increase in Na_2S concentration, and the sulfide-ion concentration increases as a consequence. The ratio Sb_2S_3:Na_2S in the saturated solutions should increase with increasing Na_2S if the hydrolysis reaction plays a significant role. The ratio does increase with increasing Na_2S concentration (Table 1). However, even in the most concentrated Na_2S solution, 0.917 mole/kg, hydrolysis is strong, and 0.4 is probably considerably less than the true value of m:n.

The strong hydrolysis of sulfide ion in water solution largely converts the sulfide ion to HS^-. Hydroxide ions are produced in quantity equivalent to HS^-. A reaction between stibnite and Na_2S solutions can therefore be written

$$m\underline{Sb_2S_3} + n\,HS^- + n\,OH^- = (Sb_2S_3)_m(S)_n^{2-} + n\,H_2O,$$

and the equilibrium constant is

$$K=[(Sb_2S_3)_m(S)_n^{2-})]/[(HS^-)^n(OH^-)^n]$$

If the S^{2-} concentration is small enough to be neglected, values for K may be calculated from the experimental data for various assumed reactions by making the approximation that concentrations can be substituted for activities. Of the reactions considered, only calculations based on

$$\underline{2Sb_2S_3} + HS^- + OH^- = Sb_4S_7^{2-} + H_2O$$

yielded reasonably constant values for K. The calculations were made as follows: If A is total Na_2S in moles per kilogram and B is total Sb_2S_2 in moles per kilogram, $A - 2B = (HS^-) = (OH^-)$. The K for the reaction can be written

$$K = B/2/(A - 2B)^2$$

The values of K calculated in this way (Table 1) range from 3.0 to 7.7, with a mean of 5.0; no particular trend of the value of K with increase in concentration of Na_2S was noted.

The following reaction is therefore tentatively proposed as being compatible with the data:

$$\underline{2Sb_2S_3} + S^{2-} = Sb_4S_7^{2-}$$

Adding to the plausibility of the postulated reaction is the existence of a solid compound having formula $2Sb_2S_3 \cdot Na_2S$, in which the mole ratio Sb_2S_3:Na_2S is 2 : 1.

R. H. Arntson
F. W. Dickson
G. Tunell
Department of Geological Sciences, University of California, Riverside

References and Notes

1. R. Fiala and N. Konopik, *Monatsh. Chem.* **81**, 504 (1950).
2. F. P. Treadwell and W. T. Hall, *Analytical Chemistry* (Wiley, New York, Engl. ed. 9, 1947), vol. 2.
3. R. H. Arntson, thesis, Univ. of California, Los Angeles, 1958.
4. C. A. Jacobson, *Encyclopedia of Chemical Reactions* (Reinhold, New York, 1946), vol. 1, p. 257.
5. Supported by grant G7405 from the National Science Foundation Institute of Geophysics and Planetary Physics, University of California, publication 221.

15 August 1966

Retrograde Melting in the System Mg-Fe-Si-O

With regard to possible retrograde melting in the system Mg-Fe-Si-O (*1*), two comments are in order.

First, the lines (*1*, figs. 1 and 2) representing equilibrium conditions for the assemblages ol+py+I+liq and py+sil+I+liq must both have positive slopes steeper than that of the line for ol+sil+I+liq and flatter than that for ol+py+sil+I. This is seen from the chemographic relations of the phases in the projected compositional triangle Fe-Mg-Si (projected from the O corner of the tetrahedron Fe-Mg-Si-O) by the methods elaborated by Schreinemakers (*2*).

When the figures are thus corrected, it becomes evident that the possibilities for "retrograde melting" are in fact significantly greater than recognized by Speidel and Nafziger. Pyroxene-iron-silica assemblages cooled at constant or increasing f_{O_2} from temperatures above 1305°C and oxygen fugacities above $10^{-11.3}$ atm (or lower, if f_{O_2} increases on cooling) will react to form melt on crossing the line py+sil+I+liq, as will pyroxene-olivine-iron assemblages in the same T-f_{O_2} region on cooling across the line ol+py+I+liq.

Second, the so-called "heat" of reaction derived by Speidel and Nafziger from the slope of the line for ol+sil+I+liq is in fact only an intermediate result in what could be a calculation of the standard heat of the reaction

$$2Fe + O_2 + SiO_2 = Fe_2SiO_4$$

if the activity coefficients of Fe_2SiO_4 in olivine and melt were accurately known as a function of temperature and composition. In the absence of such knowledge, slopes of lines on diagrams of log f plotted against $1/T$ cannot be interpreted in terms of physical heat. In any event, comparison with Darken and Gurry's (*2*) value for the standard enthalpy of formation of wustite (not the enthalpy of oxidation of metallic iron to the divalent ion, as stated) provides at best only a crude qualitative indication of the energy balance in the process under consideration.

An additional comment relates to the use of the term "retrograde melting" to describe a reaction between a gas and one or more solids to produce a liquid different in composition from either. The reaction considered here is entirely analogous to what takes place on cooling a system consisting of NaCl crystals and steam at 1 atm from 200°C to a temperature below 100°C; if there is enough H_2O, the salt crystals disappear and a liquid appears; but one would not normally call the process "retrograde melting."

P. Toulmin, III
U.S. Geological Survey, Washington, D. C.

References and Notes

1. F. A. H. Schreinemakers, *Koninkl. Ned. Akad. Wetenschap. Proc.* (Engl. ed.), **18–28** (1915–1925); see also P. Niggli, *Rocks and Mineral Deposits* (Freeman, New York, 1954).
2. L. S. Darken and R. W. Gurry, *J. Amer. Chem. Soc.* **67**, 1398 (1945); *ibid.* **68**, 798 (1946).
3. Publication approval by the director, U.S. Geological Survey.

27 June 1966

Toulmin's first comment to our report is correct if the four-phase assemblages considered could be projected onto the Mg-Fe-Si plane. However, vapor is present in equilibrium with all the phase assemblages presented (*1*, figs. 1 and 2). Oxygen must also be considered and Schreinemakers' relations for quaternary (*2*) rather than ternary systems (*2*, p. 531) must be used. The relations (*1*, figs. 1 and 2) are therefore correct and have been verified experimentally (*3*). The vapor-absent curve lies between (ol+py+sil+liq) and the metastable extension of py+sil+I+liq. Toulmin's comments on the heat of reaction are well taken. All we intended was a qualitative indication of energy relations.

D. H. Speidel
R. H. Nafziger
Department of Geochemistry and Mineralogy, Pennsylvania State University, University Park

References

1. D. H. Speidel and R. H. Nafziger, *Science* **152**, 1367 (1966).
2. F. A. H. Schreinemakers, *Koninkl. Akad. Ned. Wetenschap. Proc.* **18**, 820 (1915–16).
3. R. H. Nafziger, thesis, Pennsylvania State University, 1966.

23 August 1966