American Mineralogist, Volume 84, pages 1319–1332, 1999

Experimental determination of CO_2-H_2O activity-composition relations at 600–1000 °C and 6–14 kbar by reversed decarbonation and dehydration reactions

L.Y. ARANOVICH AND R.C. NEWTON*

Department of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Avenue, Chicago, Illinois 60637, U.S.A.

ABSTRACT

Activity-composition relations in CO_2-H_2O 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:

$CaCO_3 + SiO_2 = CaSiO_3 + CO_2$ (WQC)
calcite quartz wollastonite

$MgCO_3 + MgSiO_3 = Mg_2SiO_4 + CO_2$ (FEM)
magnesite enstatite forsterite

$Mg_3Si_4O_{10}(OH)_2 = 3\ MgSiO_3 + SiO_2 + H_2O$ (TEQ)
talc enstatite quartz

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% CO_2. Activity values of H_2O (1) and CO_2 (2) were retrieved based on the THERMOCALC 2.3 thermodynamic data set of Holland and Powell (1994), which includes equations of state of H_2O and CO_2, 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% CO_2:

$$\mathrm{R}T\ \ln\gamma_1 = (X_2)^2 \mathrm{W}\{V_1^0 V_2^{0^2}/[(V_1^0+V_2^0)(X_1V_1^0+X_2V_2^0)^2]\}$$

$$\mathrm{R}T\ \ln\gamma_2 = (X_1)^2 \mathrm{W}\{V_2^0 V_1^{0^2}/[(V_1^0+V_2^0)(X_1V_1^0+X_2V_2^0)^2]\}$$

where V_1^0 and V_2^0 are, respectively, the specific volumes of pure H_2O and CO_2 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: $W = (\mathrm{A}+\mathrm{B}T)[1-\exp(-20P)] + \mathrm{C}PT$, 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 CO_2-H_2O solutions may be reconstructed in a broad P-T-X range using any reasonably accurate equations of state of pure CO_2 and H_2O. 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.