

libria in basic solutions, the Cr + CrN buffer developed by Hallam (ms) can be used. This buffer allows us to control the fugacity of NH₃ and hence the activity of NH₄OH. Preliminary experiments have demonstrated that solutions controlled by this buffer assemblage are quite basic.

The Ag-AgCl buffer combined with a fixed f_{H_2} is probably as close to a pH buffer as we can come in a hydrothermal environment. f_{HCl} is rigorously controlled and in the pure system H-O-Cl the hydrogen ion activity, a_{H^+} , is also controlled, assuming low solubility of the buffer solids in the solution. The fugacities of the uncharged species can be calculated from the relevant equilibrium constants (eq 2 and 3) and the total pressure equation (1). Similarly, the activities of the ionic species can be calculated, using the electrical neutrality equation and the relevant dissociation constants. Using H⁺, OH⁻, and Cl⁻ as principal species, we have

$$m_{H^+} = m_{OH^-} + m_{Cl^-} \quad (17)$$

$$HCl \rightleftharpoons H^+ + Cl^- \quad K_2 = \frac{a_{H^+} \cdot a_{Cl^-}}{a_{HCl^\circ}} \quad (18)$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_3 = \frac{a_{H^+} \cdot a_{OH^-}}{a_{H_2O}} \quad (19)$$

and hence.

$$a_{H^+} = \lambda_{H^+}^{1/2} \left[\frac{a_{H_2O} \cdot K_3}{\lambda_{OH^-}} + \frac{a_{HCl^\circ} \cdot K_2}{-10^4 \gamma} \right]^{1/2} \quad (20)$$

If other species are added to the solution, such as K⁺, Na⁺ or if Ag⁺ is present in appreciable amounts, equation (17) contains additional terms, and we cannot solve for a_{H^+} without further information. On the other hand, adding salts may not significantly change equation (1), and in that case we can still calculate the fugacities of all uncharged species. In all cases, however, f_{HCl} remains rigorously specified and buffered.

The Ag-AgCl buffer is directly applicable to the study of ore solutions and of metamorphic solutions, and we expect that it can also be used to investigate igneous solutions.

ACKNOWLEDGMENTS

Work supported by NSF grant GA-1101 and by NASA grant NGR 21-001-037. We thank E. U. Franck and W. D. Gunter for helpful discussions, and J. J. Hemley and G. M. Lafon for valuable comments on the manuscript.

REFERENCES

- Burnham, C. W., Holloway, J. R., and Davis, N. F., 1969, Thermodynamic properties of water to 1000°C and 10,000 bars: Geol. Soc. America Spec. Paper 132, 96 p.
 Carmichael, D. M., 1969, On the mechanism of prograde metamorphic reactions in quartz-bearing pelitic rocks: Contr. Mineralogy and Petrology, v. 20, p. 244-267.
 Day, H. W., 1970, Redetermination of the stability of muscovite + quartz [abs.]: Geol. Soc. America Abs. with Programs, v. 2, p. 535.

- Eugster, H. P., 1970, Thermal and ionic equilibria among muscovite, K-feldspar and aluminosilicate assemblages: *Fortschr. Mineralogie*, v. 47, p. 106-123.
- Eugster, H. P., and Skippen, G. B., 1967, Igneous and metamorphic reactions involving gas equilibria, in Abelson, P. H., ed., *Researches in geochemistry*, v. 2: New York, John Wiley & Sons, p. 492-520.
- Eugster, H. P., and Wones, D. R., 1962, Stability relations of the ferruginous biotite, annite: *Jour. Petrology*, v. 3, p. 82-125.
- Fisher, G. W., 1970, The application of ionic equilibria to metamorphic differentiation: an example: *Contr. Mineralogy and Petrology*, v. 29, p. 91-103.
- Franck, E. U., 1956, Hochverdichteter Wasserdampf III. Ionendissoziation von HCl, KOH und H₂O in überkritischem Wasser: *Zeitschr. phys. Chemie*, v. 8, p. 192-206.
- 1961, Überkritisches Wasser als elektrolytisches Lösungsmittel: *Angew. Chemie*, v. 73, p. 309-322.
- Frantz, J. D., ms, 1973, Acid buffers: use of Ag + AgCl for measuring mineral-solution equilibria in the system MgO-SiO₂-H₂O-HCl: Ph.D. thesis, The Johns Hopkins Univ., Baltimore, Md.
- Garrels, R. M., and Christ, C. L., 1965, *Solutions, minerals, and equilibria*: New York, Harper and Row, 450 p.
- Greenwood, H. J., 1967, Mineral equilibria in the system MgO-SiO₂-H₂O-CO₂, in Abelson, P. H., ed., *Researches in geochemistry*, v. 2: New York, John Wiley & Sons, p. 542-567.
- Gunter, W. D., ms, 1973, An experimental study of mineral-solution equilibria applicable to metamorphic rocks: Ph.D. thesis, The Johns Hopkins Univ., Baltimore, Md.
- Hallam, M. E., ms, 1973, The origin of primitive terrestrial atmospheres: Ph.D. thesis, The Johns Hopkins Univ., Baltimore, Md.
- Helgeson, H. D., 1967, Solution chemistry and metamorphism, in Abelson, P. H., ed., *Researches in geochemistry*, v. 2: New York, John Wiley & Sons, p. 362-404.
- Hemley, J. J., 1959, Some mineralogical equilibria in the system K₂O-Al₂O₃-SiO₂-H₂O: *Am. Jour. Sci.*, v. 257, p. 241-270.
- Hougen, O. A., and Watson, D. R., 1946, *Chemical process principles charts*: New York, John Wiley & Sons, 219 p.
- Morey, G. W., and Hesselgesser, J. M., 1951, The solubility of some minerals in superheated steam at high pressures: *Econ. Geology*, v. 46, p. 821-835.
- Orville, P. M., 1963, Alkali ion exchange between vapor and feldspar phases: *Am. Jour. Sci.*, v. 261, p. 201-237.
- Poty, B. P., and Holland, H. D., 1970, Stability relations in the system MgO-SiO₂-H₂O-HCl at 500°C and 1 kb [abs.]: *Geol. Soc. America Abs. with Programs*, v. 2, p. 655.
- Presnall, D. C., 1969, Pressure-volume-temperature measurements on hydrogen from 200°C to 600°C and up to 1800 atmospheres: *Jour. Geophys. Research*, v. 74, p. 6026-6033.
- Robie, R. A., Bethke, P. M., and Beardsley, K. M., 1967, Selected X-ray crystallographic data, molar volumes, and densities of minerals and related substances: *U.S. Geol. Survey Bull.* 1248, 87 p.
- Robie, R. A., and Waldbaum, D. R., 1968, Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U.S. Geol. Survey Bull.* 1259, 256 p.
- Shaw, H. R., 1967, Hydrogen osmosis in hydrothermal experiments, in Abelson, P. H., ed., *Researches in geochemistry*, v. 2: New York, John Wiley & Sons, p. 521-541.
- Smithells, C. J., 1967, *Metals reference book*, v. 1, 4th ed.: New York, Plenum Press, 1147 p.
- Skippen, G. B., 1971, Experimental data for reactions in siliceous marbles: *Jour. Geology*, v. 79, p. 457-481.
- Wellman, T. R., 1970, The stability of sodalite in a synthetic syenite plus aqueous chloride fluid system: *Jour. Petrology*, v. 11, p. 49-71.
- Wones, D. R., and Gilbert, M. C., 1969, The fayalite-magnetite-quartz assemblage between 600° and 800°C: *Am. Jour. Sci.*, v. 267A (Schairer v.), p. 480-488.