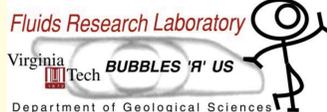


A Modified Redlich-Kwong Equation of State for H₂O-CO₂ Mixtures: Application to Fluid Inclusion Studies



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1. Introduction

The interpretation of H₂O-CO₂ fluid inclusions requires knowledge of the volumetric behaviour of such fluids on their solvus (i.e., at Th), and up to the PT trapping conditions for the inclusion. PVTX properties of H₂O-CO₂ fluids can be predicted from experimental data and/or equations of state (EOS). Our goal in this study has been to predict the PVTX properties of H₂O-CO₂ fluids both on their solvus and over as much of the geologically important PT region as is reasonable. These calculated values are then used to predict various properties of H₂O-CO₂ fluid inclusions, including total inclusion density, room temperature phase ratios, internal pressures, CO₂ homogenization temperatures and densities, melting temperatures of the CO₂ clathrate, pressure corrections and the effects of heterogeneous fluid entrapment.

2. The Modified Redlich-Kwong Equation of State for H₂O-CO₂

The modified Redlich-Kwong (MRK) equation has the form:

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)\sqrt{T}}$$

where *a* and *b* are parameters which are related to intermolecular forces. While the values of *a* and *b* can be evaluated from the critical data for pure fluids, the prediction of the corresponding terms for fluid mixtures requires some mixing rules. Redlich and Kwong retained the mixing rules originally used by Van der Waals, which for H₂O-CO₂ are:

$$a = \sum_i \sum_j X_i X_j a_{ij}$$

and

$$b = \sum_i X_i b_i$$

The *a_{ij}* "cross term" is calculated in our model from the equation of de Santis et al. (1974),

$$a_{ij} = (a_i^o a_j^o)^{1/2} + 0.5R^2 T^{5/2} K_{ij}$$

where *a_i^o* is a constant for each component. The values of the *a_i* parameters for H₂O and CO₂ are determined from EOS of the pure components using the equation of Haar et al. (1984) for the H₂O component, and that of Bottinga and Richet (1981) for the CO₂ component. The *b* values and *a_i^o* values used for the H₂O and CO₂ components are those given by de Santis et al. (1974). The *K_{ij}* term was fitted to an empirical equation:

$$K_{H_2O-CO_2} (bar^{-1}) = 82.3184 \times 10^{-4} - 16.929 \times 10^{-4} (T/10^2) + 9.0256 \times 10^{-5} (T/10^2)^2$$

The model is applicable over the PT range of validity of the two EOS for the endmember components. The EOS of Haar et al. (1984) is valid in the range T = 0-900°C, and P = 0-9 kbar; the EOS of Bottinga and Richet (1981) is valid over the range T = -50-1000°C and P = 0-8 kbar. The wide range of applicability of these EOS provides the advantage to this mixed system EOS, that it is applicable in the lower-T region, in particular at and below the H₂O critical point. The equation predicts PVT properties of fluids with a composition from 0-100 mole % CO₂.

The MRK EOS reproduces the general "shape" of the H₂O-CO₂ solvus, but does not accurately reproduce the PT conditions on the solvus. In comparison, the equation of Duan et al. (1995) and that of Paulus and Penoncello (2006) provide more accurate prediction of the PT conditions on the H₂O-CO₂ solvus. However, the MRK is computationally much simpler, and the coefficients for *K_{ij}* are the only adjustable parameters fit in this study.

The MRK EOS is used to compute fluid density on the solvus using known PTX conditions. Thus, the input data required for a typical calculation using the model presented here are the X_{CO₂} and the temperature and pressure on the solvus.

The X_{CO₂} of the fluid inclusion may be obtained using Raman analysis or room temperature phase relations. The temperature on the solvus may be obtained from the fluid inclusion homogenization temperature; the pressure may be obtained either from experimental data or an EOS (e.g., Duan et al., 1995). The isochores calculated by the MRK EOS are reasonably well-behaved and do not produce anomalous curvature at high temperature and/or pressure (Fig. 1). In addition to producing isochores, fluid density on the solvus is used in constant-volume mass-balance calculations to determine the room temperature phase ratios (Fig. 2), the CO₂ homogenization temperature (Fig. 3) and the clathrate melting temperature (Fig. 4).

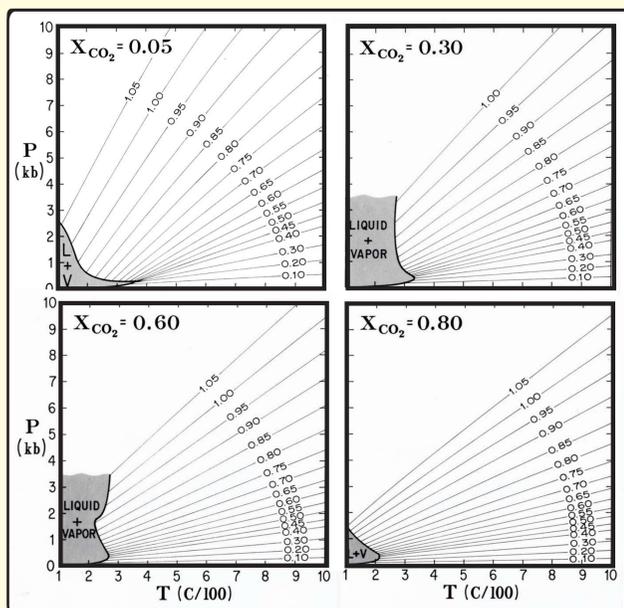


Fig. 1. Isochores of H₂O-CO₂ fluid inclusions for selected compositions, calculated using the equation of state developed in this study. Values on each isochore are densities in g/cm³. The boundary between the one-phase field and the two-phase (L+V) field is from Takenouchi and Kennedy (1964).

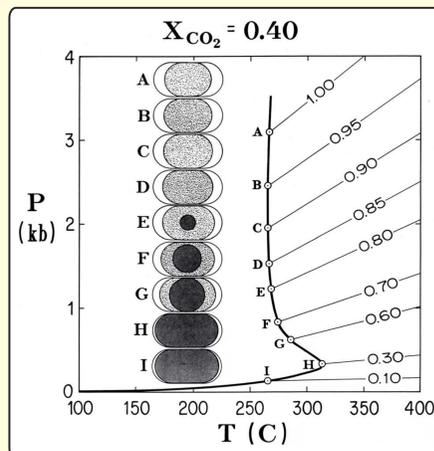
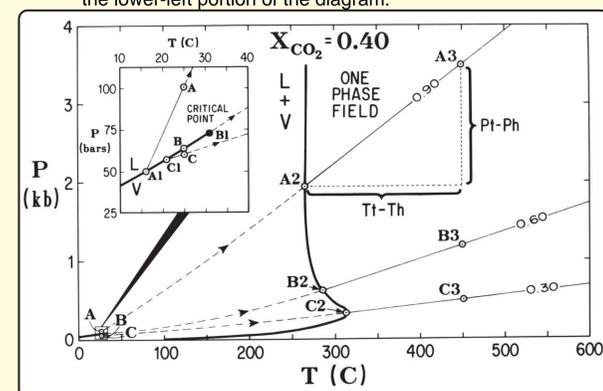


Fig. 2. (Left) Calculated phase ratios at 25°C of nine H₂O-CO₂ fluid inclusions, all having a composition of 40 mole percent CO₂, but with different temperatures and pressures of homogenization (points A-I along solvus). Inclusion densities (g/cm³) calculated from the MRK developed in this study are shown on the isochores originating at the temperature and pressure of homogenization. The clear area represents the liquid H₂O-rich phase, the stippled area represents liquid CO₂ and the shaded area represents CO₂ vapor. Solvus is from Takenouchi and Kennedy (1964).

Fig. 3. (Below) Schematic PT paths followed by three H₂O-CO₂ fluid inclusions when heated from 25°C (points A, B, C) to the homogenization temperature (points A2, B2, B3). Also shown are the calculated trapping pressures (points A3, B3, C3) of these three inclusions, assuming a common trapping temperature of 450°C. Inset shows an enlargement of the lower-left portion of the diagram.



3. Applications to Fluid Inclusion Studies

Fluid inclusion density is calculated using the MRK EOS from the known composition and solvus PT conditions. The PT projection of this density from the point of intersection of the solvus into the one-phase field defines the isochore used for pressure determinations (Fig. 1), and this density may also be used at any other PT conditions, such as room temperature, to calculate phase relations and temperatures and pressures of various other phase changes.

Fluid inclusion pressure corrections are determined using an inferred trapping temperature and extrapolating the isochore to that temperature to estimate the trapping pressure (Fig. 3).

To determine low temperature phase relations, the procedure employed in the model is to determine the internal pressure at which the constant-volume mass-balance requirement is satisfied. The molar proportions (amounts) of H₂O and CO₂ in the inclusion are known from the fluid inclusion composition, and for any pressure and temperature the amount of CO₂ dissolved in the H₂O-rich phase is known from the relationship of Dodds et al. (1956), and the volume of that phase is determined from the data of Parkinson and de Nevers (1969). The remaining volume is occupied by the CO₂ not dissolved in the aqueous phase ("free" CO₂), and thus the density of "free" CO₂ is known, which in turn determines whether the CO₂ is liquid, vapor or liquid+vapor. This treatment allows the prediction of room temperature phase ratios for any composition and trapping conditions (Fig. 2). It also allows determination of the temperature of homogenization of the CO₂ phases via intersection of the isochore corresponding to the density of "free" CO₂ and the internal pressure with the CO₂ liquid-vapor curve (Fig. 3), and determination of clathrate melting temperature via intersection of the same isochore with the clathrate phase boundary (Fig. 4). In this way, the density and homogenization temperature for fluid inclusions that decrepitate before homogenization may be estimated based on the temperature of homogenization of the CO₂ phases. In addition, homogenization temperatures and other characteristics of heterogeneously entrapped fluid inclusions can be determined from the mixing ratios of the immiscible fluid pair by the reverse procedure.

3. Summary The model developed in this study employs a modified Redlich-Kwong EOS to determine H₂O-CO₂ fluid inclusion densities at and above the solvus. Isochores originating at the temperature and pressure of homogenization and extending into the single-phase field can be calculated using this model, and can also be used to determine pressure corrections. Low-temperature phase relations can be predicted based on the fluid inclusion density determined on the solvus. An executable Fortran program implementing the EOS will be available for download at the Fluids Research Laboratory webpage, <http://www.geochem.geos.vt.edu/fluids/> in early 2010.

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