Part I

PHASE EQUILIBRIA

MOLECULAR TRANSPORT

THERMODYNAMICS

Solid-Liquid Phase of the Thallous Formate–Thallous Malonate System

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THE FEW DESCRIPTIONS of the thallous formate-thallous malonate system in the literature are contradictory. Sullivan (2) reporting on the work of Messmore, Coghill, and Anderson, referred to a mixture of equal weights of thallous formate and thallous malonate as a double salt, melting at 60° C., but presented no evidence for its existence as such. O'Meara and Clemmer (*1*) referred to a double salt resulting from mixing equimolar proportions of the salts or about 2 parts of the malonate to 1 part formate by weight. They did not report a melting point.

The thallous malonate-thallous formate system was examined by hot-stage microscopy, but there was no evidence for compound formation between the two salts. These investigations revealed a eutectic mixture which melts from 68–9° C. A phase transition of thallous formate below its melting point hampered the determination of the eutectic composition by microscopic techniques. A phase diagram for the system was plotted from data obtained from melting point determinations by the capillary method. Figure 1 shows the eutectic composition to be 54% thallous formate and 46% thallous malonate by weight. The specific gravity of the eutectic at its melting point is 4.9.

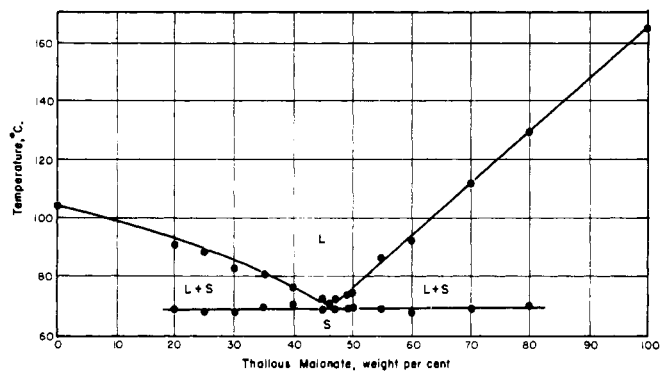

Figure 1. Solid-liquid phase diagram

EXPERIMENTAL

Reagents. Thallous formate (Eastman) melting at 102–4° C. was used without further purification after various recrystallization techniques showed no significant effect on its melting point.

Thallous malonate from various commercial sources was purified by recrystallization before use. Gradual addition of ethyl alcohol to a hot aqueous solution of the salt gave colorless crystals which melted at 163–4° C. with decomposition.

Apparatus and Technique. Thallous formate is photosenitive and hygroscopic; hence this salt and its mixtures were protected from intense light and moisture. The various thallous formate-thallous malonate mixtures were compounded in a dry box by grinding together weighed amounts of the two salts in a vitreous porcelain mortar. Thallous formate may be handled freely in air at low relative humidities without appreciable sorption of moisture.

The initial observations of mixtures of the salts were made microscopically, using a Kofler hot stage. Subsequent determinations were made in a conventional capillary melting point apparatus. The melting point determinations were repeated on the same sample for as many as four times without any appreciable change in melting point or other evidence of decomposition. However, gradual decomposition of the eutectic mixture on prolonged heating at 80° C., was observed even in the absence of air.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) O'Meara, R. G., Clemmer, J. B., U. S. Bur. Mines, Rept. Invest. No. **2897**, 1928.
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