Canadian Mineralogist
Vol. 29, pp. 767-790 (1991)

H_2O–CO_2 MIXTURES: A REVIEW OF *P–V–T–X* DATA AND AN ASSESSMENT FROM A PHASE-EQUILIBRIUM POINT OF VIEW

URS K. MÄDER*
Department of Geological Sciences, The University of British Columbia, Vancouver, British Columbia V6T 2B4

ABSTRACT

A resolution is suggested among inconsistencies between and within data sets, including *P–V–T–X* measurements, phase-equilibrium experiments and equations of state for H_2O–CO_2 mixtures. The *P–V–T–X* data of Franck & Tödheide (1959) are inconsistent with data obtained by Greenwood (1973) and Gehrig (1980), and cannot be reconciled with measured phase-equilibria in H_2O–CO_2 fluid mixtures. The data of Greenwood and Gehrig are in loose agreement, but extend only to 600 bars and do not constrain activities at higher pressures. The correction for chemical association proposed by de Santis *et al.* (1974) and adopted by Holloway (1977) and Bowers & Helgeson (1983) does not appear to be justified. Resolution of the inconsistencies among phase-equilibrium studies will require further experiments and adjustments of thermophysical properties of minerals simultaneously with fits of the mixing properties of the fluid phase. A procedure is developed for the use of experimental phase-equilibrium constraints to put limits on the fugacities of components in the fluid mixture. It is concluded that the data-base available is not yet adequate to derive a reliable equation of state for H_2O–CO_2 mixtures. Future work must include *P–V–T–X* measurements to at least 10 kbar and phase-equilibrium studies to further constrain deviations from ideal mixing and to resolve inconsistencies among existing measurements.

Keywords: water - carbon dioxide mixtures, fluids, thermophysical properties, thermodynamic properties, equations of state, phase equilibria.

SOMMAIRE

Cet article porte sur une réconciliation parmi les incompatibilités internes aux banques de données et entre celles-ci, portant sur les mesures *P–V–T–X*, les expériences sur les équilibres de phases, et les équations d'état pour les mélanges H_2O–CO_2. Les données de type *P–V–T–X* publiées par Franck & Tödheide (1959) ne concordent pas avec les données de Greenwood (1973) et de Gehrig (1980), et sont irréconciliables avec les équilibres de phases mesurés impliquant une phase fluide mixte H_2O–CO_2. Les données de Greenwood et Gehrig concordent *grosso modo*, mais ne dépassent pas 600 bars, et ne contraignent aucunement les activités à pressions plus élevées. La correction pour l'association chimique proposée par de Santis *et al.* (1974) et adoptée par Holloway (1977) et par Bowers et Helgeson (1983) ne semble pas justifiée. Une résolution des incompatibilités parmi les résultats des études des équilibres de phases nécessitera de nouvelles expériences et des ajustements aux propriétés thermophysiques des minéraux, en même temps qu'aux propriétés de mélange dans la phase fluide. Un protocole est établi pour appliquer les contraintes des équilibres de phases afin d'établir des limites sur les fugacités des composantes du mélange dans la phase fluide. La banque de données n'est pas encore adéquate pour dériver une équation d'état fiable pour les mélanges H_2O–CO_2. Les travaux futurs devront inclure des mesures des propriétés *P–V–T–X* jusqu'à au moins 10 kbar, et de nouvelles études des équilibres de phases afin de contraindre davantage les écarts à l'idéalité dans le mélange et de résoudre les incompatibilités parmi les données existantes.

(Traduit par la Rédaction)

Mots-clés: mélanges d'eau et d'oxyde carbonique, fluides, propriétés thermophysiques, propriétés thermodynamiques, équations d'état, équilibres de phases.

INTRODUCTION

C–O–H fluids are important in the study of metamorphism, fluid inclusions, properties of magmas, and evolution of oil and gas. Much of our present knowlege of H_2O–CO_2 mixtures at elevated pressures and temperatures was established during the late 1960s and early 1970s, and was stimulated by the study of progressive metamorphism of impure limestones.

Theoretical and experimental contributions combined with constraints from field observations were provided by Greenwood (1967a, b, 1969, 1973), Skippen (1971), Johannes (1969), Eugster & Skippen (1967), Trommsdorff (1972), Trommsdorff & Evans (1974), Metz (1967, 1970), among many more. About a decade earlier, *P–V–T–X* measurements on H_2O–CO_2 mixtures were ex-

---

*Present address: Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8.

tended to 2 kbar pressure (Franck & Tödheide 1959), and the two-phase region was mapped to 3.5 kbar (Tödheide & Franck 1963, Takenouchi & Kennedy 1964). Spectroscopic data and measurements of dielectric permittivity were collected in Karlsruhe by Kruse (1975) and Holzapfel & Franck (1966). Equations of state for fluid mixtures suitable for the computation of phase equilibria in geological systems were developed by Holloway (1977), Flowers (1979) and by Kerrick & Jacobs (1981). Continued efforts have steadily increased the experimental data-base (*e.g.*, Sterner & Bodnar 1991, Chernosky & Berman 1991) and supplemented field occurrences of low-variance mineral assemblages coupled with measured compositions of minerals (*e.g.*, Bucher-Nurminen 1988). With the availability of fast microcomputers and improved thermodynamic data-bases (*e.g.*, Berman 1988), efforts have been made most recently to compute petrogenetic grids for metacarbonate rocks (Carmichael 1991, Connolly & Trommsdorff 1991).

In light of these continued efforts, it is appropriate to critically examine the very foundations of thermophysical properties of H_2O–CO_2 mixtures, namely P–V–T–X measurements, equations of state and experimentally determined phase-equilibria. The purpose of this paper is to help focus on the most important measurements needed to improve and resolve the numerous inconsistencies.

THE SYSTEM CO_2–H_2O

The system CO_2–H_2O has three components, C, H, O, and contains numerous species: CO_2, H_2O, CO, O_2, H_2, CH_4, H_2CO_3, complex hydrocarbons, and the condensed phases graphite, diamond and clathrate hydrates. Despite the existence of numerous species, it is possible to take a stoichiometric approach for the binary join H_2O–CO_2, which considers only two species, CO_2 and H_2O. The experimental data, however, on which the equation is calibrated, must be known to contain only those two species. The bulk composition of the fluid may be displaced from the binary join if the fugacity of one or more species is buffered, or sources or sinks for C–H–O species exist. This is particularly significant in the case where graphite or diamond is stable (*e.g.*, Skippen & Marshall 1991, Ulmer & Luth 1991). Gain or loss of hydrogen is the most common problem encountered in experimental studies. It may be solved by buffering the fugacity of hydrogen at a very low partial pressure, removing likely sources or sinks for hydrogen, and keeping experimental run durations as short as possible. Experimentally measured volumes of CO_2–H_2O mixtures may suffer from oxygen loss due to the oxidation of the steel pressure vessel or from hydrogen loss due to diffusion or formation of metal hydrides. Under sufficiently oxidizing conditions, methane, hydrogen and carbon monoxide are present only in trivial amounts, and a binary CO_2–H_2O fluid consists chiefly of the species CO_2 and H_2O (*e.g.*, Holloway 1987, Eugster & Skippen 1967).

The two-phase region of the CO_2–H_2O binary system is encountered geologically under conditions up to lower-greenschist-grade metamorphism. The critical curve that bounds the two-phase region extends from the critical point of pure H_2O (374.15°C, 221.3 bar) to a temperature minimum (266–269°C, 2000–2450 bar, $0.37 < X(CO_2) < 0.43$), and then probably to higher temperatures with increasing pressure and increasing $X(CO_2)$ (Tödheide & Franck 1963, Takenouchi & Kennedy 1964, Sterner & Bodnar 1991). The lower branch of the critical curve extends from the critical point of pure CO_2 (31.05°C, 73.86 bar) to a lower critical end-point at somewhat higher temperature and pressure. Equations of state designed for the computation of phase equilibria at temperatures below the critical point of water must therefore account for the two-phase region.

CONSTRAINTS ON EQUATIONS OF STATE FROM THEORY AND EXPERIMENT

It is fair to state that the problem of the prediction of P–V–T properties of fluids and their mixtures is not so much due to the lack of theories and models, but to the lack of our ability to assess their relative merits. Models based on first principles are not yet sufficiently developed to test equations of state, and the body of experimental data is not large enough to distinguish between the extrapolation properties of the numerous semi-empirical equations. As a consequence, the computation of properties of fluid mixtures relies heavily on experimentally measured quantities, semi-empirical equations of state, and, in many cases, arbitrarily chosen rules for the mixing of end-member fluids.

The exact shape of the intermolecular potential as a function of temperature and pressure is not known, nor are the potentials resulting from their mutual interaction in mixtures. For this reason, most equations of state applicable to real systems are based on macroscopic models, with parameters related to the dominant intermolecular forces of attraction and repulsion. Examples are the virial-type equations, the van der Waals equation and the Redlich–Kwong (Redlich & Kwong 1949) equation with its numerous modifications.

The behavior of mixtures of gases may in some cases be described by equations in which the parameters are formed by some combination of the parameters for the pure gases. However, the equations must be mathematically and physically compatible. These "mixing rules" may be independent of the nature of the end-member gases in that they simply account for geometrical effects upon mixing. If one or more of the end-member gases deviate substantially from ideal behavior, mixing rules may be adjusted for nongeometrical effects upon mixing, such as induced dipole effects, polarizability, strong electronic interactions and chemical association (*e.g.*, Prausnitz *et al.* 1986). In most cases, only a two-body interaction parameter is developed to account for these effects. The requirement that equations of the end-member gases be compatible puts severe constraints on the possibility of introducing modifications to either end member to fit experimental data. Several equations intended for geological applications have been fit piecewise to data in order to keep equations simple [*e.g.*, Bottinga & Richet (1981) for CO_2; Holloway (1977, 1981) for H_2O; Saxena & Fei (1987) for H_2O and CO_2; Powell & Holland (1985) and Holland & Powell (1990) for the logarithm of the fugacity of H_2O and CO_2]. The tradeoff in this approach is the introduction of discontinuities to the thermodynamic functions derived from these equations of state.

An important point that is easily underestimated is the dependency of the parameters in the equation of state on the mathematical form of the equation itself. The same rules of mixing applied to a van der Waals equation and a Redlich–Kwong equation will result in different excess properties for a mixture, even though the physical justification and the underlying assumptions may be identical. Increased flexibility to fit measured volumes may be introduced by making the attractive term or the repulsive term more flexible. Thus, an equation with a simple hard-sphere repulsive term can mimic increased compressibility at high pressure by introducing a volume (or pressure) dependency on the attractive term (*e.g.*, the equation of Kerrick & Jacobs). The quality of fit to observed data alone implies nothing about the physical meaning of the variation of the parameters with *P*, *V* and *T*, or about the correctness of the mixing rules.

The number of parameters in an equation of state is not always correlated with the goodness of fit to data. In most equations, one or more parameters, such as the excluded volume, are fixed prior to regression to measured volumes (*e.g.*, Kerrick & Jacobs 1981, Holloway 1977). For some of the mathematically more complex equations, a simultaneous fit of all parameters is not possible owing to problems with numerical stability during optimization (*e.g.*, Bottinga & Richet 1981). An equation with few parameters fit simultaneously, such as the five-parameter equation presented by Mäder & Berman (1991) for CO_2, may achieve a fit comparable to a ten-parameter equation, such as that proposed by Kerrick & Jacobs (1981). A many-parameter equation may not extrapolate well, particularly if the parameters are combined empirically, for example in a power-series expansion.

Carbon dioxide

Raman spectroscopic measurements to 490°C and 2.5 kbar (Kruse 1975) indicate no significant changes in the spectrum from data at low densities. Not much is known about the extent of dissociation, ionization, or dimerization of pure CO_2 at high temperatures and very high densities.

Water

Whereas the peculiar nature and properties of water compared to other liquids are well known (*e.g.*, Franks 1972–1984, vols. I–VII), it is not well understood how these properties change with increasing pressure and temperature. Insight is gained from experimental measurements of *P–V–T* properties, dielectric permittivity, Raman and infrared spectroscopy, thermodynamic properties, and, more recently, from simulations using molecular dynamics (see also Tödheide 1972).

Water at low pressures and temperatures is dominated by hydrogen bonding, which leads to a highly structured liquid dominated by tetrahedrally coordinated molecules with an open structure similar to that in the corresponding solid, ice-I. The hydrogen bond persists to high pressures in ice (*e.g.*, ice-VII at pressures >21 kbar), with an increase in density due to distortion of the framework. The relatively low compressibility of liquid water despite the open framework indicates that the structure dominated by the hydrogen bond may persist to high pressure in the fluid state as well. There is evidence that water starts to assume compressibilities like those of unstructured liquids at a pressure between 4 and 8 kbar (Franck 1981).

The tetrahedrally coordinated network probably does not persist to high temperatures at low pressures. Spectroscopic data indicate that at supercritical conditions, H_2O has lost many of its structured characteristics. Supercritical water is, however, still polar in nature, which is important for its ability to interact with other species. No data are available on structural changes as a function of temperature at high pressures. At very high temperature and pressure (100-200 kbar), water may be largely an ionic fluid, in view of the observed monotonic increase of the ion product with pressure and temperature (Holzapfel & Franck 1966, Mitchell & Nellis 1979, and discussion in Franck 1981).

Recent progress in simulations based on molecular dynamics (Brodholt & Wood, 1990) at a density of 1 g/cm^3 and temperatures up to 2100°C (38 kbar) leads to reasonable agreement with measured volumes and transport properties. This approach may allow testing of intermolecular potential formulations and equations of state in the near future. Results of numerical simulations alone are not yet accurate enough for the purpose of thermodynamic computations.

The Haar *et al.* (1984) equation used to express the thermodynamic properties of supercritical water by Berman (1988) and in this study is thought to be reliable to at least 2500 K and 30 kbar. The equation is based on a formulation of the Helmholtz free energy as a function of temperature and density. The theoretical model and its empirical extensions obey the first and second laws of thermodynamics and thus allow for computation of any thermodynamic function by differentiation. The equation is consistent with virtually all experimental observations. Most recently, the properties of H_2O in the critical region have been addressed by Johnson & Norton (1991).

Mixtures of water and carbon dioxide

As a first approximation, inferences from $P-V-T-X$ measurements about interactions between CO_2 and H_2O may be tested against what limited spectroscopic and other data exist. From the strong depression of the critical composition curve to lower temperatures compared to water mixed with an inert gas (*e.g.*, argon, Greenwood 1961), one might expect strong chemical association up to at least 400°C and 4 kbar. The positive deviation of the volume from ideality on mixing, stemming from dispersion forces, may be reduced or even reversed by strong chemical association. Greenwood's (1969) $P-V-T-X$ measurements indicate distinct negative volumes of mixing at temperatures above 600°C and pressures below 300-400 bar (*e.g.*, see below, in Fig. 7). This would indicate that chemical association remains significant beyond 800°C, but decreases with increasing pressure. Franck & Tödheide (1959) interpreted their $P-V-T-X$ measurements in terms of deviations from a van der Waals equation of state with "geometric" rules of mixing and estimated the maximum amount of chemical association in terms of carbonic acid. De Santis *et al.* (1974) used these data to formulate a temperature-dependent equilibrium constant ($CO_2 + H_2O \rightleftharpoons H_2CO_3$) that is incorporated into their modified Redlich-Kwong equation of state and adopted by Holloway (1977), Flowers & Helgeson (1983) and Bowers & Helgeson (1983). The $P-V-T-X$ data by Franck & Tödheide are considered suspect for reasons explained below, and the de Santis *et al.* (1974) correction is not justified.

Infrared absorption and Raman spectroscopy on fluids at elevated temperature and pressure are rare, owing to obvious technical difficulties arising from the use of sapphire windows. The data available up to 2-3 kbar (Kruse 1975, and summary by Franck 1981) only show a weak band on a Raman spectrum at low temperatures, which may be assigned to carbonic acid. Spectra at higher temperatures and pressures lack clear evidence for chemical association. Read's (1975) measurements on electrical conductance suggest at least some chemical association up to the limits of his experiments at 250°C and 2 kbar.

EXISTING EQUATIONS OF STATE

In many early applications to geological problems, water and carbon dioxide have been assumed to mix ideally (*e.g.*, Eugster & Skippen 1967, Greenwood 1967b) owing to the lack of constraints on nonideality. This may result in distorted topologies in phase diagrams over a wide range of temperature, pressure and fluid composition. The most commonly used equations of state that predict $P-V-T-X$ properties of H_2O-CO_2 mixtures include that of Kerrick & Jacobs (1981) and the Holloway (1977) - Flowers (1979) equation, which are both modifications of the equation of Redlich & Kwong (1949). Holloway's equations are based on work by de Santis *et al.* (1974). Powell & Holland (1985) and Holland & Powell (1990) fitted a polynomial function for the logarithm of the fugacity to data computed with existing equations of state. The mixture is modeled by a subregular, asymmetrical solution-model for the activities, which are fitted to values computed with the Kerrick & Jacobs equation. Shmulovich *et al.* (1980) presented a virial equation and used a Margules formulation to model the excess volume of mixing as a function of composition, from which they derived the fugacities. Spycher & Reed (1988) devised a pressure-explicit virial equation applicable to calculations of hydrothermal boiling, with upper limits at 1 kbar and 1000°C. Connolly & Bodnar (1983) presented a modified Redlich-Kwong equation for the range 0-10 kbar and 100-1000°C, designed for applications to fluid-inclusion studies. Sterner & Bodnar (1991) derived a three-coefficient Margules expansion for the excess volume of mixing from their measurements on synthetic fluid-inclusions between 2 and 6 kbar and 400 to 700°C. Tabulations of P-V-T-X properties and fugacities of CO_2-H_2O mixtures were offered by Franck & Tödheide (1959), Greenwood & Barnes (1966), Greenwood (1969, 1973), Ryzhenko & Volkov (1971), Wood & Fraser (1977), Shmulovich *et al.* (1980), and Sterner & Bodnar (1991). Recent review articles on equations of state for fluids include those by Ferry & Baumgartner (1987) and Holloway (1987).

THERMODYNAMIC RELATIONSHIPS FOR FLUID MIXTURES

Whereas most standard texts cover the subject adequately (Prausnitz *et al.* 1986, Chatterjee 1991, Wood & Fraser 1977, Anderson 1977, Skippen & Carmichael 1977), they do not provide the necessary details relevant to this treatment of the phase-equilibrium experiments. The thermodynamic notation used here is summarized in Table 1.

In order to derive simple expressions for the excess properties of a mixture (*e.g.*, partial molar excess volume V_{ei}), the fugacity coefficient γ_i of a component in a mixture is best related to its pure state at temperature and pressure of interest, which yields:

$$\int_{1\,\mathrm{bar}}^{P} V_e(P,T)dP = \sum_i X_i \int_{1\,\mathrm{bar}}^{P} V_{e_i}(T)dP = \sum_i RT\ln\gamma_i(P,T,X_i). \tag{1}$$

The activity of a component with respect to the same state becomes $a_i = X_i\gamma$. Equation 1 also

TABLE 1. NOTATION FOR THERMODYNAMIC EQUATIONS

P	pressure
T	absolute temperature in Kelvin
$\Delta_R G$	Gibbs potential of a reaction
$\mathcal{G}$	Gibbs potential of a reaction diminished by the $RT\ln f$ terms of the fluid species
C_P	heat capacity at constant pressure
α	isobaric expansivity
β	isothermal compressibility
V_i°	molar volume of pure component i
V_i	partial molar volume of component i in a mixture
V_m	molar volume of a mixture
$\hat{V}$	molar volume of a mechanical (ideal) fluid mixture
V_e	molar excess volume of a mixture
V_{e_i}	partial molar excess volume of component i in a mixture
X_i	mole fraction of component i in a mixture
f_i	fugacity of component i in a mixture
f_i°	fugacity of pure component i
γ_i	fugacity coefficient of component i relative to ideal mixing at pressure and temperature of interest
a_i	activity of component i in a mixture relative to its pure state at pressure and temperature of interest
ν_i	stoichiometric coefficient of component i in a reaction
R	gas constant

Superscript * refers to a variable at some standard state
Superscript ^{id} refers to a variable in a state of ideal mixing
Superscript ^{exp} refers to an experimentally measured variable

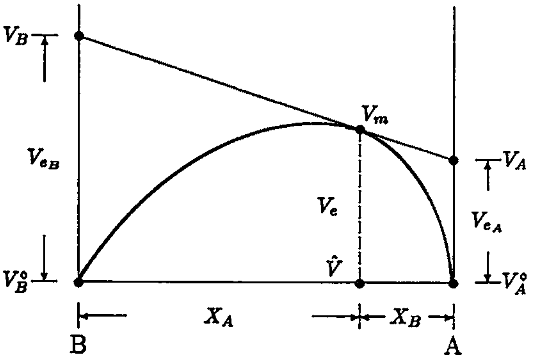

FIG. 1. Geometrical interpretation of the partial molar excess volume in a binary fluid mixture with components A and B.

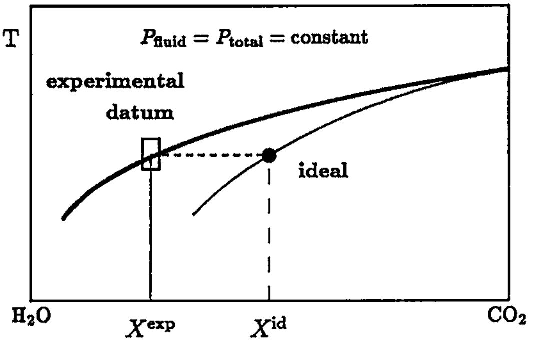

FIG. 2. Schematic diagram of a single fluid species equilibrium. The experimentally determined equilibrium curve and the computed curve assuming ideal mixing in the fluid phase are shown as a thick line and a thin line, respectively.

implies the approximate equality of unit pressure and unit fugacity. A simple geometric interpretation of the partial molar excess volume in a two-component mixture is provided in Figure 1.

In order to relate an experimentally determined phase-equilibrium position at P^{exp}, T^{exp}, X^{exp} to a hypothetical reference-position assuming ideal mixing at P^{id}, T^{id} and X^{id}, one formulates first the Gibbs potential of the reaction for both states:

$$\Delta_R G = 0 = \mathcal{G}(P^{\text{exp}},T^{\text{exp}})[\nu_j, V_j^*, S_j^*, H_j^*, (C_P)_j, \alpha_k, \beta_k] + \sum_i \nu_i RT \ln \frac{f_i(P^{\text{exp}},T^{\text{exp}},X_i^{\text{exp}})}{f_i^*} \tag{2}$$

and an analogous equation with $\mathcal{G}$ and f_i at states P^{id}, T^{id} and X^{id}. Subscript j denotes all species (solid or fluid) that take part in the reaction, k relates to solid phases only, and i is the subscript for all gaseous species. The function $\mathcal{G}$ contains all contributions to the Gibbs potential from the solid phases and the contributions from the fluid species with the exception of the volume integral ($RT \ln f$ term). Equation 2 and its analog are combined to obtain the general expression:

$$\mathcal{G}(P^{\text{exp}},T^{\text{exp}}) - \mathcal{G}(P^{\text{id}},T^{\text{id}}) = R\sum_i \nu_i \left(T^{\text{id}} \ln X_i^{\text{id}} - T^{\text{exp}} \ln \frac{f_i(P^{\text{exp}},T^{\text{exp}},X_i^{\text{exp}})}{f_i^o(P^{\text{exp}},T^{\text{exp}})}\right). \tag{3}$$

Figure 2 is an example of the special case where only one fluid component in the mixture takes part in a reaction. The deviation from ideality in an isobaric–isothermal section simplifies to:

$$\frac{f_i(P,T,X_i^{\text{exp}})}{f_i^o(P,T)} = a_i(P,T,X_i^{\text{exp}}) = X_i^{\text{id}} = \gamma_i(P,T,X_i^{\text{exp}})X_i^{\text{exp}}. \tag{4}$$

The volume integral of the partial molar excess volume with respect to pressure for this case is obtained from equation 1:

$$X_i^{\text{exp}} \int_{1\,\text{bar}}^{P} V_{e_i}(T)dP = RT \ln \frac{X_i^{\text{id}}}{X_i^{\text{exp}}} = RT \ln \gamma_i(P,T,X^{\text{exp}}). \tag{5}$$

P–V–T–X PROPERTIES CONSTRAINED BY PHASE-EQUILIBRIUM DATA

From the requirement for a reaction at equilibrium that $\Delta_R G^{P,T}$ be equal to 0, it follows that each experimental half-bracket leads to an inequality, $\Delta_R G^{P,T} < 0$ or $\Delta_R G^{P,T} > 0$, depending whether products or reactants are stable, respectively. Provided reliable thermodynamic data for all solid phases are available, each measured half-bracket of an equilibrium involving a fluid mixture will put an inequality constraint on the fugacities of the fluid species by combining the above inequalities with equation 3:

$$R\sum_i \nu_i \left(T^{\text{id}} \ln X_i^{\text{id}} - T^{\text{exp}} \ln \frac{f_i(P^{\text{exp}},T^{\text{exp}},X_i^{\text{exp}})}{f_i^o(P^{\text{exp}},T^{\text{exp}})}\right) \lessgtr \mathcal{G}(P^{\text{exp}},T^{\text{exp}}) - \mathcal{G}(P^{\text{id}},T^{\text{id}}), \tag{6}$$

where the "less than" refers to the case where products are stable. The combined bounds from many experimental half-brackets will confine an equation of state within feasible limits with respect to measured phase-equilibria. This fact may be used to test existing equations of state or to constrain adjustable parameters of a new equation using techniques of numerical optimization. Details of this method are outlined by Berman *et al.* (1986), and applied to the derivation of an equation of state for pure CO_2 by Mäder & Berman (1991).

The validity of this approach hinges on the availability of accurate thermophysical properties of minerals and pure fluids, as well as P–V–T–X measurements and phase-equilibrium experiments. Improvements on equations of state can only proceed in conjunction with improvements to the experimental data-base. Carefully documented assemblages of natural minerals can provide additional constraints and are the ultimate test in applications of computed phase-equilibria to rocks.

Thermophysical properties of minerals that are dependent on fluid properties by virtue of the available phase-equilibrium data must be fitted simultaneously with fluid properties in order to maintain self-consistency and to avoid the propagation of systematic errors into fluid properties. Whereas there is some circularity in this process, it is anticipated that every new experimental datum of high quality will guide the numerical best fit toward consistency with all available data.

P–V–T–X DATA ON H_2O–CO_2 MIXTURES

Figures 3 to 7 compare measured excess volumes of mixing with volumes computed by several equations of state. Parameters for equations of state and computer codes for their evalution were obtained from the following sources: Kerrick & Jacobs (1981), Jacobs & Kerrick (1981a), Holloway (1981) and a computer code obtained by written communication from J.R. Holloway (July, 1990). The van der Waals equation was evaluated using the following parameters and mixing rules: $a(H_2O) = 55.0 \times 10^5$, $b(H_2O) = 30.3$, $a(CO_2) = 36.8 \times 10^5$, $b(CO_2) = 43.0$, $a_{\text{mix}} = X(H_2O)^2a(H_2O) + X(CO_2)^2a(CO_2) + 2X(H_2O)X(CO_2)\sqrt{a(H_2O)a(CO_2)}$, and $b_{\text{mix}} = b(H_2O)X(H_2O) + b(CO_2)X(CO_2)$, in units of Kelvin, bar, and cm^3/mol. A positive pressure spike at 210 bar (Figs. 3A–E) in the curves computed with the Kerrick & Jacobs equation is the result of nonconvergence of the iterative root-finding procedure coded by Jacobs & Kerrick (1981a). These erroneous volumes do not affect computed fugacity coefficients for a pressure above 250 bar since the volume integration is performed algebraically, but volumes between 325 and *ca.* 415°C cannot be computed reliably below a pressure of 250 bars.

Measured volumes are represented by smoothed data provided by the individual authors where primary measurements are not reported or do not plot into the selected figures (*e.g.*, Franck & Tödheide 1959, Greenwood 1973, Gehrig 1980, Sterner & Bodnar 1991). Only a representative amount of data is plotted to avoid rendering graphs illegible. The data of Franck & Tödheide above 1.4 kbar are not included in the figures owing to large uncertainties compared to the small effect on volume of mixing at high pressures. These uncertainties are the result of not reporting P–V–T data on the pure fluids. For the computation of the excess volume below 1.4 kbar, the data on the pure gases of Kennedy (1954) and Holser & Kennedy (1958, 1959) were used; Franck & Tödheide stated that these agree to within 1% of their measurements. The same procedure had to be adopted for the data of Gehrig (1980), who reported data on mixtures between $0.1 < X(CO_2) < 0.9$, but none for the pure fluids. Error bars in Figures 3–7 represent my best estimate of uncertainty, except for measurements by Sterner & Bodnar (1991), where experimental precision is depicted.

The most striking feature apparent from inspection of Figures 3–7 is the substantial inconsistency among the data sets of Franck & Tödheide (1959), Greenwood (1973), Gehrig (1980) and Shmulovich *et al.* (1979, 1980). There is reasonable agreement, although not within stated experimental uncertainties, between the data of Greenwood (1973) and Gehrig (1980) (Figs. 4, 5). The Kerrick & Jacobs (1981) equation of state, which reproduces experimentally measured phase-equilibria quite well (Berman 1988, Jacobs & Kerrick 1981b, and discussion below), loosely approximates the data by Greenwood and Gehrig between 400 and 600°C (Figs. 3–6). I conclude that the volumes measured by Franck & Tödheide are most likely in error, particularly at pressures below 1 kbar, and should not be used. Their volumes are systematically smaller than those measured by Greenwood, Gehrig and Schmulovich *et al.* It is not possible to relate the apparently erroneous measurements of Franck & Tödheide to a single cause. The most likely problems in the experimental method that lead to underestimated volumes are thermal gradients over volumes of connections, or determination of the volume of the pressure vessel by the mercury method, or creep of Bridgman seals.

Shmulovich *et al.* (1979, 1980) measured volumes of several fluid compositions at 400 and 500°C between 0.15 and 5.7 kbar (Figs. 3, 5). Measurements by Shmulovich *et al.* (1979) at 400 and 500°C and 400–5700 bar show excess volumes significantly larger than data by Shmulovich *et al.* (1980) and Franck & Tödheide, with the exception of good agreement in the region of overlap with data by Greenwood and Gehrig at 500–600 bar (Fig. 5). At 400°C and 150–200 bar, the excess volumes of Shmulovich *et al.* (1979) are smaller than those measured by Gehrig (Fig. 3). Excess volumes measured by Shmulovich *et al.* (1979) above 700 bar pressure at 700°C (Figs. 5A, B) are difficult to reconcile with theory or phase-equilibrium data.

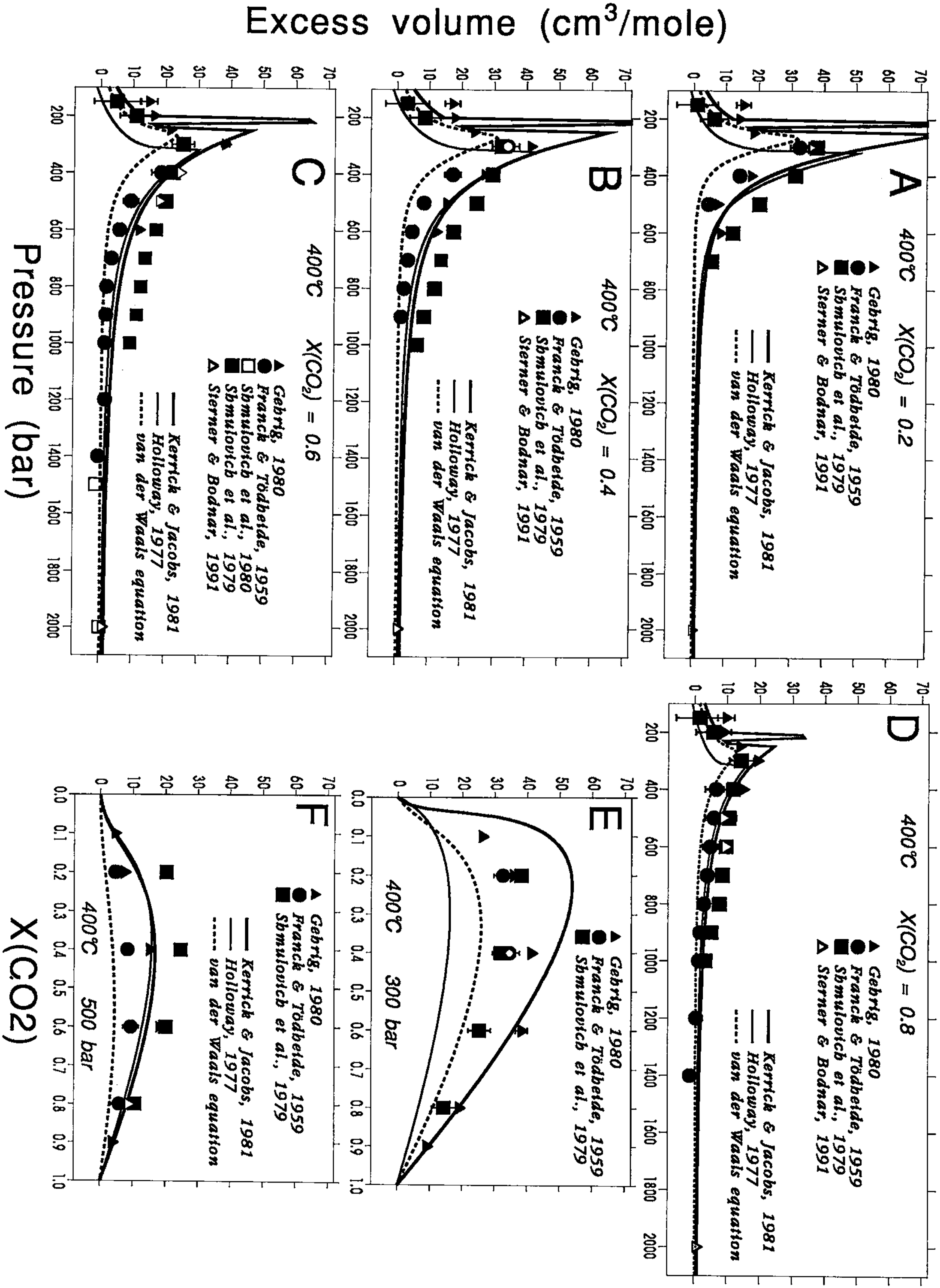

FIG. 3. Pressure *versus* excess molar volume diagrams (A, B, C, D) and fluid composition *versus* excess molar volume diagrams (E, F) of H_2O–CO_2 mixtures at 400°C. See text for discussion.

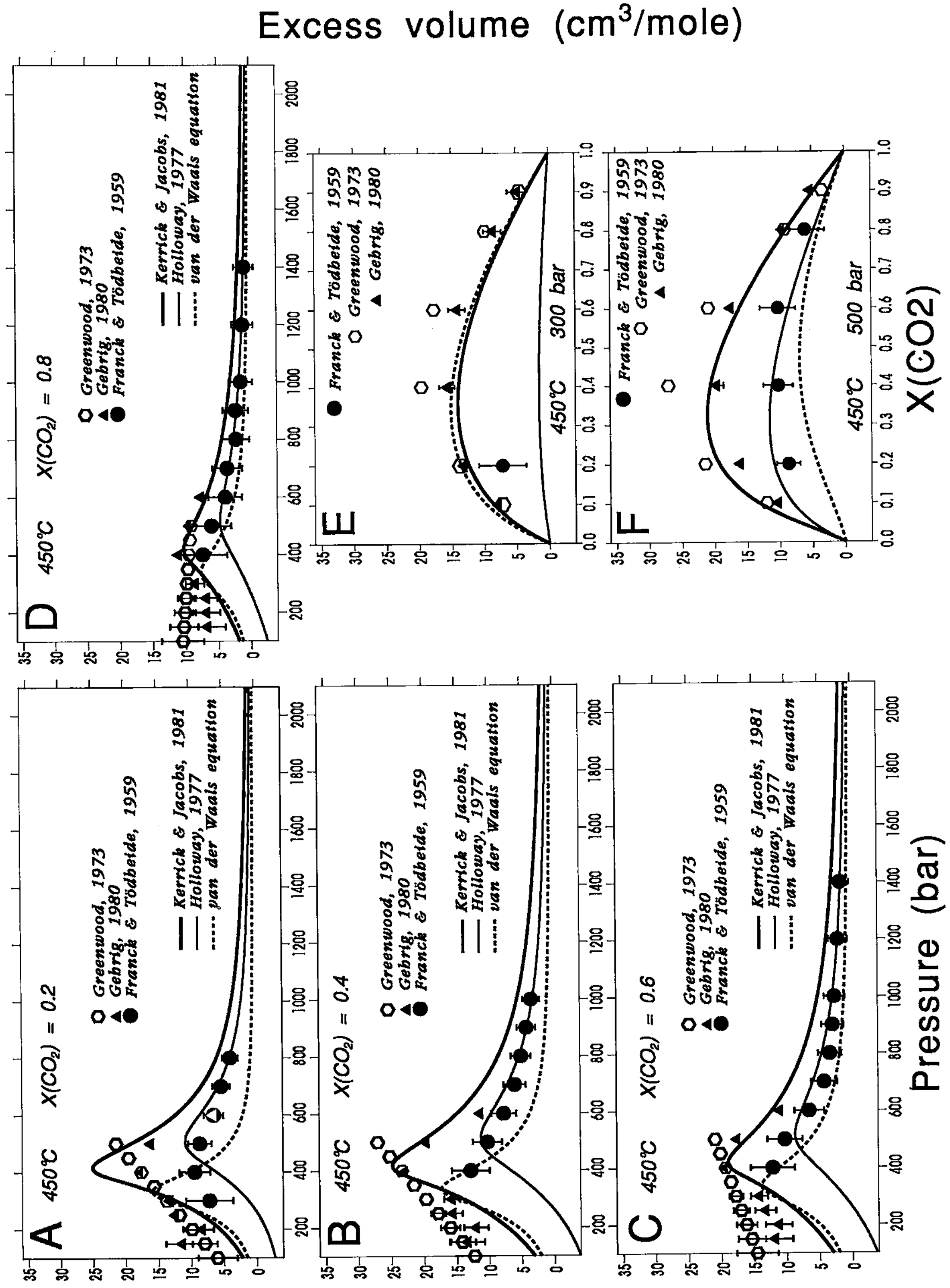

FIG. 4. Pressure *versus* excess molar volume diagrams (A, B, C, D) and fluid composition *versus* excess molar volume diagrams (E, F) of H_2O-CO_2 mixtures at 450°C. See text for discussion.

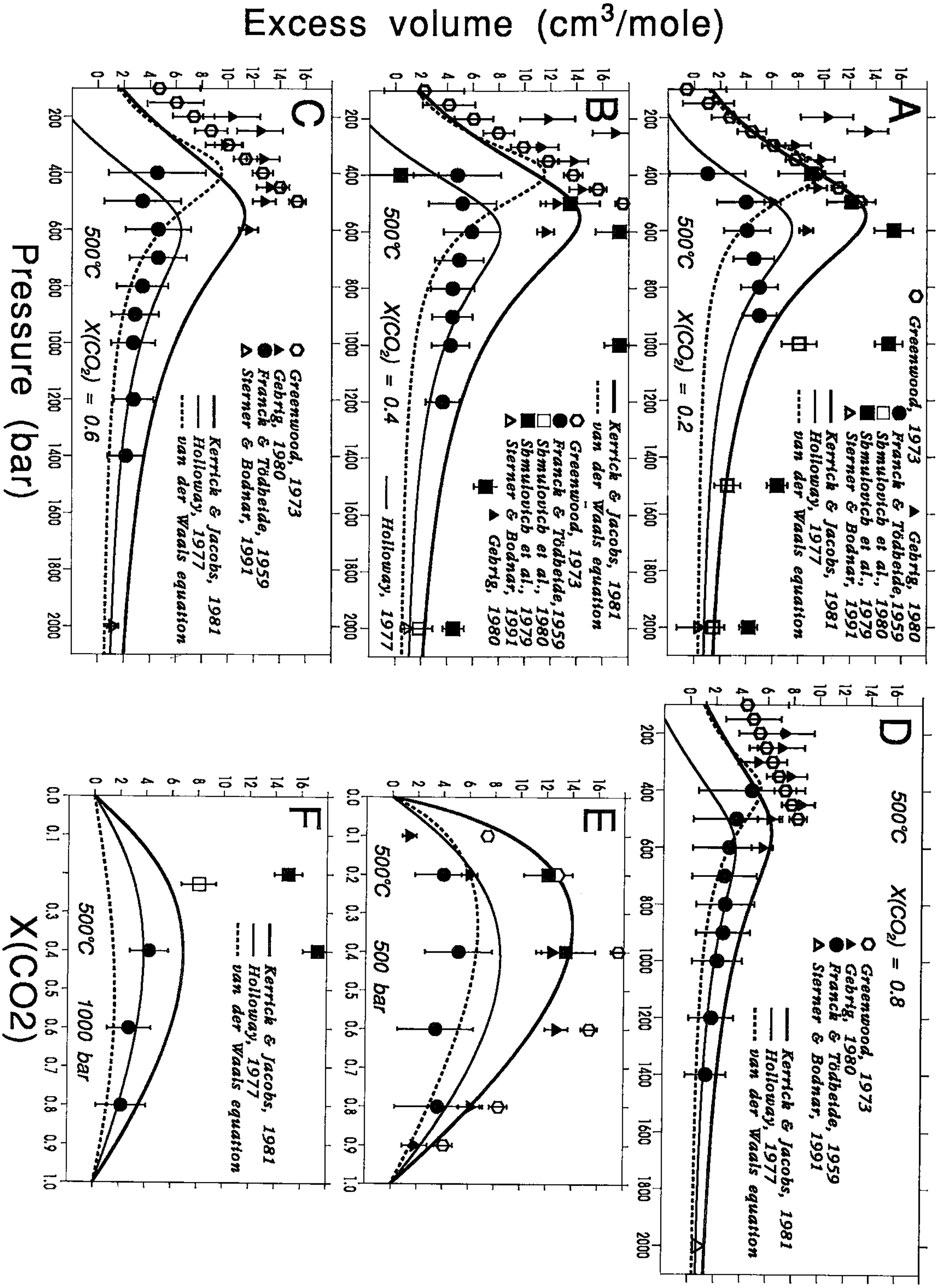

FIG. 5. Pressure *versus* excess molar volume diagrams (A, B, C, D) and fluid composition *versus* excess molar volume diagrams (E, F) of H_2O-CO_2 mixtures at 500°C. See text for discussion.

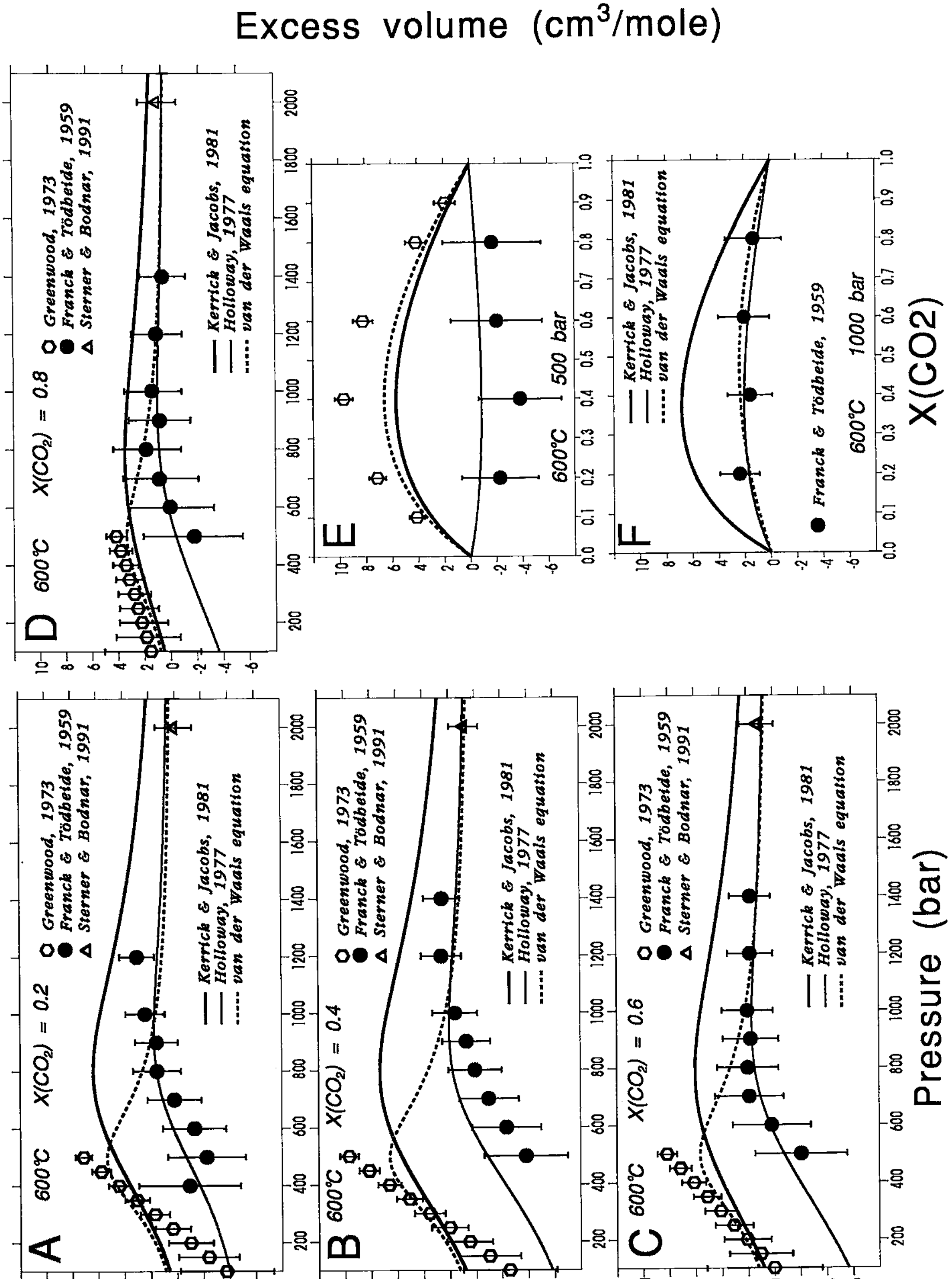

FIG. 6. Pressure *versus* excess molar volume diagrams (A, B, C, D) and fluid composition *versus* excess molar volume diagrams (E, F) of H_2O–CO_2 mixtures at 600°C. See text for discussion.

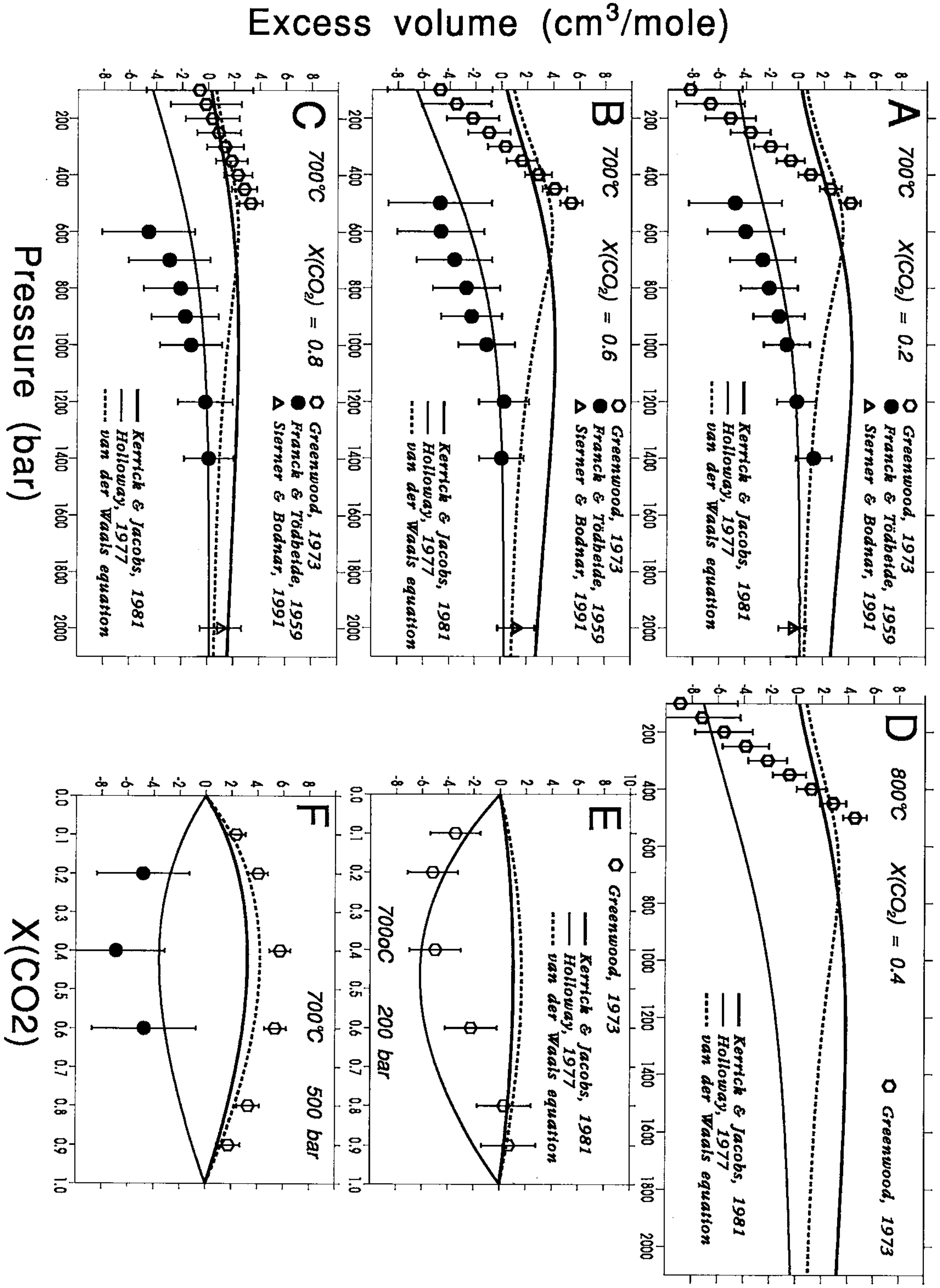

FIG. 7. Pressure *versus* excess molar volume diagrams (A, B, C, D) and fluid composition *versus* excess molar volume diagrams (E, F) of H_2O–CO_2 mixtures at 700 and 800°C. See text for discussion.

Greenwood (1969, 1973) measured negative volumes of mixing at temperatures above 600°C and pressures below 300–400 bar (Fig. 7). If these measurements are correct, significant chemical association must occur in order to reverse the positive volume-effect resulting from dispersion forces alone. The Holloway - Flowers equation, which accounts for formation of carbonic acid (de Santis *et al.* 1974), does not represent Greenwood's (1973) data well in this region.

Sterner & Bodnar (1991) derived excess volumes of mixing from measurements on synthetic fluid inclusions in quartz (2–6 kbar, 400–700°C, $0.125 < X(CO_2) < 0.875$). Only data at 2 kbar are shown in Figures 3 and 5–7. The authors computed ideal volumes with the Haar *et al.* (1984) equation of state for water and the equation of Shmonov & Shmulovich (1974) for carbon dioxide. Excess volumes were inferred to be positive, smaller than 1.3 cm^3/mol, with the exception of slightly negative excess volumes for water-rich compositions at 600 and 700°C. Uncertainties are difficult to assess because of the lack of sufficient measurements on pure fluids determined by the same method. Uncertainties of 2–3% in the measurements of Shmonov & Shmulovich (1974) on pure CO_2 (Mäder & Berman 1991) will lead to uncertainties in the excess volumes of the mixtures that are of the same magnitude as the excess volumes themselves. The important conclusion remains that fugacity coefficients up to at least 10 kbar and 700°C are dominated by relative large deviations from ideal mixing at pressures below 2 kbar.

The Kerrick & Jacobs (1981) equation is most compatible with the *P–V–T–X* data of Greenwood (1973), Gehrig (1980) and Shmulovich *et al.* (1980), and most phase-equilibrium data between 450 and 700°C (see below). The Holloway (1977, 1981) - Flowers (1979) equation is constrained to agree with data by Franck & Tödheide (1959), but underestimates deviations from ideal mixing compared to most other data.

CONSTRAINTS ON ACTIVITY – COMPOSITION RELATIONSHIPS

As an alternative approach to *P–V–T–X* measurements, one can determine directly activity–composition relationships by the use of fugacity sensors and buffering techniques. Joyce & Holloway (1987, 1989) buffered the fugacity of H_2O and analyzed the fluid mixture to obtain equilibrium $X(H_2O)$ at 2 kbar fluid pressure and 550–850°C and observed near-ideal activities for H_2O. Chou & Williams (1977, 1979a, b) used a hydrogen fugacity sensor and reported negative deviations from ideality at $X(CO_2) > 0.4$, 2–6 kbar and 600 and 700°C. A re-evaluation of the technique revealed that the data in the 1979 paper are incorrect and that deviations from ideal mixing are positive over the entire range of composition (Chou & Cygan 1990). Note that Sterner & Bodnar (1991) measured negative excess volumes on mixing for water-rich compositions at these pressures and temperatures (see above).

Walter (1963c), Shmulovich & Kotova (1980) and Ziegenbein & Johannes (1982) constrained the fugacity of CO_2 in a H_2O–CO_2 mixture from experimentally measured phase-equilibria. The results are limited by the consideration of a single equilibrium, which leads to curves of activity *versus* fluid composition at constant pressure that are polythermal, *i.e.*, the temperature is rising with increasing $X(CO_2)$. Eggler *et al.* (1979) placed constraints on the deviation from ideal mixing at 26 kbar using experiments performed in a piston–cylinder apparatus.

PHASE-EQUILIBRIUM DATA INVOLVING H_2O–CO_2 MIXTURES

Whereas the body of experimental data including H_2O–CO_2 mixtures is substantial, there are several incompatibilities among experimental studies of the same equilibrium (Table 2). One reason for this is that such experiments are technically difficult to control. There are ample possibilities for errors that remain undetected. This places obvious difficulties on selection of experiments that place reasonable constraints on the deviation from ideal mixing of the fluid phase.

The following is a summary of problems within the experimental data-base, as well as the thermodynamic data-base that Berman (1988) derived from these experiments (see also Berman 1988). Numbered phase-equilibria are keyed to Table 2.

Phase equilibria with the most disturbing inconsistencies between studies that examine the same reaction include calcite + andalusite + quartz ⇌ anorthite + CO_2 (3), calcite + quartz ⇌ wollastonite + CO_2 (1), wollastonite + calcite + anorthite ⇌ grossular + CO_2 (5), and calcite + quartz + tremolite ⇌ diopside + H_2O + CO_2 (26). Equilibria that show only a discrepancy between experiment and thermodynamic data of Berman (1988) include dolomite + tremolite ⇌ calcite + forsterite + CO_2 + H_2O (27), quartz + dolomite + H_2O ⇌ calcite + talc + CO_2 (29), magnesite + talc ⇌ forsterite + H_2O + CO_2 (31), magnesite + quartz + H_2O ⇌ talc + CO_2 (32), muscovite + quartz = sanidine + andalusite + H_2O (40), and rutile + quartz + calcite ⇌ titanite + CO_2 (46). Experiments by Manning & Bohlen (1991) corroborate the thermodynamic data for

TABLE 2. EXPERIMENTAL STUDIES OF PHASE EQUILIBRIA INVOLVING H_2O–CO_2 MIXTURES

System or Equilibrium	No	Author	P [kbar]	T [°C]	$X(CO_2)$	B88	TD	PH
Ca–Si–C–O + H_2O								
$Cal+Qtz \rightleftharpoons Wo+CO_2$	1	Zi&Jo,74	2,4,6	580–850	0.2–0.8	8	i–	G
		Gr,67a	1,2	500–720	0.0–0.9	8		ZJ
		Ja&Ke,81b	6	870	0.8–0.9	8	(i)–	
pure CO_2		Ha&Tu,56	0.3-3	570–800	–	11		
Ca–Al–Si–C–O + H_2O								
$Cal+Ky+Qtz \rightleftharpoons An+CO_2$	2	Ke&Gh,79	6	550–570	0.7	8		
		Ja&Ke,81b	6	450–580	0.0–0.8	8	(i)+	
$Cal+And+Qtz \rightleftharpoons An+CO_2$	3	Ke&Gh,79	2	410–450	0.5	8	i+	CB
		Ja&Ke,81b	2	370–450	0.1–0.7	8	i+	CB
		Ch&Be,91	1,2	340–410	0.5–0.8	–		KG,JK
$An+Cal+Qtz \rightleftharpoons Grs+CO_2$	4	Go&Gr,71	2	530–570	0.1	8		
$Wo+Cal+An \rightleftharpoons Grs+CO_2$	5	Ho,74	1,4	710–840	0.1–0.5	9	i+	
		Sh,78	1,2,4,6	610–730	0.0–0.3	9	i+	GG
		Go&Gr,71	2	580–850	0.0–0.4	9		S
$An+Cal+Crn \rightleftharpoons Gh+CO_2$	6	Ho,74	1	760–840	0.2–0.6	10		
pure CO_2		Sh,74	0.5–0.7	780–860	–	11		
$An+Cal \rightleftharpoons Grs+Gh+CO_2$	7	Ho,74	1	719–880	0.1–0.7	10	(i)–	
$An+Cal \rightleftharpoons Grs+Crn+CO_2$	8	Ho,74	1,4	750–840	0.1–0.2	10		
		Ke&Gh,79	2	680–710	0.1	10		
$Grs+Cal+Crn \rightleftharpoons Gh+CO_2$	9	Ho,74	1,4	700–840	0.0–0.2	10		
$An+Cal \rightleftharpoons Wo+Gh+CO_2$	10	Ho,74	1	760–900	0.4–0.9	10	(i)–	
pure CO_2		Sh,74	0.5–0.7	830–890	–	11		
$Grs+Cal \rightleftharpoons Wo+Gh+CO_2$	11	Ho,74	1	730–800	0.1–0.2	10		
Ca–Al–Si–C–H–O								
$Zo+CO_2 \rightleftharpoons Cal+An+H_2O$	12	St&Ni,72	2,5	430–670	0.0–0.3	9	(i)+	
		Al&Fa,82	5	480–650	0.1–0.3	9		
$Cal+Prl+H_2O \rightleftharpoons Lws+Qtz+CO_2$	13	Ni,72	4,7	310–390	0.0	–		
Ca–Mg–Si–C–O + H_2O								
$Cal+Ak \rightleftharpoons Mer+CO_2$	14	Zh,77	1	790–950	0.0–0.2	24		
$Fo+Di+Cal \rightleftharpoons Mtc+CO_2$	15	Zh,77	1	680–850	0.0–0.3	24		
pure CO_2		Wa,63a	0.1–0.5	720–880	–	25		
$Fo+Cal \rightleftharpoons Mtc+Per+CO_2$	16	Zh,77	1	730–930	0.0–0.2	24	(i)–	
pure CO_2		Wa,63b	0.1–0.7	750–900	–	25	i–	
$Di+Cal \rightleftharpoons Ak+CO_2$	17	Zh,77	1	740–880	0.1–0.4	24		
pure CO_2		Wa,63a	0.1–0.7	720–930	–	25		
$Qtz+Dol \rightleftharpoons Di+CO_2$	18	Sl,75	1,2	420–540	0.9	26		
		Ja&Ke,81b	5	570–580	0.7	26		
		Eg&Ke,81	6	600–630	0.8	26		
$Dol+Qtz+Tlc \rightleftharpoons Tr+CO_2$	19	Eg&Ke,81	6	480–560	0.1–0.2	26		
$Di+Dol \rightleftharpoons Fo+Cal+CO_2$	20	Ka&Me,80	1,3,5,10	530–870	0.9	26		

TABLE 2. CONTINUED

System or Equilibrium	No	Author	P [kbar]	T [°C]	X(CO_2)	B88	TD	P
Ca–Mg–Si–C–H–O								
Qtz+Tlc+Cal $\rightleftharpoons$ Tr+H_2O+CO_2	21	Sl,75	2	410–470	0.5	26		
Cal+Tr $\rightleftharpoons$ Dol+Di+H_2O+CO_2	22	Sl,75	5	640	0.5–0.8	26		
Dol+Tlc $\rightleftharpoons$ Fo+Di+H_2O+CO_2	23	Sk,71	1,2,2.6	500–590	0.7–0.8	26		
Cal+Qtz+Tlc $\rightleftharpoons$ Di+H_2O+CO_2	24	Sk,71	1,2,3	430–550	0.5–0.6	26		
Dol+Qtz+H_2O $\rightleftharpoons$ Cal+Tr+CO_2	25	Sl,75	2	460–500	0.8–0.9	27		
		Eg&Ke,81	6	490–600	0.1–0.7	27		
Cal+Qtz+Tr $\rightleftharpoons$ Di+H_2O+CO_2	26	Me,70	1,5	430–660	0.0–0.6	27	i+	S
		Sl,75	1,5	460–650	0.5–0.9	27		M
Dol+Tr $\rightleftharpoons$ Fo+Cal+H_2O+CO_2	27	Me,67,76	0.5,1	430–550	0.0–0.8	27	i+	
Cal+Tr $\rightleftharpoons$ Fo+Di+H_2O+CO_2	28	Ch&Be,86a	1	520–570	0.1–0.5	27		
Dol+Qtz+H_2O $\rightleftharpoons$ Cal+Tlc+CO_2	29	Me&Wi,63	2	440–510	0.3–0.9	–		
		Go&Gr,70	1,2	390–520	0.2–0.9	28	i+	
		Me&Pu,70,71	1,2,3,5	390–590	0.1–0.9	28	i(1)+	
		Sk,71	1,2	410–460	0.5–0.6	28	i(1)+	
		Eg&Ke,81	6	440–560	0.0–0.3	28		
Mg–Si–C–O + H_2O								
Mgs+En $\rightleftharpoons$ Fo+CO_2	30	Jo,69	2	560–580	0.9–1.0	35		
		El,79	26	1000–1180	0.3–1.0	–		
Mg–Si–C–H–O								
Mgs+Tlc $\rightleftharpoons$ Fo+H_2O+CO_2	31	Gr,67b	1,2	480–580	0.1–0.8	34	i*+	J
		Jo,69	0.5,1,2,4,7	470–670	0.1–0.7	34	i*±	G
Mgs+Qtz+H_2O $\rightleftharpoons$ Tlc+CO_2	32	Jo,69	1,2,4,7	330–620	0.0–0.9	34	i–	
Mgs+Tlc+H_2O $\rightleftharpoons$ Ctl+CO_2	33	Jo,69	1,2,4	330–480	0.0–0.1	35	(i)–	
Mgs+Ctl $\rightleftharpoons$ Fo+H_2O+CO_2	34	Jo,69	1,2,4	440–480	0.0–0.1	35		
Mgs+Ath $\rightleftharpoons$ En+H_2O+CO_2	35	Jo,69	2	530–560	0.9–1.0	35		
Mg–Al–Si–C–H–O								
Cal+Chl $\rightleftharpoons$ Di+Fo+Spl+H_2O+CO_2	36	Ch&Be,86a	1,2,4	550–690	0.1–0.7	33		
Dol+Chl $\rightleftharpoons$ Fo+Cal+Spl+H_2O+CO_2	37	Wk,80	1,2,3	540–620	0.7–0.8	33	i+	
		Ch&Be,86a	1,2	540–630	0.1–0.7	33		
Mgs+Chl $\rightleftharpoons$ Fo+Spl+H_2O+CO_2	38	Ch&Be,86b,89	1,2,3,4	530–670	0.2–0.7	34		
Na–Al–Si–H–O + CO_2								
Pg $\rightleftharpoons$ Ab+Crn+H_2O	39	Sv,83	1	460–510	0.1–0.4	40		
pure H_2O		Cj,70	1–7	520–670	–	37		
K–Al–Si–H–O + CO_2								
Ms+Qtz $\rightleftharpoons$ Sa+And+H_2O	40	Sv,83		450–510	0.2–0.5	40	i–	
pure H_2O		Ev,65	1–4	490–680	–	39		
		Ah,70	1–4	560–690	–	39		
		Ke,72	2	600–640	–	39		
		Cj&Jo,74	0.5–5	530–720	–	39		
K–Ca–Al–Si–C–H–O								
Cal+Ms+Qtz $\rightleftharpoons$ Sa+An+H_2O+CO_2	41	He,73	2,4,5,6,7	440–620	0.1–0.9	40		
Cal+Ms+Qtz $\rightleftharpoons$ Zo+Kfs+H_2O+CO_2	42	Jo&Or,72				–		

TABLE 2. CONTINUED

System or Equilibrium	No	Author	P [kbar]	T [°C]	X(CO_2)	B88	TD	PH
K–Mg–Al–Si–H–O + CO_2								
Phl+Qtz ⇌ En+Sa+H_2O	43	Bo,83	5	780–800	0.6–0.7	41		
pure H_2O		Wo,76	0.4–0.5	750–800	–	42	i–	WD
		Wn&Do,77	0.5	820–850	–	42	i–	W
K–Ca–Mg–Al–Si–C–H–O								
Phl+Qtz+Cal ⇌ Sa+Tr+H_2O+CO_2	44	Ho,73	2,4,6	500–650	0.1–0.7	41		
		He,75	2,4	450–520	0.6–0.7	41		
Dol+Kfs+H_2O ⇌ Phl+Cal+CO_2	45	Pu&Jo,74	2	420–540	0.1–0.9	41	(i)+	
		Pu,78	4,6	460–650	0.1–0.9	41	(i)+	
Ca–Ti–Si–C–O + H_2O								
Rt+Qtz+Cal ⇌ Ttn+CO_2	46	Ja&Ke,81b	2,6	420–620	0.1–0.8	45	i(2)+	

Key: Numbers in column 'No' are used in the text. Column 'B88' indicates the figure number of Berman (1988). Notation for column 'TD' which indicates the consistency with the thermodynamic data base of Berman (1988): inconsistent ('i'); slightly inconsistent, within uncertainties of the mineral properties or fluid properties ['(i)']; numbers in parentheses specify pressure at which inconsistencies are observed; experiments are at too high temperatures compared to Berman (1988) (+); experiments are at too low temperatures compared to Berman (1988) (–); includes revised magnesite properties of Mäder & Berman (1991) (*); Column 'PH' specifies inconsistencies amongst studies of the same equilibrium. The one–letter abbreviations key to the authors within the same group. Abbreviations for minerals are those of Kretz (1983). Abbreviations for authors: Allen & Fawcett 1982 (Al&Fa), Althaus *et al.* 1970 (Ah), Bohlen *et al.* 1983 (Bo), Chernosky & Berman 1986a, b, 1989, 1991 (Ch&Be), Chatterjee 1970 (Cj), Chatterjee & Johannes 1974 (Cj&Jo), Eggert & Kerrick 1981 (Eg&Ke), Eggler *et al.* 1979 (El), Evans 1975 (Ev), Gordon & Greenwood 1970, 1971 (Go&Gr), Greenwood 1967a, b (Gr), Harker & Tuttle 1956 (Ha&Tu), Hewitt 1973, 1975 (He), Hoschek 1973, 1974 (Ho), Jacobs & Kerrick 1981b (Ja&Ke), Johannes 1969 (Jo), Käse & Metz 1980 (Ka&Me), Kerrick 1972 (Ke), Kerrick & Ghent 1979 (Ke&Ge), Metz 1967, 1970, 1976 (Me), Metz & Puhan, 1970, 1971 (Me&Pu), Metz & Winkler 1963 (Me&Wi), Nitsch 1972 (Ni), Puhan 1978 (Pu), Puhan & Johannes 1974 (Pu&Jo), Shmulovich 1974, 1978 (Sh), Shvedenkov *et al.* 1983 (Sv), Skippen 1971 (Sk), Slaughter *et al.* 1975 (Sl), Storre & Nitsch 1972 (St&Ni), Walter 1963a, b (Wa), Widmark 1980 (Wk), Wones & Dodge 1977 (Wn & Do), Wood 1976 (Wo), Zharikov *et al.* 1977 (Zh), Ziegenbein & Johannes 1974 (Zi&Jo).

titanite suggested by Berman (1988), who could not fit the measurements at 2 kbar on equilibrium (46). Revised properties of magnesite (Trommsdorff & Connolly 1990, Mäder & Berman 1991) result in new inconsistencies with equilibria (37, 38) that were consistent with the Berman (1988) data-base. All these discrepancies cannot be explained solely by deviations of the properties of the fluid mixture from those computed from the Kerrick & Jacobs (1981) equation of state, and thus must reflect errors in experiments or thermodynamic data on the solid phases.

Slight inconsistencies that indicate possible negative deviations from ideal mixing in the fluid phase at temperatures above 750-800°C at 1 kbar pressure include brackets on equilibria in the Ca-Al-Si system (6, 7, 10, 11) and in the Ca-Mg-Si system (14, 15, 16). Consideration of the calcite I-IV transition at approximately 800°C will enhance these inconsistencies. Thermodynamic properties of the calcite polymorphs are not well constrained at present (Mäder & Berman 1991). Negative deviations from ideal mixing are consistent with Greenwood's (1969) measured negative volumes on mixing at 700 and 800°C (Fig. 7).

At temperatures below 430°C, where deviations from ideal mixing become most pronounced, constraints from phase-equilibrium data are not in accord. New data on the reaction calcite + andalusite + quartz ⇌ anorthite + CO_2 (3) (Chernosky & Berman 1991) seem to agree with the Kerrick & Jacobs (1981) equation, whereas data on dolomite + quartz ⇌ calcite + talc + CO_2 (29) demand more positive deviations from ideality. Data on reaction (32) cannot be reconciled with existing constraints on the minerals involved. The Kerrick & Jacobs (1981) equation appears to yield reasonable deviations from ideal mixing at these low temperatures. The equation cannot be utilized below 325°C for mathematical reasons.

CONCLUSIONS AND FUTURE WORK

I conclude that at present, insufficient experimental data and inadequate theoretical foundations are available on which to build a constrained empirical model that allows one to compute fugacities of H_2O–CO_2 mixtures over the range of pressure and temperature of interest to petrologists. The de Santis *et al.* (1974) correction for chemical association used by Holloway (1977) and Bowers & Helgeson (1983) is not supported by available experimental data. The Kerrick & Jacobs (1981) equation of state yields the most reasonable fugacity coefficients, even at temperatures as low as 350–400°C.

The existing body of data is sufficiently extensive that with some effort, the experimental data-base should be amenable to the proposed approach. The following problems or lack of data deserve particular attention.

P–V–T–X data

Inconsistensies among existing sets of *P–V–T–X* measurements must be resolved, and the range of pressure must be increased to at least 10 kbar by a complete series of *P–V–T–X* measurements, including pure H_2O and pure CO_2. A determination of the exact shape of the V_{excess} *versus P* hump below 2 kbar pressure is crucial.

Phase-equilibrium data

(a) Several inconsistencies amongst studies on phase-equilibria involving H_2O–CO_2 mixtures need to be resolved in order to permit refinement of thermophysical properties of solid phases, which will then provide better constraints on the fluid mixture.

(b) Phase-equilibria involving H_2O–CO_2 mixtures can be utilized to constrain deviations from ideal mixing where *P–V–T–X* data are not available.

(c) There are very few constraints from phase-equilibrium data on the activity of H_2O in a H_2O–CO_2 mixture.

Mineral properties

More extensive measurements are needed on heat capacity, expansivity, and compressibility of magnesite, calcite, brucite and talc.

Theoretical work

None of the equations of state available for fluid mixtures at higher pressures and temperatures are applicable to subgreenschist metamorphic conditions because they do not account for the two-phase region.

The concluding paragraphs are devoted to specific experimental projects that are aimed at constraining the mixing properties of the fluid phase and at improving on the thermodynamic data-base for solid phases.

5 magnesite + 1 talc ⇌ 4 forsterite + 1 H_2O + 5 CO_2

Experimental brackets by Greenwood (1967) and half-brackets by Johannes (1969) constrain the equilibrium position tightly at 1 and 2 kbar (Fig. 8), but are difficult to reconcile with the thermodynamic data-base of Berman (1988) and the revised enthalpy of magnesite (Mäder & Berman 1991). If these data are accurate, then some mineral properties must show temperature dependencies (*e.g.*, heat capacity, expansivity) that are very different from the Berman (1988) data-base, or the deviations from the Kerrick & Jacobs (1981) equation of state are larger than estimated at present. New brackets on this equilibrium would resolve these inconsistencies and place constraints on the deviation from ideal mixing in the fluid phase.

Equilibria involving margarite

This project would aim to provide constraints on the activity of H_2O in a H_2O–CO_2 mixture in a temperature range where deviations from ideality are expected to be significant (Fig. 9). Equilibria with margarite in pure H_2O have been studied by Jenkins (1984), Storre & Nitsch (1974), Nitsch *et al.* (1981), Chatterjee *et al.* (1984), and Chatterjee (1974). The two equilibria suitable for study in a fluid mixture are: 1 margarite + 1 quartz ⇌ 1

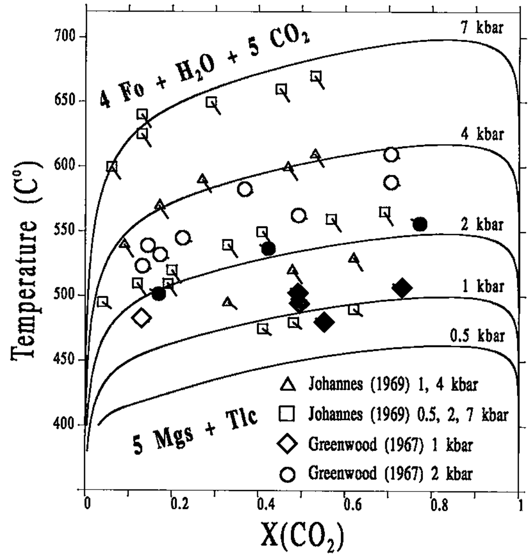

FIG. 8. Fluid composition *versus* temperature phase diagram of the equilibrium magnesite + talc = forsterite + H_2O + CO_2 at 0.5, 1, 2, 4 and 7 kbar. Filled symbols depict experimental charges with the reactant-stable phase assemblage, open symbols depict product-stable charges. Curves were computed with the Kerrick & Jacobs (1981) equation of state, the thermodynamic data of Berman (1988), and magnesite properties revised by Mäder & Berman (1991). See text for discussion of inconsistencies. The diagram was computed with GEØ-CALC (Brown *et al.* 1988).

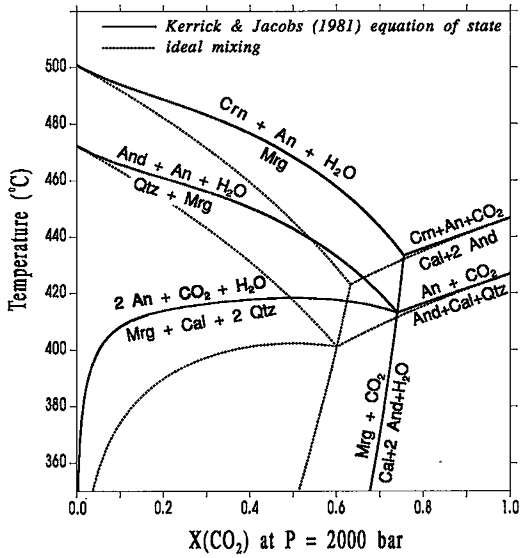

FIG. 9. Fluid composition *versus* temperature phase diagram of equilibria involving margarite, andalusite, corundum, quartz, anorthite, H_2O and CO_2 at 2 kbar pressure. The solid curves were computed with the Kerrick & Jacobs (1981) equation of state and thermodynamic data of Berman (1988). Dashed curves were computed assuming ideal mixing in the fluid phase. Reactions with zoisite or grossular that modify the diagram at very water-rich compositions are not shown. The diagram was produced with GEØ-CALC (Brown *et al.* 1988).

andalusite + 1 anorthite + 1 H_2O and 1 margarite ⇌ 1 anorthite + 1 corundum + 1 H_2O. The range accessible to experimentation at a fluid pressure of 2 kbar spans 400-500°C and $0.1 < X(CO_2) < 0.7$.

Equilibria at pressures greater than 15 kbar

Such studies, performed in a solid-media apparatus, would aim to constrain deviations from ideal mixing in the fluid phase at pressures not accessible by *P-V-T-X* measurements (*e.g.*, Eggler *et al.* 1979). The obvious disadvantages are the small volume of sample and the difficulty in controlling fluid composition, speciation in the fluid phase and diffusion of hydrogen at high temperatures. Because only the relative displacement from the equilibrium in the presence of the pure fluid is sought, some of the uncertainties arising from extrapolation of thermodynamic properties cancel. In order to resolve deviations from ideal mixing in the fluid phase, the best precision possible has to be achieved, which is about ±5 K for piston-cylinder work. Feasible studies include the reactions: 2 diaspore ⇌ corundum + H_2O (580°C at 20 kbar), forsterite + tremolite ⇌ 5 enstatite + 2 diopside + H_2O (650°C at 20 kbar), talc + forsterite ⇌ enstatite + H_2O (700°C at 20 kbar), talc ⇌ 3 enstatite + quartz + H_2O (800°C at 20 kbar), brucite ⇌ periclase + H_2O (950°C at 20 kbar), magnesite + quartz ⇌ enstatite + CO_2 (900°C at 20 kbar), magnesite + enstatite ⇌ forsterite + CO_2 (1100°C at 20 kbar), and calcite + quartz ⇌ wollastonite + CO_2 (1350°C at 20 kbar).

ACKNOWLEDGEMENTS

The author is indebted to Hugh J. Greenwood (University of British Columbia) and Robert G. Berman (Geological Survey of Canada) for support and advice during his Ph.D. research. Hugh also ensured completion of my Ph.D. on time by setting sail and venturing into new dimensions, exploring fluid properties. For that, and much more, I thank him. Financial support by NSERC to Greenwood (67-4222) and Berman (OGP 0037234) for part of this project is acknowledged. J.R. Holloway kindly supplied computer codes for the evaluation of his equation of state. The manuscript was improved at various stages by R.G. Berman, H.J. Greenwood and T.H. Brown. Terry Gordon provided stimulus by organizing an exciting "Greenwood Symposium" during the Vancouver 1989 GAC-MAC Annual Meeting. The comments made by E.L. Johnson, R.F. Martin and an anonymous reviewer were constructive and helpful.

REFERENCES

ALLEN, J.M. & FAWCETT, J.J. (1982): Zoisite - anorthite - calcite stability relations in H_2O-CO_2 fluids at 5000 bars: an experimental and SEM study. *J. Petrol.* **23**, 215-239.

ALTHAUS, E., KAROTKE, E., NITSCH, K.H. & WINKLER, H.G.F. (1970): An experimental re-examination of the upper stability of muscovite plus quartz. *Neues Jahrb. Mineral. Monatsh.*, 325-336.

ANDERSON, G.M. (1977): Fugacity, activity, and the equilibrium constant. *In* Application of Thermodynamics to Petrology and Ore Deposits (H.J. Greenwood, ed.). *Mineral. Assoc. Can., Short Course Handbook* **2**, 17-37.

BERMAN, R.G. (1988): Internally-consistent thermodynamic data for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-SiO_2-TiO_2-H_2O-CO_2. *J. Petrol.* **29**, 445-522.

______, ENGI, M., GREENWOOD, H.J. & BROWN, T.H. (1986): Deviation of internally-consistent thermodynamic data by the technique of mathematical programming, a review with application to the system MgO-SiO_2-H_2O. *J. Petrol.* **27**, 1331-1364.

BOHLEN, S.R., BOETTCHER, A.L., WALL, V.J. & CLEMENS, J.D. (1983): Stability of phlogopite - quartz and sanidine - quartz: a model for melting in the lower crust. *Contrib. Mineral. Petrol.* **83**, 270-277.

BOTTINGA, Y. & RICHET, P. (1981): High pressure and temperature equation of state and calculation of thermodynamic properties of gaseous carbon dioxide. *Am. J. Sci.* **281**, 615-660.

BOWERS, T.S. & HELGESON, H.C. (1983): Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system H_2O-CO_2-NaCl on phase relations in geologic systems: equation of state for H_2O-CO_2-NaCl fluids at high pressures and temperatures. *Geochim. Cosmochim. Acta* **27**, 1247-1275.

BRODHOLT, J. & WOOD, B. (1990): Molecular dynamics simulations of water at high temperatures and pressures. *Trans. Am. Geophys. Union (EOS)* **71**, 621 (abstr.).

BROWN, T.H., BERMAN, R.G. & PERKINS, E.H. (1988): GE0-CALC: software package for calculation and display of pressure - temperature - composition phase diagrams using an IBM or compatible personal computer. *Comp. Geosci.* **14**, 279-289.

BUCHER-NURMINEN, K. (1988): Metamorphism of ultramafic rocks in the central Scandinavian Caledonides. *Nor. Geol. Unders., Spec. Publ.* **3**, 86-95.

CARMICHAEL, D.M. (1991): Univariant mixed-volatile reactions: pressure - temperature phase diagrams and reaction isograds. *Can. Mineral.* **29**, 741-754.

CHATTERJEE, N.D. (1974): Synthesis and upper stability limit of 2*M*-margarite, $CaAl_2[Al_2Si_2O_{10}(OH)_2]$. *Schweiz. Mineral. Petrogr. Mitt.* **54**, 753-767.

______ (1970): Synthesis and upper stability of paragonite. *Contrib. Mineral. Petrol.* **27**, 244-257.

______ (1991): *Applied Mineralogical Thermodynamics: Selected Topics.* Springer-Verlag, Berlin.

______ & JOHANNES, W. (1974): Thermal stability and standard thermodynamic properties of synthetic 2*M*-muscovite, $KAl_2[AlSi_3O_{10}(OH)_2]$. *Contrib. Mineral. Petrol.* **48**, 89-114.

______, ______ & LEISTNER, H. (1984): The system CaO-Al_2O_3-SiO_2-H_2O: new phase equilibria data, some calculated phase relations, and their petrological applications. *Contrib. Mineral. Petrol.* **88**, 1-13.

CHERNOSKY, J.V. & BERMAN, R.G. (1986a): The stability of clinochlore in mixed volatile, H_2O-CO_2 fluid. *Trans. Am. Geophys. Union (EOS)* **67**, 407 (abstr.).

______ & ______ (1986b): Experimental reversal of the equilibrium: clinochlore + 2 magnesite = 3 forsterite + spinel + 2 CO_2 + 4 H_2O. *Trans. Am. Geophys. Union (EOS)* **67**, 1279 (abstr.).

______ & ______ (1989): Experimental reversal of the equilibrium: clinochlore + 2 magnesite = 3 forsterite + spinel + 2 CO_2 + 4 H_2O and revised thermodynamic properties for magnesite. *Am. J. Sci.* **289**, 249-266.

______ & ______ (1991): Experimental reversal of the equilibrium andalusite + calcite + quartz = anorthite + CO_2. *Can. Mineral.* **29**, 791-802.

CHOU, I-MING & CYGAN, R.J. (1990): Quantitative redox control and measurement in hydrothermal experiments. *In* Fluid-Mineral Interaction: A

Tribute to H.P. Eugster (R.J. Spencer & I-Ming Chou, eds.). *The Geochemical Soc., Spec. Publ.* **2**, 3-15.

______ & Williams, R.J. (1977): Activity of H_2O in CO_2–H_2O at 600°C and pressure to 8 kilobars. *Geol. Soc. Am., Abstr. Programs* **9**, 928.

______ & ______ (1979a): Activity of H_2O in supercritical CO_2–H_2O fluids. *Geol. Soc. Am., Abstr. Programs* **11**, 401.

______ & ______ (1979b): The activity of H_2O in supercritical fluids: H_2O–CO_2 at 600°C and 700°C at elevated pressures. *Proc. Xth Lunar Planet. Sci. Conf.*, 201-203.

Connolly, J.A.D. & Bodnar, R.J. (1983): A modified Redlich–Kwong equation of state for H_2O–CO_2 mixtures: application to fluid inclusion studies. *Trans. Am. Geophys. Union (EOS)* **64**, 350 (abstr.).

______ & Trommsdorff, V. (1991): Petrogenetic grids for metacarbonate rocks: pressure - temperature phase diagram projection for mixed-volatile systems. *Contrib. Mineral. Petrol.* **108**, 93-105.

Eggert, R.G. & Kerrick, D.M. (1981): Metamorphic equilibria in the siliceous dolomite system: 6 kbar experimental data and geologic implications. *Geochim. Cosmochim. Acta* **45**, 1039-1049.

Eggler, D.H., Kushiro, I. & Holloway, J.R. (1979): Free energies of decarbonation reactions at mantle pressures. I. Stability of the assemblage forsterite - enstatite - magnesite in the system MgO-SiO_2–CO_2–H_2O to 60 kbar. *Am. Mineral.* **64**, 288-293.

Eugster, H.P. & Skippen, G.B. (1967): Igneous and metamorphic reactions involving gas equilibria. *In* Researches in Geochemistry **2** (P.H. Abelson, ed.). John Wiley & Sons, New York (492-520).

Evans, B.W. (1965): Application of a reaction-rate method to the breakdown equilibria of muscovite and muscovite plus quartz. *Am. J. Sci.* **263**, 647-667.

Ferry, J.M. & Baumgartner, L. (1987): Thermodynamic models of molecular fluids at the elevated pressures and temperatures of crustal metamorphism. *In* Thermodynamic Modeling of Geological Materials: Minerals, Fluids and Melts (I.S.E. Carmichael & H.P. Eugster, eds.). *Rev. Mineral.* **17**, 323-365.

Flowers, G.C. (1979): Correction of Holloway's (1977) adaptation of the modified Redlich–Kwong equation of state for calculation of the fugacities of molecular species in supercritical fluids of geologic interest. *Contrib. Mineral. Petrol.* **69**, 315-318.

______ & Helgeson, H.C. (1983): Equilibrium and mass transfer during progressive metamorphism of siliceous dolomites. *Am. J. Sci.* **283**, 230-286.

Franck, E.U. (1981): Survey of selected non-thermodynamic properties and chemical phenomena of fluids and fluid mixtures. *In* Chemistry and Geochemistry of Solutions at High Temperature and Pressure (D.T. Rickard & F.E. Wickman, eds.). *Phys. Chem. Earth* **13-14**, 65-88.

______ & Tödheide, K. (1959): Thermische Eigenschaften überkritischer Mischungen von Kohlendioxyd und Wasser bis zu 750°C und 2000 atm. *Z. Phys. Chem., Neue Folge* **22**, 232-245.

Franks, F., ed. (1972-1984): *Water, a Comprehensive Treatise* (volumes 1-7). Plenum Press, New York.

Gehrig, M. (1980): *Phasengleichgewichte und PVT-Daten ternärer Mischungen aus Wasser, Kohlendioxid und Natriumchlorid bis 3 kbar und 550°C.* Dissertation, Hochschulverlag, Freiburg, Germany.

Gordon, T.M. & Greenwood, H.J. (1970): The reaction: dolomite + quartz + water = talc + calcite + carbon dioxide. *Am. J. Sci.* **268**, 225-242.

______ &______ (1971): The stability of grossularite in H_2O–CO_2 mixtures. *Am. Mineral.* **56**, 1674-1688.

Greenwood, H.J. (1961): The system $NaAlSi_2O_6$–H_2O–argon: total pressure and water pressure in metamorphism. *J. Geophys. Res.* **66**, 3923-3946.

______ (1967a): Wollastonite stability in H_2O–CO_2 mixtures and occurrence in a contact-metamorphic aureole near Salmo, British Columbia, Canada. *Am. Mineral.* **52**, 1669-1680.

______ (1967b): Mineral equilibria in the system MgO-SiO_2-H_2O-CO_2. *In* Researches in Geochemistry **2** (P.H. Abelson, ed.). John Wiley & Sons, New York (542-567).

______ (1969): The compressibility of gaseous mixtures of carbon dioxide and water between 0 and 500 bars pressure and 450° and 800°C. *Am. J. Sci.* **267-A**, 191-208.

______ (1973): Thermodynamic properties of gaseous mixtures of H_2O and CO_2 between 450°C and 800°C and 0 to 500 bars. *Am. J. Sci.* **273**, 561-571.

______ & Barnes, H.L. (1966): Binary mixtures of volatile components. *In* Handbook of Physical Constants (S.P. Clark, Jr., ed.). *Geol. Soc. Am., Mem.* **97**, 385-400.

Haar, L., Gallagher, J.S. & Kell, G.S. (1984): *NBS/NRC Steam Tables. Thermodynamic and*

Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units. Hemisphere Publishing Co., Washington, D.C.

Harker, R.I. & Tuttle, O.F. (1956): Experimental data on the P(CO_2)-T curve for the reaction: calcite + quartz ⇌ wollastonite + carbon dioxide. *Am. J. Sci.* **254**, 239-256.

Hewitt, D.A. (1973): Stability of the assemblage muscovite - calcite - quartz. *Am. Mineral.* **58**, 785-791.

______ (1975): Stability of the assemblage phlogopite - calcite - quartz. *Am. Mineral.* **60**, 391-397.

Holland, T.J.B. & Powell, R. (1990): An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: the system K_2O-Na_2O-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-TiO_2SiO_2-C-H_2-O_2. *J. Metamorph. Geol.* **8**, 89-124.

Holloway, J.R. (1977): Fugacity and activity of molecular species in supercritical fluids. *In* Thermodynamics in Geology (D.G. Fraser, ed.). D. Reidel, Dordrecht, Holland (161-181).

______ (1981): Compositions and volumes of supercritical fluids in the earth's crust. *In* Fluid Inclusions: Applications to Petrology (L.S. Hollister & M.L. Crawford, eds.). *Mineral. Assoc. Can., Short Course Handbook* **6**, 13-38.

______ (1987): Igneous fluids. *In* Thermodynamic Modeling of Geological Materials: Minerals, Fluids and Melts (I.S.E. Carmichael & H.P. Eugster, eds.). *Rev. Mineral.* **17**, 211-233.

Holser, W.T. & Kennedy, G.C. (1958): Properties of water. IV. Pressure - volume - temperature relations of water in the range 100-400°C and 100-1400 bars. *Am. J. Sci.* **256**, 744-753.

______ &______ (1959): Properties of water. V. Pressure - volume - temperature relations of water in the range 400-1000°C and 100-1400 bars. *Am. J. Sci.* **257**, 71-77.

Holzapfel, W. & Franck, E.U. (1966): Leitfähigkeit und Ionendissoziation des Wassers bei 1000°C und 100 kbar. *Berlin. Bunsenges. Phys. Chem.* **70**, 1105-1112.

Hoschek, G. (1973): Die Reaktion Phlogopit + Calcit + Quarz = Tremolit + Kalifeldspat + H_2O + CO_2. *Contrib. Mineral. Petrol.* **39**, 231-237.

______ (1974): Gehlenite stability in the system CaO-Al_2O_3-SiO_2-H_2O-CO_2. *Contrib. Mineral. Petrol.* **47**, 245-254.

Jacobs, G.K. & Kerrick, D.M. (1981a): APL and FORTRAN programs for a new equation of state for H_2O, CO_2 and their mixtures at supercritical conditions. *Comp. Geosci.* **7**, 131-143.

______ &______ (1981b): Devolatilization equilibria in H_2O-CO_2 and H_2O-CO_2-NaCl fluids: an experimental and thermodynamic evaluation at elevated pressures and temperatures. *Am. Mineral.* **66**, 1135-1153.

Jenkins, D.M. (1984): Upper-pressure stability of synthetic margarite plus quartz. *Contrib. Mineral. Petrol.* **88**, 332-339.

Johannes, W. (1969): An experimental investigation of the system MgO-SiO_2-H_2O-CO_2. *Am. J. Sci.* **267**, 1083-1104.

Johnson, J.W. & Norton, D. (1991): Critical phenomena in hydrothermal systems: state, thermodynamic, electrostatic, and transport properties of H_2O in the critical region. *Am. J. Sci.* **291**, 541-648.

Joyce, D.B. & Holloway, J.R. (1987): Activity - composition relations for H_2O in the system H_2O-CO_2-NaCl at high P and T by a new technique. *Trans. Am. Geophys. Union (EOS)* **68**, 450-451 (abstr.).

______ &______ (1989): Experimental activity coefficients for H_2O in H_2O-CO_2-NaCl fluids. *Trans. Am. Geophys. Union (EOS)* **70**, 495-496 (abstr.).

Käse, H.-R. & Metz, P. (1980): Experimental investigation of the metamorphism of siliceous dolomites. IV. Equilibrium data for the reaction: 1 Diopside + 3 Dolomite ⇌ 2 Forsterite + 4 Calcite + 2 CO_2. *Contrib. Mineral. Petrol.* **73**, 151-159.

Kennedy, G.C. (1954): Pressure - volume - temperature relations in CO_2 at elevated temperatures and pressures. *Am. J. Sci.* **252**, 225-241.

Kerrick, D.M. (1972): Experimental determination of muscovite + quartz stability with $P_{H2O} < P_{total}$. *Am. J. Sci.* **272**, 946-958.

______ & Ghent, E.D. (1979): P-T-X_{CO2} relations of equilibria in the system: CaO-Al_2O_3-SiO_2-CO_2-H_2O. *In* Problems in Physico-Chemical Petrology (V.A. Zakirov, V.I. Finarev & V.A. Korikovskii, eds.). *Academy of Sciences of the USSR* **2**, 32-52.

______ & 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. *Am. J. Sci.* **281**, 735-767.

Kretz, R. (1983): Symbols for rock-forming minerals. *Am. Mineral.* **68**, 277-279.

KRUSE, R. (1975): *Raman-Spektroskopische Untersuchungen and CO_2-H_2O Mischungen bis 490°C und 2500 bar.* Ph.D. thesis, Universität Karlsruhe, Karlsruhe, Germany.

MÄDER, U.K. & BERMAN, R.G. (1991): An equation of state for carbon dioxide to high pressure and temperature. *Am. Mineral.* **76**, 1547-1559.

MANNING, C.E. & BOHLEN, S.R. (1991): The reaction titanite + kyanite = anorthite + rutile and titanite - rutile barometry in eclogites. *Contrib. Mineral. Petrol.* **109**, 1-9.

METZ, P. (1967): Experimentelle Bildung von Forsterit und Calcit aus Tremolit und Dolomit. *Geochim. Cosmochim. Acta* **31**, 1517-1532.

______ (1970): Experimentelle Untersuchung der Metamorphose von kieselig dolomitischen Sedimenten. II. Die Bildungsbedingungen des Diopsids. *Contrib. Mineral. Petrol.* **28**, 221-250.

______ (1976): Experimental investigation of the metamorphism of siliceous dolomites. III. Equilibrium data for the reaction: 1 tremolite + 11 dolomite ⇌ 8 forsterite + 13 calcite + 9 CO_2 + 1 H_2O for the total pressures of 3000 and 5000 bars. *Contrib. Mineral. Petrol.* **58**, 137-148.

______ & PUHAN, D. (1970): Experimentelle Untersuchung der Metamorphose von kieselig dolomitischen Sedimenten. I. Die Gleichgewichtsdaten der Reaktion 3 Dolomit + 4 Quarz + 1 H_2O ⇌ 1 Talk + 3 Calcit + 3 CO_2 für die Gesamtgasdrucke von 1000, 3000 und 5000 Bar. *Contrib. Mineral. Petrol.* **26**, 302-314.

______ &______ (1971): Korrektur zur Arbeit "Experimental Untersuchung der Metamorphose von kieselig dolomitischen Sedimenten. I. Die Gleichgewichtsdaten der Reaktion 3 Dolomit + 4 Quarz + 1 H_2O ⇌ 1 Talk + 3 Calcit + 3 CO_2 für die Gesamtgasdrucke von 1000, 3000 und 5000 Bar". *Contrib. Mineral. Petrol.* **31**, 169-170.

______ & WINKLER, H.G.F. (1963): Experimentelle Gesteinsmetamorphose. VII. Die Bildung von Talc aus kieseligem Dolomit. *Geochim. Cosmochim. Acta* **27**, 431-457.

MITCHELL, A.C. & NELLIS, W.J. (1979): Water Hugoniot measurements in the range 30 to 220 GPa. *In* High Pressure Science and Technology. **1**. Physical Properties and Material Synthesis, 6th AIRAPT Conference (K.D. Timmerhaus & M.S. Barber, eds.). Plenum Press, New York (428-434).

NITSCH, K.-H. (1972): Das P-T-X_{CO2}-Stabilitätsfeld von Lawsonit. *Contrib. Mineral. Petrol.* **34**, 116-134.

______, STORRE, B. & TÖPFER, U. (1981): Experimentelle Bestimmung der Gleichgewichtsdaten der Reaktion 1 Margarit + 1 Quarz ⇌ 1 Anorthit + 1 Andalusit/Disthen + 1 H_2O. *Fortschr. Mineral.* **59**, 139-140.

POWELL, R. & HOLLAND, T.J.B. (1985): An internally consistent thermodynamic dataset with uncertainties and correlations. 1. Methods and a worked example. *J. Metamorph. Geol.* **3**, 327-342.

PRAUSNITZ, J.M., LICHTENTHALER, R.N. & DE AZEVEDO, E.G. (1986): *Molecular Thermodynamics of Fluid-Phase Equilibria* (2nd ed.). Prentice-Hall Inc., Englewood Cliffs, New Jersey.

PUHAN, D. (1978): Experimental study of the reaction: dolomite + K-feldspar + H_2O ⇌ phlogopite + calcite + CO_2 at the total gas pressure of 4000 and 6000 bars. *Neues Jahrb. Mineral. Monatsh.*, 110-127.

______ & JOHANNES, W. (1974): Experimentelle Untersuchung der Reaktion Dolomit + Kalifeldspat + H_2O ⇌ Phlogopit + Calcit + CO_2. Ein Methodenvergleich. *Contrib. Mineral. Petrol.* **48**, 23-31.

READ, A.J. (1975): The first ionization constant of carbonic acid from 25 to 250°C and to 2000 bar. *J. Sol. Chem.* **4**, 53-70.

REDLICH, O. & KWONG, J.N.S. (1949): On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions. *Chem. Rev.* **44**, 233-244.

RYZHENKO, B.N. & VOLKOV, V.P. (1971): Fugacity coefficients of some gases in a broad range of temperatures and pressures. *Geochem. Internat.* **8**, 468-481.

DE SANTIS, R., BREEDVELD, G.J.F. & PRAUSNITZ, J.M. (1974): Thermodynamic properties of aqueous gas mixtures at advanced pressures. *Indust. Eng. Chem. Proc. Des. Devel.* **13**, 374-377.

SAXENA, S.K. & FEI, Y. (1987): Fluids at crustal pressure and temperatures. I. Pure species. *Contrib. Mineral. Petrol.* **95**, 370-375.

SHMONOV, V.M. & SHMULOVICH, K.I. (1974): Molal volumes and equation of state of CO_2 at temperatures from 100-1000°C and pressures from 2000-10000 bars. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **217**, 206-209.

SMULOVICH, K.I. (1974): Phase equilibria in the system CaO-Al_2O_3-SiO_2-CO_2. *Geochem. Intern.* **11**(4), 883-887.

______ (1978): Stability limits of grossular and wollastonite in the H_2O-CO_2 system up to 6 kbar. *Geochem. Intern.* **14**(6), 126-133.

______ & Kotova, N.P. (1980): Influence of electrolytes on the activity of CO_2 in supercritical aqueous solutions. *Dokl. Akad. Nauk SSSR* **253**, 952-956 (in Russ.).

______, Shmonov, V.M., Mazur, V.A. & Kalinichev, A.G. (1980): P–V–T and activity concentration relations in the H_2O–CO_2 system (homogeneous solutions). *Geochem. Intern.* **17**(6), 123-139.

______, ______ & Zhakirov, I.V. (1979): P–V–T measurements in hydrous systems at high pressure and temperature. *In* Experimental Research Methods for Hydrothermal Solutions (A.A. Godikov, ed.). Nauka, Novosibirsk (81-89) (in Russ.).

Shvedenkov, G.Y., Shvedenkova, S.V., Dashevskii, Y.A. & Kalinin, D.V. (1983): Phase equilibria in the sytem containing muscovite, paragonite, alkaline feldspars, H_2O. and CO_2. *Sov. Geol. Geophys.* **24**, 428-436.

Skippen, G.B. (1971): Experimental data for reactions in siliceous marbles. *J. Geol.* **79**, 457-481.

______ & Carmichael, D.M. (1977): Mixed-volatile equilibria. *In* Application of Thermodynamics to Petrology and Ore Deposits (H.J. Greenwood, ed.). *Mineral. Assoc. Canada, Short Course Handbook* **2**, 109-125.

______ & Marshall, D.D. (1991): The metamorphism of granulites and devolatilization of the lithosphere. *Can. Mineral.* **29**, 693-705.

Slaughter, J., Kerrick, D.M. & Wall, V.J. (1975): Experimental and thermodynamic study of equilibria in the system CaO-MgO-SiO_2-H_2O-CO_2. *Am. J. Sci.* **275**, 143-162.

Spycher, N.F. & Reed, M.H. (1988): Fugacity coefficients of H_2, CO_2, CH_4, H_2O and of H_2O-CO_2-CH_4 mixtures: a virial equation treatment for moderate pressures and temperatures applicable to calculations of hydrothermal boiling. *Geochim. Cosmochim. Acta* **52**, 739-749.

Sterner, S.M. & Bodner, 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. *Am. J. Sci.* **291**, 1-54.

Storre, B. & Nitsch, K.-H. (1972): Die Reaktion 2 Zoisit + 1 $CO_2 \rightleftharpoons$ 3 Anorthit + 1 Calcit + 1 H_2O. *Contrib. Mineral. Petrol.* **35**, 1-10.

______ & ______ (1974): Zur Stabilität von Margarit im System CaO-Al_2O_3-SiO_2-H_2O. *Contrib. Mineral. Petrol.* **43**, 1-24.

Takenouchi, S. & Kennedy, G.C. (1964): The binary system H_2O-CO_2 at high temperatures and pressures. *Am. J. Sci.* **262**, 1055-1074.

Tödheide, K. (1972): Water at high temperatures and pressures. *In* Water, a Comprehensive Treatise. **I**. The Physics and Physical Chemistry of Water (F. Franks, ed.). Plenum Press, New York (463-514).

______ & Franck, E.U. (1963): Das Zweiphasengebiet und die kritische Kurve im System Kohlendioxid-Wasser bis zu Drucken von 3500 bar. *Z. Phys. Chem., Neue Folge* **37**, 387-401.

Trommsdorff, V. (1972): Change in T-X during metamorphism of siliceous dolomitic rocks of the Central Alps. *Schweiz. Mineral. Petrogr. Mitt.* **52**, 567-571.

______ & Connolly, J.A.D. (1990): Constraints on phase diagram topology for the system CaO–MgO–SiO_2–CO_2–H_2O. *Contrib. Mineral. Petrol.* **104**, 1-7.

______ & Evans, B.W. (1974): Alpine metamorphism of peridotitic rocks. *Schweiz. Mineral. Petrogr. Mitt.* **54**, 333-352.

Ulmer, P. & Luth, R.W. (1991): The graphite–COH fluid equilibrium in P, T, f_{O2} space. An experimental determination to 30 kbar and 1600°C. *Contrib. Mineral. Petrol.* **106**, 265-272.

Walter, L.S. (1963a): Experimental studies on Bowen's decarbonation series. I. P–T univariant equilibria of the "monticellite" and "akermanite" reactions. *Am. J. Sci.* **261**, 488-500.

______ (1963b): Experimental studies on Bowen's decarbonation series. II. P–T univariant equilibria of the reaction: forsterite + calcite = monticellite + periclase + CO_2. *Am. J. Sci.* **261**, 773-779.

______ (1963c): Data on the fugacity of CO_2 in mixtures of CO_2 and H_2O. *Am. J. Sci.* **261**, 151-156.

Widmark, E.T. (1980): The reaction chlorite + dolomite = spinel + forsterite + calcite + carbon dioxide + water. *Contrib. Mineral. Petrol.* **72**, 175-179.

Wones, D.R. & Dodge, F.C.W. (1977): The stability of phlogopite in the presence of quartz and diopside. *In* Thermodynamics in Geology (D.G. Fraser, ed.). D. Reidel, Dordrecht, Holland (229-247).

Wood, B.J. (1976): The reaction phlogopite + quartz = enstatite + sanidine + H_2O. *Progr. Exp. Petrol. Nat. Environ. Res. Council* **11**, 17-19.

______ & Fraser, D.G. (1977): *Elementary Thermodynamics for Geologists.* Oxford University Press, Oxford, U.K.

ZHARIKOV, V.A., SHMULOVICH, K.I. & BULATOV, V.K. (1977): Experimental studies in the system CaO–MgO–Al_2O_3–SiO_2–CO_2–H_2O and conditions of high temperature metamorphism. *Tectonophys.* **43**, 145-162.

_____ & _____ (1982): Activities of CO_2 in supercritical CO_2–H_2O mixtures, derived from high-pressure mineral equilibrium data. *In* High-Pressure Researches in Geoscience (W. Schreyer, ed.). E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, Germany (493-500).

ZIEGENBEIN, D. & JOHANNES, W. (1974): Wollastonitbildung aus Quarz und Calcit bei Pf = 2, 4 und 6 kb. *Fortschr. Mineral.* **44**, 77-79.

Received January 4, 1991, revised manuscript accepted September 7, 1991.