Table I. Triple Point Temperature of Tellurium

Triple Point Temp., °C.	Furnace Heating Rate °C./min.	Time for Melting Point Plateau, Min.	Temp. Rise On Plateau ~95%-97% °C.
449.8₁₂	0.16	90	0.08
449.7₉₉	0.35	60	0.20
449.9₃₅	1.0	30	0.24

Average 449.85; Most probable value = 449.80 ± 0.05° C.

equilibrium between the liquid and solid phases. Hence, only the melting point data are presented in Table I; the triple point temperatures given in Table I were determined from our data using the graphical method of Taylor and Rossini (6).

The plateaus for the melting point measurements (Table I) showed a gentle slope of 0.08°, 0.20°, and 0.24° C. over 95% of the plateau period for furnace heating rates of 0.16° C./min., 0.35° C./min., and 1.0° C./min., respectively. The time intervals for these plateau periods were 90, 60, and 30 minutes; the shorter time intervals are for the faster furnace heating rates.

The triple point temperature of tellurium, based on the average of all three values in Table I, is 449.85° C. The more probable value is believed to be 449.80 ± 0.05° C. since for measurement #3, the furnace heating rate may

have been too fast for thermodynamic equilibrium between liquid and solid phases. The accuracy of our measurements is estimated to be ± 0.05° C. The sample purity was estimated from the melting curves by the method of Mair, Glasgow, Rossini (5) to be mole fraction 0.99998, minimum. The presence of mole fraction 0.00002 of impurities would cause a freezing point error of 0.006° C.

Our values in Table I for the triple point temperature of tellurium are in good agreement with Machol and Westrum's value of 449.5 ± 0.3° C. and F.C. Kracek's value of 449.8 ± 0.2° C.

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Binary Melting Point Studies for Boron Bromide with Some Group IV Halides and for Germanium Bromide with Silicon Bromide

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Melting point and solubility data are presented for the binary systems boron bromide–germanium bromide, boron bromide–silicon bromide, boron bromide–germanium chloride, boron bromide–silicon chloride and germanium bromide–silicon bromide. The Group IV halides with boron bromide had simple eutectics and there was no evidence of compound formation. The germanium bromide–silicon bromide system formed a continuous series of solid solutions. Comparisons of ideal and experimental solubilities have been made.

SOLID-LIQUID equilibria of the binary systems of SnBr₄ and of SnI₄ with BBr₃ have been studied by Adamsky and Wheeler (1) and the system SiBr₄ with BBr₃ by Nisel'son and Petrusevich (8). In this paper the solid-liquid equilibria of some additional Group IV tetrahalides with BBr₃ and of the GeBr₄-SiBr₄ system have been studied by determination of liquidus curves. In the BBr₃-SiBr₄ system the eutectic point has been more precisely determined.

EXPERIMENTAL

Materials. Electronic grade chemicals were used without further purification. The BBr₃, GeCl₄ and GeBr₄ were reported to be 99.99+%, 99.999+% and 99.99+% purity, respectively, and were obtained from Eagle-Picher Company. The SiBr₄ and SiCl₄ were reported to be 99+% and were obtained from Stauffer Chemical Co.

Procedure. Mixtures of 2 ml. total volume were prepared

volumetrically from thermostated reagents, using a microsyringe calibrated in 0.02 ml. divisions. All additions were made in a dry box. Conversion from volume to weight units was made using the respective densities.

The method of determining melting points which was used was similar to that reported by Collett and Johnston (2). Mixtures were sealed in Pyrex tubes immediately after making them up and the melting temperature was taken when the last crystal disappeared. The sample tubes were vigorously stirred. Thermometers used were calibrated against a thermometer calibrated by the National Bureau of Standards. Melting temperatures were read with a reproducibility of ± 0.1° C. A five gallon unsilvered dewar was used for the constant temperature bath and dry icemethanol was used to obtain low temperatures. When not being measured samples were kept in the dark to minimize photochemical reactions.

Melting points were checked by time-temperature studies.

RESULTS AND DISCUSSION

Figure 1 shows the melting point-composition curves for the BBr_3-$GeBr_4$ and BBr_3-$SiBr_4$ systems with eutectics at 80.9 and 76.0 mole % BBr_3, respectively (-53.0° and -57.5° C.). The eutectic in the BBr_3-$SiBr_4$ system found in this study differs from that previously reported as 80.0 mole % BBr_3 at -57° C. by Nisel'son and Petrusevich (8). These curves give no evidence of molecular coordination compounds. Adamsky and Wheeler (1) found from their freezing point studies that bromine in aluminum, stannic, and arsenic bromides and iodine in stannic iodide also showed no tendency to coordinate with boron in BBr_3.

Figure 2 shows that the melting point-composition curves for BBr_3-$GeCl_4$ and BBr_3-$SiCl_4$ are also of the simple eutectic type with eutectics at 40 and 26.4 mole % BBr_3, respectively (-74° and -80.0° C.), with no evidence of compound formation. These solutions were kept frozen until their melting points were taken and presumably before any appreciable halogen exchange reaction took place.

When the BBr_3-$GeCl_4$ and BBr_3-$SiCl_4$ systems were held at room temperature a depression of their melting points was observed after about two days, indicating that halogen exchange reactions took place. The melting points became constant at a maximum depression of about 1° C. after approximately five days. The depression was only observ-
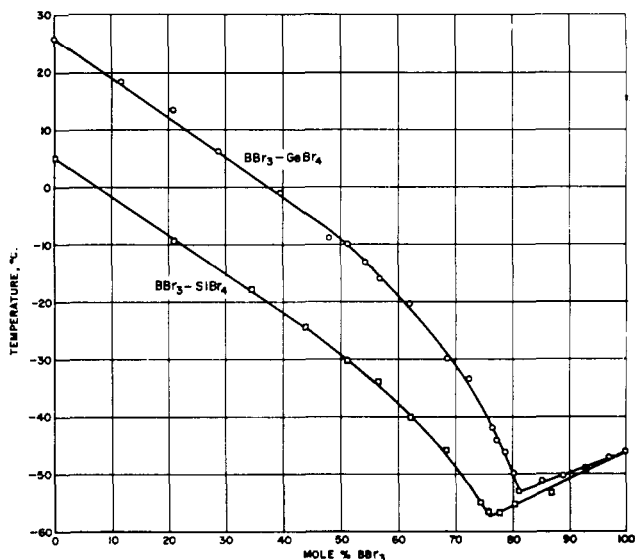
able in solutions close to 1:1 mole ratio, indicating a mass action effect on the halogen exchange reaction. Infrared spectroscopy measurements of vapors above these solutions showed BCl_3 to be present (7) confirming a halogen exchange reaction. In similar studies by Delwaulle (3) of the solidification behavior of mixtures of $GeCl_4$ and $GeBr_4$, mixed halides were observed as reaction products by Raman spectroscopy and the melting points of the solutions were also found to be changed.

If the tetrahalides in BBr_3 studied obeyed the ideal thermodynamic solubility equation (5, 10):

$$\log N = \frac{\Delta H_f}{2.303R} \left[1/T_0 - 1/T \right]$$

their heats of fusion, ΔH_f, could be determined from the slopes of the curves obtained by plotting $\log N$ as a function of $1/T$, where N is the mole fraction of the respective tetrahalide at the liquidus temperature T, and T_0 the melting point of pure tetrahalide. This equation assumes negligible solid solubility of BBr_3 in the tetrahalides and that heats of fusion are independent of temperature, namely that ΔC_p (fusion) is zero.

Curves obtained by plotting $\log N$ vs. $1/T$, determined for N as pure tetrahalide to the eutectic composition, can be seen in Figure 3. These curves have been compared with those calculated from the ideal solubility equation using the reported heats of fusion of the respective tetrahalides. The limiting slope of the experimental curve as $N \rightarrow 1$ should correspond to the ideal slope. The experimental $GeBr_4$ curve can be seen to approach closely the ideal solubility curve.
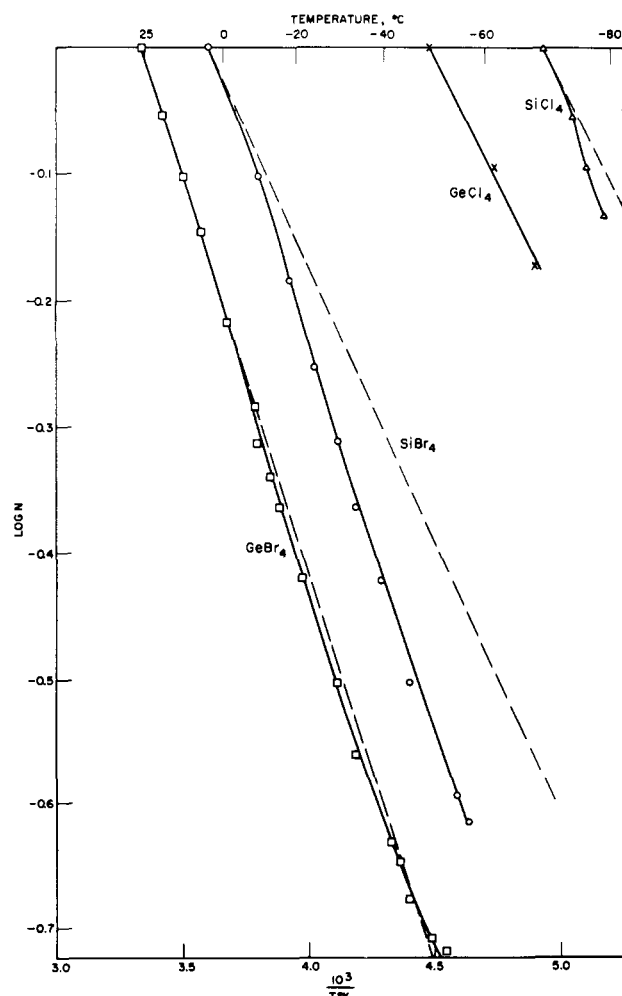

Figure 1. Melting point-composition curves for BBr_3-$GeBr_4$ and BBr_3-$SiBr_4$
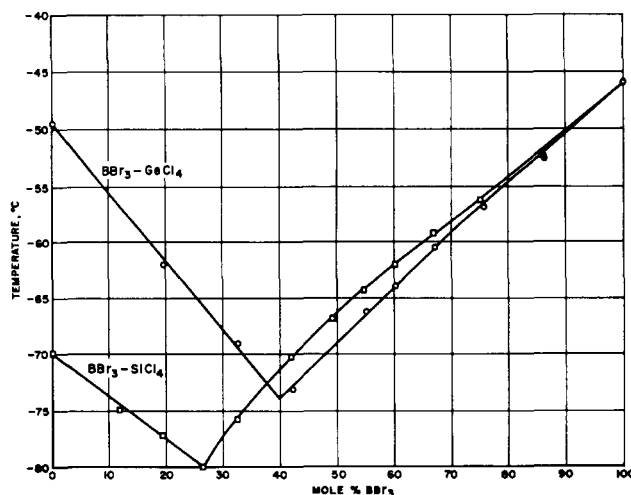
Figure 2. Melting point-composition curves for BBr_3-$GeCl_4$ and BBr_3-$SiCl_4$

Figure 3. The solubility of $GeCl_4$, $GeBr_4$, $SiCl_4$ and $SiBr_4$ in BBr_3: ---, ideal; ——, experimental

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Experimental solubility values were not obtained close enough to $N \to 1$, however, to obtain independent estimates of heats of fusion. The heats of fusion used for calculation were 2.9 ± 0.5 (6) 2.00 (4) and 1.84 (9) kcal./mole for GeBr$_4$, SiBr$_4$ and SiCl$_4$ respectively. The heat of fusion for GeCl$_4$ was not available in the literature for comparison.

The GeBr$_4$-SiBr$_4$ melting point-composition curve shown in Figure 4 is seen to be bowed upward slightly above a linear curve between the melting points of the pure components, indicating that a continuous series of solid solutions are formed in this system. The ideal liquidus and
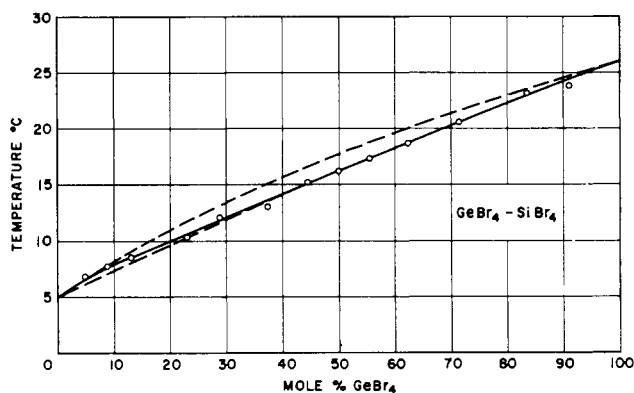

Figure 4. Experimental liquidus curve for GeBr$_4$-SiBr$_4$ compared with calculated ideal liquidus and solidus solid solution curves: ---, ideal; ——, experimental

solidus solid solution curves have been calculated (5) for this system and compared with the experimental liquidus curve in Figure 4.

ACKNOWLEDGMENT

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Formation Constants of Copper and Nickel Chelates of RAPOX

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Gravimetric estimations of copper and nickel and their separation using RAPOX (resacetophenone oxime) is described earlier (1). The colorimetric study of these complexes and their solvent extraction using cyclohexanone is partly published (2, 3). The solvent extraction method was extended to prepare a carrier free source of Cu-64, 67 from neutron irradiated zinc (4). The solubility study of these complexes in different organic solvents immiscible with water is described recently (5).

The present communication is the extension of the study of RAPOX chelates and deals with the evaluation of the formation constant of copper and nickel complexes.

EXPERIMENTAL

MATERIALS. Resacetophenone oxime was synthesized from resorcinol and crystallized from ethanol (1).

Merck's extra pure copper sulphate was used. The standard solution when analyzed (1) for copper gave 3.75×10^{-2} mole of copper per liter.

Merck's extra pure quality nickel sulfate was utilized. The analysis of the standard solution for nickel (1) gave 4.378×10^{-2} mole of nickel per liter.

Cyclohexanone was purified and distilled (6, 7).

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Freshly crystallized potassium biphthalate and B.D.H. (AnalaR) Potassium dihydrogen phosphate were used for preparing various buffer solutions.

Instruments. Lumetron photoelectric colorimeter, 402E model with monochromatic filters, was used.

For pH determinations Leeds and Northrup pH meter, Cat. No. 7666, was employed.

EVALUATION OF FORMATION CONSTANT

When an n valent metal in an aqueous medium is shaken with a chelating agent in water immiscible organic solvent, the formation of the chelate may be represented (8) by the reaction:

$$M^{-n} + n\mathrm{HR} \rightleftharpoons MR_n + nH^- \tag{1}$$
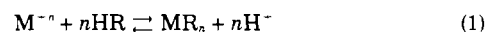
where HR stands for the chelating agent.

The over-all equilibrium constant then is given by:

$$K_M = \frac{[MR_n][H^-]^n}{[M^{-n}][HR]^n} \tag{2}$$

Substituting D for $[MR_n]/[M^{-n}]$