A Modified Redlich-Kwong Equation of State for H$_2$O-CO$_2$ Mixtures: Application to Fluid Inclusion Studies

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1. Introduction

The interpretation of H$_2$O-CO$_2$ 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. PV/TX properties of H$_2$O-CO$_2$ fluids can be predicted from experimental data and/or equations of state (EOS). Our goal in this study has been to predict the PV/TX properties of H$_2$O-CO$_2$ 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 H$_2$O-CO$_2$ fluid inclusions, including their solvus and over as much of the geologically important PT region as is reasonable. These melting temperature (Fig. 4).

6. 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 H$_2$O and CO$_2$ in the inclusion are known from the fluid inclusion composition, and for any pressure and temperature the amount of CO$_2$ dissolved in the H$_2$O-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 CO$_2$ not dissolved in the aqueous phase ("free" CO$_2"), and thus the density of "free" CO$_2" is known, which in turn determines whether the CO$_2" is liquid, vapor or liquid-vapor. This treatment allows the prediction of room temperature phase ratios for any composition and trapping conditions (Fig. 2). It also allows determination of the temperature of homogenization of the CO$_2" phases via intersection of the isochore corresponding to the density of "free" CO$_2" and the internal pressure with the CO$_2" 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 deprecate before homogenization may be estimated based on the temperature of homogenization of the CO$_2" 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 H$_2$O-CO$_2$ fluid inclusion densities at and above the solvus. Isotherms 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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References


Appendix A: Details of the calculations performed for the model developed in this study. Values on each isochore are densities in g/cm$^3$. The boundary between the one-phase field and the two-phase (L+V) field is from Takanouchi and Kennedy (1964).