

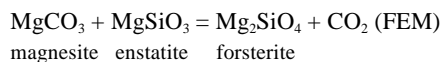
Experimental determination of CO₂-H₂O activity-composition relations at 600–1000 °C and 6–14 kbar by reversed decarbonation and dehydration reactions

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ABSTRACT

Activity-composition relations in CO₂-H₂O solutions were determined at 6, 10, and 14 kbar over broad temperature-fluid composition ranges from 70 reversed determinations of three simple-system decarbonation and dehydration reactions:



Brackets of WQC and FEM were achieved by reversing, at constant T and P , the fluid composition coexisting with the assemblages of either reaction, starting with fine-grained mixtures of reactants and products in nearly equimolar amounts and liquid water, oxalic acid, and silver oxalate as fluid sources. Brackets of TEQ were secured by reversing the reaction over narrow temperature intervals at constant P and fluid composition. All experiments were made in the piston-cylinder apparatus with NaCl or NaCl-soft glass pressure media, and all experiments with two-component fluids were buffered at hematite-magnetite. Closure intervals of reversed fluid composition averaged less than 2 mol% CO₂. Activity values of H₂O (1) and CO₂ (2) were retrieved based on the THERMOCALC 2.3 thermodynamic data set of Holland and Powell (1994), which includes equations of state of H₂O and CO₂, supplemented by several tight reversals of the end-member equilibria. A simple van Laar-type expression reproduces our composition determinations with a standard deviation of only 1.2 mol% CO₂:

$$RT \ln \gamma_1 = (X_2)^2 W \left\{ V_1^0 V_2^0 / [(V_1^0 + V_2^0)(X_1 V_1^0 + X_2 V_2^0)^2] \right\}$$

$$RT \ln \gamma_2 = (X_1)^2 W \left\{ V_2^0 V_1^0 / [(V_1^0 + V_2^0)(X_1 V_1^0 + X_2 V_2^0)^2] \right\}$$

where V_1^0 and V_2^0 are, respectively, the specific volumes of pure H₂O and CO₂ at a given (P, T), the X 's are the mole fractions, the γ 's the activity coefficients and W is analogous to a regular solution parameter: $W = (A + BT)[1 - \exp(-20P)] + CPT$, with T in K and P in kbar. The best-fit values of the constants are: $A = 12893$ J, $B = -6.501$ J/K, $C = 1.0112$ J/(K·kbar). With these formulas, the activity-concentration relations of CO₂-H₂O solutions may be reconstructed in a broad P - T - X range using any reasonably accurate equations of state of pure CO₂ and H₂O. The activity-concentration relations are closely similar to the modified Redlich-Kwong (MRK) reconstruction of Kerrick and Jacobs (1981) to pressures of 6 kbar, but the binary fluids have marginally greater positive non-ideality than the MRK predictions at 10 kbar and significantly greater non-ideality at 14 kbar. The present results can serve as a basis for reliable calculations of mineral-fluid equilibria in metamorphism of the deep crust and upper mantle.