3.5.P01

Solubility of CO_2 in water and in aqueous NaCl solutions from 0 to 100°C and from 0.1 to 100 MPa: Literature data and thermodynamic modelling

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Accurate description of the solubility of CO_2 in pure water and salt solutions is required in various scientific and technological fields, including the assessment of projects for CO_2 disposal on the sea floor or in sedimentary formations. In the present study experimental measurements of the solubility of CO_2 in pure water and NaCl solutions at pressures above 1 MPa have been assembled from more than 30 literature studies and tested for their accuracy against simple thermodynamic criteria. Some of the experimental data were discarded. Possible reasons for the observed discrepancies between datasets are discussed. The measurements of CO_2 solubility in pure water that satisfy the acceptance criteria have been correlated by a thermodynamic model based on Henry's law and on recent high-accuracy equations of state. The assumption that the activity coefficients of aqueous CO_2 are equal to unity is found to be valid up to solubilities of approximately 2 mol %. At higher solubilities the activity coefficients show a systematic trend from values greater than unity at low temperatures, to values progressively lower than unity at high temperatures. An empirical correction function that describes this trend is applied to the basic model.

Literature data on the solubility of CO_2 in NaCl solutions were fitted to the empirical Sechenov equation, where the salting-out coefficient has been made a function of temperature and of NaCl molality but not pressure. The empirical equations reproduce the experimental values of CO_2 solubility in aqueous NaCl solutions of up to 6 mol·kg^{-1} with an average deviation comparable to the experimental error. Temperature dependencies for Pitzer interaction parameters for the ternary CO_2-NaCl-H_2O system were estimated. The resulting CO_2 solubility model reproduces the experimental solubilities with a precision of better than 2 % (one standard deviation) over the entire *P-T-x* range considered and is available as a computer code. This code is particularly useful for geochemical applications, including the analysis of CO_2-bearing fluid inclusions in minerals.

3.5.P02

Thermal degassing of ammonium narrow-pore aluminosilicates: The framework defects as trap for nitrogen

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The ammonium-exchanged natural analcime $(NH_4)_{0.94}Al_{0.94}Si_{2.06}O_6$ was used to model the degassing mechanism of natural ammonium-bearing framework aluminosilicates. Thermal behaviour of NH_4-analcime has been studied by gas chromatography, IR spectroscopy and X-ray diffraction, paying attention to the interaction between ammonium and products of its decomposition (NH_3, H^+), and the framework. The de-ammoniation and dehydroxylation proceed in parallel, which evidences for the instability of the protonated analcime framework. At the initial step, the mechanism of de-ammoniation consists in thermal dissociation of NH_4^+ molecule onto NH_3 and proton (framework OH-group) and diffusion of NH_3 out of the structure, with an apparent activation energy for NH_3 desorption of 145(±13) kJ/mol. Subsequent decomposition of the framework OH-groups leads to a progressive loss of crystallinity. This step accounts for about 60 % of the total weight loss. Then, a collapse of the structure occurs.

The concentration of Lewis sites, which present coordinated unsaturated Al atoms (≡Al) [1], increases with progressive dealumination of the framework associated with the destruction of OH-groups (dehydroxylation) and corresponding (Si,Al)-O bonds. The chemical character of bonding in the ≡Al:NH_3 complexes and the non-framework Al-OH complexes makes them more stable as compared to the H-bonded NH_4^+ ions and the framework OH-groups. This causes an appreciable increase of the activation energy for NH_3 and H_2O desorption at the final step of decomposition to 270(±20) kJ/mol. This favors the conservation of a small part of nitrogen as the ≡Al:NH_3 complexe in the amorphosed aluminosilicate to higher temperatures.

The mechanism studied seems to reflect general features of the nitrogen evolution in the Earth's crust: the main portion of NH_3 is released back to the atmosphere during the metamorphic degassing at relatively low temperature (<400ºC), and a small portion (about 1% of the initial NH_3 content), strongly bonded to the amorphosed aluminosilicate, may find its way into the lower crust and mantle.

References
[1] Yin F. et al. (1997) *J.Phys.Chem.B* **101**, 1824-1830.