



Institut des Sciences de la Terre de Paris
ISTeP
UMR 7193 . UPMC - CNRS



UPMC
SORBONNE UNIVERSITÉS

Quartz solubility in H₂O-CO₂ fluids as function of H₂O density

Marie-Lola PASCAL

ISTEP, CNRS UMR-7193, UPMC, 4 Place Jussieu, 75252 Paris Cedex, France

marie-lola.pascal@upmc.fr

1. Introduction

The conventional approach to mineral solubilities and, more generally, equilibria involving dissolved species is based on equilibrium constants that depend on both pressure and temperature. For instance, dissociation of HCl is expressed by $\frac{a_{H^+} a_{Cl^-}}{a_{HCl}} = K(T, P)$. This approach combined with e.o.s. for minerals and aqueous species (e.g., the HKF model) is currently used for modelling aqueous solutions with $\rho_{H_2O} > 0.3$, i.e., neither high temperature, low pressure fluids nor gas-rich (in particular CO₂) fluids, such as volcanic gases or deep crust fluids. An alternative approach, devoid of these limitations, has been developed by Marshall and coworkers [1, 2], based on the concept of "complete" equilibrium constant, that involves the concentrations, in volume units, of all reactants including the solvent. Such constants only depend on temperature. They are independent of pressure and of the presence of non-solvating gases such as CO₂. In aqueous solutions, the solvent concentration is proportional to the water density ρ_{H_2O} , which highlights the role of H₂O density in this model.

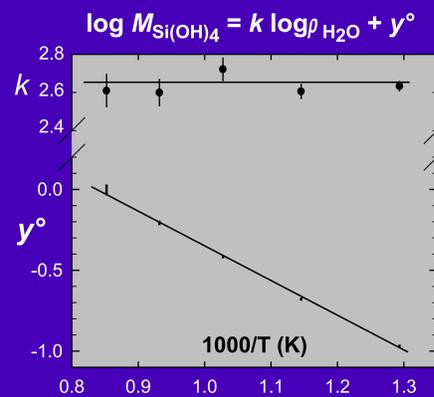
The concept of "complete" equilibrium constant was successfully applied to electrolyte dissociation at high and variable pressures and in mixtures of water with non-polar organic compounds [1,3]. Its extremely simple and general character leads to further investigate the potential interest of such a model for geological fluids. The solubility of quartz at high temperatures and pressures in the system SiO₂-H₂O-CO₂ is a convenient choice for testing the "complete" equilibrium model because

* quartz solubility in H₂O-CO₂ is well documented from 500 to 900 °C and 1.5 to 10 kbar, with CO₂ mole fractions up to 0.75 [4-10]

* quartz solubility in H₂O follows the postulated dependence on ρ_{H_2O} , regardless of pressure, as first emphasized by Kennedy [11] and expressed by the Manning's fit [12] valid up to 900 °C and 20 kbar (m = moles/kg H₂O):

$$\log m_{SiO_2} = (4.26 - 5764 T^{-1} + 1.751 \cdot 10^6 T^{-2} - 2.287 \cdot 10^8 T^{-3}) + (2.845 - 1007 T^{-1} + 3.569 \cdot 10^5 T^{-2}) \log \rho_{H_2O} \quad (1)$$

Fig. 2. Monomer Si(OH)₄ as function of ρ_{H_2O}



Fitted coefficients of the linear relation (in log units) between the monomer Si(OH)₄ concentration and H₂O density, calculated from experimental solubilities of quartz in H₂O from 500 to 900°C, 0.07 to 20 kbar. The error bars correspond to the standard errors of the fits.

2. The "complete" equilibrium constant in H₂O

If silica is dissolved as a single species according to: $SiO_2 + k H_2O = SiO_2 \cdot k H_2O^{aq}$

$$\text{the "complete" equilibrium constant is: } K^o(T) = \frac{M_{SiO_2 \cdot k H_2O}}{(M_{H_2O})^k} = \frac{M_{SiO_2 \cdot k H_2O}}{(55.51 \rho_{H_2O})^k}$$

(M = moles / liter
= $m \cdot \rho_{H_2O}$ in pure water)

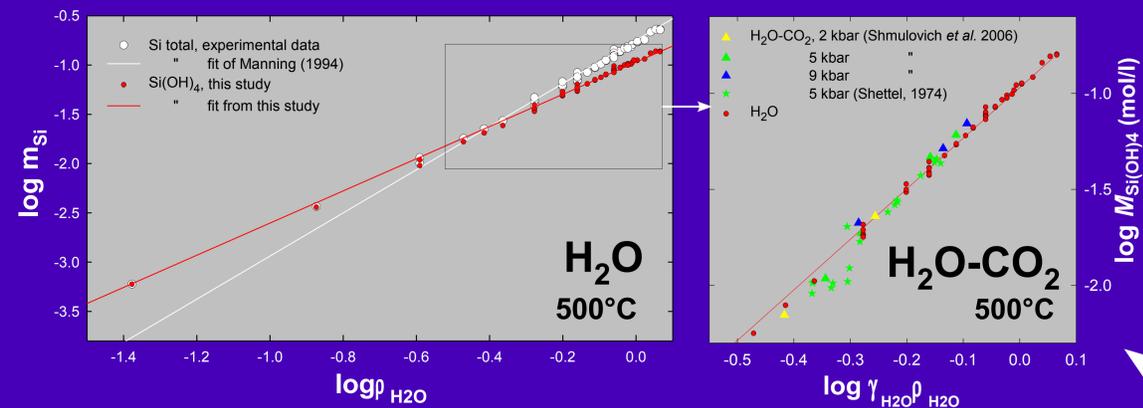
hence the observed linear relation, in pure water, between $\log m_{SiO_2}$ and $\log \rho_{H_2O}$ of Manning's fit (relation 1). However, Figure 1A shows that solubilities at $P < 0.5$ kbar ($\log \rho_{H_2O} < -0.6$) plot off the fit. This is due to the polymerization of aqueous silica at high temperature according to



evidenced from spectroscopy [13]. In the present study, the monomer concentration has been calculated for all available data of quartz solubility, from 500 to 900°C, using polymerization constants recalculated from experimental data [10,14].

Plotting the monomer concentration $m_{Si(OH)_4}$ instead of total dissolved silica m_{Si} results in a different fit that remains linear throughout the whole documented pressure range (Fig. 1A). Moreover, the coefficients of $\log \rho_{H_2O}$ in my fits of $\log m_{Si(OH)_4}$ do not depend on temperature (Fig. 2), in contrast with the coefficients of $\log \rho_{H_2O}$ in Manning's fit (1). This means that the hydration number of the monomer, k , is constant in the considered temperature range.

Fig. 1. Solubility of quartz at 500°C



A. In H₂O. Total dissolved silica (white) and monomer Si(OH)₄ (red) vs. H₂O density (in log units). Polymerization at $\rho_{H_2O} > -0.6$ results in non-linearity of total silica. In contrast, the linear dependence is closely verified by the monomer.

B. In H₂O-CO₂. The concentrations of the monomer Si(OH)₄ in H₂O-CO₂ mixtures plot close to the pure water line (red), regardless of both pressure and CO₂ mole fraction.

3. The "complete" equilibrium constant in H₂O-CO₂

For the solubilities of quartz in H₂O-CO₂ mixtures, the "complete" equilibrium constant is rewritten replacing concentrations by activities, in order to account for the polymerization of silica and the non-ideal mixing properties of the H₂O-CO₂ mixture.

$$K^o(T) = \frac{a_{SiO_2}}{(a_{H_2O})^k}$$

where $a_{SiO_2} = \gamma_{SiO_2} M_{SiO_2} = M_{Si(OH)_4}$

$$a_{H_2O} = \gamma_{H_2O} M_{H_2O} = 55.51 \gamma_{H_2O} \rho_{H_2O}$$

ρ_{H_2O} is calculated as $18 X/V$, where X is the H₂O mole fraction and V the molar volume of the mixture. Volume properties of H₂O-CO₂ fluids and γ_{H_2O} were obtained from the equation of state of Duan and Zhang [15].

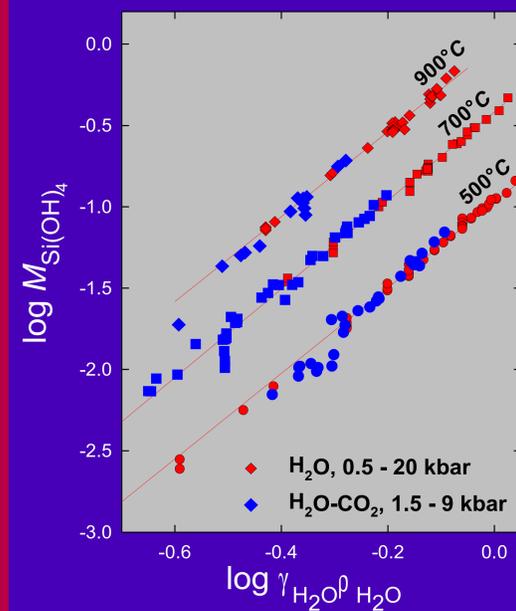
Figure 1B shows that the data at 500°C follow the same trend as the solubilities in pure water (red), regardless of pressure from 2 to 9 kbar. Similar plots at other temperatures are gathered in Fig. 3.

Perspectives

Marshall's concept of "complete" equilibrium constant can be applied not only to electrolyte dissociation, i.e., equilibria between ions and aqueous neutral species, but also to equilibria involving a solid phase and neutral aqueous species. A somewhat similar model, although including empirical coefficients and not taking the polymerization of silica into account, was recently proposed [16] for quartz solubilities in H₂O-CO₂-NaCl mixtures. This concept is therefore anticipated to apply to more complex fluid-mineral equilibria.

Provided that the involved aqueous species are identified, it might provide a simple and efficient tool for extrapolating, at any pressure and any H₂O concentration, mineral solubilities already characterized in pure water at moderate pressure, as a complement to the "density" model based on the same ideas [17].

Fig. 3. Monomer Si(OH)₄ in H₂O-CO₂



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