slope $n/0.059$, just as for a reversible wave. The ascorbic acid wave does in fact satisfy this requirement.[3] The agreement is particularly gratifying in that on the basis of the plane electrode theory, which predicted a non-linear plot, the reversible slope appeared to be a troubling anomaly. The new equation for the $E_{1/2}$ of the *average* current becomes $E_{1/2} = E_0 - (RT/2nF)\ln k - (RT/nF)\ln 0.87$. In the previous equation based on plane electrode calculations,[3] the last term was $RT/nF \ln 0.65$.

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Purification of Germanium Tetrachloride by Solvent Extraction

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Introduction.—Liquid–liquid solvent extraction methods have provided a valuable tool for the separation of impurities from many materials.[1] Since germanium tetrachloride and concentrated hydrochloric acid solutions form an immiscible extraction system,[2] a series of experiments was performed to determine the distribution ratios of a number of elements between these two phases for the purpose of developing a chemical method of purification of germanium. Other chemical methods of separation used in the past have involved the distillation of germanium tetrachloride.[3]

It is well known that traces of various impurities have a great effect upon the electrical properties of germanium metal used in semiconductor devices. In some instances it is necessary to control the significant impurities in germanium single crystals to within one part in 10 billion.[4] Consequently, it was of particular interest to study the behavior of very small amounts of impurity elements in this investigation. Radiochemical tracer techniques were used, wherever possible, in the present study, since these provided the double advantage of simplicity and sensitivity. Among the impurities known or suspected of producing an effect upon the electrical behavior of germanium, the elements antimony, arsenic, boron and copper were examined by this extraction technique.

Experimental

Batch Extractions.—Fifteen-ml. portions of germanium tetrachloride, purified by distillation (b.p. 83.1°) were placed in 30-ml. glass stoppered graduated weighing burets. No attempt was made to remove hydrogen chloride from the product since it was to be used in experiments in which it would be shaken with hydrochloric acid. The hydrochloric acid phase consisted of 15 ml. of either 6 or 12 N hydrochloric acid (reagent grade) containing the appropriate amount of impurity element. The fact that the values obtained with arsenic by adding the impurity element to either phase prior to equilibration result in the proper relation is an indication that the initial location of the impurity in the system is not significant. If the hydrochloric acid concentration is much less than 6 N, hydrolysis of germanium tetrachloride will result. Various extractions were performed at equilibration times of 5, 30 and 60 minutes. A series of extractions was performed at 0 and 25 ± 0.2° to determine the effect of temperature on the distribution. The extractors were mechanically shaken in a constant temperature water-bath for the appropriate time. To maintain a temperature of 0° the extractors were mounted in a Dewar flask containing crushed ice and the Dewar flask was mechanically shaken. Changes of phase volumes were measured and in all cases the phases were permitted to settle for 10 minutes prior to sampling.

Impurity Elements.—Of particular interest in this study was the behavior of very small amounts of impurity elements in the parts per million concentration range and lower. Consequently, whenever possible high specific activity or carrier-free radioisotopes were used as impurity elements.

Arsenic.—A standard solution of 100-ml. volume was prepared from 0.25 millicurie of processed carrier-free As^{73-74} produced by cyclotron bombardment of germanium with deuterons.[5] The chemical form of the tracer was arsenic trichloride in 12 N hydrochloric acid. Appropriate aliquots of tracer solution were used in the respective extractions to permit quantitative measurement of activity.

Antimony.—Fifteen millicuries of processed high specific activity (1751 mc./g.) Sb^{124} as antimony trichloride[5] was used to prepare a 25-ml. standard solution of antimony in 12 N hydrochloric acid. An aliquot of this solution was oxidized with $KBrO_3$ to produce pentavalent antimony.

Copper.—Ninety-five millicuries of Cu^{64} produced by irradiating 50 mg. of copper powder with neutrons in the Brookhaven pile was used to prepare a standard solution of copper chloride in 12 N hydrochloric acid (4.5 mg./ml. Cu).

Boron.—0.2858 g. of recrystallized boric acid (C.P.) was dissolved in 500 ml. of distilled water (0.1 mg./ml. B).

Radioactivity Measurements.—At least two aliquots of each phase were placed in 5-ml. screw cap vials and the γ activity was measured by means of a liquid scintillation counting technique. In the case of copper and antimony a liquid phosphor, diphenylbenzene, was used as detector. A well type thallium activated sodium iodide crystal was employed in the measurement of arsenic activity. An RCA 5819 photomultiplier tube was used in a General Electric scintillation counter. A Nuclear Instruments Model 172 scaler was used to record the counts. A sufficient number of counts was taken on each sample to give a statistical fluctuation of less than 1% from the true average rate.[6]

This arrangement permitted counting at a high geometric efficiency. No difficult sample preparation is involved and the counting rate is independent of the density of the solvent under the conditions employed.

Colorimetric Measurements.—Since the radioactive isotope of boron has an extremely short half-life, boron was determined by means of a colorimetric procedure employing carminic acid.[7] Wherever possible platinum or polyethylene apparatus was used to avoid boron contamination. A color change from bright red in the absence of boron to bluish red or blue in the presence of boron is produced. The percentage transmission was measured at 600 mμ using a Beckman Model DU spectrophotometer. Beer's Law is followed over the range from 0 to 20 μg. of boron. There is no interference from small amounts of germanium.

Miscibility of Germanium Tetrachloride in Hydrochloric Acid.—The miscibility of germanium tetrachloride in 6 and 12 N hydrochloric acid solutions was determined in order to ascertain the loss of germanium during extraction. Solutions of both 6 and 12 N hydrochloric acid were shaken with excess germanium tetrachloride for 5 minutes at 0 and 25 ± 0.2°. The germanium content of the hydrochloric acid phases was analyzed by means of a gravimetric procedure involving precipitation as the sulfide and subsequent ignition and weighing of the oxide.[8] The results of the analyses are given in Table I.

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TABLE I

MISCIBILITY OF GERMANIUM TETRACHLORIDE IN HYDROCHLORIC ACID

Equilibration temp., °C.	$GeCl_4$ in 6 *N* HCl, g./l.	Standard dev.	No. of replications	$GeCl_4$ in 12 *N* HCl, g./l.	Standard dev.	No. of replications
0	104.2	1.5	3	20.73	1.41	3
25	101.1	5.9	4	22.27	1.05	3

On the basis of calculations using 95% confidence limits there is an insignificant change in solubility of germanium tetrachloride in hydrochloric acid due to the temperature difference. On the other hand, there is a significant difference due to acid concentration. Thus, at 25° a loss equivalent to only 7.5 g. of germanium per liter of 12 *N* hydrochloric acid will result during extraction. This germanium can be recovered easily by precipitation as germanium dioxide or by extraction with carbon tetrachloride.[9]

Results and Discussion.—An examination of the results for extractions performed at temperatures of 0 and 25° and extraction times of 5, 30 and 60 minutes revealed that greater than 99.9% extraction resulted under all of the above conditions. Consequently, equilibrations for 5 minutes at 25° were selected as being practical and effective, and the data for experiments performed under these conditions are reported in Table II.

TABLE II

DISTRIBUTION OF IMPURITIES BETWEEN GERMANIUM TETRACHLORIDE AND HYDROCHLORIC ACID

Element	Initial concn., p.p.m.	HCl concn., *N*	Distribution ratio (impurity HCl / impurity $GeCl_4$)	Concn. of impurity in $GeCl_4$ phase after extraction, p.p.m.
Antimony(III)	39.3	12	8×10^3	0.003
Antimony(III)	39.3	6	8×10^4	.0005
Antimony(V)	39.3	12	4×10^3	.009
Antimony(V)	39.3	6	5×10^4	.0007
Arsenic(III)	[a]	12	2×10^3	....
Boron	6	12	[b]	Not detected
Copper	474	12	2×10^3	0.26

[a] Carrier-free tracer containing no stable material was employed. [b] Since no boron was detected in the $GeCl_4$ layer, complete extraction is assumed within the limits of sensitivity of the colorimetric procedure.

From precision studies on extractions of arsenic the values of the distribution ratios should be precise to within 35%, which is good for such trace determinations. In all of the above cases these high distribution ratios represent greater than 99.9% extraction of the impurity elements.

The extractability of arsenic trichloride increases considerably with decreasing concentrations of this substance. Allison and Muller[2] have studied the distribution of arsenic using relatively large concentrations of arsenic trichloride and found that the rate of extraction, *i.e.*, the removal of arsenic trichloride from germanium tetrachloride, increases as the extraction proceeds, although the coefficient is small in all cases. The present study, with the aid of carrier-free tracer, permitted an examination of the behavior of arsenic at extremely low concentrations of impurity element. Figure 1 shows an extension of Allison and Muller's curve with data obtained in this study. It is quite apparent that the extraction increases tremendously as the concentration of arsenic trichloride decreases, particularly at very low concentrations, thereby increasing the usefulness of this method as a means of purification, especially in the trace concentration range. This marked variation of extractability with concentration is not observed with copper, boron or antimony. In the case of antimony a concentration of 0.06 *M* antimony trichloride in the hydrochloric acid phase maintains a high degree of extraction, greater than 97%.

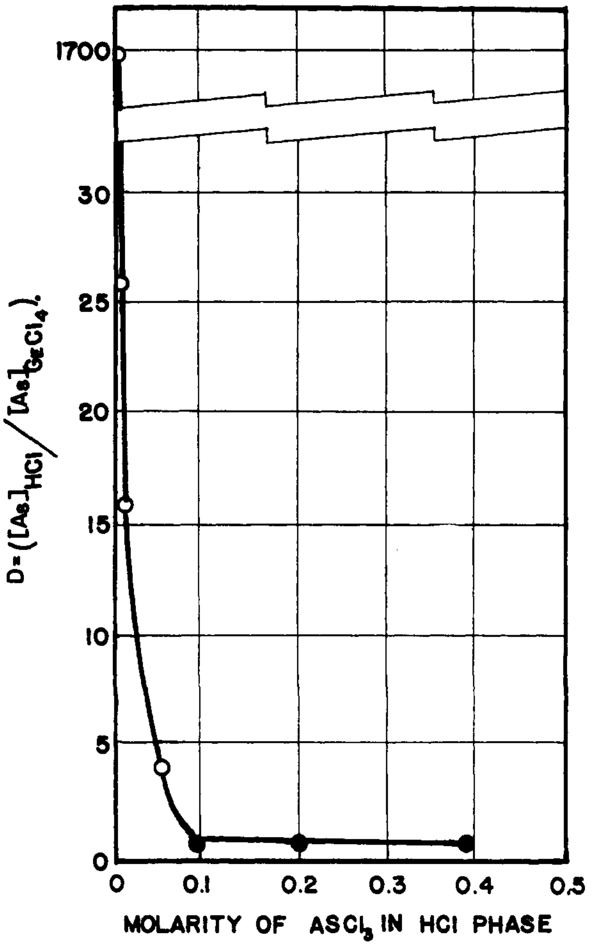

Fig. 1.—Variation of the distribution ratio with arsenic trichloride concentration: ○, data obtained from these experiments; ●, data of Allison and Muller.[2]

Conclusions.—An investigation of the distribution of trace amounts of arsenic, antimony, boron and copper between germanium tetrachloride and hydrochloric acid solutions indicates a strong preference for the latter phase. Equilibrations for 5 minutes at 25° result in greater than 99.9% extraction of these impurity elements.

In the case of arsenic, the extraction from germanium tetrachloride is rather low when large amounts of arsenic trichloride are present. The extraction increases rapidly as the concentration of arsenic trichloride decreases, approaching greater than 99.9% removal with trace amounts. A high degree of extraction is maintained in the case of the other impurities studied, independent of concentration of solute.

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Since practically all metallic impurities are soluble in concentrated hydrochloric acid solutions, it is reasonable to assume that these trace impurities will similarly result in high distribution ratios.

It is quite apparent that the effectiveness of any chemical purification scheme will be limited by the purity of the reagents employed. Thus, according to the A.C.S specifications for reagent grade hydrochloric acid (sp. gr. 1.188–1.192) used in this study, the maximum limit of arsenic impurity present is 8×10^{-7} per cent. Consequently, the use of this solvent without further purification imposes a lower limit for the removal of arsenic impurity from germanium tetrachloride, this limit being equal to or more than 5×10^{-4} parts of arsenic per million parts of germanium.

It is obvious that single batch extractions are very effective in removing the impurities under investigation from germanium tetrachloride, particularly when these impurities are present in very low concentrations. Repeated batch extractions with fresh hydrochloric acid will no doubt reduce the residual impurity considerably. Undoubtedly, a continuous system of solvent extraction could be employed with very successful results.

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Densities of Polyethylene Solutions[1]

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To obtain an estimate of the density of the amorphous regions in polyethylene at temperatures below the crystalline melting point, it is possible to extrapolate to these temperatures the (approximately) linear relation between the melt density and temperature. Confidence in this extrapolation would be increased if the resulting density could be obtained by a second independent method. To this end we have developed a precise method for measuring the densities of polyethylene solutions. The desired amorphous density is obtained by appropriate extrapolation of the specific volume–composition curve. The limited solubility of polyethylene restricts the experiments to temperatures not far below the crystalline melting point.

Previous measurements[2] of the densities of polyethylene solutions were restricted to relatively dilute solutions and were uncertain in the third decimal place. We have obtained a precision of about ±0.0002 density unit at the 95% confidence level. This is comparable to the precision attained on solid polyethylene samples at room temperature.[3]

Experimental

The polyethylene sample used in this work was that designated A-40 by others.[2,4,5] The solvent was Eastman Kodak Co. #277 *p*-xylene, m.p. 12–13°. Reischauer pycnometers (A. H. Thomas Co., #9023) were calibrated with mercury at several temperatures in the range under consideration. Corrections were applied for meniscus shape and for the buoyancy of air.

Solutions containing less than 30% polyethylene by weight were made up in glass stoppered flasks which were agitated by slow side-to-side rocking in an air oven at 90° for 12 hours. The homogeneous solutions were then poured into a 50-ml. hypodermic syringe whose barrel was wrapped with glass heating tape and maintained at 90°. An improvised needle with a 2-mm. bore was used to inject the solution into the heated pycnometer.

More concentrated solutions were too viscous to flow through the needles. They were made up directly in the pycnometers. Finely divided polyethylene and enough xylene to fill the pycnometer $^3/_4$ full at 90° were weighed in. Mixing was accomplished by slow rocking as before at 125° to reduce the viscosity of the solution. The pycnometer was then brought to 90° and filled to the graduated section. It was then cooled until the liquid level fell below the neck and rocked at this temperature until the solution was homogeneous.

Final measurements were carried out in a constant temperature bath at 90.0 ± 0.02°. The experimental data for several solutions of polyethylene A40 are listed in Table I.

Crude cloud point observations were made on the more dilute solutions by allowing them to cool in a test-tube while stirring them with a thermometer. The temperature at which the first sign of a precipitate appeared was recorded as the cloud point.

TABLE I

DENSITIES OF SOLUTIONS OF POLYETHYLENE A40 AT 90°

Wt. % polyethylene	Density	Specific vol.	Cloud point, °C.
0[a]	0.7982	1.2528	..
10.000	.8001	1.2498	68
20.000	.8020	1.2469	72
30.000	.8038	1.2441	77
44.138	.8065	1.2399	..
100	.8172	1.2237[b]	114[c]

[a] Pure *p*-xylene. [b] Obtained by least squares extrapolation. [c] Crystalline melting point by polarized light with hot stage microscope.

Discussion

Amorphous Density of Polyethylene.—A plot of specific volume against weight composition of the polyethylene solutions was a straight line with a maximum deviation of experimental points of less than 0.0002 cc./gram. This linear relationship suggests strongly that polyethylene and *p*-xylene mix without change in volume at least up to 44% polyethylene by weight. We therefore felt justified in extrapolating the line to 100% polyethylene. A least squares analysis gave a specific volume of 1.2237 ± 0.0005 (95% confidence limits) and a corresponding density of 0.8172 for amorphous polyethylene at 90.0°. This value may be compared with 0.8153 obtained by linear extrapolation to 90° of the melt density–temperature curve of another polyethylene.[6]

Estimated Heat of Fusion.—Bueche[7] has recently expressed Flory's relation[8] for the depression

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(1) A joint contribution of the Department of Chemistry, University of Delaware, and the Polychemicals Department, E. I. du Pont de Nemours & Co. Research performed by Robert Roberts in partial fulfillment of the requirements for the degree of Bachelor of Science at the University of Delaware. Presented at the Fifth Delaware Chemical Symposium, Delaware Section, A.C.S., January 17, 1953.

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