

with the value of 15.89 reported by Macalpine and Sayce.²

Summary

Solubility relationships in the ternary system

$(\text{NH}_4)_2\text{SeO}_4\text{-CuSeO}_4\text{-H}_2\text{O}$ at 25° have been determined. The double salt hydrate $(\text{NH}_4)_2\text{SeO}_4\text{CuSeO}_4\cdot 6\text{H}_2\text{O}$ is the stable phase over almost the entire range of concentrations.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Silicon Chlorobromides

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Recent studies of the silicon chlorobromides^{1,2} have increased our knowledge of these three compounds considerably; however, the information available on melting points and densities is quite scant, while boiling points are fairly well known.

A mixture of the silicon chlorobromides was prepared^{1b} by heating equal volumes of SiCl_4 and SiBr_4 over a period of seventy hours at 140° in a sealed tube. Repeated fractional distillation of the three chlorobromides provided pure samples boiling at the following uncorrected temperatures: SiCl_3Br at 78.8–79.0°, SiCl_2Br_2 at 103.8–104.1°, and SiClBr_3 at 127.0–127.3°. Portions of each pure compound were used at once in measuring densities, melting points and boiling points.

Densities, Melting Points and Boiling Points

Procedures.—Densities were measured in a calibrated 2-ml. bulb with capillary inlet bearing a reference mark; densities obtained should be accurate to one or two parts per thousand. A suitable value for carbon tetrachloride was obtained. Melting points were obtained as follows: the bulb of a calibrated toluene thermometer was immersed in about 3 ml. of pure chlorobromide in a small tube, which was itself immersed in an alcohol-bath contained in a Dewar flask. The temperature of the alcohol-bath was allowed to change slowly, with agitation of both sample and thermometer; melting points were in good accord with freezing points. Boiling points were measured to 0.2°, followed by immediate observation of the boiling point of carbon tetrachloride or water in identical equipment. *Results* of this investigation are summarized in Table I below; previous values are given when available.

(1) (a) Schumb and Anderson, *THIS JOURNAL*, **59**, 651 (1937); (b) Forbes and Anderson, *ibid.*, **66**, 931 (1944).

(2) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, pp. 962, 978, 980–981.

TABLE I

SILICON TETRACHLORIDE TO SILICON TETRABROMIDE

Com- pound	B. p., °C.		M. p. °C.	Density ²⁴	Mol. vol., ml.
	Obs.	Prev.			
SiCl_4	...	57.57 ¹	-70 ¹	1.469 ²	115.7
SiCl_3Br	80.3	80 ^{1,2}	-62 = 1	1.826	117.4
SiCl_2Br_2	104.4	104 ^{1,2}	-45.5 = 1	2.172	119.2
SiClBr_3	128.0	126–128 ^{1,2}	-20.8 = 1 ^b	2.497 ²	121.6
SiBr_4	...	153.4 ¹	+8 ¹	2.812 ²	123.7

¹ From value 1.483 at 20°, Mellor, Vol. VI, p. 962.
² Besson³ gives -39°, on a probably impure compound.
^b Reynolds' value, in Mellor, of 2.432 would give a molar volume greater than that of SiBr_4 .

Discussion.—Previously, there was some doubt as to the correct values on SiClBr_3 . This has been settled. The chief physical properties of the silicon chlorobromides are now known. In examining the liquid ranges in Table I above, we find the value is constant at $149.0 \pm 0.6^\circ$ in the last three members, SiCl_2Br_2 , SiClBr_3 , and SiBr_4 . This regularity has led to a study of liquid ranges of other mixed halides; this is now complete and should be published at a later date. Other work is in progress, including isolation of $\text{Si}(\text{OCH}_3)_3\text{SCN}$ boiling at about 170.5°.

Summary

An investigation of the chief physical properties of the silicon chlorobromides has yielded the following new values: SiCl_3Br , m. p. -62°, d^{25} , 1.826; SiCl_2Br_2 , m. p. -45.5°, d 2.172; SiClBr_3 , m. p. -20.8°, d 2.497. Boiling points of the chlorobromides have been checked also.

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(3) "International Critical Tables."

(4) Schumb and Young, *THIS JOURNAL*, **52**, 1464 (1930).

(5) Besson, *Compt. rend.*, **112**, 531, 788, 1447 (1891).