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Reactions of Silicon and Germanium with Halogens, Their Hydrides, and Organic Halogen Derivatives

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Results published up to 1972 inclusive on the kinetics and the mechanism of the reactions of silicon and germanium with halogens, their hydrides, and organic derivatives are summarised. The kinetics and the mechanism of formation of the most important organic and halogenated derivatives of silicon and germanium, which have found wide industrial application, are discussed. Published data are analysed in the light of modern views on the progress of heterogeneous catalytic reactions. A list of 163 references is included.

CONTENTS

I. Introduction 291
II. Kinetics of reactions 291
III. Mechanism of reactions 296

I. INTRODUCTION

The interaction of silicon or germanium with a halogen, its hydride, or an organic derivative is a complicated heterophase catalytic process, in which a gaseous halide reacts with a solid in the presence of a catalyst with the formation mainly of gaseous reaction products. The kinetics of such "gas–solid" processes, including the gasification of coal[1], remained for a long period a little studied field.

During the past decade, however, the reactions of silicon and germanium with halogenated hydrocarbons have found wide application in the preparation of organometallic monomers[2-4] for the industrial production of novel oligomers and polymers possessing valuable technical properties. The halogenation and the hydrohalogenation of silicon and germanium are used also in various branches of semiconductor technology[5,6].

The practical significance of these reactions has arisen during recent years from extensive investigations of the kinetics and the mechanism of the formation of silicon, germanium, organosilicon, and organogermanium halides. Thorough study of this branch of chemistry became possible when elementary silicon and germanium of the required purity became available in the necessary quantities for kinetic experiments.

The reactions of silicon and germanium with halogens and organic halides appear a fortunate example for elucidating general aspects of the reactivity of solids on treatment with gaseous reactants to form volatile products—the effects of impurities and catalytic additives, the nature of the halogen, and other factors on the activation energy, the kinetic order of the reaction, etc.

Study of the kinetics and the mechanism of several preparations of silicon and organosilicon halides, forming the basis of large-scale production[7-12], has been connected with the development of modern methods of design of reaction vessels and the modelling of chemical processes[13,14].

Earlier surveys[15-19] were concerned mainly with the reactions of silicon with alkyl chlorides and hydrogen chloride, and ignored data on reactions with other halides, as well as information on the corresponding reactions of germanium—an analogue of silicon—about which a large number of publications had already appeared. It has become necessary to analyse and generalise results on the kinetics and the mechanism of the formation of silicon, germanium, organosilicon, and organogermanium halides, which is the purpose of the present Review. The chemical properties and the methods of preparation of these compounds are not dealt with, since several special publications have appeared on this aspect[2-4,20,21].

II. KINETICS OF REACTIONS

1. Reactions of Silicon and Germanium with Halogens X_2

The reaction of halogens with silicon and germanium provides the simplest method for preparing the halides. These elements form compounds of types MX_4 and MX_2, as well as polyhalogenated silanes and germanes M_nX_{2n+2}.[21,22] Quadrivalent compounds are more characteristic of silicon; germanium typically forms both quadrivalent and bivalent halides. Under normal conditions polyhalides are formed in small quantities.

Fluorination. Silicon reacts with fluorine even at room temperature to form gaseous silicon tetrafluoride. A detailed gravimetric study of this reaction has been made on single crystals of silicon[23-25]. Initially the process is slow because of the presence of an oxide film on the surface. With a fluorine pressure of 20–150 torrs the reaction on the (111) face at 20°C is of the first order with respect to fluorine[24]. Study of the fluorination of silicon plates (99.9% pure) over the pressure range 2.8–52.5 torrs at temperatures of 75–900°C established[25] that at low temperatures (120–150°C) the activation energy was 12 kcal mole^{-1} and the order with respect to fluorine $n_{F_2} = 1$. At high temperatures the effect of external diffusion lowered the activation energy to 1.3 kcal mole^{-1} and the kinetic order to $n_{F_2} = 0.6$.

No published data are available on the kinetics of the fluorination of germanium.

Chlorination. Investigations of the chlorination of silicon and germanium[26-30] have established that the purity of the solid reactant and the presence of catalytic additions of copper influence the kinetics[26,27]. At low temperatures tetrachloro-derivatives are the main products. Table 1 lists the kinetic parameters of their formation. The results show that additions of copper to pure specimens

and impurities in technical silicon tend to enhance the reactivity of the solid. This is apparent in a sharp drop in the temperature at which reaction begins, a decrease in activation energy, and a raising of the kinetic order with respect to chlorine. The activation energies of reactions with silicon (mono- and poly-crystalline specimens with added copper) are usually higher than those for comparable specimens of germanium.

Table 1. Kinetic parameters of the formation of silicon and germanium tetrahalides.

Contact mass	Conditions of expt. T, °C	Conditions of expt. P_{X_2}, torrs	Reaction order n_{X_2}	Activation energy, kcal mole^{-1}	Ref.
fluorination					
Monocryst. Si	20	20—150	1.0	—	24
Polycryst, Si (99.9%)	120—150	3—52	1.0	12	25
chlorination					
Monocryst. Si					
Polycryst. Si (99.9999%)	20—580	—	2.0	35	28
	254—292	12—64	0.4	24.4	26
Chemically purified Si (99.8)	320—370	—	—	18	29
Technical Si (98%)	180—240	12—82	1.0	15.1	26
Polycryst. Si-Cu alloy (10% Cu)	96—115	20—68	0.6	11.6	27
Monocryst. Ge	175—258	15—160	0	25.0	30
Polycryst. Ge (99.999%)	115—142	19—70	0.4	18.1	27
Polycryst. Ge-Cu alloy (13.5% Cu)	117—160	16—70	0.7	8.4	27
iodination					
Polycryst. Ge (99.999%)	300—550	10^{-2}—10^{-4}	—	18.5	31
Polycryst. Ge	—	—	0.5	31	32

Bromination. Studies have been made on single crystals, technical silicon, and ferrosilicon (15% of iron)[33,34]. Added metals (copper, iron, cobalt, nickel, silver) lower the temperature at which bromination of monocrystalline silicon begins. Additions of copper and its bromides also enhance the reactivity of technical silicon and ferrosilicon, and tend to increase the yield of tetrabromosilane. No kinetic data have been published on the bromination of silicon or germanium.

Iodination. No kinetic data have appeared on the iodination of silicon, and results for that of germanium are contradictory. Over the temperature range in which the reaction is not complicated by diffusion the activation energy is 31 kcal mole^{-1} and the kinetic order $n_{I_2} = 0.5$.[32] The reaction on the (110), (100), and (111) faces of germanium has been ascribed[31] activation energy 18.5 kcal mole^{-1} and reaction order $n_{I_2} = 1.18$, whereas other workers[35] give $n_{I_2} = 0$. These differencies are probably due to experimental inaccuracy, since similar specimens of germanium were used and closely similar temperature ranges (280–460° and 300–500°C).[31,32]

2. Reactions of Silicon and Germanium with Hydrogen Halides HX

The main products are di-, tri-, and tetra-halogenated silicon and germanium derivatives H_2MX_2, HMX_3, and MX_4, under certain conditions with a small quantity of the monohalogeno-derivatives. The composition of the products depends on the temperature of preparation, the purity of the solid, and additions of copper, whose catalytic effect on reactions with hydrogen chloride had been noted long ago by Combes[36].

Hydrochlorination of silicon

The first kinetic study of the process was made by Trambouze[37]. The activation energy of the formation of trichlorosilane was found to be 3 and 10 kcal mole^{-1} for pure silicon and for a silicon–copper alloy. However, the higher value of 28 kcal mole^{-1} has since been obtained by Joklik and Bažant[38], who used a mixture of powdered technical silicon (98% Si) and copper (Si : Cu = 11 : 1) to prepare trichlorosilane under similar conditions over the range 180–220°C. Such contradictory values of the activation energy are due to errors of method in the earlier work[37]: experimental results obtained at the high temperatures of 250–600°C were probably distorted by diffusion factors.

Especial attention has since been paid[39-41] to improving the experimental method, and the effect of pressure has also been studied. At low temperatures silicon reacts with hydrogen chloride mainly with the formation of trichlorosilane. The variation in the surface of the solid reactant and the effect of this variation on the reaction velocity have been examined[41]. The reactivity of silicon is significantly affected by the presence of impurities. The temperature at which reaction begins and the activation energy fall as the impurity content of silicon increases in the sequence

pure (99.9999%) > purified (99.8%) > technical (98%).

In spite of a substantial difference in reactivity, the composition of the products in the region of the temperature at which reaction began was almost identical for these samples of silicon: the content of trichlorosilane in the condensate was 93–98%.

The composition of the reaction products is significantly affected by the addition of copper to the silicon. Each purity grade silicon has a definite temperature range within which the dichlorosilane content increases[41]. In the presence of copper this content rises to 30–35%.[43] The temperature ranges for the selective formation of dichlorosilane are 420–440°, 250–320°, and 220–320°C respectively for pure silicon, technical silicon, and all types of silicon in the presence of copper[43,44].

The kinetic order with respect to hydrogen chloride is close to zero with specimens of pure and purified silicon, but 0.5 with technical silicon. The reaction products —hydrogen and trichlorosilane—have no effect on the rate of the process, and the order with respect to them is zero[40].

Since the formation of trichlorosilane is almost irreversible[42], the rate equation can be written

$$r = k \cdot P_{HCl}^{n_{HCl}} .$$

The kinetic parameters of the process are affected even by small additions (0.001–0.04%) of copper to pure silicon: the temperature at which reaction begins is lowered almost by 100 deg (Table 2) and the activation energy by 6–10 kcal mole^{-1}, while the order of reaction with respect to hydrogen chloride is raised[43-45]. Table 2 reveals no correlation between the copper content and the kinetic parameters E and n_{HCl}: thus specimens with a tenfold difference in copper contents (0.04 and 0.3%) have almost the same kinetic parameters. This is probably

connected with the way in which copper is distributed during preparation of the alloys. Comparison of the reactivity of silicon of different degrees of purity showed[44] that the specific rates with pure and with chemically purified silicon are respectively around 0.01% and 1% of those with technical silicon and silicon–copper alloys.

Table 2. Effects of impurities in silicon and additions of copper on kinetic parameters of the synthesis of trichlorosilane[43–45].

Contact mass	Reaction starts at °C	Reaction order n_{HCl}	Activation energy, kcal mole^{-1}	Specific rate*, mmole m^{-2} min^{-1}
Pure Si (99.9999%)	300—320	0.0—0.1	34.4	$2.8\cdot10^{-5}$
Chemically purified Si (99.8%)	220—240	0.0—0.1	27.0	$7.1\cdot10^{-3}$
Technical Si (98.0%)	180—200	0.45—0.5	20—23	$2.7\cdot10^{-2}$
Pure Si alloyed with Cu (%)				
0.0013	250	—	27.0	—
0.04	200	0.65	24.0	—
0.08	200—240	0.24	28.4	—
0.3	180—200	0.54	24.5	—
Alloy of pure Si and Cu (%)				
2.4	180—200	0.21	29.0	$1.5\cdot10^{-1}$
8.6	180—200	0.43	23.0	$3.6\cdot10^{-1}$

*Specific rate calculated for 250 °C and p_{HCl} = 450 torrs.

Hydrochlorination of germanium

Use of copper both as an alloy[46] and as a powdered mechanical mixture[47] has a marked affect on the kinetics: the temperature at which reaction begins is lowered, and the yield of the main product (trichlorogermane) is raised. The content of tetrachlorogermane increases with rise in temperature. Formation of dichlorogermane is not observed.

Table 3. Kinetic parameters of the hydrochlorination of germanium[46,163].

Contact mass	Reaction starts at, °C	Reaction order n_{HCl}	Activation energy, kcal mole^{-1}
Pure Fe (99.9999%)	340	0.35	22—24.0
Mixture of Ge and Cu (10%) powders	300	1.0	12.5
Ge–Cu alloy (30% Cu)	180	0.8	11.4—12.3
Ge–Cu alloy (3% Cu)	210	1.3	10.2—13.1

Copper is still more effective in corresponding processes with germanium than with silicon[46]: the activation energy is roughly halved, and the kinetic order with respect to hydrogen chloride is raised from ~0.35 to 1.0 (Table 3). The value n_{HCl} = 0.8 given[46] for pure germanium is probably incorrect: repetition of the measurement has shown that n_{HCl} = 0.35.

Closely similar activation energies were obtained for reaction with germanium–copper alloys and with powdered mixtures, but reaction began at different temperatures. A more extended reactive surface of contact between copper and germanium could be regarded as most likely in the former case, or else the addition of copper tends to increase the pre-exponential factor in the reaction rate constant.

The rate of entry of germanium into reaction increases as it is consumed[18]. This is probably due to an increase in the surface area of germanium during the reaction, as was established for the hydrochlorination of silicon[41].

Hydrobromination of silicon and germanium

These processes occur similarly to hydrochlorination. Impurities in the solid reactant and additions of copper have marked effects on the kinetics. Results obtained under comparable conditions are given in Table 4. The temperature of the start of reaction and the activation energy are markedly lower in the presence of copper, while the kinetic order with respect to the gaseous reactant is higher.

Table 4. Kinetic parameters of the hydrobromination of silicon[48] and germanium[49].

Contact mass	Reaction starts at, °C	Specific rate*, mmole m^{-2} min^{-1}	Reaction order n_{HBr}	Activation energy, kcal mole^{-1}
Silicon				
Pure (99.9999%)	320	$1.2\cdot10^{-5}$	0.06—0.2	35—37
Pure Si + 10% Cu from CuCl	220	$2.9\cdot10^{-2}$	0.6—0.8	20—22
Technical (98%)	220	$1\cdot10^{-2}$	0.55—0.51	24—25
Technical Si + 10% Cu from CuCl	185	—	0.6—0.63	18.0
Germanium				
Pure (99.9999%)	325	—	0.1—0.15	24—25
Pure Ge + 10% Cu from CuCl	175	—	0.75—0.8	12.0

*At 250 °C and p_{HBr} = 300 torrs.

The value given in Table 4 for the activation energy with a pure specimen of germanium (25 kcal mole^{-1}) differs from that obtained in Ref. 50 (19 kcal mole^{-1}), the probable reason being differences in experimental conditions, primarily the higher temperature range (400–600 °C) used in this work. Raising the temperature of the hydrobromination of germanium gives rise to appreciable quantities of the tetrabromide accompanying tribromogermane[51]. The rate estimated in this paper from the loss in weight of germanium during the reaction therefore represents actually the rate of formation of two products ($HGeBr_3$ and $GeBr_4$).

Hydroiodination of germanium

Kinetic investigation of the reaction of hydrogen iodide with germanium (single crystal, (111) face) showed[52] that n_{HI} = 1 and E = 16.6 kcal mole^{-1}.

3. Formation of Organosilicon and Organogermanium Halides

The reaction of organic halides with silicon and with germanium in the presence of catalysts forms the basis of the so called direct synthesis of halogenated alkylsilanes and alkylgermanes, the chief method of obtaining organosilicon [16,22,53] and organogermanium [54,55] monomers. A mixture of products of types RMX_3, R_2MX_2, R_2MX, and $RMHX_2$ is obtained, where R = CH_3, C_2H_5, C_6H_5, etc. X = Cl, Br, and M = Si, Ge.

Highly selective preparation of these derivatives is extremely difficult in comparison with the halogenation and hydrohalogenation of silicon or germanium. Only the dimethylsilicon and dimethylgermanium dihalides can be obtained in high yields (90–95%) under fairly mild conditions. Dimethyldichlorosilane finds wide application in industry, and obviously kinetic investigations of its formation are most fully represented in the literature.

Table 5. Kinetic parameters of the synthesis of dimethyldichlorosilane.

No.	Contact mass Si + Cu (9:1)	Pressure, atm	Reaction order n_{MeCl}	Activation energy, kcal mole^{-1}	Ref.
1.	Mixed powdered Si (99.9%) + Cu	0.1—0.6	1.0	25.3	56
2.	Mixed powdered Si (98%) + Cu	1—7	1.0	20.1	57
3.	Mixed powdered Si (99.0%) + Cu from CuCl	1	1.0	26.6	16,58
4.	Si (99.98%)-Cu with added Al + Zn	4.6—12.7	1.0	25.8	16,58,59
5.	Mixed powdered Si + Cu	—	4.0	20.0	60
6.	Mixed powdered Si (99.0%) + Cu	1	1.85	9.0	61
7.	Mixed powdered Si (99.9999%) + Cu	0.15—0.9	0.96—1.1	29.0	62
8.	Mixed powdered Si (99.85%) + Cu	0.15—0.9	0.96—1.2	25.0	62
9.	Mixed powdered Si (98%) + Cu from CuCl	0.15—0.9	0.91—0.96	21.0	62
10.	Mixed powdered Si (98%) + Cu from $Cu(OH)_2$	0.15—0.9	1.1	19.2—20.0	63

Early kinetic investigations of the formation of dimethyldichlorosilane [15,56–61] disregarded the effect of the purity of the silicon, which might have been very substantial, as is evident from the above data on chlorination and hydrochlorination. Probably also because of other procedural errors, kinetic parameters obtained by different investigators varied considerably: thus values from 1 to 4 have been obtained for the order of the reaction with respect to methyl chloride, and from 9 to 27 kcal mole^{-1} for the activation energy. Although this reaction order seems [62] almost independent of the purity of the silicon, this factor nevertheless affects the activation energy (Table 5, Nos. 1, 2, and 7–9). Results for contact masses based on technical silicon, obtained by reducing copper(I) chloride and copper(II) hydroxide (Nos. 9 and 10), indicate that the chemical composition—the purity of the initial components—is of primary importance, not the mode of preparation of the contact mass.

The above experimental data are consistent with a kinetic equation of the type

$$r = K \cdot P_{MeCl}$$

for the formation of dimethyldichlorosilane. The very widely used kinetic equation proposed by Bažant et al.[56]

$$r = \frac{K \cdot P_{MeCl}}{[1 + a_{Me_2SiCl_2} \cdot P_{Me_2SiCl_2} + \sqrt{a_{MeCl} \cdot P_{MeCl}}]^2},$$

which contains the adsorption coefficients a of methyl chloride and of the product, can in several cases be considerably simplified. Kinetic data indicate first-order dependence on methyl chloride, so that the term $(a_{MeCl}P_{MeCl})^{1/2}$ can be neglected. Experimental results for the reaction under dynamic conditions with variation of P_{MeCl} from 1 to 6 atm at a low temperature could be well represented by the simplified equation [56,57], although the above term had to be taken into account with rise in temperature. This term evidently represents formally deactivation of the contact mass with rise in temperature, when the organic group undergoes appreciable pyrolysis. Published data on the retarding effect of the product $a_{Me_2SiCl_2}P_{Me_2SiCl_2}$ are contradictory. No effect of the product on reaction velocity was detected in special experiments [18] using mixtures of methyl chloride and up to 50 vol.% of dimethyldichlorosilane.

Hydrogen chloride, introduced into the reaction zone from outside [63–65] or obtained by the pyrolysis of methyl chloride [66,67] has a decisive effect on the selective formation of methyldichlorosilane under conditions of direct synthesis. Use of a mixture of methyl and hydrogen chlorides enabled the kinetics of its formation to be investigated [68] under comparatively mild temperature conditions, when the content of methyldichlorosilane in the condensate lay in the range 86–95%. The activation energy of formation of this compound from silicon of different degrees of purity was almost the same in the presence of copper (Table 6).

Table 6. Kinetic parameters of the synthesis of methyldichlorosilane [68] and ethyldichlorosilane [18].

Contact mass	Reaction order n_{RCl}	Activation energy, kcal mole^{-1}
methyldichlorosilane		
Technical Si	0.9—1.25	18.3—21.5
Technical Si + 10% Cu (mixed powders)	1.2	24.2
Technical Si + 10% Cu from CuCl	0.85	19—22
Pure Si (99.9999%) + 10% Cu from CuCl	0.9—1.1	18—20.5
ethyldichlorosilane		
Technical Si	1.2	18.3
Pure Si (99.9999%) + 10% Cu from CuCl	0.9—1.04	18—22

Technical silicon, which is sufficiently reactive for the preparation of trichlorosilane even without the addition of copper, is reactive also in the formation of methyldichlorosilane. The reaction order with respect to methyl chloride is independent of the type of contact mass and is approximately $n_{MeCl} \simeq 1$, while the activation energy lies in the range 18–24 kcal mole^{-1}.

The activation energies of formation of methyltrichlorosilane and tetrachlorosilane were estimated [18], from the

temperature dependence of the ratio of their rates of formation in the preparation of methyldichlorosilane[68], when they are present in small quantities (4–5%) among the reaction products, as respectively ~40 and 3–6 kcal mole^{-1}.

Organogermanium compounds containing hydrogen could not be obtained[68] by the reaction of germanium with methyl chloride in the presence of hydrogen chloride, and there is no information on their direct synthesis.

Voorhoeve et al.[67] obtained interesting kinetic data on the formation of methylchlorosilanes by the reaction of methyl chloride with silicon in the presence of catalytic amounts of tin and lead. In experiments with a silicon–tin contact mass (9% and 17% Sn) between 300° and 500°C the main products were methyltrichlorosilane (80–90%) and tetrachlorosilane (~10%). The activation energy of the formation of methyltrichlorosilane under these conditions was 15.6 kcal mole^{-1}.

Highly selective formation of dimethyldichlorogermane[69] results from the interaction of germanium and methyl chloride in the presence of copper. Its content in the mixture at 320–400°C is 90–98%, and is independent of the state or content (in the range 3–30%) of copper in the contact masses. The mode of preparation of the contact mass (alloy or mixture of powered germanium and copper) has no appreciable effect on the principal kinetic parameters of the process, as with silicon[62]. The kinetic order with respect to methyl chloride is n_{MeCl} = 1.5, and the activation energy 24–27.5 kcal mole^{-1}.

Comparatively little investigation has been made of the kinetics of the formation of ethylchlorosilanes. The reason is that interaction between ethyl chloride and silicon–copper contact masses yields several products in considerable quantities, which complicates interpretation of the experimental results and calculation of the kinetic parameters of the process.

Furthermore, ethyl chloride breaks down during the reaction to form ethylene and other hydrocarbons. The reaction products contain not only diethyldichlorosilane but also a large quantity of ethyldichlorosilane. The total rate of conversion of ethyl chloride on a silicon–copper contact mass is of the first order with respect to ethyl chloride[70,71]; under dynamic conditions the process is well described by the equation of Frost and Panchenkov[72]. Later Bažant and Kraus[73], on the assumption that ethylchlorosilanes and hydrocarbons (ethane and ethylene) are formed by parallel reactions, estimated activation energies respectively of 18 and 25 kcal mole^{-1} for the two overall processes.

A kinetic examination has been made also of the formation of ethyldichlorosilane as an individual reaction product on specimens of technical silicon and pure silicon in the presence of copper[18]. As with the preparation of methyldichlorosilane, a mixture of ethyl and hydrogen chlorides was used. The content of ethyldichlorosilane in the reaction products was 90–95%. The order of the reaction with respect to ethyl chloride was n_{EtCl} = 0.9–1.2, and the activation energy 18–22 kcal mole^{-1} (Table 6). As with the preparation of methyldichlorosilane, the kinetic parameters of the process are independent of additions of copper, provided that the silicon is sufficiently active in forming trichlorosilane.

No quantitative kinetic investigation has been made of the interaction of chlorobenzene with silicon–copper contact masses. Only a few data have been published on the parallel formation[15,74] of the main reaction products—phenyltrichlorosilane and diphenyldichlorosilane—and the secondary products—benzene, biphenyl, and tetrachlorosilane. Some idea of the nature of the reaction between an aryl halide and silicon can be obtained from kinetic data on the formation of phenylbromosilanes[75]. The experiments were made in a flow-type apparatus at bromobenzene pressures of 0.3–19 atm. The main product was diphenyldibromosilane, the activation energy of whose formation was 22.8 kcal mole^{-1}.

Studies[76,77] of the effect of substituents in the aryl bromide on the rate of formation of diaryldibromosilanes and aryltribromosilanes in the presence of a silicon–copper contact mass at 400°C established a linear dependence of the logarithm of the relative initial rates on the Hammett constants for the individual substituent (*p*-fluoro, *p*-chloro, hydrogen, *m*-methyl, *p*-methyl, *p*-t-butyl, and *p*-isopropyl). Kinetic equations were also obtained for the formation of di-*p*-fluorophenyldibromosilane and *p*-fluorophenyltribromosilane, regarded as occurring by parallel reactions.

Topochemical processes occurring in the solid phase are of great importance in the direct synthesis of organosilicon and organogermanium halides. Various products can be formed by interaction of copper and the solid reactant in the contact masses depending on their method of preparation. Before reaction a silicon–copper alloy consists of two phases—silicon and an intermetallic compound Cu_3Si (η-phase)[37,78–82]—the latter being formed also in contact masses from a mixture of silicon and copper(I) chloride during preliminary reduction, as well as during synthesis as the copper chloride is formed on breakdown of the organic chloride, especially in the initial (induction) period of the reaction[79,80]. It was suggested in these papers that organosilicon chlorides are indeed formed by interaction of the organic chloride with silicon liberated by breakdown of the η-phase.

The reaction of silicon–copper alloys with methyl chloride was used as example to study the kinetics of the breakdown of the η-phase[83,84], the quantity of silicon that had reacted to form methylchlorosilanes being taken as the rate of the process. It was assumed that only silicon from Cu_3Si underwent reaction. An activation energy of 16 kcal mole^{-1} was obtained; this fell to 8–10 kcal mole^{-1} in the presence of additions of 0.2% of antimony and 0.5% of arsenic, but 0.5% of titanium raised it to 28 kcal mole^{-1}. These values are extremely tentative, since silicon not combined as Cu_3Si may take part in the reaction.

Changes occurring in a silicon–copper alloy (24.7% Cu) during reaction with ethyl chloride between 280° and 360°C were monitored[81,82,85] by X-ray examination. Breakdown of the η-phase was shown to have a fairly high activation energy (30 kcal mole^{-1}) and to obey a first-order kinetic equation. The lower activation energy obtained for conversion of the ethyl chloride (20 kcal mole^{-1}) was attributed to the catalytic effect of the resulting copper.

Under conditions of direct synthesis the contact masses undergo not only structural and chemical changes but also changes in texture (grain size), specific surface, and porosity[41,86]. At higher temperatures pyrolysis of the organic groups becomes important[87–89]. Unfortunately, hardly any kinetic study has been made of the pyrolysis of organic chlorides of silicon–copper contact masses. Investigations by Bažant et al.[15,87–89] suggest a stepwise conversion of organic groups on the contact masses with the formation of polymeric products (polymethylenes, polyphenylenes, etc.).

Some data on the kinetics of the decomposition of methyl chloride on copper under dynamic conditions

appeared in a paper by Trambouze[37], who found the activation energy to vary from 4 to 7 kcal mole^{-1} depending on the type of copper. However, methane was not detected in this investigation, and a scheme was suggested in which the methyl group decomposed into carbon and hydrogen. This conclusion is inconsistent with results obtained by Bažant[89], Anderson[90], and Ivanova et al.[91] The decomposition of methyl chloride on the surface of a pure copper film sublimed in a vacuum[90] yielded hydrogen, methane, and other hydrocarbons. The activation energy of the decomposition was estimated[90,91] to be considerably lower on a silicon–copper alloy than on technical and pure silicon (respectively 14.9, 24.2, and 44 kcal mole^{-1}).

III. MECHANISM OF REACTIONS

1. Nature of Reactions

With respect to the state of aggregation of reactants and products, direct synthesis is a heterophase process. Until recently it was not clear whether the process was purely heterogeneous, occurring on the surface of the solid or heterogeneous–homogeneous, with reactive intermediates formed on the surface, passing into space, and reacting further in the gas phase.

Hurd and Rochow[92] assumed direct synthesis to be a heterogeneous–homogeneous process. They investigated the interaction of methyl chloride with silicon and copper, and suggested the formation, on the contact surface, of the reactive species CH_3 and CH_3Cu, which migrated into the gas phase and reacted with reactive silicon–chlorine intermediates (SiCl and $SiCl_2$) to give the final products. The function of copper in the suggested mechanism was to form intermediate compounds (CH_3Cu and CuCl) to act as alkylating and chlorinating agents. Rochow subsequently extended this scheme to the direct synthesis of other organosilicon halides.

An alternative view, put forward by Klebanskii and Fikhtengol'ts[78], Trambouze[37], Bažant[15], and Voorhoeve[93], regards direct synthesis as involving heterogeneous–catalytic reactions, occurring solely on the solid surface.

Certain aspects of Hurd and Rochow's mechanism appeared in several papers. At one time Andrianov et al.[94] assumed the participation of free radicals formed by dissociation of the intermediate methylcopper chloride CH_3CuCl. Holzapfel[95] considered that intermediate chlorinated compounds of silicon reacted in the gas phase. Even in the fluorination of silicon[25] it was regarded as possible that certain stages occurred in the gas phase and involved SiF and SiF_2.

The investigations of Andrianov, Golubtsov, and their coworkers[96-101] have shown that appreciable quantities of intermediate compounds of the type SiCl, $SiCl_2$, $SiCl_3$, $HSiCl_2$ may be formed in the gas phase in the reactions of copper(I) chloride and of gaseous hydrogen chloride with silicon. Thermodynamic calculations, as well as direct investigation of dichlorosilane $SiCl_2$ by mass spectrometry and ultraviolet spectroscopy, indicate comparatively high concentrations of this intermediate in the reduction of copper(I) chloride by silicon in the temperature range of direct synthesis (180°C and above)[96,97,100-102].

Attempts were made[103] to study the interaction of intermediate products in the chlorination of silicon ($SiCl_2$) with methyl chloride in the presence of copper. Ascribing great importance to copper(I) chloride, as in Hurd and Rochow's mechanism, and also allowing for the possible formation of $SiCl_2$, Andrianov, Golubtsov, et al. suggested a scheme of direct synthesis[103] in which an important part was assigned to the hypothetical compound RCl.Cu, which reacted with $SiCl_2$ to give R_2SiCl_2 and $RSiCl_3$, regenerating CuCl and Cu respectively. It is not clear from the paper where the main stages occur, in particular whether those involving $SiCl_2$ take place on the surface or in the gas phase. Alkylation stages involving R or CuR are excluded. Yet Czernotsky[104], from a study of the effect of additions of dimethyl ether on the formation of methylchlorosilanes, concludes that dimethyldichlorosilane is formed by the interaction of dichlorosilene with methyl radicals, which according to Müller and Gumbel[105] are formed from methyl chloride and copper.

Many objections have been raised against a radical mechanism of direct synthesis[15,16,93]. Special experiments in which donors or acceptors of radicals—nitric oxide[106], iodine[15], azomethane[15,58]—were introduced into the reaction mixture in the synthesis of methylchlorosilanes also did not support a radical mechanism. Comparative analysis[107] of products of the pyrolysis of chlorobenzene and by products not containing silicon also makes participation of free phenyl radicals in the synthesis of phenylchlorosilanes improbable.

Direct assessment of the homogeneous component in homogeneous–heterogeneous processes—by a method of separate calorimetry—has been used to settle the question of the nature of the reactions involved in the synthesis of silicon and germanium halides and their organic derivatives[26,27,44,108-110]. In the formation of trichlorosilane[44,110] good agreement was shown by a quantitative comparison of the rise in temperature calculated theoretically for a purely heterogeneous synthesis and observed experimentally. Consequently no significant exothermic stages take place in the gas phase. The chlorination of silicon[26], the chlorination[27] and hydrochlorination[18] of germanium, and the formation of methylchlorosilane[108,109], germanes[18], and ethylchlorosilanes[18] have been studied similarly. The results also indicate the absence of homogeneous exothermic reactions.

Thus the main stages in most of the processes investigated—for which, moreover, the most complete kinetic data are available—must be regarded as heterogeneous, taking place solely on the surface of the solid reactant.

2. Intermediate Surface Chemical Interaction

With purely heterogeneous reactions the first stage—adsorption of the gaseous reactant—may be of the most important. Rostsishevskii[113] made the first attempt at a qualitative estimate of the adsorption of methyl chloride on silicon–copper contact masses. Adsorption was found to be slight below 230°C, and was larger on alloy contact masses (15% Cu) than on a mixture of silicon and copper powders.

Bažant et al.[56] showed that methyl chloride is not adsorbed at 100°C, either on copper or on silicon, although adsorption occurs on a silicon–copper alloy (10% Cu), and at 200 torrs reaches the improbably (to the Reviewers) high value of 3.5×10^{-5} mole g^{-1}, which corresponds to roughly nine monolayers of adsorbed methyl chloride.

The adsorption of methyl chloride was studied in greater detail by Müller and Gumbel[105], who concluded that considerable adsorption occurs on the surface of a silicon–copper contact mass containing silicon–chlorine and copper–chlorine bonds (after preliminary chlorination

or remaining from the conditions of preparation of the mass). Appreciable adsorption is observed also on copper(I) chloride, which may be present in chlorine-containing contact masses. The paper contains no information on the specific surfaces of the adsorbents, and the experiments were made only at one, fairly high temperature (245–250°C), when investigations of adsorption may have been complicated by the occurrence of chemical reaction on the surface.

Contradictory views are held on the nature of the adsorption bonds holding RX to the contact masses. The concept of the dissociative adsorption of RCl is widely used in the literature on direct synthesis without adequate experimental justification. Thus adsorption on two centres of the type



is assumed by Trambouze[37] and by Bažant et al.[15]; whereas Voorhoeve[58] and Klebanskii and Fikhtengol'ts[78] take into account the electronegativity of the elements and suggest adsorption of the type



Several authors have considered the chemisorption of RCl on silicon–copper contact masses in terms of the band theory of solids. Thus Trambouze[37] used Dowden's well known views[111] concerning catalysis and chemisorption on metals. Dragojevic[112] explains chemisorption and the effect of copper and other additives in silicon on the basis of Vol'kenshtein's semiconductor theory[114], but direct experimental confirmation of the authors' conclusions is lacking; the former ignores the specific character of silicon, which has a quasi-insulated surface. Yet the discussion of adsorption on silicon–copper contact masses containing 10–20% of copper in terms of the electronic theory of semiconductor catalysis is incorrect, because such adsorbents are already strongly alloyed, degenerate semiconductors.

Work published during recent years enables a fuller assessment to be made of the character of the adsorption. Boonstra, Van Ruler[115,116], and Bootsma[117] established by a volumetric method, and Podgornyi et al.[118–124] from the contact potential difference[126], two characteristic types of adsorption of hydrogen chloride on pure polycrystalline silicon and on germanium: the γ-form involves rapid adsorption and has a lower activation energy; the β-form involves slow adsorption and requires a larger activation energy[116,119–121]. Hydrogen bromide and hydrogen iodide are adsorbed similarly[116,117]. Extremely low heats of adsorption were estimated by a chromatographic method for the low-temperature and the activated adsorption of hydrogen chloride on technical (98%) silicon[127]. The adsorption of hydrogen chloride on silicon was found to be strongly dependent on its purity, the presence of impurities, and catalytic additions of copper, the last of which promote the type of adsorption having a higher activation energy[123].

Studies have been made also of the adsorption of gaseous chlorine, chloromethane, and chloroethane[118–121] on silicon and germanium[120], as well as of chlorobenzene, vinyl chloride, and allyl chloride on silicon[122]. As with hydrogen chloride, the two forms of adsorption are found with chlorine and methyl and ethyl chlorides on pure polycrystalline silicon; but very slight adsorption effects are observed with alkyl chlorides compared with hydrogen chloride and chlorine.

Since the chemisorption of the adsorbates studied is reversible and extremely rapid even at room temperature, both on silicon and on germanium, it is evidently not the limiting stage.

With regard to the nature of the chemisorption bonds, hydrogen, methyl, and ethyl chlorides are adsorbed mainly in molecular form on silicon at room temperature[118–124]. The adsorption bond is assumed to be formed through the chlorine atom of the RCl molecule: the β-form of adsorption is effected by the donation of a pair of $3p$ electrons of the chlorine atom to a d orbital of silicon (or germanium), i.e. by a donor–acceptor bond; the γ-form corresponds to formation of a bond in which electrons from the adsorbent are directed to a $3d$ orbital of the chlorine atom. It is noteworthy in this connection that the adsorption of hydrogen halides on silicon and germanium has been assumed[115,116] to be dissociative in character.

The lack of adequate data on the first stage of surface chemical interaction—adsorption of the gaseous reactant RX—introduces some uncertainty, of course, into the description of subsequent reactions of the surface compounds on silicon (or germanium) before formation of the final products.

Two approaches have been adopted towards the stages of surface chemical interaction: the first assumes the presence of a stage limiting the whole process, and the second a steady state with no limiting stage. Thus adsorption of RX is the limiting stage in the formation of trichlorosilane and methylchlorosilanes according to Trambouze[37], and in that of ethyl-, phenyl-, and vinylchlorosilanes according to Voorhoeve[16]. However, Bažant and his coworkers[15] regard the adsorption step as extremely rapid in several processes of direct synthesis (of hydrogen-containing chlorosilanes[38], dimethyldichlorosilane[56,57], dimethyldibromosilane[127], and phenylbromosilanes[75]), assuming that the reaction velocity is limited by the surface reaction of adsorbed RX in dissociated form. Similar views were held by Müller and Gumbel[105]. The above adsorption results indicate that the opinions of the latter authors are quite well founded. Nevertheless, the hypothesis of dissociative adsorption of RX has no direct experimental support, as noted already. It has therefore been assumed in a recent series of papers[119–124] that methyl chloride is adsorbed in molecular form quite rapidly and reversibly both on silicon–copper[119] and on germanium–copper[120] contact masses. Kinetic data[62,69] on the formation of dimethyldichlorosilane (for the order with respect to methyl chloride see Section II) indicate that the activated complex of the limiting stage contains one molecule of chemisorbed methyl chloride, but in the case of dimethyldichlorogermane two methyl chloride molecules are present[18,19].

Even the simpler processes—the halogenation of silicon and germanium—are also viewed in different ways. The fluorination of silicon has been regarded[25] as limited by the adsorption stage. The iodination of germanium to the di-iodide has been represented[32] by a four-stage scheme involving dissociated forms of chemisorbed molecular iodine I_2 and bulk and surface current carriers in the crystal. The initial period of the chlorination of silicon produces linear polymeric chlorosilane molecules attached to surface atoms[128–130]. In the chlorination of germanium[30] the surface is assumed to be completely covered with the chemisorbed gaseous reactant, and the limiting stage is conversion of the surface germanium–chlorine compound; an important role is attributed to current carriers in the semiconductor.

The reactions of silicon and germanium with hydrogen halides have been more thoroughly studied. At temperatures close to the start of the reaction the hydrochlorination and the hydrobromination both of silicon and of germanium involve formation of the trihalogeno-derivative HMX_3 as main product. On the basis of adsorption data and investigations of the kinetic isotope effect in the reactions of silicon [34,131] and germanium [34,46] with HX and DX (where X = Cl, Br), and also kinetic data (Section II), the slow stage is assumed to be a surface chemical reaction of the chemisorbed hydrogen halide in molecular form. The HX molecule in the activated complex is deformed differently depending on the reactivity of the solid reactant: on highly active specimens (containing copper or an impurity) the H–X molecule is present in the activated complex essentially in a dissociated form (with the establishment of M–X and M–H bonds); on relatively inactive specimens (high-purity silicon and germanium) the state of the H–X molecule in the activated complex is similar to adsorption.

A mechanism suggested [52] for the action of hydrogen iodide on germanium, when the main product is the di-iodide GeI_2, involves as limiting stage desorption of the product formed by reaction between the surface compound HGeI and gaseous hydrogen iodide.

Alkyldichlorogermanes $RGeHCl_2$ cannot be obtained by direct synthesis [4]. Thus the desired results could not be obtained from the interaction of mixtures of methyl and hydrogen chlorides with germanium–copper contact masses over a wide range of temperatures [68]. This is probably because the surface compound GeHCl reacts rapidly with hydrogen chloride to form the surface dichloride $GeCl_2$, which reacts with methylchloride to give the final product CH_3GeCl_3. Formation of a bond with hydrogen in the direct synthesis of alkyldichlorosilanes is more probable with silicon than with germanium, owing to the specific character of the surface compound SiHCl.

Thus the first approach in interpreting surface chemical interaction in formation of the corresponding gaseous derivatives of silicon or germanium is usually based on adsorption data, but in some cases with recourse to kinetic results (type of kinetic equation representing formation of an individual product). No use at all is made of data on the selectivity of the process, which is its important characteristic [162].

In practice, however, e.g. in hydrohalogenation, the synthesis of alkyldichlorosilanes, etc., several products are very often formed simultaneously [68]. Thus, in the synthesis of methyldichlorosilane from mixtures of hydrogen and methyl chlorides, silicon tetrachloride is formed at a closely similar rate to trichlorosilane. Similarly, trichlorosilane and dichlorosilane are formed at similar rates in the hydrochlorination of silicon over a certain temperature range. In these cases, therefore, it is impossible to describe the surface chemical interaction in terms of the concept of a limiting stage.

Such more complicated situations have been discussed in recent years in terms of the Horiuti–Temkin theory of stationary reactions [132,133], which has already been widely used to describe surface chemical interaction in complicated heterogeneous catalytic reactions [13,134]. This second approach has proved extremely useful for interpreting the mechanism of the reactions

$$HCl + Si \rightarrow \text{Products}$$
$$HCl + MeCl + Si \rightarrow \text{Products} \quad .$$

It may evidently be quite effective in examining the direct synthesis of methylchlorosilanes and other organosilicon monomers [19].

It was assumed in this work that the gaseous reactant is adsorbed in molecular form, and that the intermediate surface compounds do not contain copper. A multistage mechanism was proposed for the hydrochlorination of silicon, which involved the assumed formation of the intermediate surface compounds (ZHCl), (ZHCl.HCl), (ZHSiCl), $(ZSiCl_2)$, $(ZSiCl_3)$, and (ZH), where Z denotes an active centre on the surface [133]. The process is represented by a nine-stage scheme with three independent paths

$$Si + 2HCl = H_2SiCl_2$$
$$Si + 3HCl = HSiCl_3 + H_2$$
$$Si + 4HCl = SiCl_4 + 2H_2 \quad .$$

The suggested mechanism agrees satisfactorily with kinetic data (Section II) and experimental data indicating a linear dependence of the selectivity $S = r_{II}/r_I$, the ratio of the rates by the second and first routes, on the reciprocal p^{-1}_{HCl} of the partial pressure of the gaseous reactant.

The mechanism of the more complicated reaction

$$HCl + MeCl + Si \rightarrow \text{Products}$$

has been analysed similarly [132]. Consideration is given not only to the above intermediate surface compounds but also to molecules (ZCH_3Cl) adsorbed on the silicon surface. The mechanism comprises ten stages with four independent routes

$$MeCl + HCl + Si = MeSiHCl_2$$
$$MeCl + 2HCl + Si = H_2 + MeSiCl_3$$
$$3HCl + Si = H_2 + HSiCl_3$$
$$4HCl + Si = 2H_2 + SiCl_4 \quad .$$

The kinetic equation obtained for the formation of the methyldichlorosilane is consistent with the observed first order with respect to methyl chloride. The expression for the selectivity $S = r_I/r_{IV}$ (the ratio of the rates by the first and fourth routes) was a linear function of the ratio of the partial pressures of the gaseous reactants p_{HCl}/p_{CH_3Cl}, in good agreement with experiment.

Since either (ZHCl) or (ZHSiCl) may be formed by the pyrolysis of methyl chloride, we can try to extend the multistage mechanism of the process

$$MeCl + HCl + Si \rightarrow \text{Products}$$

to the process

$$MeCl + Si \rightarrow \text{Products} \quad .$$

In particular, a possible scheme of formation of dimethyldichlorosilane may comprise the stages [19]

$$MeCl + Z \rightleftarrows ZMeCl$$
$$ZMeCl + ZMeCl \rightleftarrows ZMeCl \cdot MeCl + Z$$
$$ZMeCl \cdot MeCl + Si \rightarrow Me_2SiCl_2 + Z \quad .$$

The appearance of such byproducts as tri- and di-methylchlorosilanes can be explained by the presence of the stages

$$ZMeCl + ZMeSiMe \rightarrow Me_3SiCl + 2Z$$
$$ZMeCl + ZMeSiH \rightarrow Me_2SiHCl + 2Z \quad .$$

However, this leaves unanswered the question of the stages which will lead to formation of the intermediates (ZCH_3SiCH_3), (ZCH_3SiH), $(ZHCH_3Cl)$, and $(ZSiCl_2)$. More detailed investigations are required here on the mechanism of the pyrolysis of alkylchlorosilanes on a silicon–copper contact mass.

The idea of the formation of symmetrical derivatives such as dichlorosilane and dimethyldichlorosilane via intermediate compounds from two molecules of the gaseous

reactant is expressed in several papers, as already noted above. However, the qualitative aspect—the nature of the active centre Z—was the main concern. Thus Voorhoeve[16] suggested that the active centre in the direct synthesis of methylchlorosilanes contains two copper atoms and one silicon atom. In a series of later investigations Golubtsov et al.[135] considered that the active centre in this process is a group of the type SiCl. The theory of stationary reactions permits a quantitative approach to the inclusion of intermediate compounds of the type (ZRCl.RCl) in a multistage scheme, since its consequences can be tested experimentally. On the assumption, for example, that dichlorosilane is formed at the stage

$$ZHCl+ZHSiCl\rightarrow H_2SiCl_2+2Z,$$

in the hydrochlorination of silicon, the above selectivity $S = r_{II}/r_I$ would in general not have depended on the partial pressure of hydrogen chloride, which would have been contrary to experience.

The nature of the active centre in the kinetic analysis of multistage schemes is not significant in the Horiuti–Temkin method, since the surface is assumed to be in a steady state.

Role of copper and impurities

Comparison of kinetic data on the chlorination and hydrochlorination of silicon and germanium with data on their interaction with methyl chloride and bromide reveals the features reported below.

(*a*) Syntheses involving germanium have smaller activation energies than those involving silicon.

(*b*) A higher kinetic order with respect to the gaseous reactant is observed with germanium–copper contact masses than in the case of silicon.

(*c*) Impurities and additions of copper have a marked effect on the kinetics, lowering considerably the activation energy, and this effect is larger for reaction with germanium. Thus the order with respect to chlorine in the chlorination and hydrochlorination of silicon is higher in the presence of copper and impurities, while the activation energy falls by ~10–12 kcal mole^{-1}, i.e. by ~30% (Tables 1 and 2). The activation energy is halved with germanium. Such a relation is observed in hydrobromination (Table 4) and in the synthesis of dimethyldihalogeno-derivatives (Table 5).

(*d*) The nature of the halogen in RX (Cl or Br) has no marked effect on the kinetic parameters of the synthesis of halogenosilanes containing hydrogen or organic groups (Tables 2–4).

The decisive factor can be regarded[27,131] as the strength of the M–M bond on the surface of the solid reactant M. The higher activation energies with silicon can be explained by a more stable bond between silicon atoms, on the assumption that the same fraction of the energy of silicon–silicon and germanium–germanium bonds in the surface and adjacent layers enters as components of the activation energy[28,131]. In the hydrohalogenation of technical samples of silicon, as well as of silicon–copper and germanium–copper contact masses, the impurities and the additions of copper probably influence the energy of the M–M bond, promoting both easier rupture in the transition state and strong deformation of the H–X bond until the latter dissociates.

The effect of copper is not universal. Specimens of technical silicon even in the absence of copper are sufficiently reactive in some processes (chlorination[26], hydrochlorination[45], and hydrobromination[48] of silicon, synthesis of methyl-[68] and ethyl-dichlorosilanes[18] from mixtures of the alkyl and hydrogen chlorides). Nevertheless, specimens of high-purity silicon become considerably more active on the introduction of copper, and react at a lower temperature.

Various surface compounds of copper, regarded in several cases as independent phases, have been postulated as intermediates to explain the specific effect of copper on direct syntheses (CuR,[92] CuCl, RCuCl,[94] $HCuCl_2$,[136] Cu_3Si,[78] etc.). The role of copper is mainly to transfer chlorine atoms or R or RCl groups to the silicon atom. The regenerated copper again takes part in forming the intermediate compound.

Published mechanisms of direct synthesis do not reveal sufficiently clearly the functions of copper as a catalyst, and existing views are in some cases directly contradictory. In the first paper Hurd and Rochow[92] suggested that an indispensable condition for effective synthesis was close contact between silicon and copper phases, since rapid consumption of silicon occurred precisely at the interface. Essentially the same attitude was adopted by Bažant et al.[56,137] and also by Rossmy[138]. At the same time, beginning with the work of Klebanskii[78] and Trambouze[37] followed by the investigations of Voorhoeve[93] and of Kolster[139], silicon present as an intermetallic compound was assumed to be reactive. Andrianov, Golubtsov, et al.[140] and also Krylov and Efremov[81,82] showed that the intermediate compound acts as a donor of catalytically active copper, for contact masses not containing Cu_3Si are also catalytically active[141,142]. The functions of the copper catalyst formed by breakdown of the intermetallic compound are not clear from this work.

Such contradictory views are probably due to the absence in the above investigations of direct examination of the surface and adjacent layers of the contact masses. The reaction of hydrogen chloride, hydrogen bromide, and methyl bromide with silicon (formation of trichlorosilane[43], tribromosilane[34], methyldichlorosilane[18], and methylbromosilanes[127]) has established that copper(I) chloride, like the bromide[34], is not a catalyst, since synthesis begins only after this compound has been reduced by silicon and free copper and the Cu_3Si phase have separated.

Even a small copper content (10^{17}–10^{19} atoms cm^{-3}) proves extremely effective both for the adsorption of hydrogen chloride[124] and for sharply increasing the reactivity of the silicon[143]. This effect can be explained by a change in the collective electronic properties of the surface silicon atoms. These changes affect also the character of the adjacent layers. Thus additions of copper over the range 10^{17}–10^{20} atoms cm^{-3} lower the microhardness of a single crystal of silicon from 1250 to 700 kg mm^{-2} for a specimen with a 10^{20} atoms cm^{-3} copper content[143]. Data are also available[144,145], though less complete, on the variation of the microhardness of germanium when fairly extensively alloyed with other elements (10^{18}–10^{20} atoms cm^{-3}). A parallelism has been observed[146] between the variation of microhardness and that of specific surface energy of semiconductor crystals with covalent bonds. Such change in the state of the surface atoms should tend to enhance their reactivity, as has been observed e.g. in the synthesis of trichlorosilane. The combined electronic effect of small additions of copper, evident in the effects on the microhardness, the reactivity, and the chemisorptive power of silicon, cannot be regarded as specific to copper. This conclusion is

supported by the high reactivity of technical silicon, without the addition of copper, towards several direct syntheses (chlorination, hydrochlorination, formation of methyl- and ethyl-dichlorosilanes).

However, the change in the combined electronic properties of silicon with the introduction of small quantities of copper is insufficient for reaction with methyl chloride. Thus methyldichlorosilane is formed from a mixture of hydrogen and methyl chlorides on technical and pure silicon alloyed with copper (0.04–0.3%) in the temperature range 210–240°C, [68] which is close to the range (160–210°C) for the synthesis of trichlorosilane. But formation of dimethyldichlorosilane from methyl chloride alone and similar specimens of silicon was not observed up to 400°C. Hence it may be concluded that, in contrast to the synthesis of hydrogen-containing chlorosilanes, the formation dimethyldichlorosilane requires additional electronic changes in silicon, probably connected with the local action of copper on its surface atoms. Such an effect can be achieved only with a comparatively high content of copper in the surface and adjacent layers of silicon.

The presence of the η-phase or other intermetallic compound of silicon and copper is probably not essential for the local action of copper on the surface silicon atoms, i.e. to ensure the synthesis of dimethyldichlorosilane and probably other dialkyldichlorosilanes. In the presence of a highly active and extensive copper surface (taking into account the abnormally high rate of diffusion of copper atoms in the silicon and Cu_3Si crystal) [139], formation of an intermediate surface compound of silicon with copper may be sufficient for development of a local effect. Formation of the η-phase is a limiting case.

The long induction period in the reaction observed in practice when contact masses comprising a mixture of silicon and copper powders are used, as well as with certain alloy masses, is probably caused by formation of an active surface and of layers adjacent to the surface.

The large quantity of experimental data published on the action of impurity elements and promoters in contact masses, and also of gaseous contact poisons, represent mainly assessment of their overall and selective activity in the synthesis of hydrogen-containing halogeno-silanes and -germanes as well as corresponding organic derivatives. No quantitative data have appeared on the effect of impurities and promoters on the kinetics of the process, and therefore this question will not be examined in detail in the present Review.

The total and the selective activity of the contact masses are not significantly affected [147–149] by the usual impurities —aluminium, iron, and calcium—in silicon up to a total content of 2% and 10% of iron. However, these parameters diminish at higher contents of individual elements (1% of titanium, 2% of aluminium, 1.5% of calcium) [148]. The promoting action of individual elements (antimony, zinc, cadmium, bismuth, phosphorus, arsenic, tin, and indium) and of certain combinations (antimony plus zinc, zinc plus cadmium, antimony plus bismuth, etc.) is apparent in a higher yield of dialkyldichlorosilanes. Use of certain of these promoters (zinc, antimony, arsenic) in the synthesis of alkylhalogenogermanes [150] leads to a sharp increase in the yield of the alkyltrichloro-derivative. The yield of ethyldichlorosilane in the synthesis of ethylchlorosilanes is raised by the addition of 1.7% of aluminium, 1% of titanium, or 2% of calcium [151]. Only a certain content of promoters—not exceeding e.g. 0.001–0.005% of antimony and bismith—is optimal for the total and selective activity. Addition of higher contents of zinc and aluminium to the contact mass promotes the formation of trialkylchlorosilanes [153]. More than 0.01% of lead leads to complete deactivation of the contact mass [148,152]. Addition of aluminium and gallium increases the yield of the trimethylchlorogermane in the synthesis of methylchlorogermanes [154].

Contamination of the alkyl chloride with dimethyl ether [155], methylene dichloride [156], and sulphur dioxide [157] diminishes the activity of the contact masses.

The promoting effect of zinc, cadmium, and mercury has been explained [158] by their reaction with the organic halide in the gas phase to form their chlorides followed by transfer of a chlorine atom to copper to form cuprous chloride, which in turn is effective in the synthesis of alkylchlorosilanes by transferring its chlorine atom to silicon. However, the formation of copper(I) chloride was assumed from the content of Cu_3Si in the contact mass, although this silicide might not have been formed in this way.

Studies of the effect of promoting additions of several elements (aluminium, iron, titanium, zinc, antimony, phosphorus, arsenic, bismuth, boron, indium, gallium, tin, etc.) to samples of pure, purified, and technical silicon merit closer attention. It was concluded [159,160] from the results that promoting additives, introduced into the crystal lattice of silicon, may have either a favourable or an unfavourable effect on direct synthesis depending on their ability to react with the organic halide, and thus function as activators or inhibitors of the catalytic process.

The favourable effect of impurities and promoters in silicon has been attributed [161] to facilitation of the penetration of copper into the silicon lattice, or else the formation of silicides of low melting point.

Since the catalyst (copper) is especially sensitive to impurities, both it and surface silicon atoms can be assumed to be influenced both by gaseous impurities in the organic halide and by solid elements added to the contact masses; these effects will be still greater if a donor–acceptor type of bond can be formed on adsorption. The catalytic properties of copper and its ability to form particular compounds with silicon at the interface may be affected by adsorption on it especially of surface-active substances.

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