

calculated from a constant $-\Delta C_p$ extrapolation of existing measurements up to 90°C as summarized by Barnes et al. (1966), and including the more recent measurements by Ellis and Milestone (1967). The $K_{H_3SiO_4^-}$ of Ryzhenko (1967) used in the computation is believed to be rather uncertain. However, at the calculated pH of 9.8, $H_2SiO_4^{2-}$ is not the dominant species, and moderate errors in the second ionization constant do not significantly affect final results.

At 150°C and a total analytical Na_2S content of 0.113 m/kg Dickson (1966) reports a quartz solubility of 0.078 m/kg. For the same conditions the above model results in a total silica concentration of 0.061 m/kg. In view of the considerable (but unknown) uncertainties involved in the values of K_{H_2S} , K_{HS^-} , and K_{NaHS} , the fairly close agreement between observed and calculated solubilities indicates that complexes containing both sulfur and silica are not necessarily of major significance under the conditions tested.

While this paper was under review, Ostapenko et al. (1969) published additional data on the solubility of quartz in NaOH and Na_2S solutions at 280°C, and also came to the conclusion that silica-sulfur complexing is not quantitatively significant.

ACKNOWLEDGMENTS

We thank H.L. Barnes for a critical review of the manuscript. The work was supported by grants from the National Research Council of Canada.

REFERENCES

- Alexander, G.B., 1953. The reaction of low molecular weight silicic acids with molybdic acid. *J. Am. Chem. Soc.*, 75:5655-5657.
- Alexander, G.B., Heston, W.M. and Iler, R.K., 1954. The solubility of amorphous silica in water. *J. Phys. Chem.*, 58: 453-455.
- Anderson, G.M. and Burnham, C.W., 1965. The solubility of quartz in supercritical water. *Am. J. Sci.*, 263: 494-511.
- Anderson, G.M. and Burnham, C.W., 1967. Reactions of quartz and corundum with aqueous chloride and hydroxide solutions at high temperatures and pressures. *Am. J. Sci.*, 265: 12-27.
- Barnes, H.L., 1963. Ore solution chemistry, I. Experimental determinations of mineral solubilities. *Econ. Geol.*, 58, 1054-1060.
- Barnes, H.L., Helgeson, H.C. and Ellis, A.J., 1966. Ionization constants in aqueous solutions. In: S.P. Clark, Jr. (Editor) *Handbook of Physical Constants*, Rev. Ed. - *Geol. Soc. Am. Mem.*, 97: 401-413.
- Brintzinger, H. and Brintzinger, W., 1931. Zur kenntnis der molekulardispers gelösten Kieselsäuren und Titansäuren. *Z. Anorg. Allg. Chem.*, 196: 44-49.
- Crerar, D.A., 1968. *The Solubility of Quartz in Dilute Sodium Hydroxide Solutions at Elevated Temperatures and Pressures*. M. Sc. Thesis, University of Toronto, Toronto, Ont., 59 pp.
- Dickson, F.W., 1966. Solubilities of metallic sulfides and quartz in hydrothermal sulfide solutions. *Bull. Volcanol.*, 29: 605-628.
- Ellis, A.J. and Milestone, N.B., 1967. The ionization constants of hydrogen sulfide from 20 to 90°C. *Geochim. Cosmochim. Acta*, 31: 615-620.
- Friedman, I.I., 1948. The solubility of quartz in sodium carbonate solutions at high temperature. *J. Am. Chem. Soc.*, 70: 2649-2653.
- Gimblett, F.G.R. and Monk, C.B., 1954. E.M.F. studies of electrolytic dissociation, part 7. - Some alkali and alkaline earth metal hydroxides in water. *Trans. Faraday Soc.*, 50: 965-972.

- Goto, K., 1955. States of silica in aqueous solution. I. Polymerization and depolymerization. *J. Chem. Soc. Japan*, 76: 729–732.
- Greenberg, S.A., 1958. The nature of the silicate species in sodium silicate solutions. *J. Am. Chem. Soc.* 80: 6508–6511.
- Greenberg, S.A. and Price, E.W., 1957. The solubility of silica in solutions of electrolytes. *J. Phys. Chem.* 61: 1539–1541.
- Harned, H.S. and Owen, B.B., 1958. *The Physical Chemistry of Electrolytic Solutions*. Reinhold, New York, N.Y., 3rd ed., 803 pp.
- Helgeson, H.C., 1967. Thermodynamics of complex dissociation in aqueous solution at elevated temperatures. *J. Phys. Chem.*, 71: 3121–3136.
- Ingamells, C.O., 1966. Absorptiometric methods in rapid silicate analysis. *Anal. Chem.*, 38: 1228–1234.
- Kennedy, G.C., 1950. A portion of the system silica–water. *Econ. Geol.*, 45, 629–653.
- Kitahara, S., 1960a. The solubility of quartz in water at high temperatures and pressures. *Rev. Phys. Chem. Japan*, 30: 109–114.
- Kitahara, S., 1960b. The solubility equilibrium and the rate of solution of quartz in water at high temperatures and high pressures. *Rev. Phys. Chem. Japan*, 30: 123–130.
- Kitahara, S., 1960c. The polymerization of silicic acid obtained by the hydrothermal treatment of quartz and the solubility of amorphous silica. *Rev. Phys. Chem. Japan*, 30: 131–137.
- Kolthoff, I.M. and Sandell, E.B., 1952. *Textbook of Quantitative Inorganic Analysis*. Macmillan, London, 3rd ed., 759 pp.
- Laudise, R.A. and Ballman, A.A., 1961. The solubility of quartz under hydrothermal conditions. *J. Phys. Chem.*, 65: 1396–1400.
- Learned, R.L., Dickson, F.W. and Tunnell, G., 1967. The solubility of quartz in Na_2S and NaOH solutions at elevated temperatures and 100 bars. *Trans. Am. Geophys. Union*, 48: 249.
- Morey, G.W., Fournier, R.O. and Rowe, J.J., 1962. The solubility of quartz in water in the temperature interval from 25° to 300°C. *Geochim. Cosmochim. Acta*, 26: 1029–1043.
- Noyes, A.A., 1907. The electrical conductivity of aqueous solutions. *Carnegie Inst. Publ.*, 63.
- Ostapenko, G.T., Khetchikov, L.N. and Baliskiy, V.S., 1969. Hydrolysis of aqueous solutions of sodium sulfide and solubility of quartz in these solutions. *Geochem. Int.*, 6(1): 22–28.
- Rowe, J.J., Fournier, R.O. and Morey, G.W., 1967. The system H_2O – Na_2O – SiO_2 at 200°C, 250°C, 300°C. *Inorg. Chem.*, 6, 1183–1188.
- Ryzhenko, B.N., 1967. Determination of hydrolysis of sodium silicate and calculation of dissociation constant of orthosilicic acid at elevated temperatures. *Geokhimiya*, 2: 161–169 (in Russian). *Geochem. Int.* 4: 99–107 (English translation).
- Seidell, S. and Linke, W.F., 1965. *Solubilities of Inorganic and Metal–organic Compounds*, vol. 2. American Chemical Society, Washington, D.C., 4th ed., 1914 pp.
- Siever, R., 1962. Silica solubility, 0°–200°C and the diagenesis of siliceous sediments. *J. Geol.*, 70: 127–150.
- Sommerfeld, R.A., 1967. Quartz solution reaction: 400°–500°C, 1000 bars. *J. Geophys. Res.*, 72: 4253–4257.
- Sprauer, S.W. and Pearce, D.W., 1940. Equilibria in the systems Na_2O – SiO_2 – H_2O and Na_2O – Al_2O_3 – H_2O at 25°C. *J. Phys. Chem.*, 44, 909–916.
- Van Lier, J.A., De Bruyn, P.L. and Overbeek, J.Th.G., 1960. The solubility of quartz, *J. Phys. Chem.*, 64: 1675–1682.
- Van Loon, J.C. and Parissis, C., 1968. Rapid scheme of silicate analysis based on the lithium metaborate fusion followed by atomic absorption spectrometry. *Anal. Letters*, 1: 519–524.
- Weill, D.F. and Bottinga, Y., 1970. Thermodynamic analysis of quartz and cristobalite solubilities in water at saturation vapor pressure. *Contrib. Mineral. Petrol.*, 25: 125–132.