THE ACTIVITY OF H₂O IN SUPERCRITICAL FLUIDS: H₂O-CO₂ AT 600° AND
700°C AT ELEVATED PRESSURES. I-Ming Chou, Lockheed Electronics Co., Inc.,
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Water and carbon dioxide interact strongly with natural silicates and
oxides, particularly at the high pressures and temperatures characteristic of
igneous and metamorphic processes; these interactions may control the composi-
tions of the atmospheres of terrestrial planets, and certainly they affect
the stability of many minerals and the melting relations of rocks. Although
many studies have been done with the pure-fluids, relatively little data are
available on the mixing properties of H₂O and CO₂ under planetologically
interesting conditions.

For the binary system CO₂-H₂O, the critical curve has been determined up
to pressures of 3500 bars (1,2), and the P-V-T relations have been studied
between 300 and 2000 bars at temperatures between 400° and 750°C by Frank and
Tödheide (3) and from 1 to 500 bars between 450 and 800°C by Greenwood (4).
There is almost no experimental data at 2000 bars (only two data points from
(3)) and at higher pressures. In this study, the hydrogen fugacity sensor
technique (5,6) was employed to determine the hydrogen fugacity in CO₂-H₂O
mixtures for the redox conditions of the nickle-nickle oxide buffer at 700°C,
2 kbars and at 600°C, between 2 and 8 kbars; it is an extention of our pre-
vious work (7) at 600°C to other pressures and temperatures.

The experimental set-up and procedures as well as the starting materials
of the present work were identical to those used earlier (6). Experiments at
600°C and 2 to 8 kbars were performed using internally-heated pressure vessels
which permitted six samples with different fluid compositions in their outer
systems to be exposed at the same P-T conditions. All the runs at 700°C, 2
kbars and some of the runs at 600°C, 2 kbars were performed using conventional
20 cm cold-seal pressure vessels. The duration of the runs ranges from 1 to
4 days. After quench, the compositions of the H₂O-CO₂ gas mixtures were
determined by the weight losses of the capsules first after puncturing and
then after drying. The Cl⁻ concentrations in the sensors were measured
coulometrically on a digital chloridometer. In experiments for which the
temperature, total pressure, and oxygen fugacity are the same, the square of
the ratio of the quenched Cl⁻ concentration in a system with a mixed fluid
to that in a system with pure H₂O is the activity of H₂O. It is interesting
to note that any possible systematic errors involved in the measurements of
intensive parameters, such as P, T and (mCl⁻) lead to cancel, and that the
uncertainties associated with the aH₂O measurements are smaller in the CO₂-
rich fluids than those in the H₂O-rich fluids.

Fig. 1 shows the visual fit of the data at 600°C and 2-8 kbars; data at 2
kbars and 700°C are shown in Fig. 2. The directions of approach to equilibrium
for the two hydrogen sensors in each run are indicated by y.
. At 600°C and 2
kbars data obtained using internally-heated pressure vessels and cold-seal
pressure vessels agree well with each other. For the H₂O-rich fluids at 2 to 4
kbars, the results indicate a strong negative deviation from ideality which
has not been predicted; the deviations from ideality became progressively more
positive as the total pressure increases. At least at 2 kbars, the activity
relations are not strongly temperature dependent (compare Figs. 1 and 2). The
solid curve (Fig. 2) is the visual fit of the data and the dashed curve is
calculated from the modified Redlick-Kwong equation (8). It is apparent that
for water-rich mixtures the modified Redlick-Kwong equation is not an accurate
representation of the experimental data. Fig. 3 is the activity of CO₂ as a
function of mole fraction of water obtained from the binary Gibbs-Duhem

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relations. Throughout the whole range of compositions and pressures, there is a strong positive deviation from ideality.

Such strong deviations from ideality can only be the result of strong molecular interactions between the components of the fluid. However, thermodynamic calculations (9) indicate that under the P-T-fO₂ conditions of this study only H₂O and CO₂ are present in significant concentrations, but of course, such calculations are predictive only for species included in the calculations in the first place. If equilibrium between the fluid and sensors is reached, the measured H₂O activities are independent of the problem of speciation on the fluid phase; the speciation is only important when the H₂O activity is to be related to a bulk composition.

This non-ideal behavior of CO₂-H₂O mixtures will significantly effect dehydration and decarbonation equilibria. As an example, the stability limit of muscovite in an ideal CO₂-H₂O fluid is compared with that in actual fluids (data from this study, 9, and 10) in Fig. 4. Small amounts of CO₂ have a large destabilizing effect on hydrated minerals in planetary crusts.


Figure 1. Activity of H₂O for CO₂-H₂O mixtures at 600°C and 2, 4, 6, and 8 kilobars. The curves are visual fits to the data. The data points have been omitted for clarity.
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Figure 2. Activity of H₂O in CO₂–H₂O mixtures at 700°C and 2 kilobars. The upward and downward pointing arrowheads are the results from the two capsules which comprise the hydrogen sensor assembly. The direction of the arrowhead indicates the direction of approach to equilibrium. The dashed curve is the activity-composition relations predicted by the modified Redlich-Kwong equation (9).

Figure 3. The activity of carbon dioxide in CO₂–H₂O mixtures at 600°C and 2 and 8 kilobars, obtained from graphical integration of the binary Gibbs-Duhem and the relations in Figure 1.

Figure 4. Calculate effect of CO₂–H₂O mixing relations on the reaction, muscovite = sanidine + corundum + H₂O (10). The dashed curves-labeled X₁H₂O = 0.7, 0.8, 0.9 – are calculated assuming ideal mixing and the data of Robie, et al. (8). Solid curve-labeled X₁H₂O = 0.9 – is the calculated breakdown conditions for a constant fluid composition using the experimentally determined activity-composition relations.