mathews, 1972). Based on such values, a number of calculations for geochemical equilibria were performed. But this choice resulted in unrealistic P-V-T relationship at moderate temperature range (500–1200 K) and unreasonable RT ln f values over a large temperature and pressure range. They also set the fugacity coefficient for pure S_2 as 1.0 and calculated the nonideal mixing parameters a and b (in Holloway-Flowers MRK equation) by using the critical point of S. Obviously, these assumptions would introduce significant errors in the calculations. To express the P-V-T relationship of S_2 as precisely as possible, we estimated its critical point by searching for the relationship between the molecular entropies and critical points. Figure 4 shows such a relationship for nonpolar (O_2, H_2, CH_4, S_2, F_2, Cl_2, I_2, N_2, etc.) and polar species (H_2O, H_2S, CO_2, CO, SO_2, SO, COS, CS_2, HF, HCl, HBr, HI, etc.), from which one notes the relation of physical and thermodynamic variables of certain molecules to their electronic structures. The S atom has an electronic structure ns^2np^4, and S_2 has a d-overlapping covalence bonding very similar to that of O_2, CO, and SO, as well as of CO_2, COS, and SO_2. The statistical and thermodynamic basis for this kind of choice may be supported by more precise quantum mechanical calculation. Although the relationships are vague, we demonstrate in the following sections and further studies in heterogeneous phase equilibria (to be published in succeeding papers) that the selected values of T_{cr} and P_{cr} are reasonable and useful in the calculations of various thermodynamic equilibria in the S-bearing systems over geological temperature and pressure conditions. Our choice for S_2 is $T_{cr} = 208.15$ K, $P_{cr} = 72.95$ bars (see Fig. 4).

Because experimental P-V-T data for both S_2 and COS are not available, we assumed that S_2 and COS behave similarly to O_2, CO_2, CO, and CH_4 and applied the principle of corresponding state for S_2 and COS species, using Equations 2, 3a, 3b, and 5. For S_2 and COS we simply
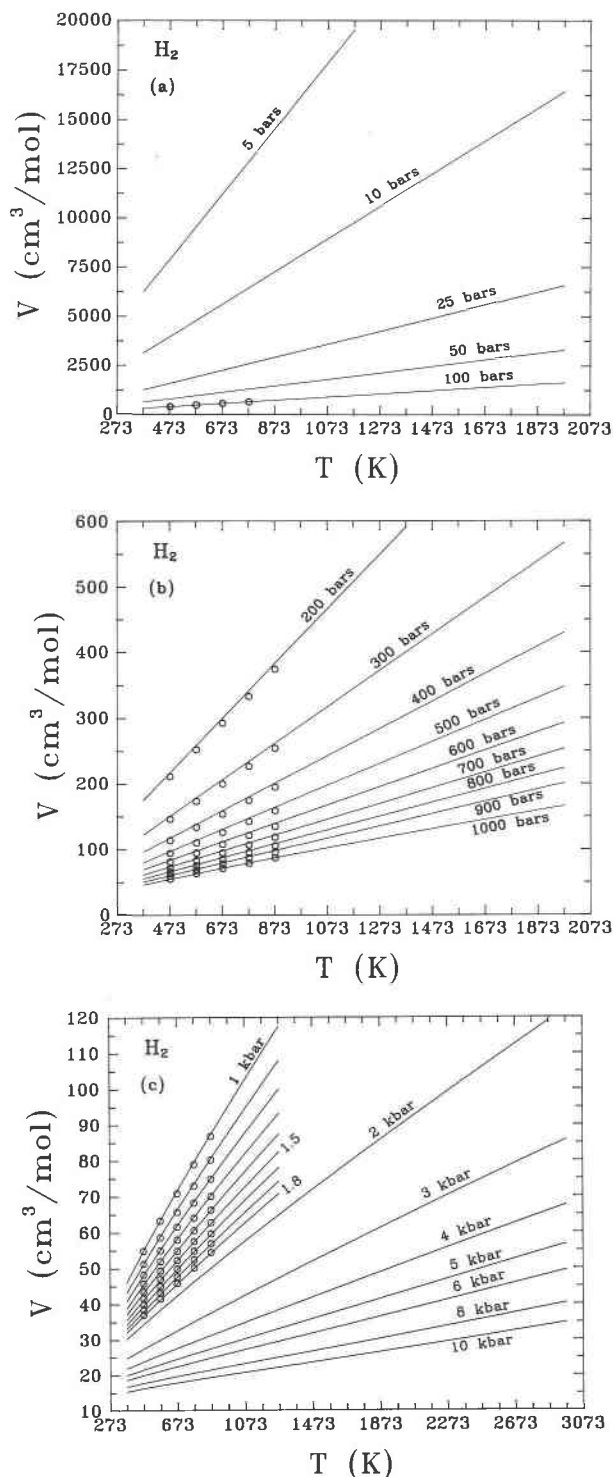

Fig. 1. P-V-T relation of H_2: (a) 1–100 bars; (b) 200 bars–1 kbar; (c) 1–10 kbar. The theoretical curves are compared with experimental data from Presnall (1969).
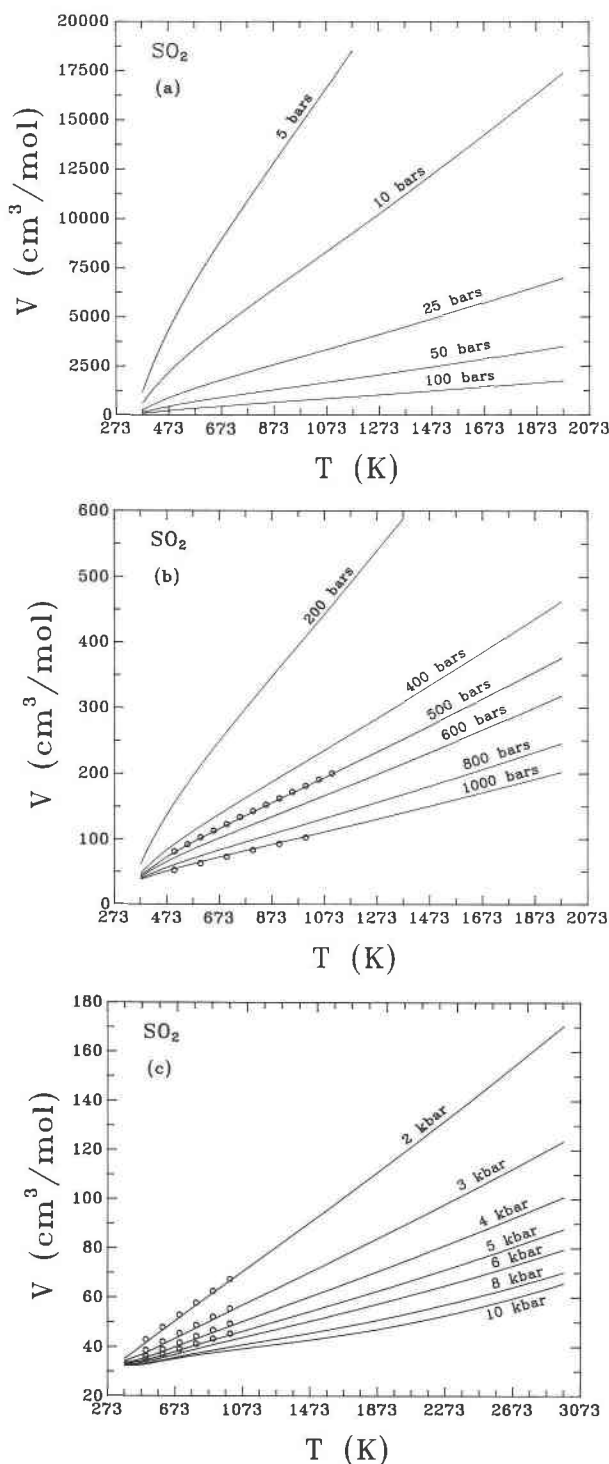
Fig. 2. P-V-T relation of SO₂: (a) 5–100 bars; (b) and (c) 200 bars–10 kbar, compared with data from Mel'nik (1978b).
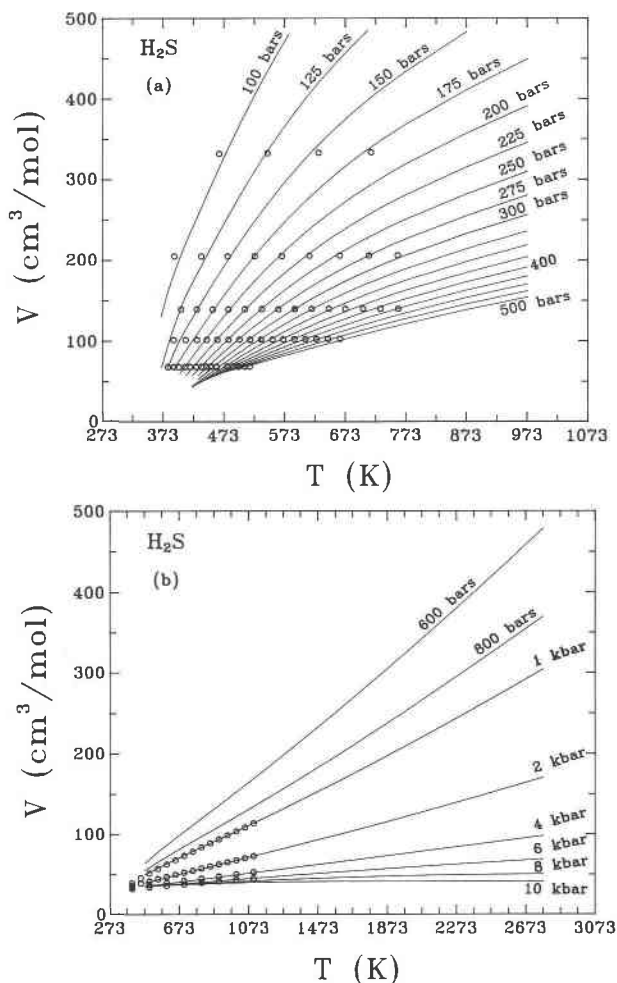

Fig. 3. P-V-T relation of H₂S: (a) 100–500 bars, compared with data from Rau and Mathia (1982); (b) 600 bars–10 kbar, compared with data from Mel'nik (1978b).

THERMODYNAMIC PROPERTIES OF PURE PHASES

The equation of state of a substance defines the functional relations among its intensive variables and physical surroundings. The thermodynamic status of the substance is constrained by the Gibbs-Duhem equation, from which all thermodynamic properties, including the Gibbs free energy, Helmholtz free energy, internal energy, fugacity, enthalpy, entropy, isobaric heat capacity, isochoric heat capacity, isothermal compressibility, and isobaric expansivity, can be calculated.

The standard thermodynamic properties, including $H^0_{f(1,298)}$, $S^0_{(1,298)}$, and $C_P(1,T)$, for all ten pure fluid phases are listed in Table 3. Saul and Wagner (1989) calculated the thermodynamic properties of H₂O as functions of temperature and pressure. For corresponding-state C-H-O gases and S-bearing species, the Gibbs free energy and fugacity, as functions of both temperature and pressure, are calculated as follows.

The Gibbs free energy of formation of a pure phase at a given temperature and pressure, referring to a standard state of 1 bar and 298.15 K, can be calculated from

adopted the same temperature-dependent coefficients as those of O₂, CO₂, CO, and CH₄ (Table 1, part a).

Tabulated data on volumes of C-H-O-S fluid species from low temperatures and pressures to high temperatures and pressures may be obtained from the authors.

$$G_f(P,T) = \int_{298}^{T}\left(\frac{\partial G}{\partial T}\right)_P dT + \int_{1}^{P}\left(\frac{\partial G}{\partial P}\right)_T dP \quad (6a)$$

or

$$G_f(P,T) = G_f(1,T) + \int_{1}^{P} V(P,T)\, dP \quad (6b)$$

where

$$G_f(1,T) = H^0_{f(1,298)} - TS^0_{(1,298)}$$

$$+ \int_{298}^{T} C_P(1,T)\, dT - T\int_{298}^{T}\frac{C_P(1,T)}{T}\, dT \quad (7)$$

and for fluid phase

$$\int_{1}^{P} V(P,T)\, dP = RT \ln f(P,T). \quad (8)$$

The fluid fugacity f and fugacity coefficient γ for pure phase are given by

$$\ln f(P,T) = \int_{P_0}^{P}\frac{Z(P,T)}{P}\, dP + \ln f(P_0,T) \quad (9)$$

and

$$\ln \gamma(P,T) = \int_{P_0}^{P}\frac{Z(P,T)}{P}\, dP - \ln P + \ln \gamma(P_0,T) \quad (10)$$

with an assumption as follows: $\gamma(P_0 = 1 \text{ bar}) = 1$; $f(P_0 = 1 \text{ bar}) = 1$.

The integral in the above equations (Eqs. 6b, 8) can be rewritten for convenience as shown below. Using Equation 2, we obtain

$$\int_{P_0}^{P}\frac{Z(P,T)}{P}\, dP = A(T)\ln\frac{P_r}{P_{0_r}}$$

$$+ B(T)(P_r - P_{0r})$$

$$+ \frac{C(T)}{2}(P_r^2 - P_{0r}^2)$$

$$+ \frac{D(T)}{3}(P_r^3 - P_{0r}^3) \quad (11)$$

where $P_r = P/P_{cr}$ and $P_{0r} = P_0/P_{cr}$.

Fig. 4. The relations between molecular entropies and critical data. (a) T_{cr} plotted against molecular entropy. (b) P_{cr} plotted against molecular entropy. Data points except for those of S_2 and SO are from Mills (1974), JANAF (1985), Prausnitz et al. (1986), Reid (1986), and Weast et al. (1988). Group symbols: open circle for the group O_2, N_2, CO, SO, S_2, and H_2; solid circle for the group CO_2, CH_4, SO_2, COS, and CS_2; plus sign for the group F_2, Cl_2, and I_2; diamond for the group HF, HCl, HBr, and HI; star for H_2O and H_2S.

TABLE 3. Thermodynamic properties $\Delta G^0_{f(1,T)}$ of pure C-H-O-S fluid phases

Phase	$\Delta H^0_{f(1,298)}$ (J/mol)	$S^0_{(1,298)}$ (J/mol·K)	$C_P(T) = a + bT + cT^{-2} + dT^2 + eT^{-3} + fT^{-0.5} + g/T$						
			a (10^2)	b (10^{-3})	c (10^6)	d (10^{-6})	e (10^8)	f	g (10^4)
H_2O	−241 818.46	188.715	0.46461	5.966	6.320	0.0	−7.957	0.0	−1.663
CO_2	−393 509.38	213.635	0.70728	−0.8822	3.464	0.0	−2.492	0.0	−1.876
CH_4	−74 809.92	186.155	1.2901	−0.4849	22.21	0.0	−22.91	0.0	−7.656
CO	−110 524.54	197.564	0.38578	0.6513	1.781	0.0	−0.9971	0.0	−0.7725
O_2	0.00	205.029	0.39450	0.5609	0.9067	0.0	0.006 039	0.0	−0.6101
H_2	0.00	130.574	0.23948	4.962	0.5279	0.0	−1.525	0.0	0.09536
S_2	128 365.12	228.070	0.38408	−0.0463	−0.4635	0.0	0.6930	0.0	−0.09936
SO_2	−296 829.70	248.111	0.71828	−2.672	2.354	0.0	−2.083	0.0	−1.642
COS	−142 088.64	231.459	0.42441	−27.573	0.70732	4.6064	−52.166	0.40721	−1.7432
H_2S	−20 627.12	205.685	0.65459	0.9168	9.326	0.0	10.54	0.0	−2.884

Note: The $\Delta H^0_{f(1,298)}$, $S^0_{(1,298)}$ for all phases are selected from Weast et al. (1988); $C_P(T)$ coefficients for C-H-O fluid phases are same as in Saxena and Fei (1987b); $C_P(T)$ coefficients for S-bearing species are assessed in this study, based on the data given in JANAF (1985); T in K. The real $C_P(T)$ coefficients equal the listed values multiplied by the relative factors. For example, $a = 0.46461 \times 10^2$ for H_2O.
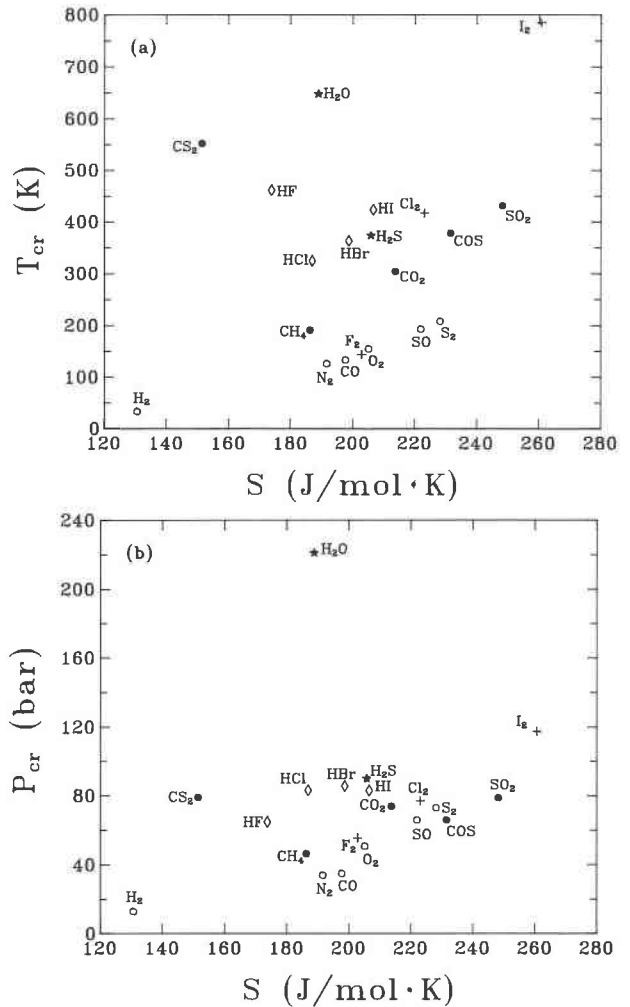
TABLE 4. Interaction energy parameters of C-H-O-S fluid species[*]

Species	a^*	σ	ϵ/κ	μ	α
1. H_2O	—	2.650	380.00	1.84	1.59
2. CO_2	0.615	3.760	424.16	—	2.65
3. CH_4	0.283	3.565	227.13	—	2.60
4. CO	—	3.760	100.20	0.10	1.95
5. O_2	0.308	3.109	194.30	—	1.60
6. H_2	—	2.960	36.70	—	0.79
7. S_2	0.3	3.0	200.0	0.0	2.0
8. SO_2	0.3	3.0	200.0	1.61	3.72
9. COS	0.3	3.0	200.0	0.0	2.0
10. H_2S	0.3	3.0	200.0	0.0	2.0

[*] The physicochemical meaning of a^*, σ, ϵ/κ, μ, α refer to Saxena and Fei (1988a), Prausnitz et al. (1986). The values for C-H-O fluid species are taken from Saxena and Fei (1988a); the values for S-bearing species are selected from Prausnitz et al. (1986) or assumed in this study (italic numbers), all of which will be taken as zero if ideal mixing is considered.

Tabulated data and plots on $RT \ln f$ of C-H-O-S fluid species from low temperatures and pressures to high temperatures and pressures may also be obtained from the authors.

INTERACTION IN FLUID MIXTURES

For ideal mixing, the activity coefficient of each component in the fluid mixture is unity, i.e.,

$$(f_i^m)_{P,T} = f_i^0 X_i = \gamma_i^0 P X_i \quad (12)$$

where $(f_i^m)P,T$ and X_i are the fugacity and mole fraction of component i in the fluid mixture and f_i^0 and γ_i^0 are, respectively, the fugacity and fugacity coefficient of pure nonideal component i. For nonideal mixing, the individual fluid fugacity $(f_i^m)_{P,T}$ is calculated by

$$(f_i^m)_{P,T} = f_i^0 a_i = \gamma_i^0 \gamma_i^m P X_i \quad (13)$$

where a_i and γ_i^m are, respectively, the activity and activity coefficient of component i in the fluid mixture.

At low temperatures and high pressures, the multicomponent fluid may be nonideal in such a way that the interactions among the components are the functions of temperature, pressure, and fluid bulk composition. Saxena and Fei (1988a) proposed a fluid mixture model for high-temperature and high-pressure C-H-O fluid, based on the intermolecular potential theory (Prausnitz et al., 1986; Reid, 1986). The main ideas can be briefly outlined as follows.

The regular solution energy parameter W_{ij} for the intermolecular mixing reaction between the ith and jth molecules can be defined as

$$W_{ij} = z[\Gamma_{ij} - \tfrac{1}{2}(\Gamma_{ii} + \Gamma_{jj})] \quad (14)$$

where Γ_{ii}, Γ_{jj}, and Γ_{ij} represent the intermolecular potentials and z denotes the coordination number. The intermolecular potential Γ consists of a Lennard-Jones potential, as given by Stockmayer (Tien and Lienhard, 1971):

$$\Gamma = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] - \frac{\mu^2}{r^3} \quad (15)$$

TABLE 5. The binary excess free energies of mixing for equimolar compositions of binary mixtures at P = 1 kbar and T = 500 °C

No.	Binary mixture	G_{ij}^{ex} (J/mol)	No.	Binary mixture	G_{ij}^{ex} (J/mol)
1.	H_2O-CO_2	1087.98	24.	CH_4-H_2S	8.16
2.	H_2O-CH_4	1094.94	25.	CO-O_2	2.72
3.	H_2O-CO	1080.25	26.	CO-H_2	32.30
4.	H_2O-O_2	1169.74	27.	CO-S_2	3.97
5.	H_2O-H_2	1238.47	28.	CO-SO_2	337.96
6.	H_2O-S_2	1189.31	29.	CO-COS	13.06
7.	H_2O-SO_2	429.46	30.	CO-H_2S	2.59
8.	H_2O-COS	1123.84	31.	O_2-H_2	2.43
9.	H_2O-H_2S	1198.42	32.	O_2-S_2	0.05
10.	CO_2-CH_4	0.95	33.	O_2-SO_2	335.30
11.	CO_2-CO	−22.31	34.	O_2-COS	1.22
12.	CO_2-O_2	22.21	35.	O_2-H_2S	−0.01
13.	CO_2-H_2	40.89	36.	H_2-S_2	1.23
14.	CO_2-S_2	24.81	37.	H_2-SO_2	336.68
15.	CO_2-SO_2	359.16	38.	H_2-COS	−0.55
16.	CO_2-COS	33.79	39.	H_2-H_2S	1.69
17.	CO_2-H_2S	23.34	40.	S_2-SO_2	335.39
18.	CH_4-CO	−7.68	41.	S_2-COS	0.73
19.	CH_4-O_2	7.77	42.	S_2-H_2S	0.02
20.	CH_4-H_2	23.64	43.	SO_2-COS	334.94
21.	CH_4-S_2	9.08	44.	SO_2-H_2S	337.06
22.	CH_4-SO_2	342.97	45.	COS-H_2S	0.99
23.	CH_4-COS	15.33			

where ϵ, σ, μ, and r are characteristic energy, equilibrium intermolecular distance, dipole moment, and length scale, respectively. Since the length scale r relates the volumetric properties of interacting molecules, Γ and therefore W_{ij} are functions of temperature and pressure.

The excess free energy G^{ex} for binary intermolecular mixing reaction is given by the van Laar equation

$$G^{ex} = W_{ij} X_i X_j q_i q_j / (X_i q_i + X_j q_j). \quad (16)$$

Then the activity coefficients γ_i can be expressed as

$$RT \ln \gamma_i = W_{ij} q_i / (1 + q_i X_i / q_j X_j)^2 \quad (17)$$

where, in turn, q_i represents the effective volumes. The activity coefficients in ternary or higher order solution are calculated from the Kohler formulation.

The excess molar volume V^{ex}, excess entropy S^{ex}, and excess enthalpy H^{ex} for binary mixtures are defined as

$$V^{ex} \equiv \left(\frac{\partial G^{ex}}{\partial P}\right)_T$$

$$= X_i X_j q_i q_j / (X_i q_i + X_j q_j)\left(\frac{\partial W_{ij}}{\partial P}\right)_T \quad (18)$$

$$S^{ex} \equiv \left(\frac{\partial G^{ex}}{\partial T}\right)_P$$

$$= X_i X_j q_i q_j / (X_i q_i + X_j q_j)\left(\frac{\partial W_{ij}}{\partial T}\right)_P \quad (19)$$

$$H^{ex} \equiv G^{ex} + TS^{ex} - PV^{ex}$$

$$= X_i X_j q_i q_j / (X_i q_i + X_j q_j)$$

$$\times \left[W_{ij} + T\left(\frac{\partial W_{ij}}{\partial T}\right)_P - P\left(\frac{\partial W_{ij}}{\partial P}\right)_T\right]. \quad (20)$$

The formulations of derivatives $(\partial W_{ij}/\partial P)_T$ and $(\partial W_{ij}/\partial T)_P$ are, however, very complicated. One can calculate the excess functions for each fluid mixture by using the free energy minimization program Solgasmix (Eriksson, 1975; Saxena and Eriksson, 1985). The mixing model is also used for the C-H-O-S fluid system here, by assuming that some of the interaction parameters for S-bearing species may be comparable to those of similar species in the C-H-O fluid. Table 3 lists the interaction energy parameters chosen for the nonideal C-H-O-S fluid in this study. Since the uncertainty in W_{ij} comes mainly from volumetric property, the applicable temperature-pressure range of intermolecular potential formulation is the same as of the pure fluid equation.

This study demonstrates the following:

1. Within the geological temperature-pressure environments, the most significant interaction energies are those in binary mixtures involving H_2O, and the next important are those in binary mixtures involving SO_2. This is because both H_2O and SO_2 have large dipole moments (1.84 and 1.61, respectively; see Table 4). The polynomial coefficients for excess energies and activities as functions of temperature, pressure, and composition regressed from intermolecular potential calculations for these nonideal (polar-polar, polar-nonpolar) binary subsystems may be obtained from the authors. As an example of the binary-excess free energy of mixing, we list such energies for equimolar compositions at a pressure of 1 kbar and temperature of 500 °C in Table 5. Table 5 also shows that the interaction energies in the binary system involving two low-polarizability molecules are negligible.

2. The interaction parameter W_{ij} decreases swiftly with increasing temperature or decreasing pressure (see Fig. 5).

3. The independently calculated P-V-T-X and P-V-T-a relations for H_2O-CO_2, H_2O-H_2, H_2O-CH_4, and CH_4-CO binary fluid mixtures are consistent with available experimental data for H_2O-CO_2 (Takenouchi and Kennedy, 1964; Greenwood, 1969, 1973; Eggler and Burnham, 1978; Eggler and Kadik, 1979; Chou and Williams, 1979; Shmulovich et al., 1980, 1982; Kerrick and Jacobs, 1981; Zakirov, 1984; Sterner and Bodnar, 1991), for H_2O-H_2 (Shaw, 1963; Seward and Franck, 1981; Smith et al., 1983; Wormald and Colling, 1985; Rimbach and Chatterjee, 1987), and for H_2O-CH_4 (Welsch, 1973; Jacobs and Kerrick, 1981a, 1981b; Smith et al., 1983). No experimental data are available for comparison for the system involving S-bearing species. The only way to check the S-bearing species is to calculate the phase equilibria in the system involving these species and compare the results with experiments.

As an example of the applicability of our mixing model, we show the comparison of calculated P-V-T-X relations of an H_2O-CO_2 binary mixture with the most recent experimental data from Sterner and Bodnar (1991) in Figure 6. Note that the experimental errors of $V_{H_2O-CO_2}$ or V^{ex} in experiments are about 0.5 to 1.0 cm³/mol; these come mainly from uncertainties in pressure (σ_{V_P}), tem-

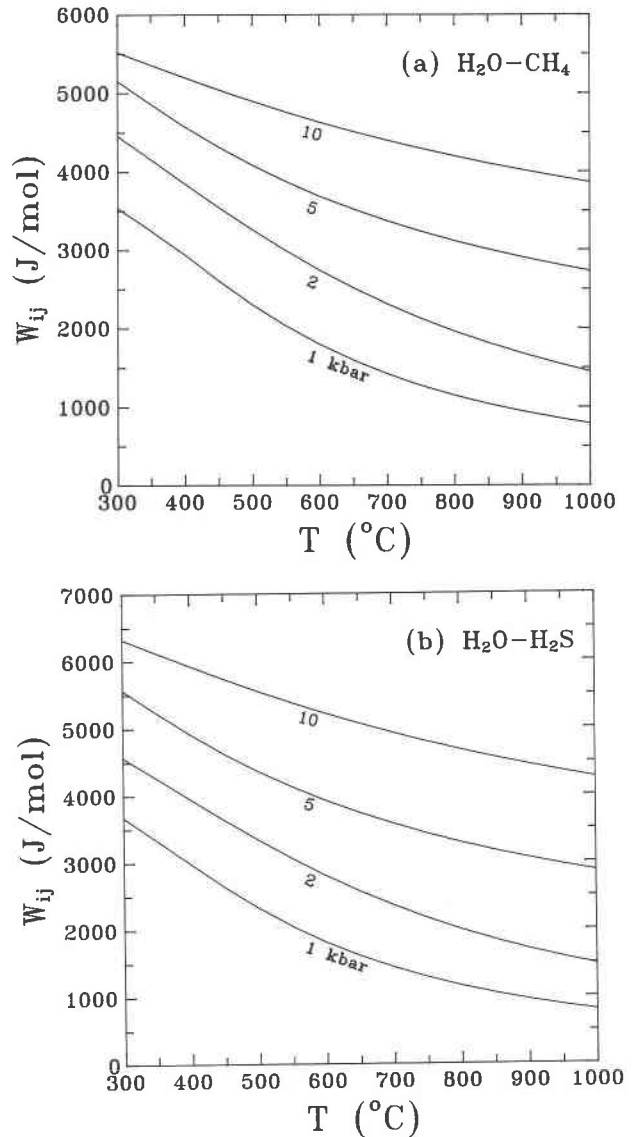Fig. 5. The temperature and pressure dependence of the binary interaction parameter W_{ij} for the (a) H_2O-CH_4 and (b) H_2O-H_2S binary mixtures.

perature (σ_{V_T}), and fluid composition (σ_{V_X}). Therefore, the fit is very good, especially at high pressures and high temperatures. The mixing data from Shmulovich et al. (1982) were discussed before by Saxena and Fei (1988a).

CONCLUSIONS

The corresponding-state equation for CO_2, CH_4, CO, O_2, H_2, S_2, SO_2, COS, and H_2S, the Saul-Wagner equation for H_2O, and the intermolecular-potential formulation for the fluid mixtures (in the calculation of low to medium temperature-pressure fluid fugacities and activities of the species in the C-H-O-S system) are recommended as a practical solution to a study of the multicomponent behavior of magmatic, metamorphic, and hydrothermal
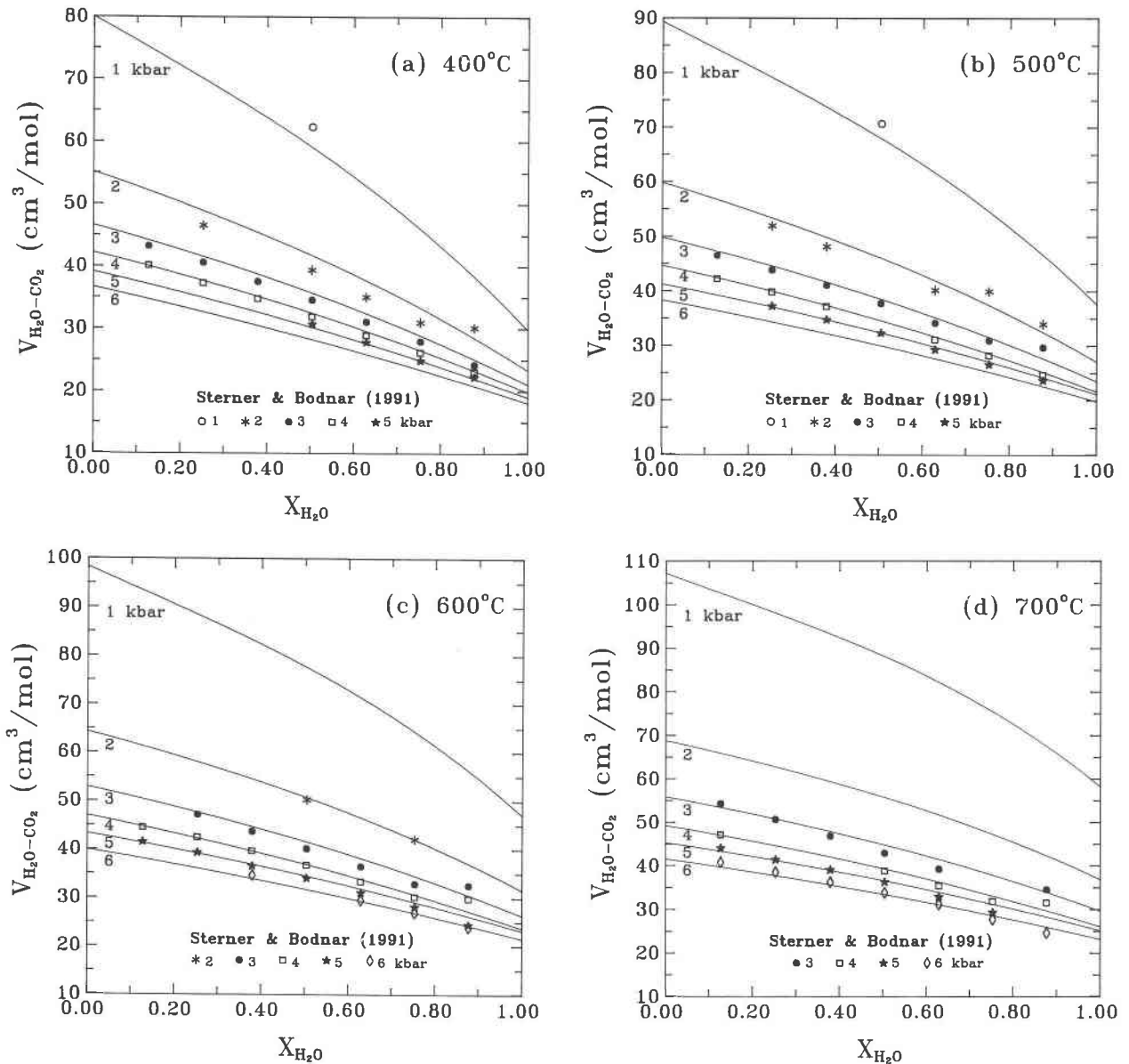
Fig. 6. *P-V-T-X* relations of H_2O-CO_2 binary mixture, compared with experimental data from Sterner and Bodnar (1991); **(a)** 400 °C, **(b)** 500 °C, **(c)** 600 °C, **(d)** 700 °C.

fluids. All the available experimental data on *P-V-T, P-V-T-X*, and *P-V-T-a* relations for C-H-O-S pure species and mixtures are reproduced well over the temperature-pressure range of geological interest.

As discussed here and in Saxena and Fei (1987a, 1987b, 1988b), this set of corresponding-state equations may be effectively and reliably applied with precision in the crustal temperature-pressure range from critical points up to 2500 K and 20 kbar. To calculate equilibria involving carbonate + silicate + oxide + sulfide + fluid, a valid C-H-O-S fluid model must be applied. This multicomponent C-H-O-S fluid model will be used in calculating buffers of f_{O_2}, f_{H_2}, f_{CO_2}, f_{CH_4}, and f_{S_2} and phase equilibria involving carbonates (including graphite), silicates, oxides, sulfides, and

fluids. The pressure-temperature range from moderate to high for fluids is covered by the molecular-dynamics simulated data of Belonoshko and Saxena (1991a, 1991b). With this work, we have extended the range to low pressures and temperatures. A computer program to calculate the compound properties of the pure fluid (*P-V-T* and fugacities) in the pressure range from 1 bar to 1 Mbar and in the temperature range from 400 to 2500 K is available from the authors.

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