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Reactivities of Copper–Germanium Alloys in the Direct Synthesis of Dimethyldichlorogermane

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The activities of the single phase alloys α (Ge in Cu), ζ (Cu_5Ge), and ϵ (Cu_3Ge) in the reaction with methyl chloride to form methylchlorogermanes were measured at 426.7°C. The alloys displayed essentially the same reactivity when compared on the basis of the same number of germanium atoms exposed to methyl chloride. Selectivity for $(CH_3)_2GeCl_2$ approached 100% at 0% conversion of germanium, thus supporting the ionic mechanism of Voorhoeve. The extent of cracking of methyl chloride could be correlated with the fraction of the surface estimated to consist of copper atoms not involved in the synthesis of methylchlorogermanes. Removal of copper from thin surface layers, probably as CuCl, was confirmed by X-ray analysis in the case of the α phase. Mechanical mixtures of alloys and free germanium showed greatly enhanced reactivities which could be explained only by the creation of additional reaction sites on the surfaces of the free germanium particles.

INTRODUCTION

The preparation of methylchlorogermanes by direct synthesis from germanium and methyl chloride in the presence of a copper catalyst was first reported by Rochow (*1*) in 1947. Since then, details of the reaction have been investigated by a number of workers (*2–6*) using mechanical mixtures of powdered germanium and powdered copper. In these studies the ratio of germanium to copper by weight ranged from 2.5:1 to 4:1. Rochow (*7*) prepared an alloy of copper and germanium by pressing a mixture of germanium and copper powders (ratio 85:21) into a disk and firing in hydrogen at 705°C. The particular intermetallic phases so found were not reported. Belij *et al.* (*8*) reported the direct synthesis of dimethyldichlorogermane from methyl chloride and copper–germanium alloys, but did not identify the alloy phases present.

From the phase diagram of the copper–germanium system (Fig. 1) it is seen that the overall compositions of the contact mixtures used in the above studies fall in the two-phase ϵ + Ge region. Copper and germanium form two Hume-Rothery "electron compounds"—Cu_5Ge (ζ phase) and Cu_3Ge (ϵ phase). The properties of these phases are listed in Table 1. In a series of investigations (*9–13*) Voorhoeve and Vlugter established that for the copper catalyzed reaction between methyl chloride and silicon, copper and silicon must be present as an intermetallic compound for copper to

TABLE 1
INTERMETALLIC PHASES IN Cu-Ge SYSTEM

Phase	Electron-atom ratio	Crystal structure
α (solid solution of Ge in Cu)		Face-centered cubic
ζ (Cu_5Ge)	1.5	Hexagonal close-packed
ϵ (Cu_3Ge)	1.75	Orthorhombically distorted hexagonal close-packed (ordered)

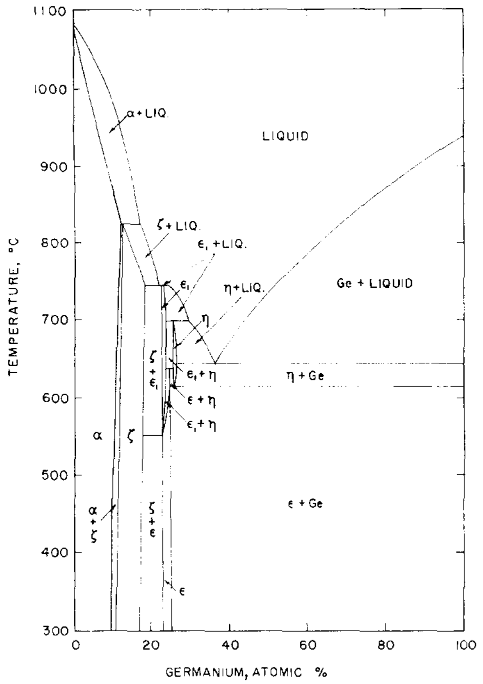

FIG. 1. Equilibrium diagram of the system copper–germanium (from "Constitution of Binary Alloys" by Hansen. Copyright 1958. Used with permission of McGraw-Hill Book Company).

function as a catalyst. Both the η phase (Cu_3Si) and the ϵ phase ($Cu_{15}Si_4$) were prepared, and were shown to have high initial reactivity and selectivity for $(CH_3)_2SiCl_2$. The object of the work reported here was to compare the activities of the single phase (α, ζ, and ϵ) copper–germanium alloys for the direct synthesis of dimethyldichlorogermane, and thus to gain additional insight into the mechanism of the reaction.

EXPERIMENTAL METHODS

Materials and Apparatus

Appropriate weights of copper (99.999 +% purity, American Smelting and Refining Co.) and germanium (resistivity 40 ohm-cm, Eagle Picher Industries) were melted together under an argon atmosphere in a nonconsumable electrode arc melter. The ingots were turned over and remelted several times to promote homogenization. Since rapid cooling in the melter caused inhomogeneous crystallization, the ingots were next sealed under vacuum in quartz tubes and homogenized in a furnace. The α and ζ phase ingots were homogenized at 700°C for 4 days, while the ϵ phase alloy was homogenized at 525°C for 3 wk. After slow cooling to room temperature, samples of the alloys were removed by filing and were subjected to chemical analysis and X-ray analysis. The samples taken for X-ray analysis were annealed under vacuum at 490°C for 3 hr to relieve strains due to filing. A Debye-Scherer camera and Cu*K*α radiation with a Ni filter were used for X-ray analysis of the α and ζ phase alloys. Cobalt *K*α radiation and an Fe filter were used for determining the crystal structures of the ϵ phase alloys. The results of these analyses are given in Table 2. A portion of the filings were screened, and alloy particles between 45 and 100 mesh were taken for testing in the reactor. The

TABLE 2
ANALYSIS OF ALLOYS

		Lattice parameters (Å)						
		Found experimentally			Literature values			
Phase	Atom % Ge	a	b	c	a	b	c	Surface area (cm²/g)
α	8.8	3.643			3.6438[a]			241
ζ	15.6	2.596		4.224	2.595[b]		4.225[b]	460
ϵ	25.0	2.636	4.571	4.202	2.645[b]	4.5532[b]	4.2025[b]	800

[a] Hume-Rothery, W., Lewin, G. F., and Reynolds, P. W., *Proc. Roy. Soc. Ser. A* **157,** 167 (1965).
[b] Schubert, K., and Brandauer, G., *Z. Metallk.* **43,** 262 (1953).

surface areas of particles in this size range were measured by the BET method using krypton as the adsorbed gas. Results of these surface area determinations are reported in Table 2.

The methyl chloride used in this study (99.5+% purity, Matheson) was passed through a drying agent (magnesium perchlorate) before being introduced into the reactor. Analysis of the methyl chloride by gas chromatography revealed trace amounts of methane, ethane, and nitrogen.

The microreactor and associated equipment (Fig. 2) were constructed according to the design of Harrison, Hall, and Rase (*14*). The reactor itself was a length of 0.25 in. o.d. stainless steel tubing immersed in a fluidized sand bed whose temperature could be controlled to within ±0.2°C. The temperature of the fluidized sand bed was measured at three positions with calibrated iron–constantan thermocouples.

Since the composition of the copper–germanium alloys was continually changing due to germanium removal, analysis of integral reactor data would be very difficult. It was decided to operate the reactor as a differential reactor. Preliminary tests showed that at 426.7°C the reaction was relatively slow, and long contact times were needed to obtain measurable conversion. Accordingly, reactor lengths of 3 to 4 in. and methyl chloride flow rates (at 760 mm Hg, 20°C) of 10 to 40 cm^3/min were selected. Under these conditions fractional conversion of the methyl chloride ranged from 0.1 to 14%. For the largest flow rate the measured pressure drop through the 3 in. packed bed, with the feed stream at atmospheric pressure, was 0.15 psi. The external transport factor calculated according to the method of Huang and Sather (*15*) was of the magnitude 1–10^{-5}. Since the analogous reaction with silicon–copper alloys was reported to be quite exothermic (*10*) a calculation was performed to check the assumption of isothermal reactor operation. The one-dimensional steady-state mass and heat balance equations were solved on a digital computer assuming a heat of reaction of -40.0 kcal/g-mole methyl chloride reacted and an activation energy of 25.0 kcal/g-mole. Using the highest reaction rate found experimentally the maximum temperature rise thus calculated was 1.2°C.

Samples of the product gas stream were removed by a sampling valve and sent to a Perkin Elmer 154D gas chromatograph for analysis. The analytical column was a 41 by 0.25 in. stainless steel tube containing silicon oil DC 500, diethyl phthalate,

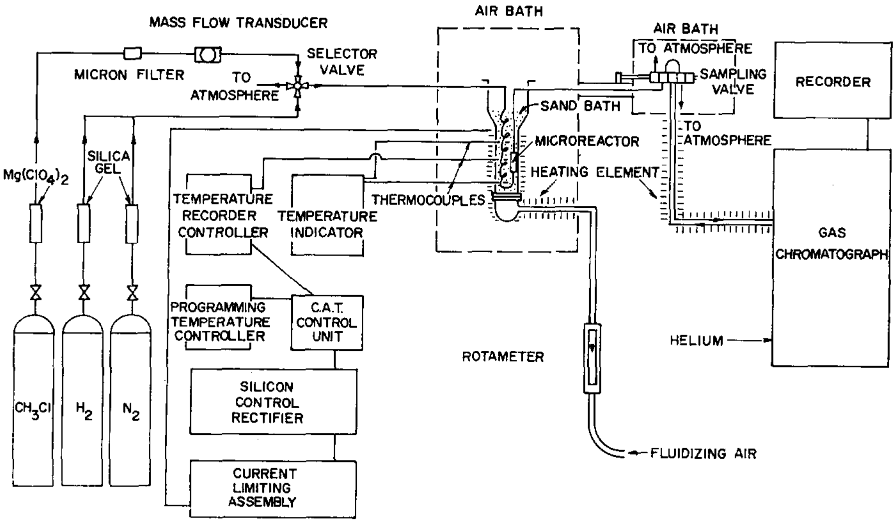

FIG. 2. Catalytic flow microreactor.

and Chromosorb WAW 60/80 mesh in the ratio 20:60:100. The elution times of some of the methylchlorogermanes were up to 60 min.

Procedure

To detect any catalytic effect of the reactor wall methyl chloride was passed through the empty reactor at 426.7°C. A small amount of hydrogen chloride and trace quantities of methane and ethane appeared in the gas chromatogram of the exit stream. At the lowest methyl chloride flow rate the cumulative amount of products other than methyl chloride was only 0.5 mole % of the exit stream. Due to the relatively long time required to complete a gas chromatographic analysis of the product gases, an intermittent mode of operation was used in testing the copper–germanium alloys. Methyl chloride was passed over the contact mass for 6 to 12 min. Then a sample of the exit gas stream was taken for analysis and simultaneously the methyl chloride feed was replaced by a stream of pure nitrogen until the gas chromatographic analysis was completed. To investigate the possibility that the alloy particles might be poisoned by impurities in the nitrogen or undergo other changes during the 60 min required for completion of the analysis, duplicate runs were performed on the ϵ phase alloy using both intermittent and continuous exposure to methyl chloride. Figure 7 shows that both methods of operation yielded essentially the same reaction rate versus germanium conversion curve.

For each alloy multiple runs having different cumulative methyl chloride contact times were performed. After each run the contact mass was removed from the reactor and a sample taken for X-ray analysis. In all runs the total moles of products found by gas chromatography were compared with the number of moles taken for analysis as calculated from the sample loop volume. The maximum discrepancy was 1.9%. The cracking of methyl chloride occurred in parallel with the formation of methylchlorogermanes as evidenced by the change in color of the contact masses from golden yellow or bluish white to gray to black during the course of the reaction.

The alloys tested varied both in germanium content and in surface area per gram. The primary purpose of this study was to investigate the ease of removal of germanium atoms from the various single phase alloys. The following definition of reaction rate was taken as most meaningful for a comparison of the intrinsic reactivities of the different phases:

$$r_g = \frac{\text{g-atom Ge reacted}}{(\text{cm}^2 \text{ alloy surface area})\ (\text{atom frac. Ge in alloy before reaction})\ (\text{min})}.$$

This definition is based on the assumption that initially the copper–germanium ratio, averaged over all surfaces of the polycrystalline particles, is roughly the same as the ratio of copper:germanium in the bulk.

RESULTS

To compare the reactivities of the alloys on the basis outlined above, it was recognized that the reaction rate–germanium conversion curves would have to be extrapolated to 0% germanium conversion. Reaction rate–germanium conversion curves determined for the α, ζ, and ϵ phase alloys (Figs. 3, 5, and 7) displayed lengthy induction periods. The distribution of methyl groups in the products (Figs. 4, 6, and 8) showed that in the period of maximum reactivity the selectivity for $(CH_3)_2GeCl_2$ approached the same limit (60–70%) for all three alloys. At the beginning of the induction period and at the end of the falling-rate period the rate of production of methylchlorogermanes was low and cracking products constituted a large percentage of the reaction products. Since the induction period was probably due to an oxide film on the germanium, attempts were made to remove the oxide film after the alloy particles were loaded into the reactor. Two methods were tried. According to Rosen-

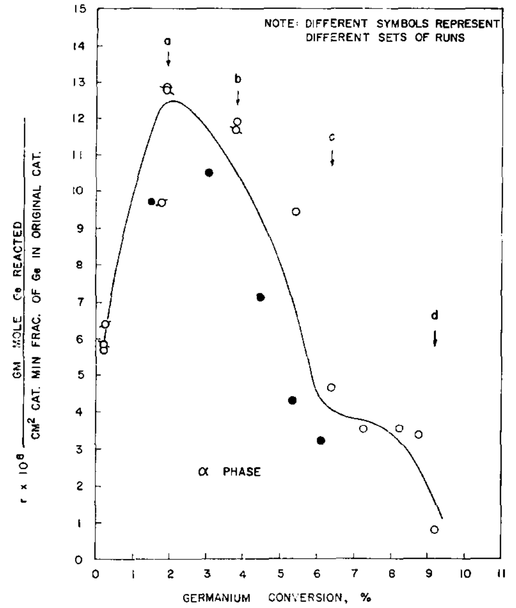

FIG. 3. Reactivity of α phase alloy. X-Ray analysis: (a) High angle lines of α phase shift slightly in the direction of higher Ge content; ζ phase lines present. (b) α Phase lines remain unchanged; ζ phase lines present. (c and d) High angle lines of α phase shift slightly in the direction of higher Cu content. No ζ phase or free Cu lines.

berg, Robinson and Gatos (*16*) GeO_2 could be removed at above 575°C by the reaction,

$$Ge + GeO_2 \rightarrow 2GeO,$$

where GeO is a relatively volatile oxide. The alloy particles in the reactor were therefore heated in a stream of nitrogen to a temperature of 575–600°C for 2 hr before being allowed to react with methyl chloride. The second method of pretreatment involved reduction with hydrogen at 590–600°C for a period of 60–80 min. The thermal pretreatment was sufficient to eliminate the induction period only for the α phase alloy. Figure 9 shows that the hydrogen pretreatment successfully eliminated the induction period for all three alloys.

The curves for the α and ζ phase alloys, when extrapolated to 0% germanium conversion, approach initial reaction rate values in the range 14×10^{-8} to 16×10^{-8}. The ϵ phase curve extrapolates to a value in the range 5×10^{-8} to 7×10^{-8}. The differences between these values are of the order of magnitude of the experimental and extrapolation errors. No significant differences between the initial reactivities of the three single phase alloys are apparent when they are compared on the basis of the reaction rate defined above.

A limited number of experiments were performed using mechanical mixtures of the powdered ζ or ϵ phases with powdered germanium. These mixtures are similar to the actual contact masses used industrially in the direct synthesis of methylchlorosilanes, and they were not pretreated to

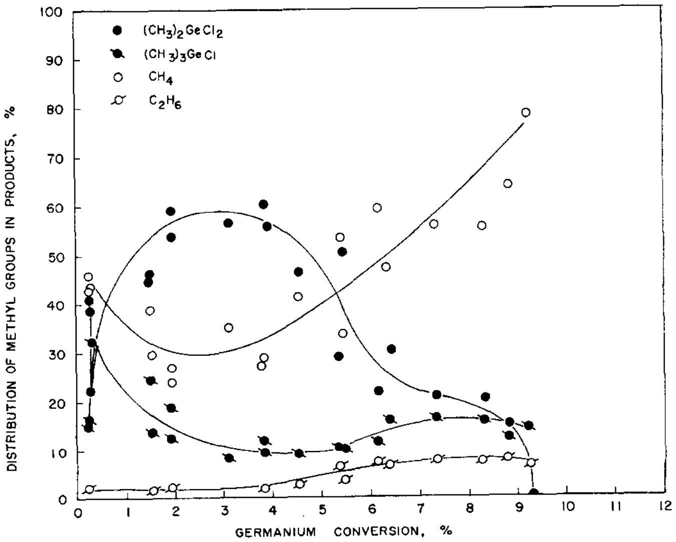

FIG. 4. Product distribution from α phase alloy.

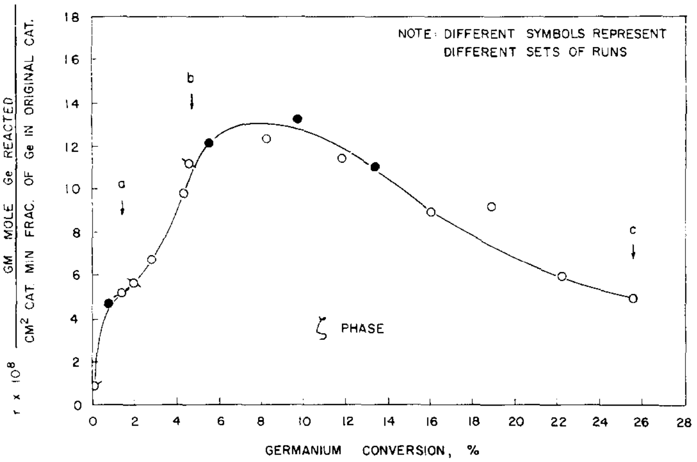

FIG. 5. Reactivity of ζ phase alloy. X-Ray analysis: (a) ζ Phase lines remain unchanged. (b) ζ Phase lines shift slightly in the direction of higher Cu content; α phase lines are present. (c) ζ Phase lines largely disappear; α phase lines are strong.

remove oxides. Using, as before, a reaction rate based on the surface area and composition of the alloy particles in the mixture, the addition of free germanium increased the maximum reactivity by 50% in the case of the ε + Ge mixtures, and by 400% in the case of the ζ + Ge mixtures (Fig. 10). Associated with these high reactivities were high selectivities for $(CH_3)_2GeCl_2$ sustained over a long period of time (Figs. 11 and 12).

DISCUSSION OF RESULTS

In studies of the reaction of methyl chloride with copper–silicon alloys Kolster, Vlugter, and Voorhoeve (*9*) attributed the continual decline in reactivity of the alloy to carbon deposited on the active sites by the cracking of methyl chloride. In this work an investigation was made of the contribution of surface depletion of germanium to the falling-rate period. A

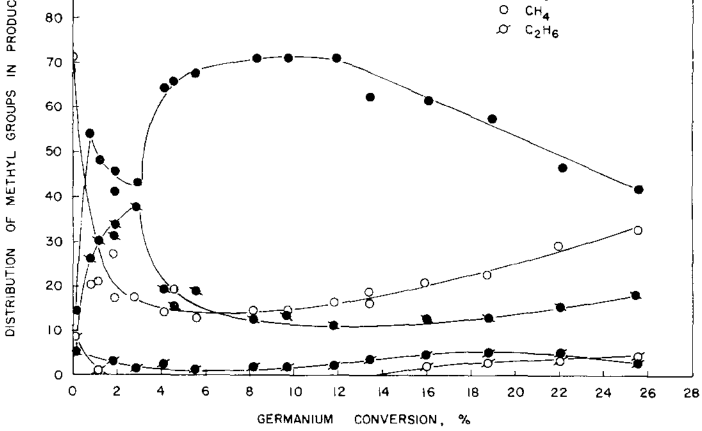

FIG. 6. Product distribution from ζ phase alloy.

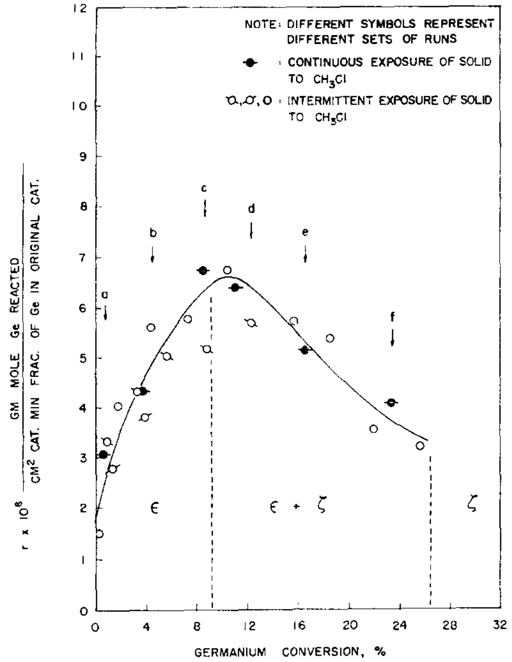

FIG. 7. Reactivity of ε phase alloy. X-ray analysis: (a) ε Phase lines; no change. (b) ε Phase lines diffuse. (c) ε Phase lines shift in the direction of higher Cu content; ζ phase lines are present. (d) ε Phase lines shift further in the direction of higher Cu content; ζ phase lines are more intense than those in (c). (e) ε Phase lines shift further in the direction of higher Cu content; ζ phase lines are more intense than those in (d). (f) ε Phase lines shift further in the direction of higher Cu content; ζ phase lines are more intense than those in (e). Note: According to stoichiometric calculations the boundary between the ε phase and the ε + ζ phases should occur at 9.11% conversion of Ge. The boundary between the ε + ζ phases and the ζ phase should occur at 26.4% conversion of Ge.

mathematical model of diffusion in a sphere with a first order surface reaction was constructed. The analogous reaction of methyl chloride with silicon–copper alloys is reported (*17*) to follow the rate equation,

$$r_0 = \frac{kK_A P_{CH_3Cl}}{[1 + (K_A P_{CH_3Cl})^{1/2}]^2},$$

at low conversions. This reduces to first order with respect to methyl chloride if $K_A \ll 1$. A sphere of diameter 0.025 cm was assumed, corresponding to the average size of alloy particles taken for testing in the reactor. The alloy particles were obtained by filing the cast and homogenized ingots and then screening the filings. The diffusivity of germanium in the α phase alloys was assumed to be the same as the diffusivity of germanium in copper. Diffusivity data for germanium in the ζ and ε phases were not available. Values had to be estimated by analogy with the copper–antimony system, which contains intermediate phases having the same crystal structures as the ζ and ε phases. Reaction rate constants were calculated using the highest values of the reaction rates obtained with the unpretreated alloys.

The results of these calculations are shown in Fig. 13 as theoretical surface germanium concentration versus cumulative reaction time. Phases found in thin surface layers* by X-ray analysis of the used contact mixtures are indicated by arrows, and are also listed in Table 3. The theoretically predicted surface concentrations do not seem in accord with the X-ray determinations of the compositions of thin surface layers. However, if the estimated diffusion coefficient for germanium in the ε phase were 2.1×10^{-10} cm²/sec rather than 5.3×10^{-10} cm²/sec, the broken curve would be calculated, which is in agreement with the X-ray data. A diffusion coefficient of 2.1×10^{-10} cm²/sec is not unreasonable.

TABLE 3

X-RAY ANALYSIS OF USED CATALYSTS

Initial phase	Cumulative reaction time (min)	Phases found in used catalyst
α	18	α + ζ
α	28	α + ζ
α	46	α
ζ	18	ζ
ζ	28	ζ + α
ε	9	ε
ε	18	ε
ε	39	ε + ζ
ε	49	ε + ζ
ε	62	ε + ζ
ε	95	ε + ζ

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* By thin surface layers are meant surface layers less than 20 μm in thickness.

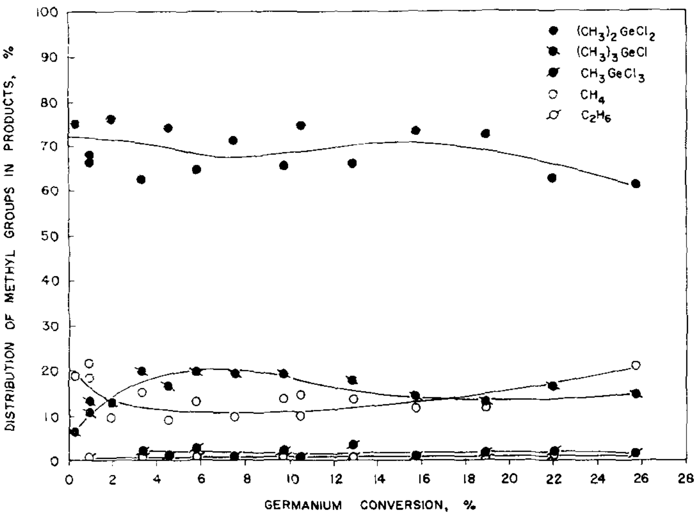


FIG. 8. Product distribution from ε phase alloy.

The diffusion coefficients estimated for the various single phase alloys at 426.7°C range over four orders of magnitude. In addition, the exact location of the theoretical curve is determined by the parameter $L' = \alpha' a/D$, and the variation in radius a from the smallest to the largest particles and the uncertainty in the rate constant α' could also account for the discrepancy. Similarly, in the case of the ζ phase alloys a change in estimated diffusion coefficient from 5.2 × 10^{-11} to 6.0 × 10^{-12} cm²/sec would be sufficient to bring the theoretical surface concentration curve into agreement with the X-ray data for thin surface layers.

The α phase, however, presents a differ-

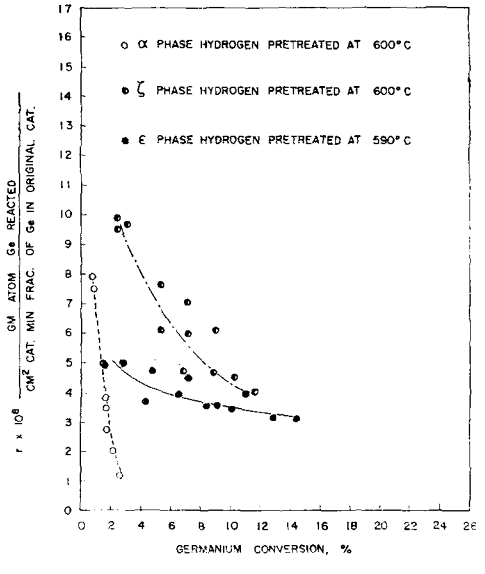


FIG. 9. Reactivities of hydrogen pretreated alloys.

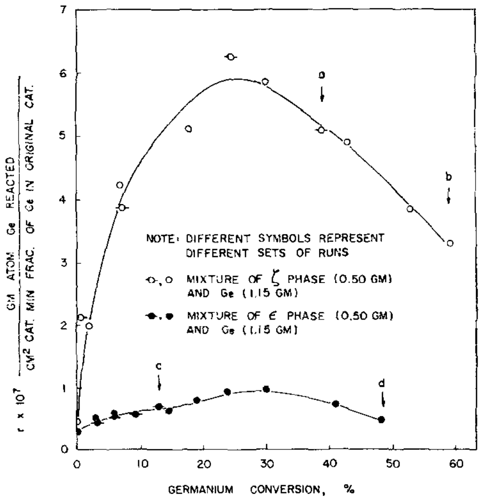


FIG. 10. Reactivities of mixtures of single phase alloys and germanium. X-ray analysis: (a) Strong ζ phase lines and α phase lines; Ge lines are strong. (b) ζ phase lines remain strong; α phase lines are strong; Germanium lines are strong. (c) ε phase lines disappear; ζ phase lines and α phase lines are strong; Germanium lines are present but weaker than the α phase and ζ phase lines. (d) ζ phase lines are weak; α phase lines are strong; Ge lines are present but weaker than the α phase lines.

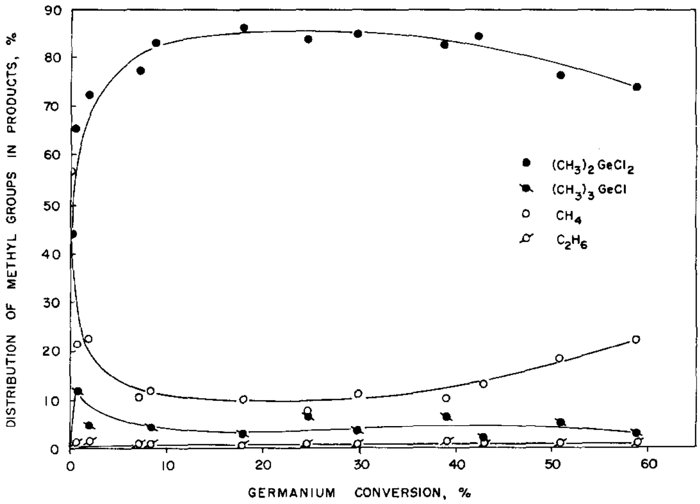


FIG. 11. Product distribution from mixture of ζ phase alloy and germanium.

ent situation. Contrary to theoretical predictions, the X-ray data reveal the presence of both the α phase and the ζ phase after 18 and 28 min of reaction. To check this result, the compositions of thin surface layers of the α phase particles were calculated from the position of the α phase lines using published X-ray data on α phase alloys of different compositions. These results are shown as a broken line in Fig. 13. They indicate either a concentration of germanium or a depletion of copper in thin surface layers of the α phase particles during the initial 30 min of reaction with methyl chloride. The following explanation, in accord with the known chemistry of the system, is offered. While germanium is being removed by reaction with methyl chloride, copper atoms on the surface are also being removed by reaction with methyl chloride to form the relatively volatile CuCl (*18*):

$$Ge + 2CH_3Cl \rightarrow (CH_3)_2GeCl_2,$$

$$Cu + CH_3Cl \rightarrow CuCl + CH_3\cdot$$

In the case of the α phase alloys, which contain 91.2 atom % copper, the second reaction predominates, and more copper atoms than germanium atoms are removed from the surface during the initial 20 min of reaction. Gradually the copper atoms are covered by products from the cracking

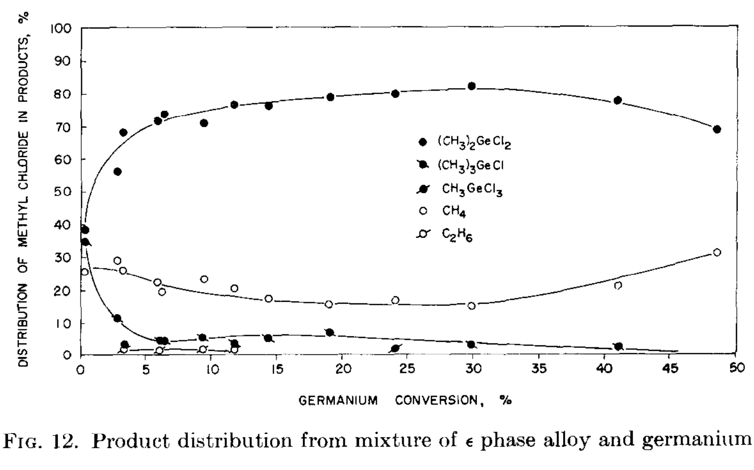


FIG. 12. Product distribution from mixture of ε phase alloy and germanium.

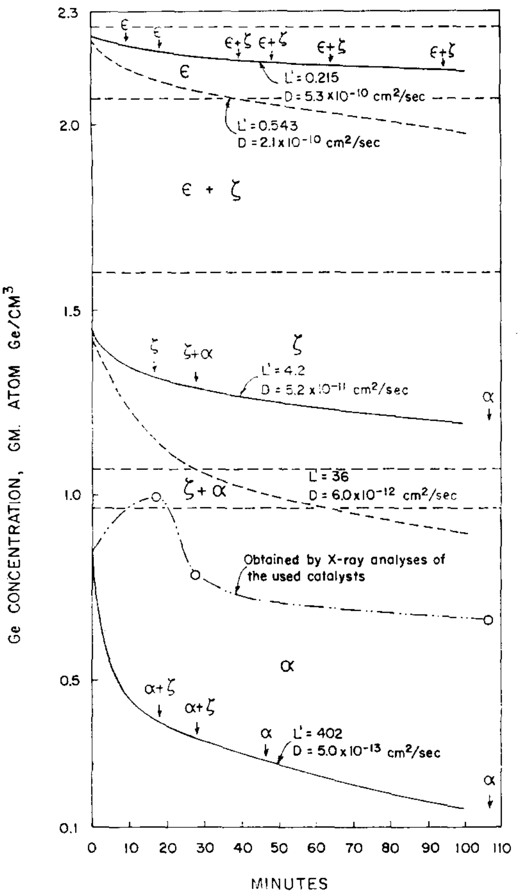
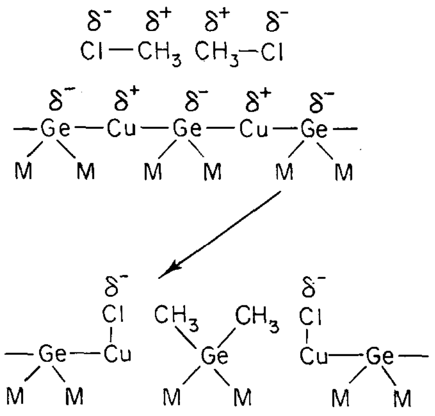


FIG. 13. Variation of surface concentration of germanium with length of reaction period as predicted by theoretical model. Phases found experimentally in thin surface layers are indicated by arrows.

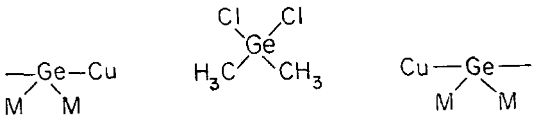
of methyl chloride. The first reaction then predominates, and the germanium concentration on the surface decreases as expected.

The above model of simultaneous surface reaction and bulk diffusion is admittedly greatly oversimplified. The possibility of significant differences between surface compositions and bulk compositions just below the surface are ignored. Nevertheless, the model is useful in attempting to relate measured rates of germanium removal, estimated bulk diffusion coefficients, and X-ray analyses of thin surface layers.

It is of interest to examine the various mechanisms proposed for the direct synthesis of methylchlorosilanes in light of the results of this study. The two main contenders are the free radical mechanism of Hurd and Rochow (*19*) and the more recent ionic mechanism of Klebansky and Fikhtengolts (*20, 21*) as fully developed by Voorhoeve (*17*). The latter mechanism, applied to the copper–germanium system, would require the assumption that atoms in the alloy are polarized so that the copper atoms carry a partial positive charge and the germanium atoms a partial negative charge. Then a dissociative chemisorption of methyl chloride would occur with the methyl group being attracted to the germanium and the Cl to the copper:



Next, by analogy with the silicon case, various internal transitions take place involving the nucleophilic attack of adsorbed Cl on the germanium substrate bonds. Ultimately the Ge–M bonds are cleaved and $(CH_3)_2GeCl_2$ is formed:



First it is necessary to examine the basic assumption of the ionic mechanism concerning the polarity of the metal atoms. Sanderson (*22*) assigns to germanium the electronegativity value 2.31 and to copper the value 1.64. Darken and Gurry (*23*) from a study of the solubility data of many elements in copper estimate a value of 1.5 for the electronegativity of copper. In

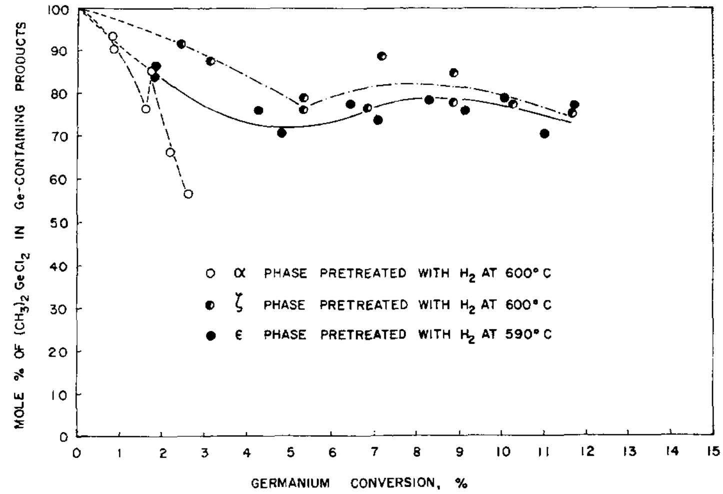
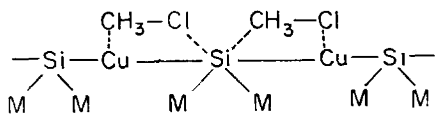


FIG. 14. Variation of selectivity for $(CH_3)_2GeCl_2$ with conversion of germanium.

either case, germanium is appreciably more electronegative than copper.

The ionic mechanism of Voorhoeve predicts the formation of $(CH_3)_2GeCl_2$ exclusively. The selectivity of the hydrogen pretreated alloys for $(CH_3)_2GeCl_2$, with respect to all germanium-containing products, is plotted versus conversion of germanium in Fig. 14. All curves extrapolate to 100% selectivity for $(CH_3)_2GeCl_2$ at 0% conversion of germanium. Similar curves are obtained for the thermally pretreated and unpretreated alloys. This indicates that $(CH_3)_2GeCl_2$ may be the only germanium-containing product initially formed, and that the other methylchlorogermanes are formed only after the alloy surface has been disrupted by removal of germanium atoms. Similar results were found by Kolster, Vlugter and Voorhoeve (*9*) for the reaction of methyl chloride with the η and ϵ phase copper–silicon alloys.

Voorhoeve (*17*) considers the formation of CH_3SiCl_3 in the analogous reaction with copper–silicon alloys as due to the relatively rare "reverse orientation" adsorption of methyl chloride:



Once this adsorption occurs the attachment of Cl to Si is relatively lasting, but the Cu–CH_3 linkage is unstable, and the methyl group easily leaves the surface. The chlorine-rich product CH_3SiCl_3 is thus produced.

We propose that in the case of $(CH_3)_3GeCl$ the adsorption occurs normally, but one of the Cl radicals is removed as CuCl before the formation of $(CH_3)_2GeCl_2$ is completed. Intrusion of a methyl group from an adjacent site or from the cracking of CH_3Cl then occurs and $(CH_3)_3GeCl$ results.

According to the ionic mechanism of Voorhoeve the direct synthesis of $(CH_3)_2GeCl_2$ would involve a germanium atom and two adjacent copper atoms. Thus, these adjacent copper atoms would presumably not be available for the cracking of methyl chloride. There should be a correlation between the number of exposed copper atoms *not* involved in the synthesis of methylchlorogermanes and the amount of cracking products (CH_4, C_2H_6) produced. Assuming that bulk and average surface compositions are roughly the same, the fraction of surface atoms representing copper atoms not involved in the synthesis of methylchlorogermanes is:

$$1 - 3 \times (\text{atom fraction Ge in original alloy}).$$

To test this assumption the rate of cracking per unit area of isolated copper atoms was defined as,

$$r_c = \frac{\text{g-moles of CH}_3\text{Cl cracked to CH}_4 \text{ and C}_2\text{H}_6}{(\text{min})\ (\text{cm}^2 \text{ catalyst surface area})\ [1 - 3 \times (\text{atom frac. Ge in original catalyst})]},$$

and is plotted versus germanium conversion in Fig. 15. The curves for the three single phase alloys appear to converge at low germanium conversion. When a 2 or a 4 is substituted for the 3 in the denominator of the above definition of reaction rate and the data are plotted in a similar manner, the curves for the three alloys are widely disparate and do not converge.

When free germanium particles were mixed with the ζ or ϵ phase particles in the contact mixture, both the reactivity and the selectivity for $(CH_3)_2GeCl_2$ were greatly increased. A simple explanation might be that the free germanium particles acted as "feeders" to supply the germanium removed from the alloy particles and thus prevent surface depletion of germanium. This explanation does not stand up under close examination. The maximum reaction rate for the ζ + Ge mixtures was four times the maximum reaction rate found by extrapolating to 0% conversion the reaction rate data for ζ phase alloys pretreated with hydrogen. The mechanical mixtures loaded into the reactor were neither pressed together nor sintered. The transport of germanium atoms from germanium particles to alloy particles by solid phase diffusion or surface transport must have been limited to those few points where the particles actually contacted each other. Also, a drastic change in the reaction mechanism due to the presence of free

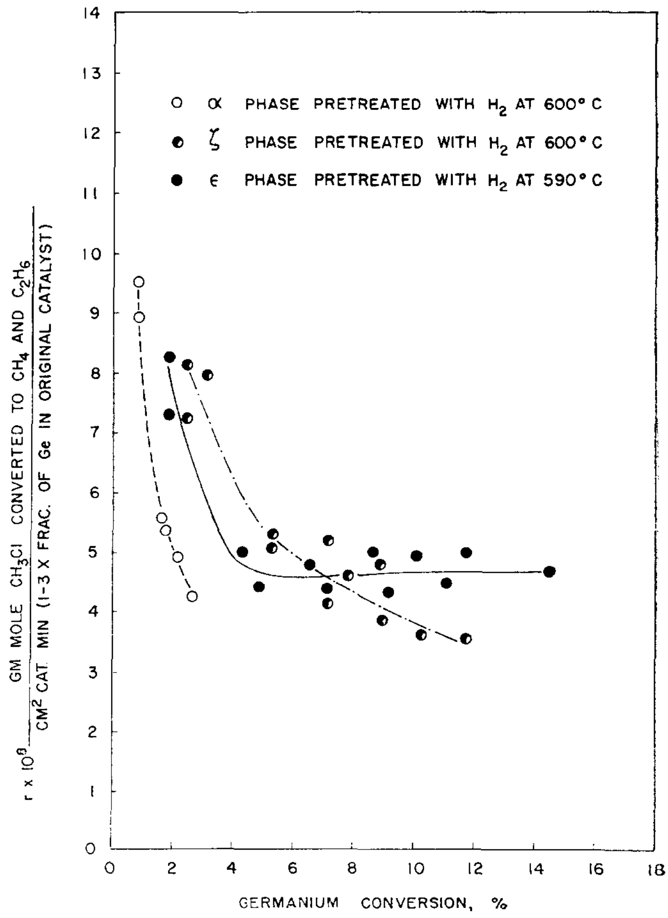


FIG. 15. Variation of rate of cracking of methylchloride with conversion of germanium.

germanium particles is unlikely. The high selectivity (95%) for $(CH_3)_2GeCl_2$ among germanium-containing products strongly supports the ionic mechanism of Voorhoeve.

The above theories having been ruled out, the only remaining explanation for the marked increase in reactivity on addition of free germanium is an increase in the number of copper–germanium pairs which are sites for the synthesis of $(CH_3)_2GeCl_2$. In the discussion of the reactivity of the pure α phase unequivocal X-ray evidence was presented indicating an initial increase in germanium concentration in thin surface layers of the alloy. This was attributed to the removal of copper by formation and sublimation of CuCl:

$$CH_3Cl + Cu \rightarrow CH_3\cdot + CuCl.$$

This would provide a mechanism for the transport of copper (as CuCl) to the particles of elemental germanium and the formation of deposits of copper on the surfaces of these particles. The peripheries of these deposits would then provide additional Cu–Ge sites for the formation of methylchlorogermanes. For the analogous reaction of methyl chloride with silicon Kolster, Vlugter and Voorhoeve (*9*) have demonstrated that a catalytically active solid can be prepared by the reaction of CuCl with silicon.

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