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Zone Melting with Reaction and Volatilization: CBr_4

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Abstract

Carbon tetrabromide was purified by zone refining. The two major impurities were $CHBr_3$ and Br_2. $CHBr_3$ was moved only slowly by zoning, with removal enhanced by volatilization from an open end of the tube. Br_2 was effectively moved by zoning, but significant new quantities were generated by thermal decomposition of the melt, even in the dark. Continued zoning greatly reduced the tendency of the CBr_4 to undergo cellular and dendritic growth, but still did not permit thermocapillary movement in a temperature gradient.

INTRODUCTION

Carbon tetrabromide was selected as a material for solidification experiments in space (*1–3*) because its low entropy of fusion causes it to solidify in a nonfaceted manner like metals (*4*). The object of these 5 to 10 min long experiments was to observe the liberation and behavior of gas bubbles during solidification in the absence of gravity. It was expected that the temperature gradient in the system would cause the bubbles to move because of the dependence of surface tension on temperature (*3*, *5*). However, no thermocapillary bubble movement occurred, which is indicative of the presence of surfactant impurities. Sufficient impurities were present to also cause the solidification front to be extremely dendritic rather than smooth (see Ref. *7*). Thus a program was begun to purify our CBr_4. Distillation was difficult because of the high melting point ($\sim 90°C$) and high volatility of CBr_4, and ineffective because some impurities appeared to have a higher volatility than CBr_4 while others had a lower volatility (*6*).

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Thus our efforts were directed toward multipass zone melting as a purification tool.

Purification of CBr_4 is complicated by its reported decomposition above 140°C and in the presence of short wavelength light below 4200 Å (*7–11*). Reaction products are primarily C_2Br_6, C_2Br_4, and Br_2, although larger molecules are no doubt eventually produced. Thus our experiments were performed in the absence of light or with light filtered through a red plastic filter. In spite of these precautions, molten CBr_4 was observed to slowly turn brown, indicating that some slow thermal decomposition occurs even at the melting point. Exposure to light greatly accelerated the process.

For solidification experiments it is also worth noting that CBr_4 crystallizes from the melt at about 90°C as an isotropic plastic crystal phase, with a transition to the monoclinic, room temperature phase at about 47°C (*12*, *13*). During solidification these phases were manifested as a transparent section just below the melt, with a chalky opaque region below that.

EXPERIMENTAL

The experiments are described in detail elsewhere (*6*). Carbon tetrabromide was obtained from Eastman, Aldrich, and K & K. It was contained in 10, 13, or 15 mm i.d. Pyrex tubes. A few experiments were also performed in 7.5 mm i.d. Teflon tubing. The results were the same as with glass, only the solid CBr_4 was easier to remove. A Fisher Zone Refiner was used with an upward zone travel rate of 6.2 mm/hr. The zone length was approximately 1 cm.

Determination of purity was made with a Model 720 F & M Dual Column Programmed Temperature Gas Chromatograph with a thermal conductivity detector. The best separation was obtained using Carbowax 20M on a solid support of Haloport F in a 2-m long, 6-mm o.d. column. Above 120°C the CBr_4 reacted to produce several small peaks in the vicinity of the CBr_4 peak. Thus an operating temperature of 85°C was used with a high flow rate ($\sim$ 100 cc/min) of the helium carrier gas. The injection port and detector lines were held at 175 at 210°C to prevent condensation of CBr_4. The injection syringe was immediately vacuum flushed with several milliliters of CCl_4 after each use to prevent clogging with CBr_4. The maximum impurity content in all samples tested was just under 3%wt. Methanol, ethanol, acetone, chloroform, CCl_4, and CS_2 were tried as solvents for the CBr_4. When the solutions were exposed to light, CBr_4 reacted when dissolved in methanol, ethanol, and acetone. In all solvents a large impurity peak was apparent at the trailing edge of the solvent peak but could not be resolved (it is thought to be bromine). Carbon tetrachloride was finally selected as a solvent.

A small air peak was assumed to go through without retention. This gave 20 sec for the carrier flow-through time, an impurity peak at ~3.2 min (identified as bromoform, $CHBr_3$), and CBr_4 at 8.3 min. No additional peaks came within 30 min, although higher molecular weight compounds should have been present. Bromoform concentrations were determined by the ratio of bromoform area to CBr_4 area, and were reproducible to within ±3%.

Bromine was analyzed with a Beckman Model 24 Spectrophotometer at 0.417 μm in CCl_4 solution (*14*). Five minutes of exposure to 0.417 μm light caused the absorption values to increase by one or two points, while the readings were normally taken in about 2 sec.

A rough idea of impurity content was also obtained by observing the planar to cellular transition, either versus distance at constant freezing rate or versus freezing rate. It is well known that the breakdown to cellular growth, and eventually dendritic growth, is more likely to occur at high impurity contents, high freezing rates, low temperature gradients, low stirring, and low distribution coefficients. While the temperature gradient at the freezing interface can be estimated from the thickness of the isotropic phase, the distribution coefficients of the impurities are unknown. Likewise, the amount of stirring is unknown. Thus the planar-cellular breakdown is an indication of purity, but could not give the actual amount of impurities.

RESULTS

Zone refining produced two visible results. Brown coloring matter was concentrated into the zone, leaving less colored yellow solid behind. Coloring of the solid increased as one moved up the tube. A few black particles were also present. These were pushed by the freezing solid unless they came to rest on a grain boundary groove, cell groove, or interdendritic space.

Some analytical results are summarized in Table 1. It was possible to zone refine only the Eastman CBr_4. Material from Aldrich and K & K displayed cellular growth from the beginning of zoning even at the lowest rate available. Little separation occurred with cellular growth, and virtually none with dendritic growth. Cellular growth was always observed to set in within 5 or 6 cm of the starting point of each zone pass on Eastman CBr_4. Note that Eastman Lot No. C6X material had approximately 6 times the $CHBr_3$ content of Lot No. A4C. Nevertheless, no difference was discernible in the onset of cellular growth. This indicates that $CHBr_3$ was not primarily responsible for cellular growth, probably because its distribution coefficient is near unity.

TABLE 1

Impurity Analysis of CBr_4

Source	Bromoform concentration (wt-%)	Light absorption at 417 μm (Br_2)	Freezing rate for onset of cellular growth (mm/hr)
Eastman Chemical Co.:			
Lot no. A4C	0.64	—	~12
Lot no. C6X	4.12	0.068	~12
Aldrich Chemical Co.:			
Lot no. 122957	0.58	0.999	>6
K & K Chemical Co.:			
Lot no. 1196	0.00	0.490	>6
Zone refined			
A4C, 2 passes	0.56	0.024	~40

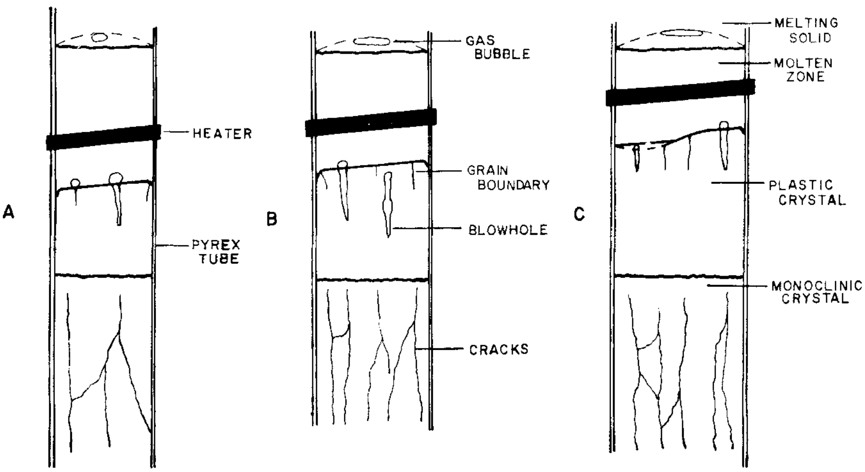

FIG. 1. Structures of zone-refined CBr_4 in 10 (A), 13 (B), and 16 (C) mm i.d. Pyrex tubes.

Five or six grains were present in each ingot, as sketched in Fig. 1. During the first few passes, gas tube "blowholes" formed at the grain boundaries. Blowholes originated by nucleation of gas bubbles, probably of air, at the freezing interface.

In one experiment, duplicate runs of 2 zone passes each were performed on CBr_4 in 10, 13, and 16 mm i.d. Pyrex tubes sealed at both ends. Cross-sectional samples 2 mm thick were taken at 1 cm intervals for gas chromatographic analysis of $CHBr_3$ content. The results are shown in Fig. 2.

The data are plotted with the original starting composition of each ingot defined as 1.0. The average relative bromoform concentrations were 1.01, 1.04, and 1.04 in the 10, 13, and 16 mm tubes, respectively. Thus the total amount of bromoform was not altered by the zoning. Note that the best separation was obtained for the 13 mm i.d. run. As tube size increases, one expects free convection stirring to increase, leading to a better separation. However, the temperature gradient decreases with increasing zone size, leading to earlier cellular growth and reduced separation. It appears that the net effect of these two phenomena is an optimum around 13 mm i.d.

On Fig. 2 is plotted a theoretical curve (*15*) for 2 zone passes with a distribution coefficient k of 0.9. An exact fit with the experimental data could not be obtained for any value of k. One explanation for this is vapor transport of volatile $CHBr_3$ up blowholes and cracks after zoning, which would tend to reduce the separation and make the concentration profiles depart from ideal.

Because bromoform is volatile, one might suspect that additional purification could be obtained by allowing volatilization from the end of the charge. This was done by leaving the top end of the tube open to the atmosphere. Results are shown in Figs. 3, 4, and 5 for 2, 4, and 12 zone passes, respectively. The average $CHBr_3$ concentration in these tubes was

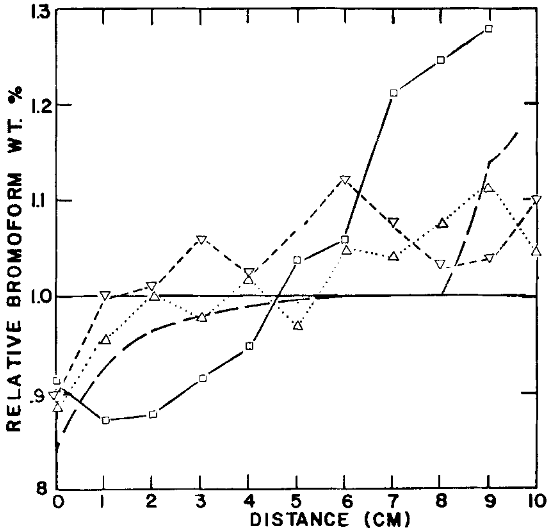

Fig. 2. Bromoform distribution after two zone passes in sealed ampules. Pyrex tubes of 10 (△), 13 (□), and 16 (▽) mm i.d. (– –) Theoretical curve for $k = 0.9$, $L/l = 10$, and $N = 2$ (*15*).

0.9, 0.82 and 0.76, respectively, showing a steady decrease of $CHBr_3$ with further zoning.

Bromine analyses were also performed, as shown in Fig. 6. The sudden increase in light absorption at approximately 5 cm down the ingot corresponds to the observed onset of cellular growth at that location. This indicates that Br_2 was largely responsible for the onset of cellular growth,

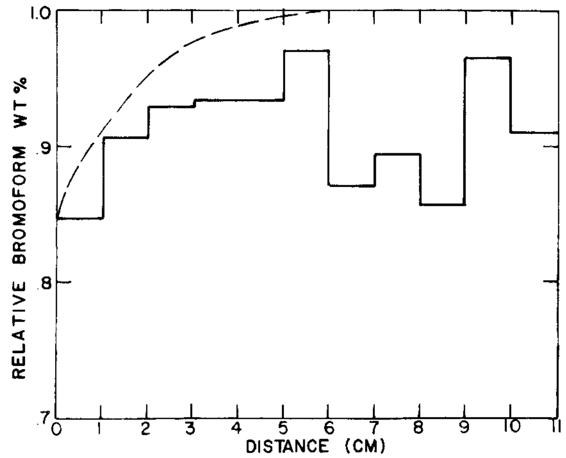

FIG. 3. Bromoform distribution after two zone passes in an open-end ampule, 10 mm i.d. (– –) Theoretical curve for $k = 0.9$, $L/l = 10$, and $N = 2$ (*15*).

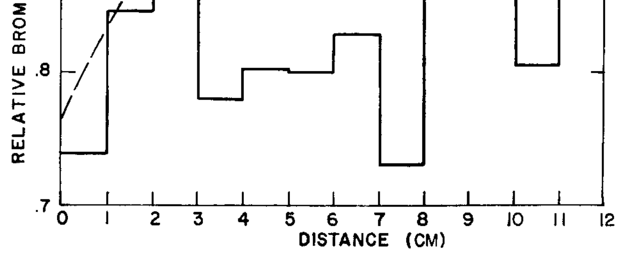

FIG. 4. Bromoform distribution after four zone passes in an open-end ampule, 10 mm i.d. (– –) Theoretical curve for $k = 0.9$, $L/l = 10$, and $N = 4$.

as would be expected from the fact that *k* for Br_2 was much lower than *k* for $CHBr_3$.

One can also see from Fig. 6 that the total amount of Br_2 increased significantly during zoning. It was in fact over 5× larger than the feed. When a zone-refined ingot was allowed to stand while sealed in its tube, microscopic reddish brown droplets of Br_2 formed in the cracks present in the monoclinic CBr_4. Removal of Br_2 would therefore have also been enhanced by operating with the top end of the tube open.

In order to produce CBr_4 suitable for space experiments, it was necessary to discard the top half of each ingot because of the enhanced Br_2 content there. Combination of several bottom halves and repeated zoning, followed by a repetition of the above, led to refined material which formed dendrites much less readily. However, gas bubbles still did not move in a temperature gradient (*2*, *3*), indicating that surfactant was still present. Therefore, in order to properly purify CBr_4, it will be necessary to find a new separation technique operating considerably below the melting point in the absence of light. Since other less sensitive organic compounds are available for the simulation of the solidification of metals, this does not appear to be a profitable direction for research.

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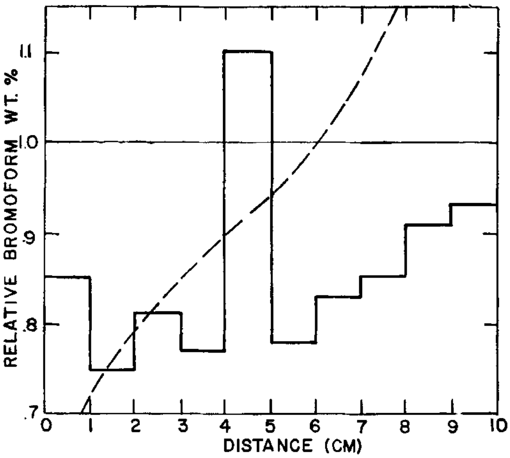

FIG. 5. Bromoform distribution after 12 zone passes in an open-end ampule, 10 mm i.d. (– –) Theoretical curve for $k = 0.9$, $L/l = 10$, and $N = 4$.

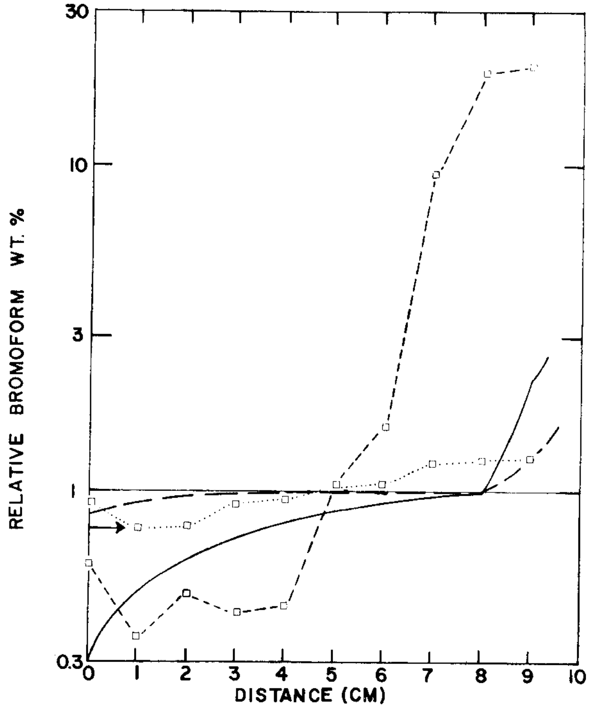

FIG. 6. Bromoform (· · ·) and Br_3 (- -) distributions after two zone passes in a sealed ampule, 13 mm i.d. (– –) $k = 0.9$. (——) $k = 0.3$.

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