direct synthesis of silanes

chlorosilanes
methylchlorosilanes
ethylchlorosilanes

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SAMENVATTING

De synthese van silanen, belangrijke grondstoffen voor silikonen, kan direct verlopen met organische halogeniden of waterstofhalogeniden en silicium en heeft zich ontwikkeld tot een technologisch belangrijk proces. De kennis van omzettingssnelheden en reactiemechanismen is echter nog verre van volledig en er is nog geen sprake van een voorspelling van optimale proceskondities op grond van gegeven uitgangsprodukten.

Dit proefschrift is een overzicht van de huidige kennis van de door koper gekatalyseerde reakties van waterstofchloride, methylchloride en ethylchlo­ride met silicium. De drie processen zijn bestudeerd op basis van hun onderlinge analogie. Waar de methylchloorsilanen-synthese een hoogste op­brengst van 90% van het difunktionele silaan - dimethyldichloorsilaan - oplevert, ontstaat bij de chloorsilanen synthese het dichloorsilaan slechts in luttele procenten van het silanen produkt. De oorzaak van dit verschil blijkt gedeeltelijk te liggen in een snelle volgreaktie, die dichloorsilaan omzet in trichloorsilaan. Wanneer de invloed van de volgreaktie wordt ver­kleind door de gassen zeer kort in kontakt te laten met het siliciumkoper­mengsel, blijkt 24 mol % toch nog slechts de hoogste selektiviteit. Een ander duidelijk verschil in de reakties is te vinden in de stabilititeit van het ontledingsprodukt van de aan chloor gebonden rest. Bij waterstof­chloride kan gemakkelijk waterstof ontstaan, waardoor het silanenprodukt een lage waterstof/chloorverhouding zal hebben. Wanneer ethylchloride wordt gekraakt tijdens de synthese van ethylchloorsilanen ontstaat onder meer etheen, zodat de ethyl/chloorverhouding in het silanenmengsel verlaagd wordt. De kraking van de methylgroep is de minst ernstige van de drie als gevolg van de hoge energie die er voor nodig is en doordat niet primair een stabiel ontledingsprodukt ontstaat. Teneinde aan deze beschouwingen kracht te verlenen, zijn thermodynamische gegevens voor de silanen verzameld en aangevuld. Daartoe worden schattingsmethoden toegepast die voor vormings­warme, warmte-inhoud en entropie een serie waarden opleveren, die door hun interne konsistentie betrouwbaarder zijn dan de afzonderlijke literatuur­waarden. De betrouwbaarheid van de methoden wordt getoetst aan koolstofver­bindingen.

Op grond van een groot aantal bekende feiten en nieuwe experimentele re­sultaten worden reaktieschema's, die in de literatuur zijn gesuggereerd,
kritisch besproken. Een belangrijk aandeel in de reakties die zich op het silicium-oppervlak afspelen, dient te worden toegeschreven aan het oppervlak ingebedde koperchloridemolekules, die een primaire chlorering van siliciumatomen bewerkstelligen. Als het reagerende waterstof- of alkylchloride daarna aan koper adsorbeert, wordt de tweede valentie van silicium gevuld door overdracht van het waterstofatoom of de alkylgroep vanuit deze geadsorbeerde toestand. Het op koper achterblijvende chlooratoom kan weer dienen voor de chlorering van een volgend siliciumatoom. Het reactie-intermediair, alkylchloorsilyl (RSiCl) wordt vervolgens met een reaktantmolecule omgezet in de dichloorverbinding. Wanneer een siliciumatoom na de eerste chlorering andermaal wordt gechloreerd, zal het ontstane dichloorsilyl (SiCl₂), dat nog aan het oppervlak is gebonden, aanleiding geven tot de trichloorverbinding.

De kinetiek gemeten voor de chloorsilanen en de methylchloorsilanensynthese is niet in tegenspraak met de veronderstelde adsorptie van het chloride aan één atoom, een koperatoom, met het chlooratoom gericht naar het koper. De alom aangehangen dissociatieve chemisorptie van RCl op twee buurplaatsen op het oppervlak volgt niet uit de kinetiek en is voor het waterstofchloride zelfs onwaarschijnlijk.

Zinkchloride, de belangrijkste promotor die in de direkte synthese wordt toegepast, bleek zijn positieve effekt beneden de eutektische temperatuur van de mengsmelt met koper(I)chloride te verliezen. Het effekt wordt daarom toegeschreven aan een verhoging van de beweeglijkheid van koper(I)- en chloorionen als gevolg van de gesmolten toestand.

In alle drie processen blijkt een relatief zeer hoge selectiviteit in de dichloorverbinding haalbaar, wanneer de kontakttijden laag worden gehouden. Naast het vermijden van het optreden van volgreakties door de korte verblijftijden, zorgt de hoge gassnelheid voor een goede temperatuurvereffening. De ontleding van het aktieve reaktie-intermediair door plaatselijk hoge temperaturen wordt daardoor tot een minimum beperkt. Het is bovendien van belang, dat de reaktanten zuurstofvrij worden gemaakt teneinde de converteerbaarheid van silicium te verhogen.
SUMMARY

The synthesis of the title compounds, which are raw materials for the manufacture of silicones, proceeds by the direct interaction of hydrogen chloride, methyl chloride, and ethyl chloride with silicon under the catalytic action of copper. The knowledge of the kinetics and the reaction mechanism is quite incomplete and a prediction of the optimum process conditions based upon the specification of the reactants is impossible at present.

This thesis discusses the three synthesis processes on the basis of their mutual resemblance. In the synthesis of methylchlorosilanes, the bi-functional silane, dimethyl dichlorosilane, is formed with a selectivity of 90%, whereas the yield of dichlorosilane in the chlorosilanes synthesis is only a few percent. Part of this difference is caused by a fast secondary reaction which converts dichlorosilane into trichlorosilane. Even by using small contact times, e.g. 0.1 seconds, to suppress the secondary conversion, the maximum selectivity does not exceed 24 mol%. Another difference can be found in the stability of the reactants to decomposition. This decreases in the order methyl chloride, ethyl chloride, hydrogen chloride. Thermodynamic considerations show that the equilibrium contents of the dichloro-compounds are low compared to the contents observed in the synthesis. To allow for thermodynamic calculations, a consistent set of data is derived from experimental data, and the gaps are filled with estimations.

On the basis of numerous experimental results, partly from the literature, the reaction schemes suggested by various investigators are discussed. The reactions on the surface have to account for the selective formation of the dichloro-compounds, which is shown to proceed differently from the formation of the trichloro-compounds. This is evident, for example, from the difference in the relation between the pressure of methyl chloride to the rates of formation of dimethyl dichlorosilane and methyltrichlorosilane. Additional evidence is the remarkable constancy of the combined contents of the dichloro-compounds in methylchlorosilanes and ethylchlorosilanes synthesis. The arguments lead to a reaction scheme which comprises transfer of copper-bound chlorine to silicon atoms as the initiating step. After adsorption of hydrogen chloride or the alkyl chloride on copper, the second silicon valency is filled by transfer of a hydrogen atom or the alkyl group from the adsorbed complex. The intermediate compound (RSiCl)
is converted into the dichloro-compound by interaction with a reactant molecule. When two subsequent chlorinations of a silicon atom occur, the resulting surface-bound dichlorosilyl \((\text{SiCl}_2)\) reacts with the reactant to form the trichloro-compound. Cuprous chloride, formed by cracking of the alkyl chloride, may be responsible for the formation of the intermediate dichlorosilyl.

The expressions describing the rates of the reactions of hydrogen chloride and methylchloride with silicon-copper do not contradict the assumed single-site adsorption of the reactant molecule on copper. Some mechanisms proposed in the literature make use of a dissociative dual-site adsorption, but this is not the only possible mechanism consistent with the kinetics. For hydrogen chloride, such dual-site adsorption seems even less probable.

As well known, zinc chloride is the most important promoter added to improve the performance of the direct synthesis. It appears to prevent the cracking of the alkylchloride. Since the effect only holds above the eutectic temperature of its mixture with cuprous chloride, it presumably improves the mobility of copper(I) and chlorine ions in the molten layer.

In a fixed bed reactor the highest selectivity in the dichloro-compounds is obtained with small contact times. The high flow rates probably increase the selectivity largely by preventing hot spots. The decomposition rate of the active reaction intermediate is hereby reduced. Thus it appears possible to conduct the synthesis of methylchlorosilanes and ethylchlorosilanes with selectivities of 90% and 75% respectively. Furthermore, the removal of oxygen from the feed allows a higher convertibility of silicon, although this phenomenon is not understood.
CHAPTER I

GENERAL ASPECTS

The economical importance of silanes, base products for silicones, is illustrated. As introduction in the field of interest, some aspects of the manufacturing of silanes are discussed. Aim and lay-out of this study are given.

I-1. Siloxanes

Alkyl- and arylchlorosilanes are the base products for polymeric siloxanes, usually named silicones. Siloxanes are prepared from the silanes by hydrolysis and consequent poly-condensation, schematically:

\[
\begin{align*}
(\equiv\text{Si-Cl}) + \text{H}_2\text{O} & \longrightarrow (\equiv\text{Si-OH}) + \text{HCl} & (\text{I.1}) \\
2 (\equiv\text{Si-OH}) & \longrightarrow (\equiv\text{Si-O-Si-}) + \text{H}_2\text{O} & (\text{I.2})
\end{align*}
\]

Alkyl-, aryl- or mixed siloxanes thus comprise a strong skeleton of silicon-oxygen bonds in the form of a chain or cyclic structure of the type:

\[
\begin{array}{c}
\text{I}
\
\equiv\text{Si-O-Si-O}\
\equiv
\end{array}
\]

The organic groups attached to the silicon atoms together with the nearly inorganic skeleton provide the special properties for which the silicones are well known, for example: high thermal stability, chemical and physiological inertness, water-repellency and independency of physical properties from temperature. A detailed survey of the chemistry and the technology of silicones has been given by Noll (80).

The economic importance is illustrated in Figure 1, where the production of silicones of some countries has been plotted after data obtained from (80) and (128). The world production of silanes in 1971 will be in the order of 85,000 tons, which follows from a rough extrapolation of the graphs. The consumption of silicones in the Netherlands is illustrated in Figure 2, according to data from (78). It can be seen that there is an increasing demand for silicones, which will reach a value of about 1,200 tons in 1971. The average price of the silicones in the Netherlands, which is
also given in Figure 2, can be estimated at about 25% higher than the price for which they can be manufactured (788, p. 329).

Figure 1. Production of silicones (t.p.a.)

Figure 2. Expenditure of silicones (t.p.a.) and price (D.Fl.) in the Netherlands

I-2. Direct synthesis

Organohalogenosilanes are mainly prepared in the so called 'direct synthesis', a reaction of an organic halide with silicon. The reaction of hydrogen chloride with silicon comes under the same heading. The processes take place at temperatures higher than about 150 °C and may be accelerated by the use of a catalyst like metallic copper. Surveys of a large number of reactions of organic halides with silicon, catalyzed by copper may be found in the literature (8, 128, 141).

Which organosilicon halide is the main product of a synthesis starting from a given organic halide is largely dependent upon the choice of the reaction conditions and of the catalyst-silicon mixture. In Table 1 the main products are listed for reactions using various catalysts in the synthesis of some (organo-)chlorosilanes.
### Table 1. The direct synthesis

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Catalyst</th>
<th>Main product</th>
<th>Alloy with Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Cu, Fe</td>
<td>HSiCl₃</td>
<td>+</td>
</tr>
<tr>
<td>MeCl</td>
<td>Cu</td>
<td>Me₂SiCl₂</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Ca</td>
<td>Me₃SiCl</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Sn, Co</td>
<td>MeSiCl₃</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Cr, Fe</td>
<td>MeSiCl₃</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>MeSiHCl₂</td>
<td>-</td>
</tr>
<tr>
<td>EtCl</td>
<td>Cu</td>
<td>Et₂SiCl₂</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>EtSiCl₃</td>
<td>+</td>
</tr>
<tr>
<td>PhCl</td>
<td>Ag</td>
<td>Ph₂SiCl₂</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>PhSiCl₃</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Cu (Cd)</td>
<td>Ph₂SiCl₂</td>
<td>+</td>
</tr>
<tr>
<td>ViCl</td>
<td>Cu, Ni</td>
<td>Vi₂SiCl₂</td>
<td>+</td>
</tr>
</tbody>
</table>

Most of the catalysts are known to form an alloy with silicon, which is indicated in the table with " + ".

Because dimethyldichlorosilane is, economically, still the most important of silanes, much research has been devoted to its preparation in the direct synthesis. It is also the difunctional silane that can be prepared with the highest selectivity:

\[
2 \text{CH}_3\text{Cl} + \text{Si (Cu)} \rightarrow (\text{CH}_3)_2\text{SiCl}_2 \text{ (90%)} \quad (I.3)
\]

Diphenyldichlorosilane follows dimethyldichlorosilane in economical importance. Its manufacture proceeds with silver as well as copper as catalyst:

\[
2 \text{C}_6\text{H}_5\text{Cl} + \text{Si (Cu, Ag)} \rightarrow (\text{C}_6\text{H}_5)_2\text{SiCl}_2 \text{ (50%)} \quad (I.4)
\]

The lack of interest in the industrial manufacturing of diethyldichlorosilane is caused principally by the limited selectivity in which it is formed in its direct synthesis:

\[
2 \text{C}_2\text{H}_5\text{Cl} + \text{Si (Cu)} \rightarrow (\text{C}_2\text{H}_5)_2\text{SiCl}_2 \text{ (65%)} \quad (I.5)
\]

Dichlorosilane, although of possible importance for the preparation of silanes and silicones with special properties is not prepared industrially. It is formed in negligible amounts in the reaction of hydrogen chloride.
with a silicon-copper mixture:

\[
2 \text{HCl} + \text{Si(Cu)} \rightarrow \text{H}_2\text{SiCl}_2 \quad (5\%)
\] (I.6)

Of the silicon-containing by-products of the direct synthesis, compounds of the type \(\text{R}_3\text{SiCl}\) and \(\text{RSiHCl}_2\) are valuable materials. Unfortunately the compound \(\text{RSiCl}_3\) is usually the main by-product; it is formed in amounts exceeding the demand.

The direct synthesis is essentially a heterogeneous reaction, as it is a reaction between a gas and a solid. When a catalyst is used, which is necessary to lower reaction temperatures and to obtain desired compounds selectively, a rather complex system appears. The usual reaction steps which can be distinguished in heterogeneous catalytic reactions in a stationary state are extended with the supply of the solid reactant:

- diffusion of gaseous reactant to the surface of the solid
- adsorption of the reactant on the surface
- diffusion of the solid reactant to the surface layer
- reaction in the adsorbed layer
- desorption of the formed product
- diffusion of the gaseous product to the gas phase.

Because of the consumption of silicon, the particles of the contact mixture, the mixture of silicon and copper with an intimate contact between the components, undergo a continuous reduction in size. This tends to increase the average catalyst content in a batch of contact mixture, when no supply of fresh silicon or removal of the excess of catalyst is provided. It is obvious that in such a system a steady state never will be reached. Also in large-scale operation a stationary state will not be maintained for long periods, in spite of supply of silicon and copper. This is caused by accumulation of impurities introduced with the reactants, and products which can not be removed from the reactor. It is for this reason that full continuous operation on industrial scale must be considered impossible if no regeneration of the solid material is performed. For a discontinuous methylchlorosilanes process, about 20 to 30 times the reactor load of silicon can be supplied before an uneconomical product composition is reached. The production has to be stopped then, and the reactor must be cooled, discharged and reloaded. In several aspects such a method of operation compares poorly with a
continuous process, with recycle of the contact mixture through a re­
generation section, where it is purified from undesired substances.
By supply of the required components it can be brought to a favour­
able composition before it is re-introduced in the reactor.

I-3. Aim and lay-out of this study

In the present work a harmonization of the knowledge of the copper-
catalyzed reactions of hydrogen chloride, methylchloride and ethylchlo­
ride with silicon is attempted. It is obvious, but not yet fully recognized
that there should exist close analogy between the behaviour of these
chlorides with respect to the function of copper and the path of the
chemical reactions. However, the structure of the chlorides already
suggests that the complexity of the reactions increase in the sequence
hydrogen chloride, methylchloride, ethylchloride.

In the following chapters not all aspects of the subjects discussed have
been reviewed in detail, as there exist rather complete papers and mono-
graphies dealing with the direct synthesis (49, 128, 147, 144). Merely
the characteristics of the processes have been considered and new experi­
mental information, as described in Chapter VII has been integrated in
the treatise. First of all, in Chapter II, the thermodynamics of silicon
compounds are reviewed and a consistent set of data is given to allow
reliable thermodynamic calculations. The silicon-copper contact mixture
is an essential component in all direct synthesis processes and it is
the subject in Chapter III. The reaction of methylchloride with silicon-
copper is discussed rather extensively in Chapter IV, where also a general
reaction scheme is developed. This explains the function of the catalyst
and of some metal chlorides, frequently applied to improve the process.
In Chapter V the chemism of chlorosilanes is discussed in relation with
that of methylchlorosilanes and in the light of newly obtained kinetic
information. The direct synthesis of ethylchlorosilanes is the subject of
Chapter VI. The experimental findings and some of the observations
described in the literature are discussed on the basis of the analogy
with the methylchlorosilanes synthesis.
The various subjects are discussed without disturbing the argumentation by experimental details. All experimental work is therefore collected in Chapter VII, and when the results are used, reference is made to the appropriate paragraph in this chapter, e.g. by (VII-1).
CHAPTER II

THERMODYNAMICS OF SILICON COMPOUNDS

Literature data on methyl-, ethyl- and phenyl-(chloro)silanes are reviewed. Based upon empirical relations using second order additivity for heats of formation, heat content and entropy, a consistent set of data is obtained for organo(chloro)silanes. The empirical relations have been tested on carbon compounds for which more experimental information is available. The heat of formation of silicon tetrachloride has been determined from the heat effect of the direct combination of the elements.

II-1. Introduction

It is remarkable that none of the modern textbooks on silicon chemistry pays attention to thermodynamics of even the simplest compounds. Yet for pure and applied (physical) chemistry in this field, knowledge of thermodynamic functions may be of great importance. In this chapter the available material on this subject is collected and discussed. Great gaps in experimentally obtained data are bridged by estimations which seem to be very reliable.

A method for estimation of the free enthalpy uses the resemblance between molecules of different compounds. It may be based upon the assumed constancy of the property of a bond between two atomic species, the value for a bond energy or any partial quantity of the molecule being derived from a compound containing only that one bond. This method, applied also to heat content and entropy leads to thermochemical quantities which, for instance, are exactly equal for isomers. Such a 'first order additivity' method neglects the mutual influence which exists between substituents in molecules with a tetravalent central atom. It implies thus linearity in the thermochemical quantities of a series of five compounds with general formula \( X_n A Y_{4-n} \). In Figures 3-5 it is demonstrated for chloromethanes that this linearity is absent for heat of formation, heat content and entropy as well. Even worse results are obtained with a 'zero order additivity' estimation in which
it is assumed that every atom in the molecule gives a characteristic contribution to the properties of the molecule, regardless of its relative position in the molecule. This rule is to some extent only true for the molecular weight of a compound. For simple molecules, i.e. two-atomic compounds the method developed by Pauling (37) using extra contributions arising from electrostatic interaction between unlike atoms, results in reasonable data. Polyatomic molecules, however, can not be treated in this way, due to the fact that in the algebraic description of the method, there appear more unknowns than there are equations. For organic compounds a number of estimation methods has been accepted, usually applying a second order additivity (56). In general these methods consider a molecule as built up from fragments, each fragment with a characteristic contribution to some physico-chemical quantity. The contributions for the fragments are derived from as many experimental data as possible, but a secondary effect is introduced as soon as some compounds give conflicting results. Extra effects must also be ascribed to characteristic deviations in the structure of the compounds. Usually these methods give fair results but they demand a large availability of experimental data. For silicon compounds not enough accurate experimental data are available. A first order additivity method then is
the alternative method to obtain approximative values for the desired compounds. This has been done by Ring and O'Neal (88). The thus obtained data, however, are incapable of predicting or describing phenomena on rearrangement equilibria. In the rearrangement as represented by reaction (II.1), an equal number of bonds between the same atoms is broken and formed

\[ 2 \text{(CH}_3\text{)}_2\text{SiCl}_2 \rightleftharpoons (\text{CH}_3)_3\text{SiCl} + \text{CH}_3\text{SiCl}_3 \]  \hspace{1cm} (II.1)

First order additivity implies, for such a reaction, an equilibrium constant, determined from symmetry-constants only. The experimentally determined value for the equilibrium constant, however, is about 20 to 30 times smaller (101, 138).

**Figure 6. Method of comparative calculation**

(Explaination see text)
Another approach is a method (104) which assumes analogy between the variation of properties in series of analogous compounds, differing only in the central atom. For example, heats of formation of chlorosilanes are derived from data for chloromethanes if at least two values for chlorosilanes are known. There are, however, two serious objections here, of which the most important one is that it is doubtful whether the bond type between carbon and its ligands is the same as between silicon and its ligands. From electron diffraction of gaseous trichlorosilane the conclusion could be drawn that the Cl-Si-Cl angle suffers less from the chlorine-chlorine repulsion than the Cl-C-Cl angle in trichloromethane (108). Furthermore, there is a practical problem regarding the accuracy of the graphic method which is used in the evaluation of the data. A demonstration is given in Figure 6. Vertical lines are drawn on the abscissa, indicating the heats of formation of the chloromethanes. Horizontal lines at the values of known chlorosilanes are drawn from the ordinate. Between interceptions of lines for corresponding compounds a straight line is drawn. The values for the unknown chlorosilanes may now be read from the newly found interceptions. The inaccuracy of the method which is already partly evident from the ratio of the scales on abscissa and ordinate can be shown as follows. The total variation between the outer chloromethanes is 7.6 kcal, whereas in chlorosilanes this amounts to 168 kcal. Owing to poor agreement of literature data for chloromethanes (see Table 3), the data must be considered to have an inaccuracy of 0.6 kcal. The corresponding error for the chlorosilanes then amounts to 15 kcal/mol. The internal consistency of the thus estimated data (104) is very poor, which may follow from a calculation of the enthalpy change of a rearrangement reaction. The disproportionation of dichlorosilane (equation II.2) for example should then have a heat effect of -49 kcal, a figure which is not likely to be right.

\[
2 \text{H}_2\text{SiCl}_2 \rightleftharpoons \text{HSiCl}_3 + \text{H}_3\text{SiCl} \quad (\text{II.2})
\]

From the considerations on this application of the method of 'comparative calculation', proposed by Karapetyants (66), it may become clear that its success will be better when the series of compared compounds have greater resemblance and when the data are numerically in the same range.
This might be the case with compounds like $\text{Me}_n\text{SiCl}_{4-n}$ and $\text{Et}_n\text{SiCl}_{4-n}$ or similar silicon compounds.

In the following paragraphs an estimation method for silicon compounds is given which is tested first on carbon compounds. Much attention has been paid to the internal consistency of the resulting data, in order to prevent conflicting results. In estimating heats of formation, use has been made of literature data on heats of formation, equilibrium constants of rearrangement equilibria, and the reaction enthalpy of the direct synthesis of methylchlorosilanes. For heat content and entropy, a new approach is presented, also using a second order additivity method.

II-2. Heat of formation of carbon compounds

Heat of formation data are estimated for methyl-, ethyl- and phenyl(chloro)silanes, based on literature data, with the use of second order additivity.

The test on carbon compounds and radicals gives better results than many other methods of estimation.

In a second order additivity method to estimate heats of formation, contributions should be considered not only from the presence of various groups or atoms in the compound but also from the mutual influence of the molecular parts. A physico-chemical quantity of compounds with a tetravalent central atom may be approximated primarily with four additive bond terms, one for each of the ligands. If all substituents have a mutual influence, it is possible to define six extra terms. If the influence between the same atoms or groups is added to their bond terms, then only terms between different substituents remain. Now the algebraic description is reduced in the number of unknowns, while the numerical results remain unchanged. Thus in a system of the type $\text{AX}_n\text{Y}_m\text{Z}_{4-n-m}$ ($m + n < 4$), consisting of fifteen compounds, there are six unknowns making it possible to estimate the larger part from knowledge of at least six suitable compounds. For two different substituents ($X$ and $Y$) the expression may be written:

$$Q(X_nY_{4-n}) = n.a(A-X) + (4-n).a(A-Y) + n.(4-n).i(X,Y) \quad \text{(II.3)}$$
The primary bond terms $a(A-X)$ and $a(A-Y)$ form the linear part of the quantity $Q$ and can for instance be derived from the molecules $AX_4$ and $AY_4$ respectively. The mutual influence term is denoted as $i(X,Y)$ and stands for the simultaneous contribution of one $X$ and one $Y$ ligand. This method is basically similar to a method proposed by Bernstein (76).

<table>
<thead>
<tr>
<th>Bond term</th>
<th>Influence term</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a(C-H)$</td>
<td>$-4.452$</td>
</tr>
<tr>
<td>$a(C-Cl)$</td>
<td>$-6.438$</td>
</tr>
<tr>
<td>$a(C-Me)$</td>
<td>$-10.002$</td>
</tr>
<tr>
<td>$a(C-Et)$</td>
<td>$-13.809$</td>
</tr>
<tr>
<td>$a(C-e)$</td>
<td>$+49.5$</td>
</tr>
<tr>
<td>$i(H,Me)$</td>
<td>$+1.024$</td>
</tr>
<tr>
<td>$i(H,Cl)$</td>
<td>$-0.215$</td>
</tr>
<tr>
<td>$i(H,Et)$</td>
<td>$+0.274$</td>
</tr>
<tr>
<td>$i(Me,Et)$</td>
<td>$-0.155$</td>
</tr>
<tr>
<td>$i(Cl,Me)$</td>
<td>$-2.104$</td>
</tr>
<tr>
<td>$i(H,e)$</td>
<td>$-0.7$</td>
</tr>
<tr>
<td>$i(Me,e)$</td>
<td>$-3.5$</td>
</tr>
<tr>
<td>$i(Cl,e)$</td>
<td>$-3.9$</td>
</tr>
</tbody>
</table>

The value of the method has first been tested for hydrocarbons and some chlorine compounds. In Table 2 the values of group contributions and influence terms are given for some methane derivatives. The data represent the best agreement with the literature data given in Table 3, column 3. The contributions were obtained by minimisation of the average standard deviation between observed and calculated data. The results of the calculation are in column 5. From the small deviations (column 6) between calculated and observed data, it is clear that application of the method to silanes is promising. It is remarkable that the estimations apply for the radicals as well. The loose electron has been considered as a substituent, with a bond energy term and a mutual influence with hydrogen, methyl, etc.
Table 3
Comparison of literature and calculated values of the enthalpy of formation at 25 °C for some carbon compounds and radicals (kcal/mol)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H_f^0 (\text{lit}) )</th>
<th>Ref.</th>
<th>( \Delta H_f^0 (\text{calc}) )</th>
<th>Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_4 )</td>
<td>-17.89</td>
<td>(22)</td>
<td>-17.81</td>
<td>-0.08</td>
</tr>
<tr>
<td>( \text{CH}_3\text{Cl} )</td>
<td>-20.66</td>
<td>(55)</td>
<td>-20.44</td>
<td>-0.22</td>
</tr>
<tr>
<td>( \text{CH}_2\text{Cl}_2 )</td>
<td>-22.4</td>
<td>(27)</td>
<td>-22.64</td>
<td>+0.24</td>
</tr>
<tr>
<td>( \text{CHCl}_3 )</td>
<td>-25.0</td>
<td>(27)</td>
<td>-24.41</td>
<td>-0.59</td>
</tr>
<tr>
<td>( \text{CCI}_4 )</td>
<td>-25.50</td>
<td>(88)</td>
<td>-25.75</td>
<td>+0.25</td>
</tr>
<tr>
<td>( \text{Me}_3\text{CCl} )</td>
<td>-25.94</td>
<td>(55)</td>
<td>-25.94</td>
<td>-0.19</td>
</tr>
<tr>
<td>( \text{Me}^2\text{C} )</td>
<td>-43.0</td>
<td>(71)</td>
<td>-42.76</td>
<td>-0.24</td>
</tr>
<tr>
<td>( \text{Me}_4\text{C} )</td>
<td>-39.70</td>
<td>(71)</td>
<td>-40.01</td>
<td>+0.31</td>
</tr>
<tr>
<td>( \text{Me}_3\text{CH} )</td>
<td>-31.5</td>
<td>(71)</td>
<td>-31.39</td>
<td>-0.11</td>
</tr>
<tr>
<td>( \text{Me}_2\text{CH}_2 )</td>
<td>-24.8</td>
<td>(71)</td>
<td>-24.81</td>
<td>+0.01</td>
</tr>
<tr>
<td>( \text{MeCH}_3 )</td>
<td>-20.24</td>
<td>(87)</td>
<td>-20.28</td>
<td>+0.04</td>
</tr>
<tr>
<td>( \text{MeCH}_2\text{Cl} )</td>
<td>-25.1</td>
<td>(88)</td>
<td>-25.83</td>
<td>+0.73</td>
</tr>
<tr>
<td>( \text{MeCHCl}_2 )</td>
<td>-29.1</td>
<td>(88)</td>
<td>-30.93</td>
<td>+1.83</td>
</tr>
<tr>
<td>( \text{Et}_2\text{CH}_2 )</td>
<td>-35.0</td>
<td>(88)</td>
<td>-35.42</td>
<td>+0.42</td>
</tr>
<tr>
<td>( \text{Et}_3\text{CH} )</td>
<td>-45.34</td>
<td>(88)</td>
<td>-45.06</td>
<td>-0.28</td>
</tr>
<tr>
<td>( \text{Et}_4\text{C} )</td>
<td>-55.4</td>
<td>(112)</td>
<td>-55.24</td>
<td>-0.16</td>
</tr>
<tr>
<td>( \text{MeEtCH}_2 )</td>
<td>-30.15</td>
<td>(88)</td>
<td>-30.27</td>
<td>+0.12</td>
</tr>
<tr>
<td>( \text{Me}_2\text{EtCH} )</td>
<td>-36.92</td>
<td>(88)</td>
<td>-36.25</td>
<td>-0.67</td>
</tr>
<tr>
<td>( \text{Me}_3\text{EtC} )</td>
<td>-44.35</td>
<td>(88)</td>
<td>-44.28</td>
<td>-0.07</td>
</tr>
<tr>
<td>( \text{Me}_2\text{Et}_2\text{C} )</td>
<td>-48.17</td>
<td>(88)</td>
<td>-48.24</td>
<td>-0.07</td>
</tr>
<tr>
<td>( \text{MeEt}_3\text{C} )</td>
<td>-51.38</td>
<td>(88)</td>
<td>-51.89</td>
<td>+0.51</td>
</tr>
<tr>
<td>( \text{MeEt}_2\text{CH} )</td>
<td>-41.02</td>
<td>(88)</td>
<td>-40.81</td>
<td>-0.21</td>
</tr>
</tbody>
</table>

Radical

<table>
<thead>
<tr>
<th>Radical</th>
<th>( \Delta H_f^0 )</th>
<th>Ref.</th>
<th>Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C} )</td>
<td>+171</td>
<td>(87)</td>
<td>+198</td>
</tr>
<tr>
<td>( \text{CH} )</td>
<td>+142</td>
<td>(66)</td>
<td>+141.9</td>
</tr>
<tr>
<td>( \text{CH}_2 )</td>
<td>+90</td>
<td>(66)</td>
<td>+88.7</td>
</tr>
<tr>
<td>( \text{CH}_3 )</td>
<td>+34.0</td>
<td>(66)</td>
<td>+34.0</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_5 )</td>
<td>+25.7</td>
<td>(66)</td>
<td>+25.7</td>
</tr>
<tr>
<td>( \text{i-C}_3\text{H}_7 )</td>
<td>+17.6</td>
<td>(66)</td>
<td>+17.5</td>
</tr>
<tr>
<td>( \text{t-C}_4\text{H}_9 )</td>
<td>+6.8</td>
<td>(66)</td>
<td>+9.0</td>
</tr>
<tr>
<td>( \text{CCI}_3 )</td>
<td>+18.6</td>
<td>(66)</td>
<td>+19.5</td>
</tr>
</tbody>
</table>

*Ref. indicates reference number.*
Though in Table 3 only data have been given for compounds with known heats of formation in order to enable a comparison, it should be emphasized that the results suggest reliable extension to many more carbon compounds. Heat of formation data for hydrocarbons, covered by the contributions given in Table 2, and for which no experimental data exist may be calculated with the use of equation (II.3).

II-3. Heat of formation of silicon compounds

For silicon compounds of the same type as the carbon compounds discussed above, the results for bond terms and influence terms are given in Table 4. The bond terms are based upon the available data on heats of formation. The influence terms have been chosen on the basis of a number of known equilibrium constants. The free enthalpy change of rearrangement reactions can be shown to contain only influence terms, heat content and entropy. The free enthalpy change of reaction (II.1), for example, can be represented as:

$$\Delta g_0^{298} = \Delta h_f^0(\text{Me}_3\text{SiCl}) + \Delta h_f^0(\text{MeSiCl}_3) - 2 \Delta h_f^0(\text{Me}_2\text{SiCl}_2) + T.\Delta s_0^{298} \quad \text{(II.4)}$$

Introduction of equation (II.3) in which $Q$ can be $\Delta h_f^0$ leads to:

$$\Delta g_0^{298} = -2i(\text{MeCl}) - T.\Delta s_0^{298} \quad \text{(II.5)}$$

Equation (II.5) is made suitable for other temperatures by introducing the heat content and appropriate entropy of reactants and products, as discussed in paragraphs II-4 and -5. Values for the experimentally determined equilibrium constants have been compared with calculations via equation (II.5). The agreement appeared quite satisfactory (727 and V-2). In Table 5 the experimentally obtained data may be compared with the estimates. Resultant data for some silicon compounds covered by the group contributions as given in Table 4 are given in the appendix (Table 48). The data differ somewhat from earlier results, as new experimental work became available (51,52,92).
The reliability of the data is different for different substituents present in the compounds. Due to the availability of literature data, the expected possible errors increase in the order H, Me, Et, Ph.

The advantage of the proposed method is that the estimated data are completely consistent in that they predict the free enthalpy change of rearrangements with an accuracy of better than 1 kcal (727), which is not the case if the individual experimental data are used. Also the conflicting results for the silicon-carbon bond energy (34) disappear upon introduction of the estimated data.

As for the difference between estimated and experimentally obtained data it appears that for some methylchlorosilanes the estimated data are more negative than the literature data. The direct synthesis of methylchlorosilanes, however, was shown to have a heat effect that is even somewhat larger than can be calculated from the estimations. This suggests that some bond terms might even be more negative.

Heats of formation of silicon compounds have been measured by various methods. A classic method is to calculate the heat of formation of a substance from the observed heat of combustion. For compounds that are

<table>
<thead>
<tr>
<th>Bond term</th>
<th>Influence term</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(Si-H) + 1.9</td>
<td>i(H,Me) + 0.1</td>
</tr>
<tr>
<td>a(Si-Cl) - 40.1</td>
<td>i(H,Cl) - 0.6</td>
</tr>
<tr>
<td>a(Si-Me) - 13.0</td>
<td>i(H,Et) 0</td>
</tr>
<tr>
<td>a(Si-Et) - 14.0</td>
<td>i(Cl,Me) - 2.0</td>
</tr>
<tr>
<td>a(Si-Ph) + 23.0</td>
<td>i(Cl,Et) 0</td>
</tr>
<tr>
<td>a(Si-e) + 27.1</td>
<td>i(Cl,Ph) - 4.5</td>
</tr>
<tr>
<td></td>
<td>i(H,Ph) 0</td>
</tr>
<tr>
<td></td>
<td>i(H,e) + 2.4</td>
</tr>
<tr>
<td></td>
<td>i(Me,e) + 5.8</td>
</tr>
<tr>
<td></td>
<td>i(Cl,e) - 1.6</td>
</tr>
</tbody>
</table>
Table 5

Values for enthalpy of formation of gaseous silicon compounds at 25 °C (kcal/mol)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_f^{\text{O(lit)}}$</th>
<th>Ref$^b$</th>
<th>method$^c$</th>
<th>$\Delta H_f^{\text{O(calc)}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH$_4$ silane</td>
<td>+ 7.3 (60)</td>
<td>dir</td>
<td>+ 7.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ 7.8 (22)</td>
<td>dir</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- 11.3 (13)</td>
<td>comb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiHCl$_3$ trichlorosilane</td>
<td>-117.4 (134)</td>
<td>hydr</td>
<td>-120.2</td>
<td></td>
</tr>
<tr>
<td>SiCl$_4$ tetrachlorosilane</td>
<td>-163.2 (13)</td>
<td>hydr</td>
<td>-160.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-153.7 (47)</td>
<td>hydr</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-160.3 VII-13</td>
<td>dir</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeSiCl$_3$ methyltrichlorosilane</td>
<td>-150.5 (47)</td>
<td>hydr</td>
<td>-139.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-139.7 (62)</td>
<td>comb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me$_2$SiCl$_2$ dimethyldichlorosilane</td>
<td>-108.4 (33)</td>
<td>hydr</td>
<td>-114.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-111.1 (51)</td>
<td>comb</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-104.8 (47)</td>
<td>hydr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me$_3$SiCl trimethylchlorosilane</td>
<td>-80 (47)</td>
<td>hydr</td>
<td>- 85.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- 84.7 (13)</td>
<td>hydr</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- 84.6 (52)</td>
<td>comb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeSiHCl$_2$ methyldichlorosilane</td>
<td>-99.7 (51)</td>
<td>comb</td>
<td>- 96.4</td>
<td></td>
</tr>
<tr>
<td>Me$_2$SiHCl dimethylchlorosilane</td>
<td>-73.5 (51)</td>
<td>comb</td>
<td>- 68.6</td>
<td></td>
</tr>
<tr>
<td>Me$_4$Si tetramethylsilane</td>
<td>- 77 (111)</td>
<td>comb</td>
<td>- 52.0</td>
<td></td>
</tr>
<tr>
<td>Me$_3$SiH trimethylsilane</td>
<td>- 67 (171)</td>
<td>comb</td>
<td>- 36.8</td>
<td></td>
</tr>
<tr>
<td>Me$_2$SiH$_2$ dimethylsilane</td>
<td>- 49 (171)</td>
<td>comb</td>
<td>- 21.8</td>
<td></td>
</tr>
<tr>
<td>EtSiH$_3$ ethylsilane</td>
<td>- 29 (111)</td>
<td>comb</td>
<td>-  8.3</td>
<td></td>
</tr>
<tr>
<td>MeSiH$_3$ methylsilane</td>
<td>+  1 (52)</td>
<td>imp</td>
<td>-  7.0</td>
<td></td>
</tr>
<tr>
<td>Et$_2$SiH$_2$ diethylsilane</td>
<td>- 44 (111)</td>
<td>comb</td>
<td>- 24.2</td>
<td></td>
</tr>
<tr>
<td>Et$_3$SiH triethylsilane</td>
<td>- 47 (171)</td>
<td>comb</td>
<td>- 40.1</td>
<td></td>
</tr>
<tr>
<td>Et$_4$Si tetraethylsilane</td>
<td>- 45 (111)</td>
<td>comb</td>
<td>- 56.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- 58.2 (72)</td>
<td>comb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EtSiCl$_3$ ethyltrichlorosilane</td>
<td>-124 (42)</td>
<td>comb</td>
<td>-134.3</td>
<td></td>
</tr>
<tr>
<td>Ph$_2$SiCl$_2$ diphenyltrichlorosilane</td>
<td>-52.2 (22)</td>
<td>hydr</td>
<td>- 52.2</td>
<td></td>
</tr>
<tr>
<td>Ph$_4$Si tetraphenylsilane</td>
<td>+ 96 (17)</td>
<td>comb</td>
<td>+ 92.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ 90 (113)</td>
<td>comb</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Radical

<table>
<thead>
<tr>
<th>Radical</th>
<th>$\Delta H_f^{\text{O}}$</th>
<th>Ref$^b$</th>
<th>$\Delta H_f^{\text{O}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>+108.4 (13)</td>
<td></td>
<td>+108.4</td>
</tr>
<tr>
<td>SiCl</td>
<td>+ 48 (55)</td>
<td></td>
<td>+ 34</td>
</tr>
<tr>
<td>SiCl$_2$</td>
<td>- 37.7 (55)</td>
<td></td>
<td>- 35.6</td>
</tr>
<tr>
<td>SiCl$_3$</td>
<td>- 99 (109)</td>
<td></td>
<td>-100.4</td>
</tr>
<tr>
<td>SiH$_3$</td>
<td>+ 40 (109)</td>
<td></td>
<td>+ 40</td>
</tr>
<tr>
<td>SiMe$_3$</td>
<td>+ 5.6 (48)</td>
<td></td>
<td>+ 5.5</td>
</tr>
</tbody>
</table>

$^a$ Me denotes CH$_3$, Et - C$_2$H$_5$, Ph - C$_6$H$_5$. $^b$ Some of the data were not
unstable relative to their elements the heat of decomposition can be measured. For disilane (Si₂H₅) the heat of formation from measurement of the heat of combustion appeared to be -35.8 kcal/mol (38), whereas the decomposition into the elements resulted in +17.1 kcal/mol (22). The results differ by as much as 53 kcal/mol. The difference between results obtained by both methods applied to silane, amounts to 18 kcal. Probably, errors in the combustion method arise from the undefined state of the combustion products, caused, for example, by the incomplete combustion of silicon. Therefore, the direct measurement of the heat of decomposition will produce a better figure.

Another method is to measure the heat of hydrolysis of an organochlorosilane. This still requires measurement of the heat of combustion of the hydrolysate, which may vary in composition, i.e. the degree of polymerization. The argument that polymerization of the silanols has no enthalpy change (33) must be considered incorrect. Equation (II.6) schematizes this polycondensation.

\[ 2 (\equiv Si-OH) \rightarrow (\equiv Si-O-Si\equiv) + H_2O \quad (II.6) \]

If it is compared with an analogous reaction like the formation of dimethylether from methanol (equation II.7), which has a heat effect of -26 kcal in gasphase (25 °C), it becomes clear that such consequent use of bond additivity is rather speculative.

\[ 2 CH_3OH \rightarrow CH_3-O-CH_3 + H_2O \quad (II.7) \]

A method with a simplicity which is comparable to that of the decomposition into the elements is the measurement of the reaction heat of a direct combination of the elements. This is only possible for silicon tetrachloride, which is formed rapidly from chlorine and metallic silicon at elevated temperatures. The results of such a measurement

\[ ΔH°(SiO"-amorph) = -216.1 \text{ kcal/mol (72).} \]
has been taken as the 'best value' for this compound, as it lies well within the range indicated by data obtained from hydrolysis (VII-13).

II-4. Heat content

First order additivity in heat content assumes proportionality between the heat content and the number of substituted ligands. That this may lead to large errors is shown in Figure 4, where the value of $H^0_{298} - H^0_0$ of chloromethanes is plotted versus the number of chlorine atoms in the molecules. The calculation of the heat content of the compound $H_2ACl_2$ (A=C, Si) from the values of $AH^0_4$ and $ACl^0_4$, using first order additivity is about 15% too high. Knowledge of data for the extremes enables interpolation; when extrapolation would be required the relative errors may be larger.

The deviation from linearity in such a series of compounds is caused by non-linear terms in the thermodynamic functions. The equations for calculation of thermodynamic functions contain contributions from translation, rotation and vibration of the molecule. For this last contribution, knowledge is required of the fundamental vibration-frequencies of the molecule. This information can be obtained from Raman and infrared spectroscopy, but only for simple molecules. The assignment of the frequencies becomes much more complicated when the number of atoms and complexity of the molecules increase. For the most useful part of the heat content, the increment in the function from 298 K

![Figure 7. Additive part of heat content of chlorosilanes (kcal/mol)](image)
to \( H^0_{T-298} \), a good approximation can be obtained when a non-linear term is introduced, which contains the natural logarithm of the molecular weight. The relation to calculate a heat content in this manner is equation (II.8):

\[
(H^0_{T-298})(X^AY_{4-n}) = n.\Phi(A-X) + (4-n).\Phi(A-Y) - \frac{3}{2} R (T-298) \ln(M) \quad (II.8)
\]

Though the theoretical meaning of the molecular weight term in this case is obscure, it is evident from Figure 7, where the \( H_{600} - H_{298} \), minus this term, is plotted for chlorosilanes, that the result is very satisfactory. The points representing the additive part of the heat content now lie on a straight line. There are enough literature data available to evaluate \( \Phi \)-values for the most interesting substituents in silane. They are given in Table 6 for temperatures of 400, 500, 600 and 700 K and contain 298 K as a basis. From these values the heat content data for a number of organochlorosilanes could be calculated, which have been collected in the appendix in Table 48.

### Table 6

<table>
<thead>
<tr>
<th>Bond</th>
<th>Temp. (K) 300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-H</td>
<td>0</td>
<td>0.553</td>
<td>1.165</td>
<td>1.820</td>
<td>2.443</td>
</tr>
<tr>
<td>Si-Cl</td>
<td>0</td>
<td>0.961</td>
<td>1.933</td>
<td>2.923</td>
<td>3.923</td>
</tr>
<tr>
<td>Si-Me</td>
<td>0</td>
<td>1.287</td>
<td>2.729</td>
<td>4.315</td>
<td>5.933</td>
</tr>
<tr>
<td>Si-Et</td>
<td>0</td>
<td>1.904</td>
<td>4.108</td>
<td>6.552</td>
<td>9.226</td>
</tr>
<tr>
<td>Si-Ph</td>
<td>0</td>
<td>3.023</td>
<td>6.641</td>
<td>10.773</td>
<td>15.318</td>
</tr>
</tbody>
</table>

**II-5. Entropy**

For entropy the first order additivity of bond-contributions has proved more reliable than is the case for heat of formation and heat content, provided that contributions from the symmetry of the molecule are accounted for (see Figure 5). Yet the accuracy will be increased if another non-linear term is introduced. This should contain the natural logarithm of the molecular weight, as was done for the heat content.
The relation enabling the calculation of entropy from bond-contributions, symmetry and the molecular weight of the substance, which best fits the experimental data was shown before (127) to be:

\[ S^0(x_nAy_{4-n}) = n \varphi'(A-X) + (4-n) \varphi'(A-Y) - R \ln \sigma + \frac{3}{2} R \ln(M) \] (II.9)

As for the meaning of the molecular weight term, the statistical thermodynamic function for entropy actually contains this term as part of the translational contribution (56), whereas the symmetry term is contained in the rotational contribution.

Values for \( \varphi' \) for some substituents in silanes for temperatures 298, 400, 500, 600 and 700 K are given in Table 7. Entropies for a number of silicon compounds have been calculated from these data and are given in the appendix in Table 48.

### Table 7

<table>
<thead>
<tr>
<th>Bond</th>
<th>298</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-H</td>
<td>10.872</td>
<td>11.672</td>
<td>12.410</td>
<td>13.09</td>
<td>13.72</td>
</tr>
<tr>
<td>Si-Cl</td>
<td>17.175</td>
<td>18.789</td>
<td>20.135</td>
<td>21.24</td>
<td>22.19</td>
</tr>
<tr>
<td>Si-Et</td>
<td>27.075</td>
<td>31.613</td>
<td>35.565</td>
<td>39.34</td>
<td>42.87</td>
</tr>
<tr>
<td>Si-Ph</td>
<td>33.095</td>
<td>40.543</td>
<td>47.495</td>
<td>54.21</td>
<td>60.51</td>
</tr>
</tbody>
</table>
CHAPTER III

THE CONTACT MIXTURE AND ITS SURFACE

In all contact mixtures, Cu₂Si is likely to occur, but it deteriorates the mechanical strength. Results on adsorption of various compounds indicate that most heats of adsorption are only slightly more negative than the heats of condensation.

III-1. Introduction

In the direct synthesis, the surface of the silicon-catalyst mixture is the place where the reacting halide adsorbs, where a silicon atom is produced from the inner part of the solid, its bonds with the substrate are broken and replaced by bonds with molecular fragments of the reactant, and from where the silane molecule finally desorbs. It is of particular interest to consider the phenomena on the surface in order to give some elucidation on the direct synthesis. In the following chapters the overall processes will be discussed. In this chapter their common basis, the contact mixture, will be considered.

III-2. Preparation of the silicon-copper contact mixture

The starting materials for the silicon-copper contact mixture are silicon and copper or copper compounds. Starting from elemental silicon and copper the most simple method is to mix the components in the form of powders. On industrial scale this method is frequently used. A more intimate mixture is obtained when it is heated in a reducing or inert atmosphere to induce sintering or even to melt it. When the molten mixture has been cooled, it has to be ground in order to obtain a sufficiently high specific surface area. Particles of sieve fraction of 50 - 300 microns, with a specific surface area in the order of 0.1 m²/g will perform well in both a fluidized or fixed bed reactor. The above and other methods to obtain a contact mixture have been described by Rochov, who first used the mixture in alkylchlorosilanes synthesis (69).
For laboratory purposes, a well defined contact mixture may be obtained from silicon and cuprous chloride. When this mixture is heated at temperatures above 260 °C, the cuprous chloride will be reduced to metallic copper (equation III.1) by part of the silicon. The copper deposits on the silicon particles.

\[ 4 \text{CuCl} + n \text{Si} \rightarrow 4 \text{Cu} + \text{SiCl}_4 + (n-1) \text{Si} \]  

(III.1)

Contact mixtures thus obtained perform reproducibly in a direct synthesis of alkylchlorosilanes \((727)\). Continued heating at 400 °C after the reduction of cuprous chloride improves the convertibility of the silicon, although an induction period, in which no silanes are formed, may occur. The improvement has been credited to a better dispersion of the components. When the contact mixture is not subjected to prolonged heating, no induction period is observed \((VII-5, VII-8-3)\), while the surface of the contact mixture will remain slightly chlorinated \((VII-3-2)\).

It can not be determined whether an induction period arises from oxidation of the surface by traces of oxygen in the inert gas during the treatment at high temperature, or from complete removal of chlorine from the surface.

Another copper compound applied in the preparation of a contact mixture is cupric oxide, which has to be reduced by hydrogen in order to obtain metallic copper in an active contact mixture. Many copper compounds convertible into metallic copper have been tested by researchers and are the subject of a part of the patent literature \((see e.g. (747))\).

All preparation methods lead to finely divided copper over or in the silicon, the elements being in intimate contact. Already at about 300 °C, silicon and copper are able to form an alloy, the \(\eta\)-phase:

\[ 3 \text{Cu} + \text{Si} \rightarrow \text{Cu}_3\text{Si} \]  

(III.2)

The structure and the formation of this compound by diffusion has been investigated by Kolster \((68)\). He showed that \(\text{Cu}_3\text{Si}\) is the only intermetallic compound formed when silicon and copper are in contact. It is formed at the phase boundary between silicon and \(\text{Cu}_3\text{Si}\) \((68, p. 177)\) and this comes about because copper is the only diffusing component, whereas the silicon atoms are practically immobile. The diffusion coefficient
of copper through the η-phase layer has already a high value at 343 °C: D = 2.4x10^{-12} \text{ m}^2/\text{s}. From the diffusion coefficients at different temperatures the activation energy could be determined to be 21 kcal/mol, a surprisingly low value for diffusion in solids (68, p. 169).

With this knowledge it is not surprising that the contact mixture which is active in a direct synthesis, conducted at 300 °C or higher, may contain part or all of the copper in the form of η-phase. This was discovered already in 1956 (67, 114) and lead to the conclusion that the ability of alkylchlorosilanes formation was solely due to the occurrence of Cu₃Si. Experimental evidence has been furnished that the contact mixture must contain η-phase to be reactive (67), but also that contact mixtures need not be reactive when they contain η-phase (70, 100). And even contact mixtures in which no η-phase could be detected have been shown to be active in the direct synthesis (47, 58).

The conclusion with respect to the function of Cu₃Si seem not very unanimous. It has, however, to be recognized that the high diffusion rates in the alloy guarantee a sufficient availability of atoms of both the reactant silicon and the catalyst copper on the surface. It is from this philosophy that a group of Russian authors proposed that break-down of Cu₃Si, a reaction with an activation energy of 30 kcal/mol (70), produce the copper atoms which exert a catalytic function on the reaction of an alkylchloride with silicon (69, 70, 117).

### III-3. Adsorption on contact mixtures and silicon

Results on heats of adsorption obtained from kinetic measurements seem inaccurate. More direct methods yield data in better agreement with each other; the values indicate that the interaction with the surface of the contact mixture is of a physical nature.

The adsorption equilibrium constant of methylchloride has been determined indirectly from kinetic investigation in the direct synthesis of methylchlorosilanes (59, 129). The values which are obtained with such a method are strongly dependent upon the rate equation chosen to describe the kinetics. When a series of kinetic measurements is assumed to be described by an equation based upon dissociative chemisorption
of the methylchloride on two active sites of the surface, a value of the adsorption equilibrium constant can be calculated (see IV-5):

\[ K_{\text{MeCl}} = 0.0091 \text{ atm}^{-1} \quad (295 \, \text{°C}) \]

When, however, a kinetic equation is chosen which comprises one-site adsorption of methylchloride, the same set of experimental results furnishes a value:

\[ K_{\text{MeCl}} = 0.029 \text{ atm}^{-1} \quad (295 \, \text{°C}) \]

The only significance of the data is that in the first case 9% and in the second about 3% of the active surface is assumed to be covered with methylchloride molecules at 1 atm. partial pressure. Such data refer to a relation between coverage and adsorption equilibrium constant as is given in equation (III.3):

\[ K_A = \frac{\theta^n}{p_A(1-\theta)^n} \quad (\text{III.3}) \]

In this equation \( n \) is the number of sites involved in the adsorption of one adsorbent molecule.

For different contact mixtures, different adsorption equilibrium constants can be determined, indicating that the numeric value of such data has merely a qualitative meaning. The performance of a contact mixture depends upon so many factors that empirical approach for large scale application will always be required.

From the temperature dependence of the adsorption equilibrium constant, obtained from the afore-mentioned type of kinetic measurement, the heat of adsorption may be determined. Joklik and Bazant (55) quote a value of -4.7 kcal/mol for methylchloride on a technical silicon-copper mixture (11.9% Cu) between 280 and 320 °C. By means of pulse chromatography the heat of adsorption on the contact mixture (10% Cu) could be determined for temperatures below 120 °C (VII-2). Also for some other compounds of interest the heat of adsorption has been determined by gas-solid chromatography. Data extended with some from the literature are given in Table 8.

Inspection of the collected data on methylchloride adsorption shows that the data are wildly scattered. The larger negative values for
Table 8
Heat of adsorption of gaseous chlorides (kcal/mol)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_{\text{ads}}$</th>
<th>Temp (°C)</th>
<th>$\Delta H_{\text{cond}}$</th>
<th>Ref.</th>
<th>Adsorbate</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCl</td>
<td>-4.7 (-21)</td>
<td>280-320</td>
<td>-3.6</td>
<td>(59)</td>
<td>Si + 11.9% Cu</td>
</tr>
<tr>
<td></td>
<td>(-23)</td>
<td>280-370</td>
<td></td>
<td>(64)</td>
<td>Si + 10% Cu</td>
</tr>
<tr>
<td></td>
<td>-7.5</td>
<td>71-97</td>
<td></td>
<td>(72)</td>
<td>Si + 10% Cu</td>
</tr>
<tr>
<td></td>
<td>-6.4</td>
<td>100-170</td>
<td></td>
<td>VII-4</td>
<td>Si</td>
</tr>
<tr>
<td>EtCl</td>
<td>-8.5</td>
<td>70-121</td>
<td>-4.2</td>
<td>VII-2</td>
<td>Si + 10% Cu</td>
</tr>
<tr>
<td>HCl</td>
<td>-4.7</td>
<td>20-110</td>
<td></td>
<td>(54)</td>
<td>Si + 8.7% Cu</td>
</tr>
<tr>
<td></td>
<td>-5.0</td>
<td>98-132</td>
<td></td>
<td>VII-2</td>
<td>Si + 10% Cu</td>
</tr>
<tr>
<td></td>
<td>-5</td>
<td>130-150</td>
<td></td>
<td>(54)</td>
<td>Si</td>
</tr>
<tr>
<td></td>
<td>-4.4</td>
<td>20</td>
<td></td>
<td>VII-9</td>
<td>Si + 5% Cu</td>
</tr>
<tr>
<td>Me$_2$SiCl$_2$</td>
<td>(-2.7)</td>
<td>280-370</td>
<td>-7.3</td>
<td>(59)</td>
<td>Si + 10% Cu</td>
</tr>
<tr>
<td></td>
<td>-11.2</td>
<td>280-320</td>
<td></td>
<td>(59)</td>
<td>Si + 11.9% Cu</td>
</tr>
<tr>
<td></td>
<td>-8.9</td>
<td>74-96</td>
<td></td>
<td>VII-2</td>
<td>Si + 10% Cu</td>
</tr>
<tr>
<td>MeSiCl$_3$</td>
<td>-10.3</td>
<td>87-119</td>
<td>-7.5</td>
<td>VII-2</td>
<td>Si + 10% Cu</td>
</tr>
<tr>
<td>SiCl$_4$</td>
<td>-8.0</td>
<td>60-85</td>
<td>-7.2</td>
<td>VII-2</td>
<td>Si + 10% Cu</td>
</tr>
<tr>
<td>PhCl</td>
<td>-12.3</td>
<td>170</td>
<td>-8.4</td>
<td>(8)</td>
<td>Si + 30% Cu</td>
</tr>
<tr>
<td>PhBr</td>
<td>-15.1</td>
<td>170</td>
<td>-9.0</td>
<td>(8)</td>
<td>Si + 30% Cu</td>
</tr>
<tr>
<td></td>
<td>-12.5</td>
<td>170</td>
<td></td>
<td>(8)</td>
<td>Si</td>
</tr>
<tr>
<td></td>
<td>-14.5</td>
<td>170</td>
<td></td>
<td>(8)</td>
<td>Cu</td>
</tr>
</tbody>
</table>

a) interpretation of observed kinetics
b) estimated heat of reaction of: CH$_3$Cl + Cu-Si $\rightarrow$ CuCl + Si-CH$_3$.
Recalculation with a recently determined value for $E$(Si-Si) = 54.2 kcal/mol (73) yields $\Delta H_{\text{ads}}$ = -10 kcal/mol
c) obtained by pulse chromatography
d) from adsorption isotherms
e) calorimetric determination
f) value assumed to apply only to MeSiCl$_3$ but was determined for the average silanes product
g) disregarded data, see text
the heat of adsorption, however, should probably be disregarded. The value -21 kcal/mol stems from kinetic data between 280 and 370 °C and was obtained by hand-performed curve-fitting in the assumed kinetic equation (IV-5). Consequently, the overall activation energy appeared to be -0.9 kcal/mol, which is hardly a rational value. This also refers to the obtained heat of adsorption of the average silanes product: -2.7 kcal/mol, a value even less negative than the heat of condensation of the compounds. The value -23 kcal/mol, calculated for the heat of chemisorption of methylchloride may deviate from the true value because of the used bond strength in the silicon-lattice. With a recently determined value of the silicon-silicon bond energy (see footnote b) of Table 8) one arrives at -10 kcal/mol. The reliability of such an estimation is, however, limited. The more reliable experimental data indicate that the heat of adsorption of methylchloride is about -6 (±2) kcal/mol.

The result for hydrogen chloride agrees reasonably well with a value from the literature (54), also obtained by pulse chromatography. For silicon specimens of varying purity, values ranging from -4.0 to -6.0 kcal/mol have been calculated from the experimental results. For silicon-copper alloys with 8.7% of copper, values of -4.5 to -5.0 kcal/mol have been determined. A calorimetric determination revealed a value of ΔH_ads = -4.4 (±0.4) kcal/mol for hydrogen chloride at 20 °C (VII-9-4). It can be concluded that the heat of adsorption of hydrogen chloride is about -4.5 kcal/mol.

At temperatures above 220 °C an activated form of sorption has been observed for hydrogen chloride on silicon and silicon-copper (VII-3-3, (54)) and for methylchloride on silicon (VII-2-3). In both cases the adsorbed amounts increase with rise of temperature. The rather low values for the heats of adsorption compared to the heats of vaporization (Table 8, column 4) suggest that physical adsorption is dealt with in the low temperature range. The low heat of adsorption of methylchloride derived from kinetic data between 280 and 320 °C (-4.7, (59)) also indicates a low-energetic interaction. The activated adsorption observed by Ivanova (54) and as described in VII-3-3 would indicate an endothermic chemisorption, with a positive value for the heat of adsorption. In the
case of description in terms of dissociative chemisorption, an endothermic reaction of the halide with the silicon surface has to be considered, which is improbable. For the two possibilities as schematized in equations (III.4) and (III.5), a heat of reaction can be estimated at -16 and -21 kcal/mol respectively.

\[
\begin{align*}
2 \text{Si} + \text{HCl} & \rightarrow \text{SiH} + \text{SiCl} \\
\text{Si} + \text{HCl} & \rightarrow \text{SiCl} + \frac{1}{2} \text{H}_2
\end{align*}
\]

(III.4)  
(III.5)

It is much more probable that the increasing sorption capacities with rise in temperature are due to etching, i.e. an increase of the active surface area by reaction of the chloride with the silicon. The negative slope in the Arrhenius-graph is then to be associated with the combined effect of the etching process and the adsorption, phenomena with an opposite temperature dependency. The value which emerges from the slope of the Arrhenius-graph for the adsorption of methylchloride as well as hydrogen chloride is 10 kcal/mol (VII-3-3). If the heat of adsorption of the chloride is subtracted from this value, the result gives the activation energy of the etching process, being about 15 kcal/mol. It is remarkable that the amounts of chlorine found on the surface of the silicon after etching by hydrogen chloride and by methylchloride are about the same (VII-3-3).

From experiments where the change of pressure is observed with time, the phenomenon can be studied more closely. Müller and Gümbl tested various silicon-copper mixtures at 245 °C, a temperature where the silanes formation will not yet take place. The adsorbed amounts of methylchloride increase with time and reach equilibrium values after 5 - 30 minutes. The course of the adsorption shows close resemblance with the adsorption on pure silicon (VII-4-2). At temperatures below 235 °C the pressure reaches an equilibrium value after 10 - 12 minutes. Above this temperature methylchloride reacts with both silicon (VII-4-2) and contact mixture (728, p. 128), which follows from the continued drop of the pressure after the initial rapid adsorption. It may be seen also from the presence of cracked products in the gas sample after some hours of contact between methylchloride and silicon at about 300 °C (VII-4-2).
Table 9

Adsorption of methylchloride at elevated temperatures (after 15 min. adsorption)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>% Cu</th>
<th>PCH$_3$Cl (atm.)</th>
<th>ads. amount (10$^{-3}$ Nml/g)</th>
<th>adsorbate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>245</td>
<td>20</td>
<td>0.18</td>
<td>2</td>
<td>techn. Si + techn. Cu</td>
<td>(86)</td>
</tr>
<tr>
<td>245</td>
<td>20</td>
<td>0.18</td>
<td>90</td>
<td>techn. Si + CuCl</td>
<td>&quot;</td>
</tr>
<tr>
<td>245</td>
<td>20</td>
<td>0.18</td>
<td>2</td>
<td>pure Si + techn. Cu</td>
<td>&quot;</td>
</tr>
<tr>
<td>245</td>
<td>20</td>
<td>0.18</td>
<td>90</td>
<td>pure Si + CuCl</td>
<td>&quot;</td>
</tr>
<tr>
<td>245</td>
<td>20</td>
<td>0.18</td>
<td>20</td>
<td>techn. Si + CuCl</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(heated at 850 °C)</td>
<td>&quot;</td>
</tr>
<tr>
<td>245</td>
<td>20</td>
<td>0.18</td>
<td>2</td>
<td>(same, at 1150 °C)</td>
<td>&quot;</td>
</tr>
<tr>
<td>245</td>
<td>20</td>
<td>0.18</td>
<td>90</td>
<td>pure Si + techn. Cu</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(16 hrs reaction)</td>
<td>&quot;</td>
</tr>
<tr>
<td>245</td>
<td>0</td>
<td>0.18</td>
<td>100</td>
<td>techn. Si (1 hr Cl$_2$-etching at 200 °C)</td>
<td>&quot;</td>
</tr>
<tr>
<td>235</td>
<td>0</td>
<td>0.10</td>
<td>0.95</td>
<td>pure Si</td>
<td>VII-4-2</td>
</tr>
<tr>
<td>250</td>
<td>0</td>
<td>1.0</td>
<td>25</td>
<td>pure Si</td>
<td>VII-3-3</td>
</tr>
<tr>
<td>291</td>
<td>0</td>
<td>0.2</td>
<td>5</td>
<td>pure Si</td>
<td>VII-4-2</td>
</tr>
<tr>
<td>350</td>
<td>0</td>
<td>1.0</td>
<td>100</td>
<td>pure Si</td>
<td>VII-3-3</td>
</tr>
</tbody>
</table>

Table 9 lists the amounts of adsorbed methylchloride for silicon-copper mixtures and for silicon under various conditions. The data in the table have no quantitative significance due to the unknown specific surface area of the samples. The influence of the type of contact mixture and of temperature, may, however, follow from comparison of the data.

Considering the present results the following conclusions seem justified:

- The heat of adsorption of methylchloride is -6 kcal/mol, a value higher than the heat of condensation and lower than the estimated heat of dissociative chemisorption.

- Etching requires an overall-activation energy of 10 kcal/mol, which is appreciably smaller than that of the silanes formation. The value probably combines the heat of adsorption and the activation energy required for the increase of the reactive surface area, which is 15 kcal/mol.
- Due to etching, the amounts of hydrogen chloride or methylchloride adsorbed increase with time of contact and with temperature.
- Contact mixtures prepared from silicon and cuprous chloride remain to a high degree superficially chlorinated (VII-3-2) and show higher adsorption of methylchloride than mixtures of silicon and copper powder.
- Heating of an active contact mixture decreases the adsorption capacity.
- Adsorption of methylchloride on silicon proceeds via a single site mechanism (VII-4-3).

**III-4. On the particle size distribution**

Due to shrinkage during formation of Cu₃Si, the contact mixture suffers from considerable erosion, which leads to formation of small particles. The particle size distribution of contact mixture to be supplied in order to account for consumption by reaction resembles that of the original mixture.

A contact mixture prepared by melting of silicon and copper leads to a rather homogeneous alloy with copper present in the bulk of the resulting particles. In otherwise prepared contact mixtures, the copper is deposited on the surface of the contact mixture particles. Kolster expects that the shrinkage of Cu₃Si during the formation of silicon and copper, which causes cracks in the silicon, is responsible for the presence of small copper-rich particles in a freshly prepared contact mixture (68, p. 180). It is a satisfactory explanation for the fact that free copper can be found in a reacting contact mixture. If contact between silicon and copper should exist, the diffusion of copper is fast enough to convert all copper into Cu₃Si even during consumption of silicon by formation of silanes. Indeed, during the preparation of a contact mixture from cuprous chloride and silicon a change of the particle size distribution can be observed, which is shown in Figure 8. The solid lines represent the proportional composition of the original silicon specimen (see VII-5-2). The dotted lines give the same for the contact mixture (with 10.7% copper) prepared from it. The particle size distribution was obtained by sieve analysis. The relative errors in the measurements amount to 5%. 
It is evident from the diagrams that a considerable amount of dust is formed (1.5 wt %) with particle size smaller than 60 microns.

The formation of small particles can also be demonstrated by measuring the specific surface area of a specimen of silicon of 50 - 75 microns and of a 10% copper containing contact mixture prepared from such a fraction. A permeametric determination (method according to (7)) revealed a value of 0.071 m²/g for the acid-washed silicon specimen. By reaction with cuprous chloride, the weight increased by 10% and the specific surface area by 18% (0.084 m²/ 1.1 g contact mixture).

The mechanical strength of the contact mixture has been tested by sieving a 9.5% copper containing contact mixture over a 60 microns sieve. The starting silicon was of sieve fraction 105 - 150 microns. The amounts of dust and the copper content are given in Table 10.

<table>
<thead>
<tr>
<th>Time of sieving (hrs)</th>
<th>Amount of dust (g/100g.hr)</th>
<th>Cu-content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>Si-Cu</td>
</tr>
<tr>
<td>1</td>
<td>0.13</td>
<td>0.33</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>0.46</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>0.68</td>
</tr>
<tr>
<td>4</td>
<td>0.04</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>0.43</td>
<td>74</td>
</tr>
<tr>
<td>6</td>
<td>0.21</td>
<td>75</td>
</tr>
</tbody>
</table>

For comparison, a sample of the original silicon has been subjected to the same treatment. The Table shows that an appreciable amount of copper-rich dust is formed from the contact mixture.
Erosion of a contact mixture by fluidization is even more severe. Figure 9 shows the amount of dust formed by fluidization with 2.5 and 5 times the rate of minimum fluidization versus time. The average copper content of the dust appeared to be 42%, about the same as that of the entrained dust during a direct synthesis (VII-5-3). The change of the particle size distribution of this contact mixture sample, as it was determined by sieve analysis is shown in Figure 10.

**Figure 9. Dust formation by fluidization**

- a- doubling of gas rate

**Figure 10.**

Particle size distribution before (solid lines) and after 80 min. fluidization

When a contact mixture is subjected to reaction with methylchloride in a fluidized bed process, the change in the particle size distribution shows about the same features as that from the fluidization alone. In Figure 11a the diagrams are drawn for the mixture before (solid lines) and after 47% of silicon conversion. The change in the amounts of the fractions shown in Figure 11b, based upon an initial amount of 100 g of the mixture. The shaded areas represent the supply, required to compensate for the consumed silicon. The spectrum to be supplied resembles closely that of the starting mixture. As the copper content had increased from 11.1 to 15.9%, it follows that the entrainment of dust, which contained 48% of copper in this experiment is not capable of keeping the copper content on a constant level. The supplied contact mixture should, for this reason, have a lower copper content than the reacting contact mixture.
Particle size distribution before (solid lines) and after conversion of 47% of the silicon. a- in percent, b- in grams per 100 g of contact mixture before reaction.
IV-1. Introduction

Dimethyldichlorosilane, the most important of the methylchlorosilanes because of its application in the manufacturing of silicones, can be prepared from methylchloride and metallic silicon, with copper as catalyst. In addition to the catalyst, often other inorganic compounds such as metals or metal chlorides are added as promoters to accelerate the reaction in the desired direction. Impurities present in the metallic silicon and copper or in the methylchloride may also have a large effect upon selectivity and reactivity as has been discussed extensively in the literature (e.g. 86, 89, 100, 128, p. 130).

The reaction of methylchloride with a contact mixture of silicon and copper (reaction IV.1) proceeds at temperatures between 260 and 370 °C and is conducted to obtain dimethyldichlorosilane as the main product.

\[
2 \text{CH}_3\text{Cl} + \text{Si} (\text{Cu}) \rightarrow (\text{CH}_3)_2\text{SiCl}_2 \quad \text{(IV.1)}
\]

The maximum selectivity (mol % of dimethyldichlorosilane) up to now is 90%; 10% is made up of compounds listed in Table 11. However, a widely varying composition may be obtained, depending upon the conditions under which the synthesis is carried out, i.e. temperature, pressure, type of reactor and the quality of the contact mixture.

The influence of temperature is manifested principally above 360 °C. In that range the cracking of methylchloride and products becomes noticeable. This causes an increase in the chlorine-content of the silanes product, and also leads to tar-formation which blocks the active surface and causes the appearance of considerable amounts of gaseous hydrocarbons and hydrogen in the product mixture.
Table 11
The main compounds in the product of a methylchlorosilanes synthesis. The order is roughly in decreasing content.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethyldichlorosilane</td>
<td>(CH$_3$)$_2$SiCl$_2$</td>
<td>70.2 °C</td>
</tr>
<tr>
<td>methyltrichlorosilane</td>
<td>CH$_3$SiCl$_3$</td>
<td>66.1 °C</td>
</tr>
<tr>
<td>trimethylchlorosilane</td>
<td>(CH$_3$)$_3$SiCl</td>
<td>57.3</td>
</tr>
<tr>
<td>methyldichlorosilane</td>
<td>CH$_3$SiHCl$_2$</td>
<td>41.9</td>
</tr>
<tr>
<td>tetrachlorosilane</td>
<td>SiCl$_4$</td>
<td>57.6</td>
</tr>
<tr>
<td>trichlorosilane</td>
<td>SiHCl$_3$</td>
<td>31.8</td>
</tr>
</tbody>
</table>

As the cracking of methylchloride presumably proceeds according to reactions (IV.2) or (IV.3), the result is a decreased content of methyl groups in the silanes product.

\[
\begin{align*}
\text{CH}_3\text{Cl} + \text{Cu} & \rightarrow \text{CuCl} + \frac{1}{2} \text{CH}_4 + \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{C} \quad \text{(IV.2)} \\
\text{CH}_3\text{Cl} \ (\text{Cu}) & \rightarrow \frac{1}{2} \text{CH}_4 + \frac{1}{2} \text{C} + \text{HCl} \quad \text{(IV.3)}
\end{align*}
\]

The cuprous chloride or hydrogen chloride formed will rapidly chlorinate silicon, leading to a higher chlorine/methyl ratio in the silanes product. The influence of pressure upon the product composition, however small, lies in the differing order in which the partial pressure of methylchloride appears in the rate equations for the various methylchlorosilanes, which will be shown in IV-5. Because of the large heat effect of the direct synthesis of methylchlorosilanes (about 90 kcal/mol Si) it is of importance to control the temperature of the reactor by sufficient heat transport to the reactor wall and proper cooling of the latter. This may be accomplished in a fluidized bed reactor. In case of high conversion-rates in a fixed bed reactor where heat transport is appreciably smaller, local overheating of parts of the contact mixture may occur, resulting in increased cracking of reactant and products, thus lowering the selective formation of dimethyldichlorosilane.

The method of preparation of the contact mixture determines how well the reactant silicon and the catalyst copper are mixed. In case of poor homogeneity, enhanced cracking of methylchloride occurs on copper-rich particles. The quality of the contact mixture is also determined by the impurities, which are contained in both the silicon and the copper. The presence of small amounts of impurities can have a large effect upon
the performance of the mixture.

It is virtually impossible up to now, to predict a methylchlorosilanes product composition and reaction rates, given the reaction conditions and the specification of the contact mixture, as there are not only many contradictory experimental results reported in the literature, but also the reproducibility of experiments in laboratory synthesis is rather poor, as has been recognized before (128, p. 187).

The complicated and capricious course of the chemical reactions taking place in the direct synthesis led to the fact that many propositions for a reaction mechanism have been made, all of them able to explain certain phenomena, none of them able to explain all phenomena. The details given by some authors have inspired the question, stated by V. Bazant (8): 'Were you there and did you see what the active sites and activated complexes looked like?'

IV-2. Characteristics of the methylchlorosilanes synthesis

Some hard facts regarding the methylchlorosilanes synthesis are extracted from own observations and from phenomena described in the literature.

A large amount of literature is available with opinions of the authors about the mechanisms according to which the methylchlorosilanes are formed. When the observed phenomena and the various mechanisms are considered, contradictions appear, which may or may not be caused by unnoticed or unnoticeable differences in experimental circumstances as for example differences in the quality of the reactants. This has prevented up to now that a harmonious conclusion about the reaction mechanism has been drawn. In this section some facts will be discussed, which are partly based on information from literature and which come partly from own observations as described in Chapter VII. Elucidation furnished by other experiments with other chlorides than methylchloride, but closely related because of apparent analogy has also been drawn into consideration. In collecting the material, doubtful and contradictory results have been avoided, but some will be dealt with later.
a. Copper acts as catalyst in the reaction of metallic silicon with:
- methylchloride
- ethylchloride
- phenylchloride
- chlorine
- hydrogen chloride
- various other organic halides

Observations:
1. Methylchloride reacts in the absence of copper only at temperatures higher than 370 °C (67), mainly forming methyltrichlorosilane and cracked products (VII-5-5).
2. Methylchloride already reacts at 270 °C (67) with properly prepared silicon-copper contact mixtures, mainly forming dimethyldichlorosilane.
3. Ethylchloride does not react with silicon in the absence of copper at temperatures below 310 °C (67); with copper present, diethyldichlorosilane is formed even at a temperature just above 200 °C (77).
4. Phenylchloride will not react with pure silicon up to 500 °C, while a silicon-copper contact mixture, containing e.g. 30% by weight of copper will form phenylchlorosilanes between 420 and 480 °C (8).
5. Reaction of chlorine and hydrogen chloride (24, 86, 114) with silicon is substantially accelerated by even small amounts of copper, contained in the silicon (VII-11).
6. Isopropylchloride reacts with silicon at about 200 °C. With copper present the reaction temperature is lowered by about 100 degrees (67).

b. Copper is catalytically active when it is dispersed finely over or in the silicon.

Observations:
1. When a direct synthesis is carried out with a mechanical mixture of silicon and copper, an induction period of some hours may be observed (85).
2. Eta-phase and epsilon-phase, intermetallic compounds of overall formula Cu₃Si and Cu₁₅Si₄ respectively, show a very short or no induction period (85).
3. Contact mixtures prepared from silicon and cuprous chloride at temperatures above 270 °C where metallic copper is deposited on the silicon particles are highly reactive (127).

4. The induction period can be drastically shortened when the contact mixture of silicon and copper is heated for some time at 1150 °C in a vacuum (86).

c. The surface of a reacting contact mixture is strongly chlorine-containing.

Observations:
1. Hydrogen chloride partly adsorbs irreversibly on silicon and silicon-copper particles; upon heating, most of the hydrogen will be freed. The chlorine can not be removed from the surface up to a temperature of 380 °C (VII-4-1).

2. Etching with chlorine or hydrogen chloride before the start of the direct synthesis shortens the period during which no silanes are formed (85 and VII-6-2).

3. Contact mixtures, prepared in situ from cuprous chloride and silicon show no induction period (VII-5-2) and contain up to 0.06 wt % of chlorine (VII-3-2).

4. Contact mixtures which have been reacting for some time with methylchloride always contain substantial amounts of chlorine. Up to 8% of cuprous chloride has been found (45). Typical amounts of carbon, hydrogen and chlorine in a spent contact mixture are e.g. 1.2, 0.1 and 0.2 wt % respectively (123).

5. Alkoxyalkanes react with silicon-copper contact mixtures after exposure to hydrogen chloride. The produced organosilanes contain chlorine, and the production ceases when the chlorine has been consumed (147).

d. Copper will react at elevated temperatures with a number of gaseous chlorides, forming cuprous chloride.

Observations:
1. Cuprous chloride is formed from chlorine and hydrogen chloride at temperatures above 92 °C (97).
2. Ethylchloride decomposes under catalytic action of copper into ethylene and hydrogen chloride. The latter will react with copper, forming cuprous chloride (s).

e. At the temperature of the direct synthesis, methylchloride reacts with metallic copper, forming cuprous chloride and cracked products.

Observations:

1. Copper is transported in a stream of methylchloride at temperatures above 250 °C.(86, 86) The copper will be found in the cold part of the reaction tube in the form of cuprous chloride (86). Methylchloride decomposes readily over copper at temperatures above 350 °C(87).

2. Sulfidation of copper during the direct synthesis increases reactivity because blocking of the active surface by free copper and cracked products formed by action of free copper is hindered (727, p. 62).

3. The start of a direct synthesis with a contact mixture containing copper that is not finely divided over the silicon particles, is characterized by enhanced cracking (86), low initial content of dimethyldichlorosilane and a relatively high content of methyltrichlorosilane.

4. When methyldichlorosilane is led over copper powder at 360 °C, it is partly converted into methyltrichlorosilane and dimethyldichlorosilane. Substituting the nitrogen which is used as a diluent gas by methylchloride, decreases the conversion about ten times (82), due to occupation of the surface by methylchloride.

5. The free enthalpy change of the cracking of methylchloride on copper (equation IV.2) is -38.1 kcal/mol (600 K); thermodynamically this is somewhat more favourable than cracking with hydrogen chloride formation (equation IV.3), of which the free enthalpy change is -35.0 kcal/mol (600 K).

f. The product mixture obtained in a direct synthesis may deviate strongly from the thermodynamic equilibrium composition.

Observations:

1. At 300 °C the content of dimethyldichlorosilane may be as high as 90 mol %, while at that temperature the equilibrium concentration
is 78 mol % (see Figure 15).

2. Only at very long residence times is an active contact mixture able to disproportionate a methylchlorosilanes mixture to obtain the equilibrium composition (132).

3. The content of methyldichlorosilane may reach the value of 40 mol % (VII-5-2) at times, while the thermodynamic equilibrium allows only for about 1 mol % at 350 °C (IV-6, Figure 15).

g. The different methylchlorosilanes are formed in parallel reactions in the direct synthesis.

Observations:
1. The residence time of the gases in a fixed bed reactor has no influence upon the product composition above values for the residence time of 0.5 sec (VII-6-2).

2. In fluid-bed experiments only a minor tendency to decrease selectivity with some per cent can be observed when the average residence time increases from 3 to 30 sec (127, p. 83).

3. Admixture of dimethyldichlorosilane to the methylchloride feed effectuates no influence on the product composition after correction for the supplied silane (132). The temperature during this experiment was 350°C.

h. Silanes containing two chlorine atoms are formed in a different manner than those containing one or three chlorine atoms.

Observations:
1. The average content of dimethyldichlorosilane in a product mixture obtained from a direct synthesis is between 70 and 90 mol %. Small local variations in the conditions, presumably the temperature, easily change the ratio between dimethyldichlorosilane and methyldichlorosilane. The contents of the other products, however, remain remarkably constant (VII-5, -6).

2. In the direct synthesis of ethylchlorosilanes, the sum of the contents of diethyldichlorosilane and ethyldichlorosilane does not vary so much as each of the contents, while the content of ethyltrichlorosilane is rather constant (VII-8-4, Figure 58).
3. Addition of ethylene to ethylchloride reacting with a contact mixture decreases the content of ethyltrichlorosilane, but has no influence upon the ratio of diethyldichlorosilane to ethyldichlorosilane (VII-8-4).

4. The rates of formation of methyltrichlorosilane and trimethylchlorosilane show linear dependence of the methylchloride partial pressure, whereas the rate of formation of dimethyldichlorosilane and methyl­dichlorosilane shows a significant deviation from linearity (IV-5, Figures 13 and 14).

i. The activation energy of the reaction of methylchloride with contact mixtures is about 26 kcal/mol and decreases with increasing content of impurities in the mixture.

Observations:

1. Contact mixtures prepared from very pure copper and silicon but containing zinc chloride and aluminium chloride as promoters show an activation energy of 26.6 kcal/mol (727, p. 79).

2. For a mixture prepared from 12% copper with 3.8% impurities and pure silicon the activation energy is 25.3 kcal/mol (59).

3. Technical silicon, containing more than 1.3% impurities in combination with (10%) copper shows an activation energy of 20.1 kcal/mol (64).

j. Cracking of methylchloride during the direct synthesis does not produce methyl radicals in the gas phase.

Observations:

1. Toluene addition during a methylchlorosilanes direct synthesis does not alter the amount of methane formed, and does not produce detectable amounts of dibenzyl. This indicates that methane is formed in the adsorbed layer on the contact mixture surface (VII-6-4).

2. Addition of a small amount of iodine to methylchloride reacting with a contact mixture decreases the reaction rate substantially by poisoning the contact mixture. If methyl radicals were present, they would react with iodine and form methyliodide which is not expected to exert any influence (788, p. 261).
3. Azomethane produces methyl radicals when it decomposes in contact with a reacting contact mixture. The effect of such generation of methyl radicals appeared to be a decrease in reactivity, indicating that methyl radicals are not involved in the silanes formation (727).

IV-3. Reaction mechanism

Some reaction mechanisms proposed by various investigators comprise the hypothesis that the reacting (alkyl)chloride (RCl) will adsorb on two sites of the active surface, for which in fact no direct experimental evidence exists. The fact that the amount of methylchloride adsorbed on a surface with atomically distributed silicon and copper is higher at 100 °C than on either silicon or copper alone (59) does not imply dissociative chemisorption. Moreover, the amount of methylchloride which is able to adsorb on various contact mixtures was shown not to be related to the reactivity of the mixtures (85).

\[
\begin{align*}
\text{Rochov:} & \quad R...Cl \\
& \quad : \\
& \quad Cu...Cu \\
\text{Klebansky:} & \quad R...Cl \\
& \quad : \\
& \quad Si...Cu \\
\text{Voorhoeve:} & \quad R...Cl \\
& \quad : \\
\text{Bazant:} & \quad R...Cl \\
& \quad : \\
\text{Dragojevic:} & \quad R...Cl \\
& \quad : \\
& \quad Cu...Si
\end{align*}
\]

The difference in the direction of the chemisorption suggested in (b) and (c) results from a difference in opinion about the charge distribution on adjacent silicon and copper atoms. Klebansky and Voorhoeve produce arguments to explain that the silicon atom has a negative charge compared to the copper atom (67, 727 p. 127). The opinion of the Prague school of
Bazant is that the silicon atom is more positive than the copper atom based upon the electronegativity values (Si: 1.8, Cu: 1.9) assigned by Pauling (63, 97 p. 69). Dragojevic, using the Wolkenstein theories on the semiconductor properties of catalysts also assumes the silicon atom positive with respect to the neighbouring copper atom (78, 33). Of these contrary opinions, the arguments in favour of the copper atom being positive with respect to the silicon are the most convincing. Golubtsov c.s. assume the adsorption of the alkylchloride on copper (45). Rochov and Hurd have suggested the formation of copper methyl (CuCH₃) and copper chloride (CuCl) from dissociative chemisorption of methylchloride (96). The filling of the silicon valencies is then supposed to proceed via successive chlorinations and methylations by copper chloride and copper methyl respectively. The actual presence of CuCH₃ under direct synthesis conditions, however, has been shown to be doubtful (45). There is also little agreement in the opinions about the sequence in which the silicon valencies are filled with chlorine atoms and methyl groups in order to reach the observed amazingly high selectivity. In the triangular diagram in Figure 12, the various routes to obtain the five possible methylchlorosilanes (MeₙSiCl₄₋ₙ) have been schematized. If the reaction steps really consist in sequential chlorinations and methylations, the diagonal lines represent these steps. Downward to the left is a chlorination, to the right is a methylation. Dotted vertical lines represent the simultaneous substitution of two silicon-lattice bonds by one methylchloride molecule. The scheme does not contain the hydrogenation steps responsible for the formation of hydrogen containing silanes. All routes leading to dimethyldichlorosilane find support in the literature but little or no experimental proof could be given. Elucidation of the route actually taken in the formation of any methylchlorosilane would require the quantitative detection of the intermediate surface compounds and determination of the rate constants of the separate reaction steps, which may turn out to be very difficult. There is some evidence for the route, suggested by Golubtsov (44), starting with two chlorinations, in which dichlorosilene (SiCl₂) is formed, and concluded with two methylations. The intermediary compound which is claimed to be stable under direct synthesis conditions was detected with the aid of ultraviolet adsorption measurements (45). It may, however, not be excluded that small amounts of poly-chlorosilanes, e.g. Si₃Cl₈, have been detected, which if present,
Figure 12. Surface reactions in alkylchlorosilanes-formation

might give rise to the same observations under the conditions of the experiment. The existence of surface-bound silicon dichloride, rather than the proposed dichlorosilene in the gas phase which must be expected to be highly unstable (see also V-2), does not imply that dimethyl-dichlorosilane is proceeded by this compound. Surface-bound silicon dichloride may very well be the intermediate for the production of silanes containing more than two chlorine atoms (VII-8-3). Though it is difficult to decide in favour of one single route (Figure 12) to obtain dimethyl-dichlorosilane with the observed selectivity, it is certain that there is no statistical distribution of chlorine atoms and alkyl groups over the silicon atoms. This would lead to a selectivity of 37.5 mol %, meaning in fact that only the entropy is determining. With pure statistical distribution the ratios between the silanes would become:

\[
\text{Me}_4\text{Si} : \text{Me}_3\text{SiCl} : \text{Me}_2\text{SiCl}_2 : \text{MeSiCl}_3 : \text{SiCl}_4 = 1 : 4 : 6 : 4 : 1
\]

This is not even the case in the gas phase, where the equilibrium concentration of dimethyldichlorosilane is 74 mol % at 330 °C (Figure 15), with silicon present in excess. This indicates that dimethyldichlorosilane is somewhat more stable than the other methylchlorosilanes. The distribution of chlorine and methyl over methylchlorosilanes in the adsorbed state can not be expected to differ much from the distribution in the gas phase. In terms of the steps schematized in Figure 12 this implies that the
rates of desorption of the methylchlorosilanes \((v,w,x,y,z)\) are about the same.

In conclusion, the rates of the surface steps \(n\) through \(u\) should be responsible for the ca 90% appearance of dimethyldichlorosilane in the adsorbed layer. The precursors of dimethyldichlorosilane in this scheme must accordingly react with nearly maximum selectivity via step \(q\) or \(r\), preceeded by either \(i\) and \(j\), or \(k\) and \(l\). When the routes are considered via the extreme possibilities \(\tilde{\text{SiCl}}_2\) or \(\tilde{\text{SiR}}_2\), the necessity arises that the rates of steps \(h\) or \(m\) respectively are extremely low. The same applies to the steps \(p\) and \(s\). That this is very improbable can be explained as follows.

Firstly the intermediates can be expected to be highly reactive because they carry part of the energy gained in the preceeding substitutions. A statistical completion of the valencies would then rather follow, forming \(\tilde{\text{RSiCl}}_3\) from \(\tilde{\text{SiCl}}_2\) and \(\tilde{\text{R}_3\text{SiCl}}\) from \(\tilde{\text{SiR}}_2\), because of equal availability of \(R\) and \(Cl\) in the surface layer. Secondly, taking \(\tilde{\text{SiCl}}_2\) for instance, the electron density on the silicon atom will be decreased by the electron attracting ability of the two chlorine atoms \((\text{35})\), thus facilitating subsequent substitutions to be chlorinations rather than methylations. The occurrence of this phenomenon has been observed already in the rearrangement of ethylchlorosilanes \((\text{120})\). Starting with \(\tilde{\text{SiMe}}_2\), the next probable substitution is another methylation because of the positive inductive effect of the methyl groups, which tends to make the silicon atom slightly negative. This effect can be observed for instance in the Grignard synthesis of alkylchlorosilanes. Alkylation of tetrachlorosilane by an alkylmagnesium halide leads mainly to highly alkylated products, even if tetrachlorosilane is added in excess. The sole possibility resulting from this argument is that the formation of adsorbed dimethyldichlorosilane proceeds via simultaneous methyl- and chlorine substitution on the active surface compound \(\tilde{\text{RSiCl}}\), for instance by interaction with a methylchloride molecule

\[
\tilde{\text{RSiCl}} + \text{RCl} \rightarrow \tilde{\text{R}_2\text{SiCl}}_2
\]

Because of the high energy of the intermediate \(\tilde{\text{RSiCl}}\), obtained from the preceeding substitutions, the reaction can be expected to proceed fast and without the necessity of a catalyst. The slowest step of the overall reaction then should lie in the formation of the intermediate \(\tilde{\text{RSiCl}}\).
There is yet another argument for the existence of $\text{RSiCl}^{\text{A}}$ as the only surface compound responsible for the dimethyldichlorosilane formation. Dimethyldichlorosilane seems energetically stabilized, relative to methytrichlorosilane and trimethylchlorosilane, by the presence of the same number of chlorine atoms and methyl groups. Together with the entropy-gain from the differences in symmetry, the free enthalpy is more negative than could be expected from bond additivity (II-2). The surface compound $\text{RSiCl}^{\text{A}}$ is in the same position between $\text{SiCl}^{\text{A}}_{2}$ and $\text{SiR}^{\text{A}}_{2}$, as $\text{R}_{2}\text{SiCl}_{2}$ in the series $\text{R}_{n}\text{SiCl}_{4-n}^{\text{A}}$, and an extra stabilization is to be assigned to the presence of R and Cl together in the intermediate, added to the entropy-gain from the differences in symmetry of the structures.

The above considerations were given in order to avoid some of the contradictions applying to some reaction schemes. Next, account has to be made for the formation of $\text{RSiCl}^{\text{A}}$ being the most probable reaction intermediate in the formation of dimethyldichlorosilane.

Discrimination between step-by-step reaction b-e or c-f (in extenso: via $\text{SiCl}^{\text{A}}$ or $\text{SiR}^{\text{A}}$) and simultaneous methylation and chlorination is only possible when the second step (e or f) is the slower of the two. Otherwise there is formally no difference between a slow b/c followed by a fast e/f and the direct interaction with adsorbed methylchloride. Again the argument that a primary chlorination or methylation induces respectively subsequent chlorination or methylation has to be considered. It advocates the direct interaction of a silicon atom with methylchloride in an activated state. But now the function of the catalyst has to be introduced. This can be either activation of the silicon atom, e.g. by 'lifting it towards the gas phase', thus decreasing the necessary energy to break a silicon-lattice bond, or it activates the methylchloride by releasing the carbon-chlorine bond. The first mechanism does not explain the difference in behaviour of different alkylchlorides towards the silicon-copper system, so the catalytic function of copper must at least partly be associated with interaction with the alkylchloride. Moreover, a silicon atom in the surface-layer has already an energy higher than that of the average silicon atom in the crystal because part of its valence electrons are unpaired. For this reason, the addition of the first ligand can be expected to proceed fast and without requiring the activation by a catalyst. From the high bond energy between the halogen
and silicon, as well as the observed presence of cuprous chloride on
the surface of a silicon-copper particle, and the initiating influence
of addition of chlorine and hydrogen chloride, the obvious conclusion
should be drawn that the first silicon valency is to be filled by a
chlorine atom. After initiation, chlorine atoms have to be supplied
either directly by methylchloride, but this would involve the formation
of a methyl radical, or by superficially chlorinated copper. The result-
ing reaction intermediate need not be reactive because of the stable
gemetry of the monochlorinated lattice-bound silicon atom. The subse-
quent substitution of a silicon-lattice bond is likely to require a
deliberate amount of energy. If the scheme under discussion holds,
the following step, being relatively slow, must proceed fully in favour
of the reaction intermediate RSiCl. This will be the case if in this
stage an alkylchloride molecule is available with the chlorine part
bound to a catalyst atom and the alkyl group already slightly released
from the chlorine. From the known interaction between alkylchlorides
(and hydrogen chloride) and copper, under extreme conditions leading
to cuprous chloride formation, this alkylation (or hydrogenation) by
the alkylhalide-copper complex becomes obvious.

IV-4. Survey of the developed reaction scheme

'As if you were there...'

From the preceding considerations it seems likely that the following
schemes apply to the formation of methylchlorosilanes.

1. The formation of dimethyldichlorosilane:

\[
\begin{align*}
\text{Si} + \text{CuCl} & \rightarrow \text{SiCl} + \text{Cu} \\
\text{Cu} + \text{CH}_3\text{Cl} & \rightarrow \text{Cu(ClCH}_3) \\
\text{SiCl} + \text{Cu(ClCH}_3) & \rightarrow \text{CH}_3\text{SiCl} + \text{CuCl} \\
\text{CH}_3\text{SiCl} + \text{CH}_3\text{Cl} & \rightarrow \text{(CH}_3)\text{2SiCl}_2
\end{align*}
\]

First of all the surface of the contact mixture has to be activated.
During this initial period active silicon atoms are chlorinated by
transfer of chlorine from cuprous chloride formed by cracking of methyl-
chloride or previous treatment with chlorine or hydrogen chloride (step 1).
For a contact mixture prepared in situ from cuprous chloride and silicon this active state may have been reached during the preparation. The propagation steps forming dimethyldichlorosilane consist of adsorption of methylchloride with the chlorine atom directed to copper (step 2). The slowest step, which determines the rate of the overall reaction is transfer of the methyl group from the copper-methylchloride complex to the chlorinated silicon atom (step 3). This transfer requires breaking of the carbon-chloride bond and is responsible for the main fraction of the activation energy. In this step cuprous chloride is regenerated, which is capable of chlorination of another silicon atom according to step 1. Step 4 represents the final methylchlorination, either by adsorbed or gaseous methylchloride. Desorption of dimethyldichlorosilane will now follow.

2. The formation of methyl dichlorosilane:

\[
\begin{align*}
\text{Si} + \text{CuCl} & \rightarrow \text{SiCl} + \text{Cu} \\
\text{Cu} + \text{CH}_3\text{Cl} & \rightarrow \text{Cu(ClCH}_3\text{)} \\
\text{SiCl} + \text{Cu(ClCH}_3\text{)} & \rightarrow \text{HSiCl} + \text{CuCl} + \frac{1}{2} \text{CH}_4 + \frac{1}{2} \text{C} \\
\text{HSiCl} + \text{CH}_3\text{Cl} & \rightarrow \text{CH}_3\text{SiHCl}_2
\end{align*}
\]

The scheme resembles that of the formation of dimethyldichlorosilane, except in the result of the rate determining step (7), where the methyl group does not survive the attempt of transfer. This will occur on local hot spots and the result is a hydrogenation instead of a methylation. The HSiCl undergoes methylchlorination, after which methyldichlorosilane may desorb (step 8).

3. The formation of methyl trichlorosilane:

\[
\begin{align*}
\text{Si} + \text{CuCl} & \rightarrow \text{SiCl} + \text{Cu} \\
\text{Cu} + \text{CH}_3\text{Cl} & \rightarrow \text{Cu(ClCH}_3\text{)} \\
\text{Cu(ClCH}_3\text{)} & \rightarrow \text{CuCl} + \frac{1}{2} \text{CH}_4 + \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{C} \\
\text{SiCl} + \text{CuCl} & \rightarrow \text{SiCl}_2 + \text{Cu} \\
\text{SiCl}_2 + \text{CH}_3\text{Cl} & \rightarrow \text{CH}_3\text{SiCl}_3
\end{align*}
\]

When the adsorbed methylchloride enters in a cracking reaction (step 11) the 1 : 1 ratio of methyl over chlorine is disturbed. The excess of
cuprous chloride will perform two chlorinations instead of one (steps 9 and 12). Reaction of silicon dichloride \( \text{SiCl}_2 \) with methylchloride leads to methyltrichlorosilane (step 13), which will desorb.

4. Formation of higher alkylated silanes:

\[
\begin{align*}
n \text{Cu(\text{ClCH}_3)} + \text{Si} & \rightarrow \text{Si(\text{CH}_3)_n} + n \text{CuCl} & (14) \\
2 \text{CH}_3\text{SiCl} & \rightarrow \text{Si(\text{CH}_3)_2} + \text{SiCl}_2 & (15) \\
\text{Si(\text{CH}_3)_2} + \text{CH}_3\text{Cl} & \rightarrow (\text{CH}_3)_3\text{SiCl} & (16)
\end{align*}
\]

In case of a local shortage of reactive chlorine, e.g. due to the presence of metals such as Fe, Ca, Cd, Zn, Al, etc., the formation of small amounts of \( \text{Si(\text{CH}_3)_2} \) becomes possible. Also disproportionation of \( \text{CH}_3\text{SiCl} \) (step 15) which may be catalyzed by Friedel Crafts-type catalysts, has to be considered as a possible source of dimethylsilyl.

IV-5. Kinetics of methylchlorosilanes synthesis

The kinetic equation for the formation of dimethyldichlorosilane in accordance with the proposed reaction mechanism, with one site adsorption of methylchloride, is in better agreement with experimental data than the equation based upon dual site adsorption. The formation of methyltrichlorosilane appears to be first order in methylchloride.

At small partial pressures of methylchloride a nearly linear relationship between the rate of formation of methylchlorosilanes and the methylchloride pressure has been found (59). Voorhoeve measured the reaction rates at pressures up to 26 atmospheres in a fixed bed at 295 °C (127, p. 92). He concluded that the rate of formation of methylchlorosilanes may be well described by the rate equation proposed by Bazant (59):

\[
R = \frac{k \cdot K_A \cdot P_A}{(1 + \sqrt{K_A \cdot P_A + K_R \cdot P_R})^2} \quad (IV.5)
\]

This equation represents a dissociative chemisorption of the reactant on two sites of the surface with a reaction on the surface as the slowest step. When the product partial pressures are nearly zero, the initial rate is given by:
The dissociative chemisorption of methylchloride requires two neighbouring sites on the surface of the contact mixture. Although this is not conflicting with the essentials of the reaction scheme as proposed in IV-4 it has been pointed out that it is not the most probable way of adsorption (IV-3). It is therefore interesting to examine the experimental results that led to the above kinetic equation, in order to check whether the rate equation based upon one site adsorption will cover the results as well or perhaps even better.

From the arguments given in IV-3 leading to the proposed reaction scheme, it follows that the rate equation for the formation of dimethyldichlorosilane should account for the formation of methyldichlorosilane as well. It should not, however, account for the formation of methyltrichlorosilane and other products, the formation of which is accompanied or preceded by methylchloride break-down. For this reason the amount of methylchloride forming dimethyldichlorosilane and methyldichlorosilane has been calculated from the experimental data of Voorhoeve (727, p. 92), which cover a large methylchloride pressure range (Table 12). Not only equation (IV.6) but also equation (IV.7) is a good representation of the experimental data, which is shown in Figure 13.

\[
R_0 = \frac{k \cdot K_A \cdot P_A}{(1 + \sqrt{K_A \cdot P_A})^2}
\]  

\[\text{(IV.6)}\]

The solid line is drawn according to equation (IV.6), where \(k = 1.07 \text{ g MeCl/g Si.hr} \) and \(K_A = 0.0091 \text{ atm}^{-1}\); the dotted line is calculated from equation (IV.7), with \(k_1 = 0.26 \text{ g MeCl/g Si.hr} \) and \(K_A = 0.029 \text{ atm}^{-1}\).

The lines largely coincide in the lower part of the figure which obscures a distinction. Equation (IV.7) represents the initial rate for a reaction with single site adsorption of methylchloride and with the rate determining reaction in the surface layer. For non-zero product pressure the original rate equation consistent with the reaction scheme in IV-4 (steps 1 - 8) is:
Table 12. Initial reaction rates\(^a\) for different products.
Calculated from (727, p. 92)

<table>
<thead>
<tr>
<th>(p_{\text{CH}_3\text{Cl}})</th>
<th>(r_D)</th>
<th>(r_T)</th>
<th>(r_M)</th>
<th>(r_{\text{DH}})</th>
<th>(r_Q)</th>
<th>(r_{\text{TH}})</th>
<th>(r_{D+\text{DH}})</th>
<th>(r(1))</th>
<th>(r(2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.9</td>
<td>97.09</td>
<td>20.09</td>
<td>2.07</td>
<td>5.85</td>
<td>2.64</td>
<td>1.06</td>
<td>102.9</td>
<td>111.3</td>
<td>114.4</td>
</tr>
<tr>
<td>22.8</td>
<td>94.83</td>
<td>18.61</td>
<td>2.32</td>
<td>11.18</td>
<td>3.06</td>
<td>0.72</td>
<td>106.0</td>
<td>103.2</td>
<td>104.9</td>
</tr>
<tr>
<td>19.8</td>
<td>93.57</td>
<td>16.91</td>
<td>1.78</td>
<td>11.31</td>
<td>5.67</td>
<td>1.42</td>
<td>104.9</td>
<td>94.6</td>
<td>95.1</td>
</tr>
<tr>
<td>16.6</td>
<td>79.38</td>
<td>13.11</td>
<td>1.61</td>
<td>9.14</td>
<td>4.67</td>
<td>1.19</td>
<td>88.5</td>
<td>84.3</td>
<td>83.9</td>
</tr>
<tr>
<td>13.5</td>
<td>66.07</td>
<td>9.64</td>
<td>1.30</td>
<td>8.55</td>
<td>4.65</td>
<td>1.75</td>
<td>74.6</td>
<td>73.0</td>
<td>72.1</td>
</tr>
<tr>
<td>13.5</td>
<td>63.45</td>
<td>9.50</td>
<td>1.07</td>
<td>6.77</td>
<td>3.09</td>
<td>1.28</td>
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<td>72.1</td>
</tr>
<tr>
<td>10.4</td>
<td>52.62</td>
<td>7.10</td>
<td>0.90</td>
<td>4.67</td>
<td>2.51</td>
<td>1.13</td>
<td>57.3</td>
<td>60.1</td>
<td>59.3</td>
</tr>
<tr>
<td>10.4</td>
<td>57.13</td>
<td>7.90</td>
<td>1.01</td>
<td>4.30</td>
<td>3.66</td>
<td>0.81</td>
<td>61.4</td>
<td>60.1</td>
<td>59.3</td>
</tr>
<tr>
<td>7.0</td>
<td>39.74</td>
<td>5.43</td>
<td>0.56</td>
<td>1.94</td>
<td>2.32</td>
<td>1.76</td>
<td>41.7</td>
<td>43.8</td>
<td>43.5</td>
</tr>
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<td>4.2</td>
<td>29.92</td>
<td>3.70</td>
<td>0.39</td>
<td>1.48</td>
<td>1.78</td>
<td>1.10</td>
<td>31.4</td>
<td>28.2</td>
<td>28.6</td>
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<tr>
<td>4.2</td>
<td>24.79</td>
<td>3.12</td>
<td>0.27</td>
<td>1.23</td>
<td>0.90</td>
<td>0.98</td>
<td>26.0</td>
<td>28.2</td>
<td>28.6</td>
</tr>
</tbody>
</table>

\(^a\) column 1 in atm; column 2 - 10 in g MeCl/kg Si.hr converted in product: 
D= \(\text{Me}_2\text{SiCl}_2\), T= \(\text{MeSiCl}_3\), M= \(\text{Me}_3\text{SiCl}\), DH= \(\text{MeSiHCl}_2\), Q= \(\text{SiCl}^\_\), TH= \(\text{SiHCl}_3\).

\[ r_{D+\text{DH}} = r_D + r_{\text{DH}}, r(1) \text{ is calculated from equation (IV.7), } r(2) \text{ is calculated from equation (IV.6).} \]

\[
R = \frac{k'_1.\theta(\text{SiCl}).K_A.p_A}{1 + K_A.p_A + K_R.p_R} \quad (IV.8)
\]

The product \(k'_1.\theta(\text{SiCl})\) equals \(k_1\) in (IV.7). From the graph (Figure 13) it becomes obvious that the experimental data do not permit a clear distinction between both rate equations. From the standard deviation of the experimental data from the calculated lines some difference appears. For the equations comprising two site adsorption and one site adsorption the standard deviations are respectively 5.1 and 4.7 (arbitrary units). These figures speak slightly but not decisively in the advantage of the one site kinetic equation. The study reveals that it is rather difficult to decide in favour of a certain reaction mechanism on the basis of measured kinetics. The given facts, however, do support the proposed reaction step schematizing the adsorption of methylchloride on a copper atom in the surface layer of the silicon-copper contact mixture. The rate determining step consists of the reaction of the adsorbed methylchloride molecule with a chlorinated silicon atom. If the rate of conversion of methylchloride into methyltrichlorosilane is plotted versus the pressure of methylchloride a nearly straight line
Figure 13  
Rate of formation of Me₂SiCl₂ + MeSiHCl₂  
experimental data from (127), lines calculated: 1- assuming single site adsorption, 2- dual site adsorption

Figure 14  
Rate of formation of MeSiCl₃ (T) and Me₃SiCl (M)

is obtained (Figure 14). This indicates that within the experimental error the formation of methyltrichlorosilane is of first order in methylchloride, with a rate equation as given by:

\[ R_0 = k_2 \cdot p_A \]  

(IV.9)

From the scheme in IV-4 (steps 9 - 13) equation (IV.10) would follow:

\[ R = k_2' \cdot \theta(SiCl₂) \cdot p_A \]  

(IV.10)

The equation includes the assumption that reaction of a methylchloride molecule with \( SiCl₂ \) is the slowest step of the series (IV-4, step 13). From the data in Table 12 the reaction rate constant for the methylchloride conversion into methyltrichlorosilane appears to be: \( k_2 = 0.00078 \) g MeCl/g Si.hr.atm.
IV-6. Thermodynamic considerations

For maximum selectivity in dimethyldichlorosilane, the temperature should be as low as possible. Increase of temperature lowers the methyl content and increases the chlorine content in the silanes mixture. The equilibrium contents of Si-H containing compounds are extremely low.

With the data derived in Chapter II, computations can be performed on the equilibrium of a mixture of methylchlorosilanes (Appendix I). When the equilibrium composition is calculated with initial equi-molecular amounts of dimethyldichlorosilane and methylchloride (Si:Cl:C = 1:3:3) a surprising result is obtained. At 300 °C the molar percentages of dimethyldichlorosilane, methyltrichlorosilane and tetrachlorosilane are 8.2, 84.9 and 6.9 respectively with regard to the silicon compounds. The reason is simply that the calculation was performed without the possibility of elemental silicon participating. Such a calculation thus applies to a gas phase equilibrium. Because of the fact that occurrence of elemental carbon was allowed for, the resulting carbon deposition accounts for part of the disturbed Cl:CH₃ balance. Column 2 in Table 13 shows the partial pressure of the compounds as they were computed in this manner. The atomic ratios in the gas phase at equilibrium appeared to be Si:Cl:C = 1:3:2.4. The main compounds in the gas can be seen to be methane, methyltrichlorosilane, hydrogen, dimethyldichlorosilane and tetrachlorosilane, decreasing in content in the given order.

A more realistic computation has been carried out by allowing silicon to participate. This approaches a situation that may occur when a reactive contact mixture is equilibrated with methylchloride, i.e. the equilibrium with silicon present in excess and with initial CH₃:Cl = 1:1. Table 13 (columns 3-6) contains the resulting data for the temperature range between 300 and 400 °C and 1 atmosphere pressure. In Figure 15 a plot is made of the concentrations of the main silanes, based on a total of 100 for the silanes. Table 13 also lists the equilibrium-ratio Si:Cl:C in the gas phase. The data show that the Cl:Si ratio increases with temperature, and that the C:Cl ratio of the gas mixture is below unity. The C:Cl ratio in the silanes product is even smaller and decreases from 0.91 at 300 °C to 0.72 at 400 °C, an indication that some cracking is favoured thermodynamically.
Figure 15
Equilibrium composition of methylchlorosilanes.
D- Me₂SiCl₂, DH- MeSiHCl₂, T- MeSiCl₃, MH- Me₂SiHCl,
Q- SiCl₄, M- Me₃SiCl, TH- SiHCl₃

A number of remarkable facts appear upon comparison with the usual composition of the product of a direct synthesis.
- Selectivity with kinetic control can be higher than seems thermodynamically justified.
- The amounts of methyldichlorosilane, tetrachlorosilane and trichlorosilane are thermodynamically much smaller than is observed in some experiments.
- The equilibrium contents of methyltrichlorosilane and trimethylchlorosilane are very close to the contents in the practice of the direct synthesis.
- The equilibrium composition of the gas phase without possibility of interaction with silicon resembles the product composition of the uncatalyzed reaction between silicon and methylchloride (VII-5-4).
Table 13. Equilibrium pressures in reaction of methylchloride with silicon\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>300 °C(^b)</th>
<th>300 °C</th>
<th>333 °C</th>
<th>367 °C</th>
<th>400 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>5.57x10(^{-1})</td>
<td>1.17x10(^{-1})</td>
<td>1.63x10(^{-1})</td>
<td>2.06x10(^{-1})</td>
<td>2.38x10(^{-1})</td>
</tr>
<tr>
<td>MeSiH(_2)(_Cl)</td>
<td>9.69x10(^{-5})</td>
<td>4.47x10(^{-3})</td>
<td>7.00x10(^{-3})</td>
<td>1.03x10(^{-2})</td>
<td>1.37x10(^{-2})</td>
</tr>
<tr>
<td>MeSiH(_2)(_Cl)</td>
<td>3.11x10(^{-9})</td>
<td>1.63x10(^{-5})</td>
<td>3.52x10(^{-5})</td>
<td>6.80x10(^{-5})</td>
<td>1.12x10(^{-4})</td>
</tr>
<tr>
<td>Me(_2)(_SiHCl)</td>
<td>6.11x10(^{-7})</td>
<td>1.45x10(^{-3})</td>
<td>1.88x10(^{-3})</td>
<td>2.20x10(^{-3})</td>
<td>2.11x10(^{-3})</td>
</tr>
<tr>
<td>MeSi(_3)</td>
<td>7.36x10(^{-15})</td>
<td>4.36x10(^{-9})</td>
<td>1.37x10(^{-8})</td>
<td>3.65x10(^{-8})</td>
<td>7.67x10(^{-8})</td>
</tr>
<tr>
<td>Me(_2)(_SiH(_2))</td>
<td>7.42x10(^{-13})</td>
<td>1.97x10(^{-7})</td>
<td>4.01x10(^{-7})</td>
<td>7.00x10(^{-7})</td>
<td>9.95x10(^{-7})</td>
</tr>
<tr>
<td>Me(_3)(_Si)</td>
<td>3.41x10(^{-11})</td>
<td>4.26x10(^{-6})</td>
<td>5.48x10(^{-6})</td>
<td>6.07x10(^{-6})</td>
<td>5.91x10(^{-6})</td>
</tr>
<tr>
<td>Me(_4)(_Si)</td>
<td>6.63x10(^{-10})</td>
<td>3.61x10(^{-5})</td>
<td>3.03x10(^{-5})</td>
<td>2.14x10(^{-5})</td>
<td>1.39x10(^{-5})</td>
</tr>
<tr>
<td>Me(_2)(_SiCl)</td>
<td>4.57x10(^{-5})</td>
<td>4.88x10(^{-2})</td>
<td>3.77x10(^{-2})</td>
<td>2.65x10(^{-2})</td>
<td>1.78x10(^{-2})</td>
</tr>
<tr>
<td>Me(_2)(_SiCl(_2))</td>
<td>3.21x10(^{-2})</td>
<td>6.68x10(^{-1})</td>
<td>5.86x10(^{-1})</td>
<td>4.89x10(^{-1})</td>
<td>3.95x10(^{-1})</td>
</tr>
<tr>
<td>MeSi(_3)(_Cl)</td>
<td>3.37x10(^{-1})</td>
<td>1.35x10(^{-1})</td>
<td>1.59x10(^{-1})</td>
<td>1.86x10(^{-1})</td>
<td>2.09x10(^{-1})</td>
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<tr>
<td>SiCl(_4)</td>
<td>2.72x10(^{-2})</td>
<td>2.14x10(^{-4})</td>
<td>4.23x10(^{-4})</td>
<td>8.43x10(^{-4})</td>
<td>1.57x10(^{-3})</td>
</tr>
<tr>
<td>SiH(_2)(_Cl(_3))</td>
<td>1.29x10(^{-4})</td>
<td>1.14x10(^{-4})</td>
<td>2.60x10(^{-4})</td>
<td>5.58x10(^{-4})</td>
<td>1.08x10(^{-3})</td>
</tr>
<tr>
<td>Si(_2)(_Cl(_2))</td>
<td>7.10x10(^{-8})</td>
<td>7.37x10(^{-6})</td>
<td>1.97x10(^{-5})</td>
<td>4.87x10(^{-5})</td>
<td>1.01x10(^{-4})</td>
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<tr>
<td>SiH(_3)(_Cl)</td>
<td>4.63x10(^{-12})</td>
<td>5.45x10(^{-8})</td>
<td>1.85x10(^{-7})</td>
<td>5.61x10(^{-7})</td>
<td>1.35x10(^{-6})</td>
</tr>
<tr>
<td>Si(_4)</td>
<td>3.14x10(^{-17})</td>
<td>4.11x10(^{-11})</td>
<td>1.95x10(^{-10})</td>
<td>7.63x10(^{-10})</td>
<td>2.20x10(^{-9})</td>
</tr>
<tr>
<td>H(_2)Cl</td>
<td>1.61x10(^{-4})</td>
<td>6.56x10(^{-7})</td>
<td>2.47x10(^{-6})</td>
<td>8.29x10(^{-6})</td>
<td>2.32x10(^{-5})</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>7.60x10(^{-25})</td>
<td>2.75x10(^{-29})</td>
<td>1.70x10(^{-27})</td>
<td>7.83x10(^{-26})</td>
<td>2.25x10(^{-24})</td>
</tr>
<tr>
<td>H(_2)</td>
<td>5.10x10(^{-2})</td>
<td>2.37x10(^{-2})</td>
<td>4.48x10(^{-2})</td>
<td>7.83x10(^{-2})</td>
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<tr>
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<td>6.21x10(^{-14})</td>
<td>4.37x10(^{-13})</td>
<td>2.56x10(^{-12})</td>
<td>1.17x10(^{-11})</td>
</tr>
</tbody>
</table>

\(\text{Si} : \text{Cl} : \text{C}\)

| gas phase | 1:3:2.4 | 1:2.11:2.04 | 1:2.15:2.04 | 1:2.22:2.05 | 1:2.30:2.13 |
| silanes    | 1:3:1.01 | 1:2.10:1.90 | 1:2.15:1.83 | 1:2.22:1.76 | 1:2.30:1.67 |
| initial    | 1:3:3   | c)         | c)         | c)         | c)         |

\(^a\)pressures in atm., total pressure 1 atm., gases assumed ideal, computed with data from (55, 38, 121) and with method as given in Appendix I

\(^b\)computed with elemental carbon as the only solid phase considered

\(^c\)initial Cl : CH\(_3\) = 1 : 1, elemental silicon in excess, see text
IV-7. Implications of the reaction schemes

The role of cuprous chloride is discussed in the view of the preceding considerations. When its function is an initiating chlorination of silicon, a number of phenomena are easily understood.

The reaction schemes presented (IV-4) follow from a consideration of the main characteristics of the direct synthesis (IV-2) and from a discussion of the sequence of distribution of the substituents over the silicon valencies from a logical point of view (IV-3). They offer not only a relatively simple explanation of the formation of silanes but also furnish the explanation for a number of phenomena, which seemed contradictory. Now it is interesting to discuss some of the features of the developed reaction scheme, mainly regarding to methylchlorosilanes.

- As for the formation of dialkyldichlorosilanes, the reaction scheme does not require a two site adsorption of the reactant. The two site adsorption is doubtful if it is realized that the chance of adsorption of a methylchloride molecule, with its carbon-chlorine bond parallel to a silicon-copper bond, must be much smaller than the chance of adsorption of a methylchloride molecule with its chlorine atom directed to a copper atom. The chlorine atom, being the negative part of an alkylchloride molecule possesses an electron cloud, which is able to interact with the copper atom whereas the electrons on the adjacent carbon atom are screened by its hydrogen ligands. For the reaction of hydrogen chloride with a contact mixture, which is likely to proceed in an analogous way, the argument for a single site adsorption is even stronger, when the spherical geometry of the molecule is taken into account.

- Various gaseous chlorides react with silicon-copper contact mixtures. The minimum reaction temperature seems to decrease with increase of the polarizability of the bond of chlorine with the rest of the molecule (87). This may be related with the ease of formation of a complex between copper and the chloride.
- In the suggested schemes there is a transfer of copper-bound chlorine to silicon. One of the arguments against the scheme proposed by Rochov and Hurd (86), which also contains this transfer, is that the solid-solid reaction between cuprous chloride and silicon would not proceed at temperatures lower than 260 °C. According to Müller, however, this reaction will already start at 180 °C under favourable conditions (86). Furthermore, large differences exist between the suggested chlorine transfer and the reaction between particles of silicon and particles of cuprous chloride. An important difference is the state of the surface. When crystalline silicon enters in a reaction with cuprous chloride, the silicon surface is covered with a protective layer of silicon dioxide, which inhibits the reaction at low temperatures. When the temperature is increased, etching by gaseous cuprous chloride will make a part of the silicon surface available and the exothermic reaction will from then on proceed violently. The surface of a contact mixture reacting with methylchloride, however, is already active as the etching procedure, either by cracking of methylchloride during the induction period or by initiating etching with hydrogen chloride or chlorine, has already taken place. The rate of reaction of such an active surface will be substantially higher than that of an oxidized surface. Another difference is that in the case of the reaction of silicon with cuprous chloride, the contact between the particles of both compounds depends upon particle size and the homogeneity of the mixture. This is by far inferior to that of cuprous chloride molecules formed from copper atoms which were already incorporated in the surface of the particle. The degree of contact thus largely determines the rate of the reaction. Thirdly the rate of transport of cuprous chloride via the gas phase is determined by the temperature. This may be the main reason that the reaction is seen to start only above 260 °C, when the distance between reacting particles requires transport through the gas phase.

- The ratio between the amounts of dialkyldichlorosilane and alkyldichlorosilane, experimentally often a poorly reproducible figure, is determined by the fraction of the alkyl groups undergoing break-down during the transfer to silicon. The sum of the rates of formation of the two compounds is given by equation (IV.8), if the activation energy of the process is required for the weakening of the carbon-chlorine bond in the copper-alkylchloride complex and the weakening of the silicon-
lattice bond.

The given reaction schemes apply also to the reaction of chlorine and hydrogen chloride (V-5) with silicon in the presence of copper. Because of the weak bond in the chlorine molecule, it is to be expected that chlorine reacts the fastest of all chlorides (see also VII-11). In this system no other transfer of chlorine than via cuprous chloride could explain the catalytic action of copper:

\[
\begin{align*}
2 \text{Cu} & \stackrel{\Lambda}{\rightarrow} 2 \text{CuCl} \\
\text{Si} + 2 \text{CuCl} & \stackrel{\Lambda}{\rightarrow} \text{SiCl}_2 + 2 \text{Cu} \\
\text{Cl}_2 + \text{SiCl}_2 & \stackrel{\Lambda}{\rightarrow} \text{SiCl}_4
\end{align*}
\]

In the case of the hydrogen chloride reaction, the chance of loss of a hydrogen atom during the rate determining step:

\[
\text{SiCl} + \text{Cu(ClH)} \rightarrow \text{HSiCl} + \text{CuCl}
\]

explains the lower content of dichlorosilane in this process than that of dimethyldichlorosilane in the methylchlorosilanes synthesis:

\[
\text{Cu(ClH)} \rightarrow \text{CuCl} + \frac{1}{2} \text{H}_2
\]

It is an indication that the stability of the surface complex Cu(ClH) is much lower than that of Cu(ClCH₃) or Cu(ClC₂H₅). This could already be understood from the reactivity of hydrogen chloride with copper which is higher than the reactivity of methylchloride with copper. The much lower possible reaction temperature of the chlorosilanes synthesis is completely consistent with this argument.

Attempts to increase the rate of formation of alkyl dichlorosilane by reacting with mixtures of hydrogen chloride and alkylchloride have failed (67). This indicates that no formation of, for example methyl dichlorosilane is possible via:

\[
\text{ClSiCH}_3 + \text{Cu(ClH)} \rightarrow \text{CH}_3\text{SiHCl}_2 + \text{Cu}
\]

This may be explained by the low stability of the complex Cu(ClH) at the temperatures where the methylchlorosilanes synthesis is carried out. The main source of the hydrogen containing silanes will be when the Si-H bond is established in the rate determining step, during pyrolysis of the methyl group in an attempt to methylate silicon monochloride:
The effect to be expected from admixture of hydrogen chloride is an increase of the $\text{SiCl}_2$-fraction (see also V-6), resulting in enhanced methyltrichlorosilane formation (IV-4-3). Only at the lowest possible reaction temperature has the complex $\text{Cu(ClH)}_2$ a chance to enter into reaction with $\text{SiCl}_4$ before it decomposes. This must be the basis of the patent describing the reaction of a mixture of methylchloride and hydrogen chloride (1:5:1) with a contact mixture containing 7% of copper and 1.5% of nickel. At 250 - 260°C the product is claimed to consist of 40.6 wt % methylidichlorosilane and 9.1 wt % dimethyldichlorosilane. At 280 - 290°C the data are 32 and 8.5 wt % respectively.

The formation of alkyltrichlorosilane according to the reaction scheme in IV-4-3 finds support in the literature. The content of methyltrichlorosilane in the product mixture is usually close to the equilibrium value, but this is certainly not caused by a secondary disproportionation reaction, which has to be considered as slow. Due to the fact that the content of methyltrichlorosilane is usually much larger (about 10 times, see, for example Table 12, IV-5) than that of trimethylchlorosilane, the disproportionation of $\text{CH}_3\text{SiCl}_3$ (IV-4-4) only yields a fraction of the $\text{SiCl}_2$ that is required for the methyltrichlorosilane formation. The larger part stems from the interaction between cuprous chloride and silicon:

$$2 \text{CuCl}_2 + \text{Si} \rightarrow 2 \text{Cu} + \text{SiCl}_2$$

The cuprous chloride is generated by cracking of methylchloride or reaction of hydrogen chloride with free copper. It can be transported through the gas phase and assists in improvement of the dispersion of copper over the surface of the particles. That the content of methyltrichlorosilane tends to increase with temperature is caused by the increased vapour pressure of cuprous chloride and the faster decomposition of the copper-methylchloride complex, resulting in an increased coverage by $\text{SiCl}_2$. The latter is also the effect to be expected from the presence of hydrogen chloride. In the ethylchlorosilanes synthesis, it is the lower stability of the copper-ethylchloride complex that causes an unfavourably high $\text{SiCl}_2$-concentration on the surface, giving rise to 15 to 25% of ethyltrichlorosilane in the silanes product.
Addition of hydrogen to the alkylchloride feed will cause a reduction of cuprous chloride according to:

$$2 \text{CuCl} + \text{H}_2 \rightarrow 2 \text{Cu} + 2 \text{HCl}$$  \hspace{1cm} (IV.18)

The liberated hydrogen chloride reacts rapidly with the available active reaction sites (ClSiMe and SiCl₂) giving a temporary increase in reactivity, but it soon kills the reaction because of the consumption of propagatory CuCl. An analogous effect has been observed with the addition of hydrogen sulphide (727). Small amounts of this additive have a beneficial effect because of the conversion of free copper:

$$2 \text{Cu} + \text{H}_2\text{S} \rightarrow \text{Cu}_2\text{S} + \text{H}_2$$  \hspace{1cm} (IV.19)

thus preventing part of the cracking due to its presence. With the increase of the content of hydrogen sulphide in the methylchloride feed, a decrease of reactivity follows because it also reacts with cuprous chloride:

$$2 \text{CuCl} + \text{H}_2\text{S} \rightarrow \text{Cu}_2\text{S} + 2 \text{HCl}$$  \hspace{1cm} (IV.20)

This is once more an indication of the important rôle of cuprous chloride in the reaction steps leading to alkylchlorosilanes. Moreover, the effect of a temporary addition of 3.2 mol % hydrogen sulphide to methylchloride (727, p. 65) is in complete agreement with the expectations: a sharp increase of reactivity and content of methyltrichlorosilane and methyldichlorosilane (formation of hydrogen chloride by reaction IV.20) and decrease of the content of dimethyldichlorosilane from 90 wt % to 35 wt %.

That copper does not seem the best catalyst in the phenylchlorosilanes synthesis follows from a consideration of the reaction schemes in IV-4. The temperature where the carbon-chlorine bond can be broken to allow a transfer of the phenyl group from the copper-phenylchloride complex to a chlorinated silicon atom is about 420 - 460 °C. Below this temperature, no phenylchlorosilanes are formed. At the reaction temperature of the phenylchlorosilanes synthesis, both the vapour pressure of cuprous chloride and its rate of reaction with silicon are high to such a degree that the concentration of SiCl is low relative to the concentration of SiCl₂. The result is a considerable cracking of the phenylchloride on the excess of free copper and a continuously disturbed phenyl/chlorine balance on the surface and thus of the silanes mixture.
When silver is used as a catalyst, part of the problem is solved. The chlorination of silicon is much slower because of the lower vapour pressure of silver chloride, and the ratio of SiCl₂/SiCl is smaller. The miscibility of silicon with silver atoms, however, is much smaller than with copper atoms because silver is not known to form alloys with silicon. The resulting poor distribution of the catalyst over the silicon surface will not provide high reaction rates.

IV-8. The promoting effect of zinc chloride

The molten layer of promoting metal chlorides improves the mobility of copper(I) and chlorine ions. It thus provides a uniform chlorination of silicon and a proper distribution of copper over the surface.

One of the most commonly used promoters seems to be zinc or zinc chloride. It is the subject of, and mentioned in, a large number of publications and patents (e.g. 3, 29, 69, 73, 75, 83, 127), and it is probably applied by all manufacturers of dimethyldichlorosilane. When zinc is added as a metal it initially exhibits an increase of the methyl/chlorine ratio in the silanes product because of its high affinity for chlorine. It can be easily calculated that 1 wt % of zinc performs only an increase of the average methyl/chlorine ratio of 0.005 over a silicon conversion of 80%. The main influence comes from the presence of zinc chloride in the contact mixture, the beneficial effect being already noticeable when its content is 0.1%. Such an amount corresponds roughly with a layer with a thickness of about 15 Ångström when the specific surface area of the contact mixture is 0.2 m²/g. Because there is no knowledge of the boundary tension of liquid zinc chloride against a contact mixture surface it can not be determined whether it can completely cover the surface. When zinc chloride vapour is added to the methylchloride feed, an equilibrium concentration of 0.33 (+ 0.04) wt % zinc chloride will remain adsorbed on the silicon surface at 350 °C (123). This large amount is a strong indication that zinc chloride may wet the surface sufficiently to guarantee a large coverage.
The effect of the presence of zinc chloride is that the convertibility of silicon is substantially increased, together with an enhanced reactivity of the contact mixture (VII-5 Figures 37, 38, VII-6-3). A group of Russian investigators recently developed a reaction scheme to explain the effect of some metal chlorides (ZnCl₂, CdCl₂, HgCl₂) by their chlorination of copper (47):

\[ \text{ZnCl} + \text{Cu} \rightarrow \text{Zn} + \text{CuCl} \]  

The monochloride of the metals is regenerated in the gas phase by interaction with the organic chloride:

\[ \text{Zn} + \text{RCl} \rightarrow \text{ZnCl} + \text{R} \]  

A thermodynamic calculation shows that the presence of atoms of such an unnoble metal is very improbable under direct synthesis conditions (VII-12-1). Moreover, all explanations in terms of enhanced cleavage of the carbon-chlorine bond seem very unlikely, because it would imply the formation of large amounts of cracked products and thus an increase of the chlorine/methyl ratio in the silanes product. Actually, the cracking of methylchloride under the catalytic action of zinc chloride is negligible compared to its positive influence on the process. When methylchloride was reacted for 55 hours with a batch of 8.2 g of silicon with a constant concentration of 0.33 wt % zinc chloride at a temperature of 350 °C, only 25 mg of cracked hydrocarbons was deposited on the silicon (723). No methylchlorosilanes could be detected in the product gas. The behaviour of a contact mixture promoted with zinc chloride suggests in fact the opposite of enhanced cracking.

This follows immediately when the tar contents of the entrained dust from promoted and unpromoted contact mixtures are compared. In Figure 16, drawn according to data from VII-5-2, this is illustrated. The points represent the average amount of tar (carbon + hydrogen) in the entrained dust of some fluidized bed experiments.

About the same influence was observed from the presence of cadmium chloride in a contact mixture (76, 139, 140, VII-8-4,
This promoter was shown to improve the ratio trimethylchlorosilane/methyltrichlorosilane and to increase the convertibility of silicon substantially. It also allows a copper-catalyzed phenylchlorosilanes synthesis to be conducted with a high yield of diphenyldichlorosilane (139).

Not only the alkylchlorosilanes synthesis is promoted by zinc chloride. The reaction of chlorine with a silicon-copper contact mixture is also accelerated by its presence (VII-12). This provides evidence that the function of zinc chloride lies in the transfer of chlorine. From the observation that the effect ceases below the eutectic temperature of the mixture of cuprous chloride and zinc chloride (242 °C (53)), it follows that not a reaction in the gas phase (47) but one on the surface of the particles must be considered (VII-12).

The above arguments advocate that the promoting effect of zinc chloride lies in its ability to dissolve cuprous chloride. The melt provides, firstly, proper distribution of cuprous chloride over the surface and consequently a higher reaction rate per unit weight of contact mixture. Secondly, the mobility of copper(I) and chlorine ions is improved, which ensures rapid chlorination of silicon atoms appearing in the surface layer. Thirdly, by decreasing the amount of free cuprous chloride in the solid state as well as in the gas phase, cracking of alkylchlorides and of the less stable higher alkylated silanes is substantially lowered.

In the practice of the direct synthesis, the melt will not consist purely of zinc chloride and cuprous chloride. As iron and aluminium are usually present in the silicon, the promoting molten layer will contain ferric chloride and aluminium chloride as well. Study of the chemical reactions comprising methylchloride and the silanes in such ternary or quaternary metal chloride systems may reveal additional information to elucidate the reaction mechanism of the direct synthesis.

The given elucidation of the functioning of zinc chloride presumably also applies to cadmium chloride. Although the eutectic melting point of the mixture of cuprous chloride and cadmium chloride is 408 °C (53), the melting point of ferric chloride is sufficiently low (306 °C) and its content usually sufficiently high (0.5 wt %) to ascertain the ternary mixture to be in the liquid state at the temperature of the direct
synthesis. That cadmium chloride seems to be such an excellent promoter in the copper-catalyzed phenylchlorosilanes synthesis is readily understood from this conception. Fusion of cuprous chloride with cadmium chloride will lower the concentration of cuprous chloride in the gas phase and consequently the over-chlorination of silicon atoms. This decreases the chance of cracking of phenylchloride on free copper. The phenyl/chlorine ratio in the surface layer is not disturbed and the product will show a favourable content of highly phenylated products.

IV-9. The course of the direct synthesis

The direct synthesis of methylchlorosilanes and ethylchlorosilanes in a fixed or fluidized bed reactor proceeds schematically according to Figure 17. Examples of the course of this process can be found in the literature (127, 128, 139) and in VII-5-3.

Figure 17
chematic course of a direct synthesis

Five stages can be roughly distinguished in the batch process, without extra supply of silicon or copper. An explanation in view of the preceding considerations will now be attempted.

a. The induction period, in which no methylchlorosilanes are formed. In this stage some methylchloride undergoes cracking on copper. The cuprous chloride or hydrogen chloride formed will etch the oxidized contact mixture surface (II-3, VII-3), thus exposing reactive superficially chlorinated silicon. The occurrence of the induction period can be prevented by treatment with chlorine, hydrogen chloride or by heating for some time at high temperatures (86).

b. A period of increasing reactivity and selectivity (content of dimethyl dichlorosilane). The fraction of the contact mixture surface which is active in the dimethyldichlorosilane formation increases, by continued etching and improving distribution of catalyst and promoters over the surface of the silicon particles. Transport of copper proceeds via diffusion of the metal and through the gas phase in the form of cuprous...
chloride. The cracking of methylchloride which precedes the etching, causes a high initial methyltrichlorosilane content which gradually decreases in this stage of the process. For contact mixtures which are heated for some time at 400 °C this period is drastically shorter (127, p. 60). When the traces of oxygen, usually present in methylchloride have been removed, selectivity will also commence at a higher level (VII-5-2).

c. A period with nearly constant reactivity and selectivity, with a minor tendency of improvement of reactivity and deterioration of the selectivity. In this stage, the supply of silicon to the surface by the diffusion process in the catalyst layer is sufficiently rapid to keep up with the surface reaction. The slight increase of the reactivity per unit weight of silicon is caused by the increase of the specific surface area of the particles with decreasing particle size.

d. A remarkable feature in the course of the direct synthesis has been observed by Zock (139). It is a sharp increase of reactivity at a stage where most of the silicon has been converted and just before the complete fall of both reactivity and selectivity. The phenomenon can sometimes be observed also in the work of other investigators but has not been recognized as characteristic. It may be speculated that this stage is related to the state of complete coverage of the silicon particles with \( \eta \)-phase crystallites for which Voorhoeve (127, p. 54) predicts the beginning of the fall in activity. According to the findings of Kolster (68), \( \eta \)-phase is formed at the boundary between silicon and \( \eta \)-phase by diffusion of copper through the \( \eta \)-phase layer. The formation of \( \text{Cu}_3\text{Si} \) from silicon and copper gives a volume contraction of 12% and therefore this process initiates the formation of bursts and cracks in the \( \eta \)-phase layer and between the layers of \( \eta \)-phase and silicon. The latter will hamper further copper diffusion and facilitates the breaking loose of small \( \eta \)-phase particles. When this occurs, the surface nearly consisting only of highly reactive \( \eta \)-phase (127, p. 109), increases rapidly in surface area and the activity increases accordingly.

e. Shortly after the highly reactive period the silicon in the reactive particles, which mainly consist of \( \eta \)-phase and copper, is converted.
No reactive silicon is available and methylchloride cracking on copper will continue the blocking of the surface, accompanied by an increasing formation of methyltrichlorosilane. In this stage both reactivity and selectivity fall rapidly. The overall percentage of convertible silicon depends strongly upon the conditions of the synthesis, i.e. the quality of reactants and catalyst and the presence of promoting elements or salts. The convertibility is decreased when traces of oxygen contaminate the methylchloride feed, because accumulation of oxides effectuates an accelerated cracking (VII-5-2). Evaporation of zinc chloride will lower its content and thus its wholesome effect. If its presence could be prolonged - by lowering the temperature, or by supply - the convertibility of silicon would be enhanced (VII-6-3).
CHAPTER V

CHLOROSILANES

Analogy between chlorosilanes and methylchlorosilanes synthesis in reaction mechanism, kinetics and product composition seems absent. The explanation for this phenomenon lies partly in the fast conversion of dichlorosilane into trichlorosilane, but the latter is still the main product at short contact times. The reaction schemes proposed for alkylchlorosilanes synthesis apply satisfactorily.

V-1. Application and preparation of chlorosilanes

Chlorosilanes, compounds of the type $H_nSiCl_{4-n}$ (n=0,1,2,3) can be used as precursors to a number of organochlorosilanes, which are otherwise difficult to obtain. Trichlorosilane, for instance can be converted into organochlorosilanes by means of a Grignard synthesis, which is schematized in the equation:

$$HSiCl_3 + n \text{RMgBr} \rightarrow HSiR_nCl_{3-n} + n \text{MgBrCl} \quad (V.1)$$

The hydrogen atom in the resulting product offers possibilities for further preparative work (90, 128). Addition by olefins and substitution of aromatic compounds, using Friedel Crafts-type catalysts (39), also enable the preparation of a large number of compounds.

$$XYZSi-H + CH_2=CH-R \rightarrow XYZSi-CH_2-CH_2-R \quad (V.2)$$

$$XYZSi-H + C_6H_5-R \rightarrow XYZSi-C_6H_4-R + H_2 \quad (V.3)$$

Tetrachlorosilane and trichlorosilane find an important application in the manufacture of metallic silicon of high purity for the semiconductor industry. The preparation of pure silicon proceeds at high temperatures (circa 1000 °C) by reduction of chlorosilanes with hydrogen or by pyrolysis. Some papers have already appeared on the kinetics (7) and the thermodynamics (40, 104) of the reduction of chlorosilanes with hydrogen.

Preparation of chlorosilanes proceeds by reaction of hydrogen chloride with silicon at temperatures above 170 °C. The minimum temperature of
the reaction depends upon the presence of additives or impurities, which can have a large influence on the process (105). Already in 1896 copper has been mentioned as a catalyst for the reaction (24). The reaction product mainly consists of trichlorosilane, but depending upon the conditions, also the other chlorosilanes appear in varying content (VII-7). The occurring overall reactions are given in Table 14.

Table 14. Overall reactions in chlorosilanes synthesis

<table>
<thead>
<tr>
<th>Equation</th>
<th>Reaction Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V.4)</td>
<td>$3 \text{HCl} + \text{Si} \rightarrow \text{HSiCl}_3 + \text{H}_2$</td>
</tr>
<tr>
<td>(V.5)</td>
<td>$2 \text{HCl} + \text{Si} \rightarrow \text{H}_2\text{SiCl}_2$</td>
</tr>
<tr>
<td>(V.6)</td>
<td>$4 \text{HCl} + 2 \text{Si} \rightarrow \text{H}_3\text{SiCl} + \text{HSiCl}_3$</td>
</tr>
<tr>
<td>(V.7)</td>
<td>$4 \text{HCl} + \text{Si} \rightarrow \text{SiCl}_4 + 2 \text{H}_2$</td>
</tr>
</tbody>
</table>

Tetrachlorosilane may be obtained directly from the reaction of chlorine with silicon, a process which is also catalyzed by copper (VII-11). The reaction proceeds according to:

$$2 \text{Cl}_2 + \text{Si} \rightarrow \text{SiCl}_4 \quad (V.8)$$

Also compounds containing more than one silicon atom may be found in the product of the chlorosilanes synthesis, for instance hexachlorodisilane. Its formation proceeds schematically according to:

$$6 \text{HCl} + 2 \text{Si} \rightarrow \text{Si}_2\text{Cl}_6 + 3 \text{H}_2 \quad (V.9)$$

Some introductory information about the product composition and reaction rates in the direct synthesis of chlorosilanes under various conditions may be found in Table 15. The table is a list of some results published in the literature and as obtained by own experimental work (VII-7).

Table 15. Experimental results in chlorosilanes synthesis

<table>
<thead>
<tr>
<th>Reference:</th>
<th>Solid reactant:</th>
<th>Particle size:</th>
<th>Reactor type:</th>
<th>Temperature (°C):</th>
<th>Reaction rate (mmol Si/g.min):</th>
<th>Product composition:</th>
</tr>
</thead>
<tbody>
<tr>
<td>(14, 48)</td>
<td>very pure Si, no Cu</td>
<td>50 - 250</td>
<td>fluid-bed</td>
<td>331</td>
<td>0.0021</td>
<td>1 - 2</td>
</tr>
<tr>
<td>(14, 48)</td>
<td>techn. Si, no Cu</td>
<td>50 - 250</td>
<td>fluid-bed</td>
<td>240</td>
<td>0.0043</td>
<td>1 - 2</td>
</tr>
<tr>
<td>(14, 48)</td>
<td>amorph Si, no Cu</td>
<td>50 - 250</td>
<td>fluid-bed</td>
<td></td>
<td></td>
<td>10 - 20</td>
</tr>
<tr>
<td>(60)</td>
<td>techn. Si, 5 % Cu</td>
<td>50 - 250</td>
<td>fluid-bed</td>
<td></td>
<td></td>
<td>10 - 20</td>
</tr>
<tr>
<td>(106)</td>
<td>techn. Si, 3 % Cu</td>
<td>150 - 300</td>
<td>fixed bed</td>
<td>180 - 220</td>
<td>0.007</td>
<td>0.5</td>
</tr>
<tr>
<td>VII-7</td>
<td>techn. Si, no Cu</td>
<td>125 - 150</td>
<td>fixed bed</td>
<td>170 - 350</td>
<td>0.011</td>
<td>150 - 210</td>
</tr>
<tr>
<td>VII-7</td>
<td>techn. Si, 5 % Cu</td>
<td>150 - 210</td>
<td>fixed bed</td>
<td>260</td>
<td>0.13</td>
<td>260</td>
</tr>
<tr>
<td>VII-7</td>
<td>techn. Si, 3 % Cu</td>
<td>150 - 210</td>
<td>fixed bed</td>
<td>260</td>
<td>0.13</td>
<td>260</td>
</tr>
</tbody>
</table>

a) and 8 - 37 % polychlorosilanes
Some characteristics follow from a consideration of the data in the table:
- copper catalyzes the reaction,
- reactivity is higher when the silicon contains impurities,
- trichlorosilane is the main reaction product.

Compared with the maximum dimethyldichlorosilane yield of the methylchlorosilanes synthesis, which is about 90%, the content of the dichlorocomound in the chlorosilanes synthesis is very low. For this lack of analogy between the two processes no explanation has been given until now. The attention of the investigators has mainly been focussed on the formation of trichlorosilane, this being the main product of the synthesis.

The present chapter will discuss the direct synthesis of chlorosilanes from hydrogen chloride and silicon, catalyzed by copper. Attention is paid to the discrepancy between the composition of a chlorosilanes product and the equilibrium composition. Secondary reactions will be considered to account for this discrepancy, in a section devoted to the kinetics. The kinetic equations are discussed in relation with the probable reaction schemes.

V-2. Thermodynamic considerations

Estimated and experimentally obtained data on the free enthalpy change of some reactions agree well. The equilibrium content of dichlorosilane is much smaller than can be observed in practice. Thermodynamics favour the formation of tetrachlorosilane.

Studies on the chemical equilibria in chlorosilanes are of interest to the manufacturers of chlorosilanes and semiconductor-pure silicon. Therefore, the thermodynamic functions of the compounds involved have to be evaluated. The lack of full experimental data on heats of formation of the chlorosilanes, however, hampers reliable equilibrium calculations. The missing data have then to be obtained by an estimation method, applied for instance, by Shaulov c.s. (104). This method has been discussed in II-1. The results for the chlorosilanes must be considered doubtful because of their lack of internal consistency. When bondenergies are assumed constant to enable estimation of heats of formation, the internal consistency of the thermodynamic functions improves.
A study based upon estimations obtained in this way has been carried out \( (146) \). The results are likely to be much closer to reality than the equilibrium constants calculated by Shaulov. Still better results are obtained by a second order additivity method of which the discussion and the results are in II-3 and Appendix II respectively.

Experimentally the matter has been approached by Ashen \( (7) \). He found that in the system of compounds:

\[
\text{SiCl}_4, \text{HSiCl}_3, \text{H}_2\text{SiCl}_2, \text{H}_2 \text{ and HCl}
\]
equilibrium is achieved at temperatures above 700 °C without using a catalyst. No solid silicon was deposited up to 900 °C. In this temperature region the molefractions of tetra-, tri- and dichlorosilane appeared to be 0.57, 0.43 and 0.15 respectively. In the region of 700 to 900 °C no significant change of the molar ratios has been observed. This could already be expected from the small heat effect of the disproportionation reaction (equation V.10), which is 1.3 kcal.

\[
2 \text{ HSiCl}_3 \rightarrow \text{H}_2\text{SiCl}_2 + \text{SiCl}_4 \quad (V.10)
\]

In Table 16 the enthalpy change of the reaction, as calculated from heat content data \( (55) \) and heat of formation data (Appendix II) has been given in the first row. From the same references the free enthalpy change of this reaction for temperatures from 500 to 1100 K has been calculated. Compared with the experimental value \( \Delta G_{\text{exp}} = 1.6 \) (± 0.6) kcal/mol for the temperature region 1000 - 1200 K \( (7) \), the

<table>
<thead>
<tr>
<th>Equil. (V.10)</th>
<th>Temp. (K)</th>
<th>( \Delta H^0 )</th>
<th>( \Delta G^0 )</th>
<th>( K )</th>
<th>( \Delta G^\exp )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SiCl}_4 \rightarrow \text{HSiCl}_3 + \text{H}_2 \text{SiCl}_2 )</td>
<td>500</td>
<td>1.24</td>
<td>2.29</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>1.26</td>
<td>2.50</td>
<td>0.12</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>1.27</td>
<td>2.71</td>
<td>0.14</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1.29</td>
<td>2.92</td>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>1.30</td>
<td>3.12</td>
<td>0.17</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1.31</td>
<td>3.32</td>
<td>0.19</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>1.32</td>
<td>3.52</td>
<td>0.20</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Equil. (V.11)</th>
<th>Temp. (K)</th>
<th>( \Delta H^0 )</th>
<th>( \Delta G^0 )</th>
<th>( K )</th>
<th>( \Delta G^\exp )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SiCl}_4 \rightarrow \text{HSiCl}_3 + \text{H}_2 \text{SiCl}_2 )</td>
<td>500</td>
<td>-17.01</td>
<td>-13.19</td>
<td>5.9x10^4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>-16.75</td>
<td>-12.46</td>
<td>3.1x10^4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>-16.54</td>
<td>-11.75</td>
<td>4.7x10^3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>-16.35</td>
<td>-11.08</td>
<td>1.0x10^3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>-16.21</td>
<td>-10.43</td>
<td>3.3x10^2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>-16.09</td>
<td>-9.79</td>
<td>1.4x10^2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>-16.0</td>
<td>-9.17</td>
<td>6.7x10^1</td>
<td>-</td>
</tr>
</tbody>
</table>

In Table 16, thermodynamic constants of equilibria \( (V.10) \) and \( (V.11) \), the...
agreement is satisfactory. The equilibrium constant calculated from the estimated value at 1100 K is in error with a factor 2, which is a reasonable result, taking also into account that the concentration of dichlorosilane could not be measured because of calibration difficulties. The agreement between experimental and calculated data is better even for the reaction of hydrogen chloride with trichlorosilane (equation V.11). The data are in Table 16.

\[ \text{HSiCl}_3 + \text{HCl} \rightarrow \text{SiCl}_4 + \text{H}_2 \quad \text{(V.11)} \]

Table 17. Theoretical composition of a chlorosilanes mixture.

<table>
<thead>
<tr>
<th>Compound</th>
<th>200 °C</th>
<th>300 °C</th>
<th>400 °C</th>
<th>500 °C</th>
<th>600 °C</th>
<th>800 °C</th>
<th>1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCl(_4)</td>
<td>35.9</td>
<td>36.5</td>
<td>37.2</td>
<td>37.8</td>
<td>38.6</td>
<td>38.4</td>
<td>37.2</td>
</tr>
<tr>
<td>SiHCl(_3)</td>
<td>18.2</td>
<td>17.3</td>
<td>16.4</td>
<td>15.5</td>
<td>14.3</td>
<td>13.7</td>
<td>12.3</td>
</tr>
<tr>
<td>SiH(_2)Cl(_2)</td>
<td>0.86</td>
<td>0.95</td>
<td>0.98</td>
<td>1.0</td>
<td>0.99</td>
<td>0.98</td>
<td>0.90</td>
</tr>
<tr>
<td>SiH(_3)Cl</td>
<td>0.004</td>
<td>0.006</td>
<td>0.008</td>
<td>0.010</td>
<td>0.012</td>
<td>0.013</td>
<td>0.014</td>
</tr>
<tr>
<td>SiCl(_2)</td>
<td>(1.0\times10^{-14})(2.1\times10^{-11})(4.5\times10^{-9})(2.4\times10^{-7})(4.9\times10^{-6})</td>
<td>0.059</td>
<td>1.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>(7.9\times10^{-7})(2.0\times10^{-5})(1.9\times10^{-4})(9.9\times10^{-4})(3.5\times10^{-3})(0.021)(0.07)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(^a)</td>
<td>45.0</td>
<td>45.1</td>
<td>45.4</td>
<td>45.6</td>
<td>46.0</td>
<td>46.9</td>
<td>48.6</td>
</tr>
<tr>
<td>Cl:Si(^b)</td>
<td>3.64</td>
<td>3.65</td>
<td>3.66</td>
<td>3.68</td>
<td>3.70</td>
<td>3.78</td>
<td>3.89</td>
</tr>
</tbody>
</table>

Table 18. Theoretical composition of a chlorosilanes mixture.

<table>
<thead>
<tr>
<th>Compound</th>
<th>200 °C</th>
<th>300 °C</th>
<th>400 °C</th>
<th>500 °C</th>
<th>600 °C</th>
<th>800 °C</th>
<th>1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCl(_4)</td>
<td>32.2</td>
<td>32.9</td>
<td>34.6</td>
<td>35.2</td>
<td>35.7</td>
<td>35.7</td>
<td>33.6</td>
</tr>
<tr>
<td>SiHCl(_3)</td>
<td>22.7</td>
<td>20.6</td>
<td>19.7</td>
<td>18.8</td>
<td>17.9</td>
<td>16.4</td>
<td>14.4</td>
</tr>
<tr>
<td>SiH(_2)Cl(_2)</td>
<td>1.35</td>
<td>1.47</td>
<td>1.54</td>
<td>1.54</td>
<td>1.54</td>
<td>1.48</td>
<td>1.34</td>
</tr>
<tr>
<td>SiH(_3)Cl</td>
<td>0.007</td>
<td>0.012</td>
<td>0.016</td>
<td>0.02</td>
<td>0.023</td>
<td>0.027</td>
<td>0.027</td>
</tr>
<tr>
<td>SiCl(_2)</td>
<td>(7.6\times10^{-15})(1.6\times10^{-11})(3.4\times10^{-9})(1.8\times10^{-7})(3.7\times10^{-6})</td>
<td>0.069</td>
<td>1.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>(7.6\times10^{-7})(1.9\times10^{-5})(1.8\times10^{-4})(9.5\times10^{-4})(3.4\times10^{-3})(2.1\times10^{-2})(6.8\times10^{-2})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(^a)</td>
<td>43.6</td>
<td>43.0</td>
<td>43.3</td>
<td>44.7</td>
<td>45.0</td>
<td>46.5</td>
<td>49.3</td>
</tr>
<tr>
<td>Cl:Si(^b)</td>
<td>3.55</td>
<td>3.51</td>
<td>3.53</td>
<td>3.61</td>
<td>3.64</td>
<td>3.74</td>
<td>3.94</td>
</tr>
</tbody>
</table>

\(^a\)mol % silicon withdrawn from the gas phase, \(^b\)atomic ratio Cl:Si in the gas phase
The thermodynamic data for the chlorosilanes as have been derived seem reliable enough to allow a calculation of the equilibrium composition of a chlorosilanes mixture. In Tables 17 and 18 the theoretical composition considering the most interesting compounds is listed for the temperature range between 200 and 1000 °C and 1 atmosphere total pressure. The tables are from calculations where the initial atomic ratios Cl:H = 1:1 and Cl:H = 1:2 have been introduced respectively. The calculations were performed with the method as described in Appendix I.

Some interesting facts follow from the tables:
- Tetrachlorosilane is under all circumstances the main compound. Doubling of the H:Cl ratio decreases its content in the chlorosilanes mixture from 65 to 57 mol % at 200 °C and from 75 to 68 mol % at 1000 °C.
- The content of silicon dichloride remains negligible below 800 °C.
- The equilibrium Cl:Si ratio in the gas phase varies between 3.5 and 4, increasing with increasing temperature, decreasing when excess of hydrogen is present.

It is obvious that the formation of tetrachlorosilane is favoured thermodynamically, although it usually appears only in small amounts in the chlorosilanes synthesis. Compared to the methylchlorosilanes system, the equilibrium concentration of the dichloro-compound is low. Yet, the content of dichlorosilane may, under special conditions, exceed the equilibrium content substantially (VII-7 and Table 15). This is caused by the kinetics of the process, which prevents a shift of the product mixture in the direction of the equilibrium composition by secondary reactions.

V-3. Kinetics in the gas phase

Unocatalyzed secondary reactions convert dichlorosilane into trichlorosilane faster than trichlorosilane into tetrachlorosilane.

In the chlorosilanes synthesis the product seems to show no typical analogy with that of the methylchlorosilanes synthesis. The content of the dichloro-compound is very low, although sometimes higher than should
follow from thermodynamics. It is possible that this difference is caused by a secondary reaction, which converts dichlorosilane into trichlorosilane. In the methylchlorosilanes synthesis no fast secondary reactions could shift the product composition in the direction of the equilibrium, but this may be caused by the small differences between the actual and the thermodynamic composition. That tetrachlorosilane is not formed in high amounts, in contrast with the thermodynamic prediction, indicates that the rate of conversion of trichlorosilane into tetrachlorosilane is negligible.

The kinetic data of (7) allow some elucidation on a part of the gas phase kinetics. Based upon the kinetic expressions (equations V.13 and V.15) which were determined at 1000 K and the heat effect of the corresponding reactions, first of all the activation energy of the reverse reactions has been calculated.

\[
\frac{d(H_2SiCl_3)}{d(t)} = 2 \times 10^{10} (HSiCl_3) \cdot \exp\left(\frac{-51,000}{RT}\right) \text{ [mol}.1^{-1}.s^{-1}] \quad (V.13)
\]

\[
\frac{d(HSiCl_3)}{d(t)} = 7.8 \times 10^{10} (SiCl_4) \cdot (H_2)^{1/2} \cdot \exp\left(\frac{-55,000}{RT}\right) \quad (V.15)
\]

For this calculation, the relation between the activation energy of a chemical reaction \(E_1\) and the activation energy of the reverse reaction \(E_{-1}\) has been assumed to be given by the following expression:

\[
\Delta H_R(T) = E_1 - E_{-1} \quad (V.16)
\]

From the fundamental relation as given by equation (V.17) and the entropy data for the compounds concerned, the pre-exponential terms of the kinetic expression for the reverse reactions have been calculated.

\[
\frac{k_{\infty,1}}{k_{\infty,-1}} = \exp(\frac{\Delta S}{R}) \quad (V.17)
\]

The relations thus obtained (equations V.19 and V.21) for the reactions of dichlorosilane and trichlorosilane with hydrogen chloride apply to a temperature of about 1000 K, where the original data were obtained.
\[
\begin{align*}
\text{H}_2\text{SiCl}_2 + \text{HCl} & \rightarrow \text{HSiCl}_3 + \text{H}_2 \quad \text{(V.18)} \\
\frac{d(\text{HSiCl}_3)}{d(t)} & = 2.3 \times 10^9 \exp(-33,600/RT) \cdot (\text{HCl}) \cdot (\text{H}_2\text{SiCl}_2) \quad \text{(V.19)} \\
\text{HSiCl}_3 + \text{HCl} & \rightarrow \text{SiCl}_4 + \text{H}_2 \quad \text{(V.20)} \\
\frac{d(\text{SiCl}_4)}{d(t)} & = 3.3 \times 10^9 \exp(-38,900/RT) \cdot (\text{HCl}) \cdot (\text{HSiCl}_3) \quad \text{(V.21)}
\end{align*}
\]

In these expressions the presence of the concentrations of hydrogen chloride and the chlorosilanes is speculative, as there is no experimental evidence that the discussed reactions are of the first order with respect to the reactants. In the temperature region of the direct synthesis of chlorosilanes the expressions change slightly with respect to the numeric values. For the correction, the variation of enthalpy and entropy of the activated state with the temperature has been taken as the arithmetic mean of the variations of the enthalpy and entropy of the components with the temperature.

\[
\begin{align*}
\frac{d(\text{HSiCl}_3)}{d(t)} & = 1.7 \times 10^9 \exp(-33,200/RT) \cdot (\text{HCl}) \cdot (\text{H}_2\text{SiCl}_2) \quad [500 \text{ K}] \quad \text{(V.22)} \\
\frac{d(\text{SiCl}_4)}{d(t)} & = 2.4 \times 10^9 \exp(-38,400/RT) \cdot (\text{HCl}) \cdot (\text{HSiCl}_3) \quad [500 \text{ K}] \quad \text{(V.23)}
\end{align*}
\]

Although the evaluated expressions may contain a systematic error due to assumptions used in the evaluation, it can be concluded that at 500 K the rate of conversion of dichlorosilane into trichlorosilane is about 100 times higher than the rate of conversion of trichlorosilane into tetrachlorosilane, when all concentrations are taken to be unity or equal. An interesting feature of the derived data is that the activation energy of the trichlorosilane formation from dichlorosilane and hydrogen chloride has exactly the value of the activation energy of the trichlorosilane formation from very pure silicon and hydrogen chloride, which is 33.2 kcal/mol at about 600 K (48).

If equation (V.22) holds, the rate of formation of trichlorosilane in the gas phase with for example \(p_{\text{HCl}} = 0.2\) and \(p_{\text{H}_2\text{SiCl}_2} = 0.2\) is given by:

\[
\frac{d(p_{\text{HSiCl}_3})}{d(t)} = 2.2 \times 10^{-7} \quad \text{atm.s}^{-1} \quad \text{(V.24)}
\]
It is evident that this rate of reaction is too small to contribute to a change of the product composition under the conditions of the direct synthesis. The surface of the contact mixture, however, is undoubtedly able to lower the activation energy of this secondary formation of trichlorosilane considerably.

V-4. Kinetics of the reaction of hydrogen chloride with silicon-copper

The kinetic equations describing the formation of dichlorosilane and trichlorosilane have been determined. The compounds are formed in parallel reactions but dichlorosilane reacts rapidly on the surface of the contact mixture, forming trichlorosilane.

As the essential reaction steps in the synthesis of chlorosilanes proceed on the surface of the silicon particles, the process has to be regarded as heterogeneous catalysis, with the particularity that the larger part of the catalyst is also reactant. In such a process the following kinetic steps must be considered:

1. Diffusion of hydrogen chloride from the gas phase to the surface of the contact mixture particles.
2. Adsorption of hydrogen chloride on an active site.
3. Diffusion of silicon to the surface of the particle.
4. Reaction steps on the surface to form chlorosilanes in adsorbed form.
5. Desorption of chlorosilanes.
6. Diffusion of chlorosilanes to the gas phase.

In the synthesis of methylchlorosilanes it has been shown that the diffusion steps 1 and 6 are not rate-determining (127). The contact mixture is not porous - specific surface areas rarely exceed 1 m²/g - so the only possibility for diffusion control is limitation of the reaction by film-diffusion. That this is not at all imaginary in the chlorosilanes synthesis can be seen by comparing the results of various investigators on the matter of the activation energy. In Table 19 some data are given. It is unacceptable that some of the lower values for the overall activation energy apply to the actual rate determining step. The obvious explanation is that, in cases of an observed extremely low activation energy, limitation by film-diffusion plays a rôle.

With respect to step 3, the description should in fact be: diffusion
Table 19. Activation energy of chlorosilanes synthesis

<table>
<thead>
<tr>
<th>Reference</th>
<th>Activation energy (kcal/mol)</th>
<th>Temperature (°C)</th>
<th>Solid reactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>(48)</td>
<td>27.4 - 29.4</td>
<td>240</td>
<td>techn. Si, no copper</td>
</tr>
<tr>
<td></td>
<td>33.2</td>
<td>330</td>
<td>pure Si, no copper</td>
</tr>
<tr>
<td>(114)</td>
<td>3</td>
<td>400 - 600</td>
<td>Si + Cu</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>250 - 300</td>
<td>Si-Cu alloy</td>
</tr>
<tr>
<td>(60)</td>
<td>28</td>
<td>180 - 220</td>
<td>techn. Si, 10 % Cu</td>
</tr>
<tr>
<td>(39)</td>
<td>19.7</td>
<td>250 - 300</td>
<td>techn. Si, no copper</td>
</tr>
<tr>
<td>VII-7</td>
<td>16 ± 7</td>
<td>220 - 260</td>
<td>techn. Si, 5 % Cu</td>
</tr>
<tr>
<td>VII-10</td>
<td>24 ± 2</td>
<td>172 - 198</td>
<td></td>
</tr>
</tbody>
</table>

of copper to the inner of the particle. It has namely been proved by tests with silicon-copper diffusion couples with markers, that copper is the diffusing component of the system (126). For the methylchlorosilanes formation at 343 °C it was calculated (68, p.179) that the rate of diffusion in the solid, i.e. the supply of silicon atoms to the surface, is about 3 orders in magnitude higher than is necessary for the chemical reaction. This implies that in the methylchlorosilanes synthesis this step has no rate control. A similar calculation for the chlorosilanes synthesis at 260 °C reveals that the diffusion rate is more than 100 times higher than the consumption of silicon by the chemical reaction. This excludes that diffusion in the solid is the slowest reaction step in a normally conducted chlorosilanes synthesis. Evidence has been obtained that reaction of chlorine with silicon-copper is at 215 °C controlled by the diffusion in the solid (VII-11).

As the formation of chlorosilanes is accompanied by a considerable heat production (-52 kcal/mol trichlorosilane, equation V.4), the desorption of the products - step 5 - is not likely to be rate-controlling, due to the high energy of the products in the adsorbed state. The heat of desorption of trichlorosilane will not differ much from that of tetra-chlorosilane, which is 8 kcal/mol (III-3). The heat of formation of adsorbed trichlorosilane, about -60 kcal/mol is far in excess of this value. Experimental support of this conclusion is the observed absence of the influence of admixture of trichlorosilane upon the rate of the
chlorosilanes formation (48).

The remaining possibilities are that adsorption - step 2 - or the surface reaction are rate-determining. In both cases the Hougen and Yang-schemes (137) suggest a rate equation which contains the partial pressure of the reactant. Equation (V.25) is a relation, similar to the one that has been derived for the formation of dimethylchlorosilane (IV-5). It implies that the reactant adsorbs on one active site on the surface and that a subsequent surface reaction is the slowest step.

\[ R = \frac{kK_A \cdot p_A}{1 + K_A \cdot p_A + K_R \cdot p_R} \] (V.25)

A recent publication (48) deals with the kinetics of the hydrogen chloride reaction with silicon of high purity and with 'purified' technical silicon. The authors concluded that the reaction order in reactant and products is close to zero. Only at very small hydrogen chloride pressure has a reaction order in hydrogen chloride of 0.51 been observed (39). The former observation is in contradiction with a rate equation comprising the adsorption of hydrogen chloride as the slowest step. It does support, however, a kinetic description involving a reaction step on the surface as the slowest, such as equation (V.25). An explanation of the observed small dependency of the partial pressure of hydrogen chloride can be found in the high degree of coverage of the active surface by molecules of the reactant. On examination of equation (V.25), it can be seen that if the product \( kA \cdot pA \) is large compared to \( 1 + KR \cdot pR \), the dependency of the partial pressure of reactant \( A \) disappears. This may be the case for the reaction of hydrogen chloride with silicon, which shows the following estimation of the adsorption equilibrium constant of hydrogen chloride.

From a gaschromatographic study of the adsorption of hydrogen chloride on silicon some information about the coverage of the surface was obtained (54). At a hydrogen chloride pressure of 30 mm of mercury and a temperature of 150 °C, \( 10^{-6} \) mol was adsorbed per gram of technical silicon with specific surface area 0.1 m²/g. If the number of silicon surface atoms in the (1 1 1)-plane, which is most favoured thermodynamically (147), is taken to be \( 8 \times 10^{18} \) per m² (19), the coverage of the surface, when \( 6 \times 10^{17} \) molecules (= \( 10^{-6} \) mol) are adsorbed is 0.75. The adsorbed amount on silicon-copper contact mixtures at 230 °C is of
roughly the same magnitude (69). Introducing the above figures in the equation for the equilibrium constant of adsorption of hydrogen chloride on silicon (V.26), a value:

$$K_{HCl} = 76 \text{ atm}^{-1}$$

is obtained, valid for a temperature of 150 °C. The value is sufficiently high to obscure the influence of the hydrogen chloride pressure down to a partial pressure of 0.1 atm.

$$K_{HCl} = \frac{\theta_{HCl}}{P_{HCl} \cdot (1-\theta_{HCl})} \quad (V.26)$$

The apparent lack of analogy with the methylchlorosilanes synthesis with respect to the kinetics is thus partly caused by the high adsorption equilibrium constant of hydrogen chloride, which causes a high degree of coverage of the surface. The equation describing the rate of reaction of hydrogen chloride with silicon-copper now follows from (V.25) and is valid for not too small pressures of hydrogen chloride:

$$R = \text{constant} \quad (V.27)$$

The reaction products, principally dichlorosilane and trichlorosilane, are formed in amounts varying with the time of reaction (VII-7). In the experiments, very short contact times were applied, i.e. below 0.5 s. At the smallest contact time, the highest content of dichlorosilane was formed: 24 mol %. In a study by Bazant c.s. (60) on the mechanism of the copper catalyzed hydrogen chloride reaction with silicon, formation of the products di-, tri- and tetrachlorosilane in parallel reactions is suggested. The highest dichlorosilane content found was about 6 mol % at 220 °C and with a contact time of 44 s. The experiments were conducted with contact times of more than 3 s. Cause of the contradictory results may be partly the difference between the ranges of contact time studied.

The present insight and the newly obtained kinetic information (VII-7) enable some elucidation on the chemical reactions playing a rôle in the chlorosilanes synthesis and allow the determination of some kinetic parameters. The reactions responsible for the product of the chlorosilanes synthesis are given in Table 20. The rates of formation of dichlorosilane and trichlorosilane, considering in this instance only the reactions
Table 20. Reactions occurring in the chlorosilanes synthesis

<table>
<thead>
<tr>
<th></th>
<th>Reaction</th>
<th>Rate Expression</th>
<th>( k_x )</th>
<th>( k_y )</th>
<th>( k_z )</th>
<th>( k_w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 2 \text{HCl} + \text{Si} ) (Cu) ( \rightarrow ) ( \text{H}_2\text{SiCl}_2 )</td>
<td>( k_1 ) ( \rightarrow ) ( \text{H}_2\text{SiCl}_2 )</td>
<td>(V.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( 3 \text{HCl} + \text{Si} ) (Cu) ( \rightarrow ) ( \text{HSiCl}_3 + \text{H}_2 )</td>
<td>( k_2 ) ( \rightarrow ) ( \text{HSiCl}_3 + \text{H}_2 )</td>
<td>(V.4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( \text{H}_2\text{SiCl}_2 + \text{HCl} ) (Si,Cu) ( \rightarrow ) ( \text{HSiCl}_3 + \text{H}_2 )</td>
<td>( k_3 ) ( \rightarrow ) ( \text{HSiCl}_3 + \text{H}_2 )</td>
<td>(V.18)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( 4 \text{HCl} + \text{Si} ) (Cu) ( \rightarrow ) ( \text{SiCl}_4 + 2 \text{H}_2 )</td>
<td>( k_4 ) ( \rightarrow ) ( \text{SiCl}_4 + 2 \text{H}_2 )</td>
<td>(V.7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>( \text{HSiCl}_3 + \text{HCl} ) (Si,Cu) ( \rightarrow ) ( \text{SiCl}_4 + \text{H}_2 )</td>
<td>( k_5 ) ( \rightarrow ) ( \text{SiCl}_4 + \text{H}_2 )</td>
<td>(V.20)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1, 2 and 3 are given by the relations:

\[
\frac{d(p_{\text{H}_2\text{SiCl}_2})}{d(t)} = k_1 \cdot p_{\text{HCl}} - k_3 \cdot p_{\text{H}_2\text{SiCl}_2} \cdot p_{\text{HCl}} \quad (V.28)
\]

\[
\frac{d(p_{\text{HSiCl}_3})}{d(t)} = k_2 \cdot p_{\text{HCl}} + k_3 \cdot p_{\text{H}_2\text{SiCl}_2} \cdot p_{\text{HCl}} \quad (V.29)
\]

As the exponents of the hydrogen chloride pressure are close to zero \((a,c,d \approx 0)\) and reaction 3 is assumed to be of first order in dichlorosilane, the relations may be written:

\[
\frac{d(p_{\text{H}_2\text{SiCl}_2})}{d(t)} = k_1 - k_3 \cdot p_{\text{H}_2\text{SiCl}_2} \quad (V.30)
\]

\[
\frac{d(p_{\text{HSiCl}_3})}{d(t)} = k_2 + k_3 \cdot p_{\text{H}_2\text{SiCl}_2} \quad (V.31)
\]

For very short contact times, the molar ratio between trichlorosilane and dichlorosilane in the product will approach the value \( k_2/k_1 \). In Figure 18 the molar ratios are plotted versus contact time for two experiments at 260 °C and a 5 wt % copper-containing contact mixture (VII-7). The line intercepts the ordinate at a value of 3.1. In Table 21 the calculated ratios of the \( k_2/k_1 \) values for some other experiments are listed. The data were obtained by the method of least squares, assuming a linear relationship between the molar ratios and the contact time, which is permitted for the low values of the contact time. As an average value will be taken:

\[
\frac{k_2}{k_1} = 3.1 \quad [260 \degree \text{C}, 5 \text{ wt } \% \ \text{Cu}] \quad (V.32)
\]
The ratio between trichlorosilane and dichlorosilane is also the rate of the silicon conversion, which was determined to be:

$$R = 0.126 \pm 0.012 \text{ mmol Si/g Si min \ [260 °C]} \text{ (V.27)}$$

Summing equations (V.30) and (V.31) and introducing equation (V.32), enables calculation of the rate constants. For the conversion of (mmol.g\(^{-1}.min^{-1}\)) into (atm.s\(^{-1}\)), the molar volume of the chlorosilanes at 260 °C and 1 atm was taken: 0.047 m\(^3\) and the void volume of the contact mixture: 0.41 cm\(^3\).g\(^{-1}\). Thus 1 mmol.g\(^{-1}.min^{-1}\) = 1.92 atm.s\(^{-1}\).

$$k_1 = 0.06 \text{ atm.s}\(^{-1}\) \text{ [260 °C]}$$

$$k_2 = 0.18 \text{ atm.s}\(^{-1}\) \text{ [260 °C]}$$

The values are expected to be accurate within 20%. Integration of equations (V.30) and (V.31) gives (V.33) and (V.34). Fitting the equations to the experimental results (VII-7) yields values for \(k_3\), which are also given in Table 21.

$$p_{H_2SiCl_2} = \frac{k_1}{k_3} (1 - \exp(-k_3.t)) \text{ (V.33)}$$

$$p_{HSiCl_3} = (k_1 + k_2).t - \frac{k_1}{k_3} (1 - \exp(-k_3.t)) \text{ (V.34)}$$
For 260 °C an average value follows:

\[ k_3 = 2.1 (\pm 0.8) \text{ s}^{-1} \]

Introducing the evaluated rate constants into equations (V.33) and (V.34) and converting the partial pressures into mol percentages, gives:

\[ \text{mol} \% (\text{H}_2\text{SiCl}_3) = \frac{12.1}{t} (1 - \exp(-2.1xt)) \]  

(V.35)

Already after a contact time of 10 seconds the dichlorosilane content will be as low as 1.2 mol %, which is consistent with the findings of Joklik and Bazant (60).

The range of contact times studied does not permit evaluation of the constants \(k_4\) and \(k_5\). The qualitative conclusion that can be drawn is that their numerical value must be several orders of magnitude smaller than the values of \(k_1\) and \(k_2\), because of the negligible amounts of tetrachlorosilane formed at short contact times at 260 °C.

V-5. Mechanism of the reaction of hydrogen chloride with silicon-copper

In analogy to the methylchlorosilanes formation the initiating step, being a chlorination of silicon by cuprous chloride is proposed. Surface-bound silicon dichloride is the precursor of trichlorosilane.

A transcription of the scheme as given for the reaction of methylchloride with silicon under catalytic action of copper should account for the differences in the product composition of the processes. It is evident from the available information that the schemes have to comprise the formation of dichlorosilane and trichlorosilane, as they appear as the only products formed in primary reactions. Because of a rather fast secondary reaction, converting dichlorosilane into trichlorosilane, and a slower one converting trichlorosilane into tetrachlorosilane, the literature seemed only concerned about trichlorosilane.

The formation of trichlorosilane is believed to proceed via a surface compound of type \(\text{SiCl}_2\) according to equation (V.36) (60):

\[ 2 \text{HCl} + \text{Si} \xrightarrow{\Delta} \text{SiCl}_2 + \text{H}_2 \]  

(V.36)

With one more hydrogen chloride molecule, trichlorosilane is formed:
HCl + SiCl₂ $\xrightarrow{\text{A}}$ HSiCl₃ \hspace{1cm} (V.37)

The scheme is the analogue of that for the formation of alkyltrichlorosilane (IV-4). Another reaction scheme from the literature proposes an initiation reaction of hydrogen chloride with aluminium, forming aluminium chloride and surface-bound silicon monohydride (105). Aluminium is often present as an impurity of silicon. The second step is reaction of the silicon hydride with copper. Then the silicon atom is sufficiently reactive for successful hydrogen chloride attack, to form chlorosilanes and chloropolysilanes. For the formation of chloropolysilanes, compounds of general formula SiₙCl₉₋₂n+₂, by reaction of chlorine with silicon at low temperatures the plausible mechanism has been given already in 1914 by Martin (80). When the surface of a silicon crystal is chlorinated to the extent that a chain of silicon atoms binds two chlorine atoms each, the chain may leave the surface when the atoms at the ends are chlorinated once more. A schematic representation of the intermediate state is as follows:

![Schematic representation of intermediate state](image)

At the lowest possible reaction temperature of about 180 °C, the longest chains can be expected, because enhanced cleavage of the silicon-silicon bonds will occur with increasing temperature. Polychlorosilanes containing as much as 14 silicon atoms have been detected at 180 °C (8). At 350 °C the reaction of chlorine with silicon leads almost exclusively to tetrachlorosilane. Polychlorosilanes with some chlorine atoms substituted by hydrogen, are obtained by reacting hydrogen chloride with silicon or silicon-copper (105).

It can be stated conclusively that the occurrence of doubly chlorinated silicon atoms on the silicon surface is evident when hydrogen chloride or chlorine are involved. For the formation of trichlorosilane this is an argument in favour of the scheme as is given in the equations (V.36) and (V.37). The reaction intermediate SiₐCl₂ is presumably formed from silicon and cuprous chloride; the motivation has largely been given in IV-3 and IV-7. The scheme, completely analogous to the scheme in IV-4-3
for the primary formation of trichlorosilane is as follows:

\[
\begin{align*}
CuCl + \text{Si} & \rightarrow SiCl + Cu \quad (1) \\
HCl + Cu & \rightarrow Cu(\text{ClH}) \quad (2) \\
Cu(\text{ClH}) & \rightarrow CuCl + \frac{1}{2}H_2 \quad (3) \\
CuCl + SiCl & \rightarrow SiCl_2 + Cu \quad (4) \\
Cu(\text{ClH}) + SiCl_2 & \rightarrow HSiCl_3 + Cu \quad (5)
\end{align*}
\]

The copper-hydrogen chloride complex decomposes partly - step 3 - thus creating an excess of chlorinated copper, so that part of the SiCl will be chlorinated once more - step 4. Reaction of silicon dichloride with hydrogen chloride leads to trichlorosilane.

The formation of dichlorosilane:

\[
\begin{align*}
CuCl + \text{Si} & \rightarrow SiCl + Cu \quad (6) \\
HCl + Cu & \rightarrow Cu(\text{ClH}) \quad (7) \\
Cu(\text{ClH}) + SiCl & \rightarrow HSiCl + CuCl \quad (8) \\
Cu(\text{ClH}) + HSiCl & \rightarrow H_2SiCl_2 + Cu \quad (9)
\end{align*}
\]

The formation of monochlorinated silicon is believed to initiate the process. Cuprous chloride is regenerated during step 8 and will rapidly chlorinate silicon atoms appearing in the surface layer. After adsorption of a hydrogen chloride molecule on a copper atom - step 7 - a hydrogen atom from the copper-hydrogen chloride complex will substitute a silicon-lattice bond - step 8. This formation of the reaction intermediate HSiCl is believed to be the slowest step of the process. Hydrochlorination by adsorbed hydrogen chloride will form dichlorosilane in adsorbed state - step 9 - and desorption follows.

The secondary formation of trichlorosilane proceeds on the contact mixture surface. This is evident from the small value of the rate of reaction (V.18) in the gas phase (see V-3) compared to that when a contact mixture surface is present (see V-4).
Adsorbed dichlorosilane undergoes dehydrogenation - step 11 - and forms an extra amount of silicon dichloride.

The above schemes comprise the reaction rate constants $k_2$ and $k_1$ in the rates of steps 5 and 9, provided these steps are rate determining. The ratio $k_2/k_1$ thus equals the ratio of monochlorinated and dichlorinated silicon atoms on the surface. The secondary reaction rate constant $k_3$ is related to the adsorbed amount of dichlorosilane and its rate of decomposition, step 11.
CHAPTER VI

ETHYLCHLOROSILANES

The direct synthesis of ethylchlorosilanes can be conducted with a selectivity of 76% in a fixed-bed process at 350 °C when high gas-velocities are applied. Admixture of ethylene will suppress the formation of ethyltrichlorosilane.

VI-1. Introductory considerations

Ethylchlorosilanes may serve as precursors of silicones as do methyl- and phenylchlorosilanes. The resulting ethylsilicones have a disadvantage compared to the other groups, consisting in the relatively low stability of the ethyl group. Above 140 °C ethylsilicones will suffer from oxidation when exposed to air. This is about 60 degrees C lower than the stability limit of methylsilicones and 160 degrees C lower than that of phenylsilicones. The economic importance might, however, grow because ethylchloride is cheaper than methylchloride. Moreover, for one weight unit of ethylsilicones, 1.54 weight unit of diethyldichlorosilane is required; this figure is more favourable than for methylsilicones from dimethyldichlorosilane, where it is 1.75. In equation (VI.1) such theoretical conversion is schematized:

\[
(C_2H_5)_2SiCl_2 + H_2O \rightarrow ((C_2H_5)_2SiO)n + 2 HCl \quad (VI.1)
\]

For purposes where the thermal stability is not the principal requirement, ethylsilicones may become a cheaper alternative when the base products, the ethylchlorosilanes could be manufactured for the same or even somewhat higher price as methylchlorosilanes. Ethyldichlorosilane is an interesting compound owing to the presence of a silicon-hydrogen bond, which furnishes possibilities for substitution of the hydrogen atom by aromatic groups or addition of olefinic groups. A number of patents on this topic appeared (e.g. 30, 32, 34). After such a conversion, hydrolysis and polycondensation may yield silicones with special properties.
Ethylchlorosilanes can be prepared in a direct synthesis from ethylchloride and silicon. The process is catalyzed by copper, which was discovered in 1945 by Rochov. Some of the compounds which are found in the product of the reaction between ethylchloride and silicon can be thought to be formed according to the overall schemes given in Table 22.

**Table 22. Overall reactions in the ethylchlorosilanes synthesis.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \text{C}_2\text{H}_5\text{Cl} + \text{Si} \rightarrow (\text{C}_2\text{H}_5)_2\text{SiCl}_2$</td>
<td>(VI.2)</td>
</tr>
<tr>
<td>$3 \text{C}_2\text{H}_5\text{Cl} + \text{Si} \rightarrow \text{C}_2\text{H}_5\text{SiCl}_3 + 2 \text{C}_2\text{H}_4 + \text{H}_2$</td>
<td>(VI.3)</td>
</tr>
<tr>
<td>$2 \text{C}_2\text{H}_5\text{Cl} + \text{Si} \rightarrow \text{C}_2\text{H}_5\text{SiHCl}_2 + \text{C}_2\text{H}_4$</td>
<td>(VI.4)</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl}$</td>
<td>(VI.5)</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{Cl} \rightarrow 2 (\text{CH}_x) + (2-x) \text{H}_2 + \text{HCl}$</td>
<td>(VI.6)</td>
</tr>
<tr>
<td>$3 \text{HCl} + \text{Si} \rightarrow \text{SiHCl}_3 + \text{H}_2$</td>
<td>(VI.7)</td>
</tr>
</tbody>
</table>

Because of the ease of the catalytic cracking of ethylchloride (equations VI.5 and VI.6), the chemistry of the direct synthesis of ethylchlorosilanes is more complicated than that of methylchlorosilanes. In the product not only the compounds are found, as given by the schemes in Table 22, but numerous other compounds, such as methane, ethane and butane as cracked products, methylchlorosilanes, mixed methyl-ethylchlorosilanes and compounds containing more than one silicon atom. An extensive listing of the products is given in (62).

The selectivity of the process is low compared to that of the methylchlorosilanes synthesis. The highest contents of diethyl dichlorosilane reported up to now is 65%, the rest is made up mainly from ethyltrichlorosilane, ethyldichlorosilane, etc. Table 23 gives some experimental results obtained by various investigators. The data do not give more than a general impression of the obtainable selectivity and reactivity. They do indicate, however, that the employed temperatures lie between 300 and 360 °C, that the copper content should be below 15% and that a fluidized bed reactor seems preferable.

As for additives to or impurities in the contact mixture about the same applies as in the methylchlorosilanes synthesis. Small amounts of metals
or metal chlorides may have a large influence upon reactivity and selectivity. Calcium, aluminium, titanium and cobalt usually increase the reactivity and decrease selectivity \((776, 27)\). Lead, bismuth and antimony in concentrations of 0.001% \((776)\) and zinc, nickel, lithium and zirconium in concentrations of 0.1 - 3% increase selectivity but decrease the reactivity \((776, 74)\). Manganese, phosphorus and lead, bismuth and antimony in concentrations higher than 0.005% can be considered as poisonous, while iron contents up to 10% show no influence \((776)\). Not only is the effect of an additive dependent upon its concentration, but also upon possible other impurities or additives. Contact mixtures with 0.1 - 0.5% zinc chloride or cadmium chloride have been shown to perform as favourably in ethylchlorosilanes synthesis \((VII-8)\) as in methylchlorosilanes synthesis \((VII-5, 786)\). Their promoting effect in the latter process has been discussed in IV-8.

<table>
<thead>
<tr>
<th>Temp ((^\circ C))</th>
<th>Cont. mixture</th>
<th>Reactor type</th>
<th>DH(^a)</th>
<th>DH(^a)</th>
<th>T(^a)</th>
<th>Reactivity(^b)</th>
<th>Ref.</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>pills</td>
<td>fixed b.</td>
<td>26</td>
<td>18</td>
<td>27</td>
<td>((66)) 1945</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>powder</td>
<td>fixed b.</td>
<td>40</td>
<td>30</td>
<td>30</td>
<td>((67)) 1952</td>
<td></td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>alloy</td>
<td>fluid-b.</td>
<td>20</td>
<td>18</td>
<td>50</td>
<td>184 ((6)) 1956</td>
<td></td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>&quot;</td>
<td>&quot;</td>
<td>38</td>
<td>23</td>
<td>24</td>
<td>400 &quot; &quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>&quot;</td>
<td>&quot;</td>
<td>48</td>
<td>26</td>
<td>18</td>
<td>500 &quot; &quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>&quot;</td>
<td>&quot;</td>
<td>30</td>
<td>34</td>
<td>30</td>
<td>395 ((6)) 1957</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>&quot;</td>
<td>stirred b.13</td>
<td>37</td>
<td>14</td>
<td>39</td>
<td>44 &quot; &quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>&quot;</td>
<td>fixed b.</td>
<td>13</td>
<td>13</td>
<td>3</td>
<td>30 &quot; &quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>&quot;</td>
<td>&quot;</td>
<td>13</td>
<td>13</td>
<td>3</td>
<td>30 &quot; &quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>365</td>
<td>fluid-b.</td>
<td>fixed b.</td>
<td>36</td>
<td>25</td>
<td>39</td>
<td>((11)) 1960</td>
<td></td>
<td></td>
</tr>
<tr>
<td>365</td>
<td>&quot;</td>
<td>fluid-b.</td>
<td>41</td>
<td>16</td>
<td>157</td>
<td>((11)) 1962</td>
<td></td>
<td></td>
</tr>
<tr>
<td>365</td>
<td>&quot;</td>
<td>&quot;</td>
<td>18.3</td>
<td>25</td>
<td>36</td>
<td>500 &quot; &quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>Si+Cu(^{\dagger})</td>
<td>&quot;</td>
<td>64</td>
<td>8</td>
<td>21</td>
<td>((46)) 1963</td>
<td></td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>Si+Cu(^{\dagger})</td>
<td>fixed b.</td>
<td>75</td>
<td>10</td>
<td>15</td>
<td>135 ((VII-8-5)) 1966</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{\dagger}\)Composition of product in wt \%, D - Et\(_2\)SiCl\(_2\), DH - EtSiHCl\(_2\), T - EtSiCl\(_3\)

\(^{\dagger}\)in g silanes/kg contact mixture. hour

\(^{\dagger}\)prepared from Si + CuCl.
VI-2. The influence of the temperature

The influence of the temperature on the combined content of the dichloro-compounds is negligible. The overall activation energy for the ethylchlorosilanes formation is 20 kcal/mol, which is about 5 kcal/mol lower than for the methylchlorosilanes formation.

As the most favourable temperature of reaction of ethylchloride with a silicon-copper contact mixture rather high values are suggested in the literature. For the temperature where the highest selectivity is claimed to be reached, values of 355 °C (118), 370 °C (118) and 380 °C (74) are reported. The highest selectivity mentioned in the literature was, however, obtained at 320 °C in a fluidized bed reactor (46), while in a fixed bed at 330 °C an unparallelled selectivity of 75 mol% has been obtained (VII-8-5). As an illustration of the influence of the temperature, Figure 19 gives the contents of diethyldichlorosilane and ethyldichlorosilane in an experiment (ECS-10) where the temperature was increased step-wise from 260 to 300 °C. In the reaction of methylchloride with a contact mixture, the lowest possible reaction temperatures seem to give the highest selectivity. It may not be excluded that some secondary reaction comprising ethyldichlorosilane and diethyldichlorosilane is responsible for this difference.

When the content of ethyltrichlorosilane is considered, it is evident that this is hardly influenced by the temperature, which is shown with the upper line in Figure 20 (data in VII-8-4). As the product of the ethylchlorosilanes synthesis mainly consists of the three afore-mentioned compounds, it follows that the combined content of diethyldichlorosilane and
ethyl dichlorosilane is not influenced by the temperature either. When a large amount of experimental results is studied it even becomes doubtful, whether a relation exists between the ratio of diethyl dichlorosilane and ethyl dichlorosilane and the temperature.

The activation energy for the formation of ethyl chlorosilanes has been determined at \(21 \pm 2\) kcal/mol for an alloy containing 24% copper \((70, 118)\) and 18 kcal/mol for a mixture of silicon and 10% copper \((77)\).

For a contact mixture containing 4 - 6% copper, prepared from cuprous chloride and silicon and containing about 1% cadmium chloride, a value of \(20 \pm 3\) kcal/mol was determined \((VII-8-4)\).

Compared to values of the activation energy quoted for the reaction of methyl chloride with contact mixture, there appears to be a difference of about 5 kcal/mol. It may be speculated that this difference is caused by the higher polarizability of the carbon-chlorine bond in ethyl chloride than the one in methyl chloride (see also IV-7).

From experiments with small contact times it can be concluded that diethyl dichlorosilane, ethyl dichlorosilane and ethyl trichlorosilane are formed in parallel reactions \((VII-8-5)\). The formation of these compounds have been schematized in the equations \((VI.2 - VI.4)\). The analogy with the methyl chlorosilanes synthesis is obvious. Compounds of the same type are formed in only slightly different amounts. The same remarkable scattering is found also in the contents of the dichloro-compounds \((VII-8-4)\). Furthermore there is no significant influence of the temperature upon the content of ethyl trichlorosilane, which means that the activation energy applies to the formation of all three compounds. For the formation of cracked gases during the ethyl chlorosilanes synthesis, Bazant has determined an activation energy of 25 kcal/mol \((77)\). This
value comes from the gas production not only accompanying the formation of ethyltrichlorosilane and ethyldichlorosilane but also that accompanying the formation of trichlorosilane and tetrachlorosilane. It is thus probably related with the primary decomposition of ethylchloride (equation VI.5), which does not play an important role when the temperature is kept moderate and well under control.

VI-3. Decomposition of ethylchloride

Thermodynamically, ethylchloride should decompose completely under the conditions of the direct synthesis. Ethylene, when added to the feed adsorbs on silicon and prevents part of the silicon-catalysed cracking.

Cracking of ethylchloride is to be considered as the main complication of the direct synthesis of ethylchlorosilanes:

\[
\text{C}_2\text{H}_5\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl} \quad \text{(VI.5)}
\]

Uncatalyzed decomposition, i.e. the reaction in the gas phase, is a slow process with a considerable activation energy. The rate of reaction is given by (148):

\[
R = 3.8 \times 10^7 \exp\left(-\frac{-32,000}{R_T}\right)(\text{C}_2\text{H}_5\text{Cl}) \quad \text{[400 - 500 °C]} \quad \text{(VI.8)}
\]

It is an endothermic non-radical reaction (\(\Delta H_R = 14.2 \text{ kcal/mol (15)}\)); the hydrogen atom in the resulting hydrogen chloride comes from the second carbon atom (148). From the rate equation it follows that the cracking in the gas phase will not contribute appreciably to the reactions.

Cracking under catalytic action of copper proceeds with formation of hydrogen chloride, ethylene, ethane and hydrogen (5, temperature not mentioned). Up to 320 °C, silicon is not capable of ethylchloride cracking (11), although at 320 °C small amounts of ethylchlorosilanes were formed in the reaction of ethylchloride with silicon (142). Differences in the purity of the silicon specimens may well account for the discrepancy, as it has been established, that many metals and metal chlorides act as catalysts for the decomposition (11, 119, 149, 150). Amongst these are substances often present in the contact mixture, such
as aluminium chloride, ferric chloride, zinc chloride and cuprous chloride.

When technical silicon is used in the contact mixture, and the synthesis is conducted above 320 °C, it is very probable that the cracking of ethylchloride participates in the reactions. When the decomposition equilibrium of ethylchloride is considered (VI.9), it suggests itself at first sight that the presence of ethylene effectuates a shift of this equilibrium towards ethylchloride.

\[ \text{C}_2\text{H}_5\text{Cl} \rightleftharpoons \text{C}_2\text{H}_4 + \text{HCl} \quad (\text{VI.9}) \]

The high value of the equilibrium constant, however, at the temperature of the direct synthesis (\( K = 112 \) at 300 °C (75)), makes it doubtful that addition of ethylene could influence the equilibrium. For instance, at 300 °C the partial pressure of hydrogen chloride, allowed by the presence of silicon, is \( 2 \times 10^{-5} \) (Table 17, p. 80). The equilibrium ratio ethylene/ethylchloride can then be calculated at \( 5.6 \times 10^6 \), and accordingly the addition of ethylene is useless. The arguments indicate, that according to thermodynamics, ethylchloride should decompose completely. This was also shown by an attempt to compute the equilibrium composition in the ethylchlorosilanes system, as was done for methylchlorosilanes (IV-6) and chlorosilanes (V-2). The resulting product at equilibrium consisted purely from chlorosilanes and cracked products. That ethylchlorosilanes are actually formed is therefore a result of the kinetics of the process which obviously appears to prevent complete cracking. Yet, addition of ethylene does influence the product composition, which may follow from Figure 20, where the lower line represents the concentrations of ethyltrichlorosilane for various temperatures when ethylene was added to the ethylchloride-feed (VII-8-4). Presence of ethylene increases the sum of the contents of diethyl dichlorosilane and ethyldichlorosilane from 70 to 80%. Comparable experiments with nitrogen as diluent showed that it is not caused by the dilution (142, VII-8-4). Additional information comes from a study of the combined interaction of ethylchloride and ethylene with silicon. The presence of ethylene largely suppresses the formation of chlorosilanes, while considerable amounts of chlorosilanes are formed without ethylene (142). The latter is also the case when a mixture of hydrogen chloride and ethylene is reacted.
with silicon or silicon-copper (179, 142). It is obvious that in the first case, ethylchloride decomposition is prevented, as it is in all probability hydrogen chloride which gives rise to the chlorosilanes.

From the above considerations, it is clear that ethylene influences the kinetics of the decomposition of ethylchloride on the surface by some preferential adsorption on active sites, capable of this decomposition. As it is observed on silicon as well as on silicon-copper, it is not very speculative, to state that the preferential adsorption of ethylene proceeds on silicon atoms. It prevents cracking of ethylchloride on silicon atoms, and thus lowers the amount of $\text{SiCl}_2$, the intermediate for the formation of ethyltrichlorosilane. When the adsorbed state of ethylene is schematized as:

![Ethylene Adsorption Diagram](image)

the occurrence of silanes of the type $\text{R}_2\text{Si-CH}_2\text{-CH}_2\text{-SiR}_2$ is readily understood (62).

It seems very interesting to investigate the influence of admixture of ethylene upon the direct synthesis of methylchlorosilanes.

VI-4. Secondary reactions in ethylchlorosilanes synthesis

Unlike the methylchlorosilanes synthesis, the product mixture is presumably influenced by secondary reactions, involving the dichlorocompounds.

A number of theoretical possibilities can be suggested to explain a change in the product composition as obtained by primary reactions. Considering the main compounds arising from the interaction of ethylchloride with silicon, i.e. diethylidichlorosilane, ethyltrichlorosilane, ethyldichlorosilane, ethylene and trichlorosilane, some of the overall reactions as listed in Table 24 may have importance.

From the values of the free enthalpy change, given in the table, it follows that not all reactions seem thermodynamically feasible, but the estimated thermodynamic data on ethylchlorosilanes (see II-3) may
Table 24. Secondary reactions

<table>
<thead>
<tr>
<th></th>
<th>Reaction</th>
<th></th>
<th></th>
<th></th>
<th>(\Delta G^\circ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((C_2H_5)_2SiCl_2) (\rightarrow) (C_2H_5SiHCl_2 + C_2H_4)</td>
<td>250 °C</td>
<td>350 °C</td>
<td>450 °C</td>
<td>7.8</td>
</tr>
<tr>
<td>2</td>
<td>(C_2H_5SiCl_3) (\rightarrow) (HSiCl_3 + C_2H_4)</td>
<td></td>
<td></td>
<td></td>
<td>9.2</td>
</tr>
<tr>
<td>3</td>
<td>(2(C_2H_5)_2SiCl_2) (\rightarrow) (C_2H_5SiCl_3 + (C_2H_5)_3SiCl)</td>
<td></td>
<td></td>
<td></td>
<td>-0.30</td>
</tr>
<tr>
<td>4</td>
<td>(SiHCl_3 + HCl) (\rightarrow) (SiCl_4 + H_2)</td>
<td></td>
<td></td>
<td></td>
<td>-13.0</td>
</tr>
<tr>
<td>5</td>
<td>(C_2H_5SiCl_2 + C_2H_5Cl) (\rightarrow) ((C_2H_5)_2SiCl_2 + HCl)</td>
<td></td>
<td></td>
<td></td>
<td>-8.8</td>
</tr>
<tr>
<td>6</td>
<td>(SiHCl_3 + C_2H_5Cl) (\rightarrow) (C_2H_5SiCl_3 + HCl)</td>
<td></td>
<td></td>
<td></td>
<td>-10.2</td>
</tr>
<tr>
<td>7</td>
<td>((C_2H_5)_2SiCl_2 + HCl) (\rightarrow) (C_2H_5SiCl_3 + C_2H_6)</td>
<td></td>
<td></td>
<td></td>
<td>-24.5</td>
</tr>
</tbody>
</table>

be inaccurate for some kcal, so the results must be used with some reservation.

Experimental support for the actual appearance was furnished for the reactions 1, 2 and 6. Reactions 1 and 3 deal in fact with the stability of the key-compound diethyldichlorosilane. Its thermal stability is rather high, and it cannot be decomposed when led over contact mixtures which have been made inactive by contact with air. Already at 300 °C, however, a mixture consisting of silicon and cuprous chloride is capable of some decomposition of diethyldichlorosilane. Table 25 lists the composition of the product when diethyldichlorosilane, diluted with nitrogen, is led over such a mixture with a contact time of 15 seconds. No decomposition of diethyldichlorosilane was observed when it was brought in contact with a mixture of cuprous chloride and quartz powder up to 400 °C. After reduction of the cuprous chloride in the mixture by hydrogen, still no decomposition occurred up to 400 °C. Above

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Composition (wt %)</th>
<th>EtSiCl_3</th>
<th>EtSiHCl_2</th>
<th>Et_2SiCl_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td></td>
<td>3</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td>310</td>
<td></td>
<td>5</td>
<td>40</td>
<td>55</td>
</tr>
<tr>
<td>320</td>
<td></td>
<td>3</td>
<td>46</td>
<td>51</td>
</tr>
</tbody>
</table>
400 °C all tested mixtures, including inactive mixtures and alloys of silicon and copper appeared to induce decomposition under formation of ethyldichlorosilane and ethyltrichlorosilane.

The reverse of reaction 1 proceeds under quite different circumstances. At ethylene-pressures of 26 - 112 atm and a temperature of 300 °C part of the ethyldichlorosilane can be converted into diethyldichlorosilane after some hours of reaction (30, 32). No catalysts of the Friedel Crafts-type (e.g. AlCl₃) should be present in order to avoid cracking of the products (37). The same applies to the reverse of reaction 2. At 300 °C more than half the trichlorosilane can be converted in 16 hours of reaction with ethylene-pressures between 26 and 78 atm. (37).

Reaction 3 represents a rearrangement. In analogy to the methylchlorosilanes system the participation of this reaction must be considered of negligible importance under the conditions of the direct synthesis.

Reaction 6 was studied in the gas phase and appeared to proceed at 360 °C with a contact period of 1.5 seconds (25). From the larger part of the trichlorosilane introduced, however, tetrachlorosilane was formed. This can be credited to reaction 4, which proceeds fast at 360 °C (V-3). The authors assume the conversions to proceed via radical interactions. Above 450 °C the compound diethylchlorosilane was also claimed to be formed. This observation, however, must be considered doubtful because of the low stability of the substance and the improbability of its gas-chromatographic separation when ethyltrichlorosilane is present (VII-8-2). The occurrence of hexachlorodisilane seems much more probable under the experimental circumstances and this may account for the misinterpretation of the analysis. When reaction 6 already proceeds in the gas phase, it will certainly participate when a reactive surface is available. The reaction does not contribute, however, to a favourable product composition, as the resulting hydrogen chloride will not give rise to dichloro-compounds.

Reaction 5 is the analogue of 6. As the content of ethyldichlorosilane is usually much higher than that of trichlorosilane, its contribution to the formation of diethyldichlorosilane can not be excluded. It would provide a satisfactory explanation of the sometimes observed increasing ratio diethyldichlorosilane/ethyldichlorosilane with increasing temperature (VII-8-4 and Figure 19, p.97). Differences between the temperature depen-
dency of the rates of reactions 1 and 5 may account for the fact that reaction 1 does not play an important rôle in the temperature region below 300 °C. The same applies to the reactions 2 and 6, which also function in opposite directions. Their net effect will depend upon the excess in the amount of ethylchloride but it is actually a decomposition of ethylchloride.

Reaction 7 is included to show a theoretical possibility which is highly favoured thermodynamically. There is, however, no experimental result available, although ethane is always present in considerable amounts in the cracked gases (779).

VI-5. Conclusions

The copper-catalyzed reaction of ethylchloride with silicon shows close resemblance with that of methylchloride. Not only the optimum conditions of both processes are about the same, but also the activation energy and the reaction rates differ only slightly. Even the distribution of the ethylchlorosilanes in the product, apart from a somewhat lower selectivity is essentially the same as in the methylchlorosilanes product. Under the conditions of the direct synthesis, ethylchloride will decompose and the reaction schemes for the formation of ethylchlorosilanes thus comprise the formation of ethylene and the reaction of the hydrogen chloride formed. The relevant arguments in favour of the reaction schemes have been discussed in IV-3 and IV-5, the schemes have been given in IV-4.

Reliable kinetic information is hard to obtain, due to the complexity of the system. The primary formation of ethylchlorosilanes has to be studied more extensively under conditions as described in VII-8-5 and may lead to a further demonstration of the analogy to the methylchlorosilanes formation.
CHAPTER VII

EXPERIMENTS

The techniques used to obtain some of the information discussed in the preceding chapters are described. Each section in this chapter contains the results of a set of experiments, with a discussion of the results. Reference is made to the chapter where the results are placed in the context of the subject discussed.

VII-1. Specification of the silicon and the contact mixture

The silicon used in the experiments was technical silicon with main impurities: 0.4% Fe, 0.1% Al, 0.3% Ca + Mg, and traces of Cu, Ti, Cd, Sr, Ni, Mn, and K, which could only be detected by X-ray fluorescence. As, Sb, Pb, Bi, Sn and P could not be detected, which means that their concentrations are smaller than 0.05%. Only minor modifications have sometimes been applied:

- Iron, introduced by the grinding procedure was usually removed by fluidizing the silicon for some hours with air at room temperature, while a permanent magnet was hanging in the upper part of the bed. This treatment reduces the iron-content to about 0.2%.

- Chemical purification of the silicon was carried out by extraction with hydrochloric acid on a steam bath and subsequent washing with distilled water. The iron-content decreased substantially when the extraction was performed for some days. The iron-content may become as low as 0.001%. Also the aluminium content decreases somewhat by this treatment, for example, down to 0.04%.

- In order to obtain a sharper sieve fraction, the silicon has sometimes been washed with distilled water. Frequent decantation removed most of the fines. After filtration and drying at 120 °C the appearance of the dust-free specimen was brighter than the same unwashed.

Cuprous chloride was prepared by a standard method (127, p.154).

Contact mixtures were prepared from silicon, cuprous chloride and additives, if required, by thorough mixing. In a glass reactor the mixture was slowly heated under a stream of inert gas until the re-
duction of cuprous chloride started. This occurred usually between 260 and 300 °C. The start of the reaction was indicated clearly by a temperature-rise of the mixture and by the production of tetrachlorosilane, according to the equation:

\[ n \text{ Si} + 4 \text{ CuCl} \rightarrow 4 \text{ Cu} + (n-1) \text{ Si} + \text{ SiCl}_4 \]  

(VII.1)

Depending on the purpose of the contact mixture, a direct synthesis experiment could be started right away, or the mixture was allowed to cool to room temperature and stored in a vacuum exsiccator above sulfuric acid. In the latter case contact with air was not avoided, which may have caused the quality of the contact mixture to deteriorate. When a test was conducted with a charge of such a contact mixture, it was usually etched for some minutes with hydrogen chloride in the course of heating to the required reaction temperature. A small stream of hydrogen chloride was then added to the inert gas stream when the temperature was between 130 and 160 °C. This sufficiently activated the contact mixture to prevent the occurrence of an induction period.

VII-2. Pulse chromatography to obtain heats of adsorption (III-3)

The heat of adsorption of several chlorides on silicon-copper contact mixtures has been determined below 132 °C. The values increase from -5 to -10 kcal/mol in the sequence HCl, MeCl, SiCl₄, EtCl, Me₂SiCl₂, Me₂SiCl₃

-2-1. Introduction

When a pulse of a compound is carried by a stream of inert gas through a column containing a powdered solid, interaction between the compound and the surface of the solid will cause a difference between the retention times of the compound and the inert gas. The operation of this "gas-solid" chromatography is analogous to gas-liquid chromatography, applied for analytical purposes.

The residence time of an inert gas pulse (tₙ) is also the time that the adsorbent pulse remains in the gas phase. This is a measure of the opportunity to adsorb. The difference between the residence times of
adsorbent \( t_r \) and inert gas \( t_m \) is the time that the adsorbent is in the adsorbed state; it is a measure of the opportunity to desorb. The relations can be written as follows:

\[
\text{amount adsorbed} = \text{adsorption rate} \times \text{adsorption time} \quad \text{(VII.2)}
\]

\[
\text{amount desorbed} = \text{desorption rate} \times \text{desorption time} \quad \text{(VII.3)}
\]

For the column it holds that the total amounts adsorbed and desorbed are equal:

\[
\frac{\text{ads.rate}}{\text{des.rate}} = \frac{t_r - t_m}{t_m} \quad \text{(VII.4)}
\]

The quantities "adsorption rate" and "desorption rate" are closely related to \( k_{\text{ads}} \) and \( k_{\text{des}} \) (the rate constants in equations (VII.5) and (VII.6)).

\[
r_{\text{ads}} = k_{\text{ads}} \cdot p_A \cdot (1 - \theta) \quad \text{(VII.5)}
\]

\[
r_{\text{des}} = k_{\text{des}} \cdot \theta \quad \text{(VII.6)}
\]

These relations apply to the Langmuir-type of adsorption \(^{37}\) and furnish the adsorption equilibrium constant in case \( r_{\text{ads}} = r_{\text{des}} \):

\[
K_A = \frac{k_{\text{ads}}}{k_{\text{des}}} = \frac{\theta}{p_A \cdot (1 - \theta)} \quad \text{(VII.7)}
\]

It has been shown \(^{28}\) that there is a linear dependence between the ratio \( (t_r - t_m)/t_m \) and \( K_A \), the proportionality determined by the gas velocity \( (u) \), the available surface area \( (A) \), the number of active sites per unit of surface area \( (N_s) \), and the pulse volume \( (V) \):

\[
K_A = \frac{t_r - t_m}{t_m} \cdot F(u, A, N_s, V) \quad \text{(VII.8)}
\]

By measuring the retention time at various temperatures, the heat of adsorption of the compound may be calculated using the expression:

\[
K_A = K^0 \cdot \exp\left( \frac{-\Delta H_{\text{ads}}}{R_g T} \right) \quad \text{(VII.9)}
\]
From (VII.8) and (VII.9) follows:

\[
\ln\left(\frac{t_r - t_m}{t_m}\right) = - \frac{\Delta H_{\text{ads}}}{R T} + \ln\left(\frac{R^0}{F}\right)
\]  

(VII.10)

Plotting the left-hand side of (VII.10) versus 1/T yields \(\Delta H_{\text{ads}}\).

It can be expected that the volume of the pulse influences the value \((t_r - t_m)/t_m\) for a given adsorbent. The dependency is shown in Figure 21, where the relative retention of ethylchloride is plotted versus the amount injected, for various temperatures. Extrapolation to zero pulse volume seems rather speculative, especially for the lower temperatures. For this reason, the suggestion in the literature that a theoretically justified relative retention is obtained by extrapolation to zero pulse volume (23) has not been followed. It is clear that for different pulse volumes different adsorption heats will be determined if the heat of adsorption is dependent upon the coverage of the surface. It will appear possible to make an extrapolation to zero pulse volume for the heats of adsorption, which seems more reliable than for the relative retention.

Figure 21
Relative retention of ethylchloride

-2-2. Method of measurement

A stainless steel tube of length 3.20 m and inner diameter of 7 mm was filled with a silicon-copper contact mixture containing 10% copper, prepared from silicon of sieve fraction 50 - 75 microns and cuprous chloride. The column contained about 150 g of the mixture and comprised part of a gaschromatographic system, with katharometer-detection and argon or hydrogen as carrier gas. The temperature could be kept constant within 1 degree C. Before a series of pulses was fed to the column, the contact mixture was subjected to a treatment with hydrogen chloride. The free space in the column was filled with hydrogen chloride and with both ends
closed the column was then heated to 300 °C to create a reactive surface. Upon cooling, the gas was replaced by the carrier gas until a stable base line of the recorder of the gaschromatograph was obtained and the temperature had become constant.

Injection of the pulses of both liquid and gaseous compounds was accomplished by means of a hypodermic syringe. The tube was filled in a nitrogen atmosphere, to prevent moisture or oxygen from deactivating the column. In spite of these precautions, however, the activity of the column slowly decreased with time, and this may be one of the main sources of error in the measurements. For each compound tested, the column was reactivated by hydrogen chloride treatment.

The retention time $(t_r)$ has been taken as the time between the injection and the appearance of the peak-maximum. The moment of injection is clearly indicated on the recorder chart by the response of the katharometer on the injection in the system. The retention time of nitrogen which in most cases is injected together with the sample was taken as the residence time in the column $(t_m)$. To enable the relative retention $( (t_r - t_m)/t_m )$ to be determined as a function of the pulse volume, the peak area of the adsorbent has been used, calculated from peak-height and peak-width at the middle of the peak.

-2-3. Results

When silicon (without copper) is used as adsorbate, the relative retention is so close to zero, that experiments are useless.

Using a silicon-copper contact mixture, the relative retention is measurable, and decreases with increasing temperature. The highest temperature of the column applied for each compound was determined by the possibility to measure a substantial difference between the retentions of inert gas and adsorbent. At the lowest value of the relative retention (about 0.02) the error arising from the substraction of $t_r$ and $t_m$ becomes unacceptable.

For each compound, between 50 and 80 measurements were performed at different temperatures. The curves representing the experiments with
Figure 22
Relative retention as function of pulse volume for various temperatures.
Temperatures in °C, pulse volume expressed in cm$^2$ peak area.

methylchloride, hydrogen chloride, dimethyldichlorosilane, methyltrichlorosilane and tetrachlorosilane are given in Figures 22-a, b, c, d and e, respectively, drawn from tabulated data (124). In all cases the spread of the points indicate an absolute error in the value of the relative retention of ± 0.01. The error in the peak areas can be estimated as ± 0.4 cm$^2$, mainly caused by the inaccuracy of the measurement of the peak-width. The value of $\Delta H_{ads}$ was calculated for various pulse volumes (expressed as the surface area of the peaks in the chromatograms). The results are given in Table 26 and Figure 23.
### Table 26.
Heat of adsorption for various adsorbent pulse volumes (kcal/mol)

<table>
<thead>
<tr>
<th>Compound</th>
<th>MeCl</th>
<th>EtCl</th>
<th>HCl</th>
<th>Me₂SiCl₂</th>
<th>MeSiCl₃</th>
<th>SiCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>peak area (cm²)</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>Temp.range (°C)</td>
<td>71 - 97</td>
<td>70 - 121</td>
<td>98 - 132</td>
<td>74 - 96</td>
<td>87 - 119</td>
<td>60 - 85</td>
</tr>
</tbody>
</table>

From the plots in Figure 23, there appears to be a tendency of increased heat of adsorption with smaller pulse volumes, a phenomenon that is likely to be related with the influence of the surface coverage upon the heat of adsorption. Extrapolation to zero pulse volume has been performed graphically and the data are given in column 2 of Table 26. Although there is no justification that the extrapolated values have more significance than the average values of the heats of adsorption, these are the data which have been taken as the results of the measurements. The relative error in the heats of adsorption can be estimated at 10 - 20%.

### VII-3. Determination of surface-bound chlorine (III-3, IV-2)

A contact mixture preparation at 380 °C from silicon and cuprous chloride results in a fully chlorinated surface. Etching with hydrochloride or methylchloride is a process with an activation energy of 10 kcal/mol, and starts already below 200 °C.

-3-1. Introduction

Several methods have been suggested to shorten the induction period in
the direct synthesis of alkylchlorosilanes (IV-2). They have in common the introduction of chlorine to the surface of the contact mixture, for example by etching with hydrogen chloride or chlorine. Also a contact mixture prepared in situ from silicon and cuprous chloride shows only an induction period when it has been heated for a long time. Both processes are chlorinations of silicon, resulting in the formation of silicon chlorides. Boonstra (79) has shown that from adsorption of hydrogen chloride on very pure silicon at room temperature, a fast coverage of a monomolecular layer is obtained, whereupon further adsorption proceeds slower, the total amount adsorbed being proportional to the logarithm of time. At elevated temperatures the adsorption is immediately followed by formation of gaseous silicon chlorides. It is presumably a stepwise chlorination of the silicon that leads to the formation of, for example, tetrachlorosilane:

\[
\text{Si} \rightarrow \text{SiCl} \rightarrow \text{SiCl}_2 \rightarrow \text{SiCl}_3 \rightarrow \text{SiCl}_4 \rightarrow \text{SiCl}_4
\]

When the resulting tetrachlorosilane is removed from the reaction zone the available chlorine will react until no more is left, but an "equilibrium" amount will remain in chemisorbed state, i.e. bound to the surface. This amount has been determined for a contact mixture prepared from silicon and cuprous chloride and for silicon that has been etched with hydrogen chloride and methylchloride. As it must be expected that there is a temperature-influence upon the amount of surface-bound chlorine, the etching experiments have been done at various temperatures.

-3-2. Remaining chlorine from reaction of silicon and cuprous chloride

Portions of 200 mg of powdered cuprous chloride were mixed thoroughly with silicon (90 - 120 microns) in amounts of 2 - 14 g. In this way contact mixtures were prepared containing between 1 and 7% of copper. The mixtures of silicon and cuprous chloride were kept for 1 hour at 380 - 400 °C in a stream of nitrogen to remove the silicon chlorides formed. The reaction proceeds mainly according to:

\[
n \text{Si} + 4 \text{CuCl} \rightarrow 4 \text{Cu} + \text{SiCl}_4 + (n-1) \text{Si} \quad \text{(VII.1)}
\]

After cooling to room temperature the contact mixture was removed from the reactor and was leached with water. It was assumed that all surface-bound chlorine or unreacted cuprous chloride would be converted by the
the water treatment into hydrochloric acid. The amount of chlorine in the water was determined by titration with a silver nitrate solution. The experimental data are given in Table 27.

Table 27.
Amount of chlorine remaining in contact mixtures

<table>
<thead>
<tr>
<th>silicon (gram)</th>
<th>cuprous chloride (gram)</th>
<th>residual chlorine (mg)</th>
<th>chlorine (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.03</td>
<td>0.220</td>
<td>0.7</td>
<td>0.032</td>
</tr>
<tr>
<td>2.18</td>
<td>0.204</td>
<td>1.9</td>
<td>0.082</td>
</tr>
<tr>
<td>4.04</td>
<td>0.209</td>
<td>1.3</td>
<td>0.031</td>
</tr>
<tr>
<td>6.01</td>
<td>0.204</td>
<td>4.8</td>
<td>0.078</td>
</tr>
<tr>
<td>6.01</td>
<td>0.202</td>
<td>5.3</td>
<td>0.086</td>
</tr>
<tr>
<td>8.03</td>
<td>0.206</td>
<td>3.9</td>
<td>0.048</td>
</tr>
<tr>
<td>10.12</td>
<td>0.204</td>
<td>8.8</td>
<td>0.086</td>
</tr>
<tr>
<td>13.93</td>
<td>0.207</td>
<td>10.8</td>
<td>0.077</td>
</tr>
</tbody>
</table>

The table shows that there is an increase in the residual chlorine content of the contact mixture with the amount of silicon, which means that the chlorine content per unit weight of contact mixture is roughly constant and about $0.065 \pm 0.022$ wt %.

3-3. Residual chlorine from etching of silicon with hydrogen chloride and methylchloride.

In a static system comprising a reaction vessel, and connections for adsorbent, vacuum, outlet, air inlet and a mercury manometer, a batch of 10 - 20 g of iron-free silicon powder can be kept in an adsorbent atmosphere. Figure 24 shows the schematic representation of the system. The reaction vessel is heated by immersion in a bath of paraffin oil or Wood's metal. After introduction of the silicon powder in the sample holder, the system is kept under vacuum for at least 15 minutes until the required temperature is reached. Then hydrogen chloride is admitted. A small stream of hydrogen chloride is allowed to flow from inlet to outlet.
outlet in order to keep a constant pressure during the treatment. After closure of the hydrogen chloride inlet and outlet, the system is evacuated at a pressure less than 1 mm of mercury for 15 minutes. The sample holder with the vacuum connection still open is then allowed to cool by removal of the heating bath. Air is introduced to the system, the sample holder is removed, the silicon is washed with water, filtered, and the amount of chlorine in the filtrate is determined potentiometrically.

In preliminary experiments, the influence of some of the experimental parameters has been checked:

- Within the experimental error, there was no influence of the time of degassing if this time exceeded 10 minutes.
- The time of hydrogen chloride etching was not important. The same results were obtained for adsorption times of 4, 15 and 70 minutes at 21 °C.
- No adsorption of hydrogen chloride on the inner wall of the reaction vessel could be determined.
- For silicon samples of different sieve fractions the variation of the adsorbed amount at room temperature was within the limits of the experimental error (see Table 28).

<table>
<thead>
<tr>
<th>Sieve fraction (microns)</th>
<th>Adsorbed amount (mg HCl/g Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 - 75</td>
<td>0.023</td>
</tr>
<tr>
<td>75 - 90</td>
<td>0.026</td>
</tr>
<tr>
<td>90 - 125</td>
<td>0.024</td>
</tr>
<tr>
<td>125 - 150</td>
<td>0.027</td>
</tr>
<tr>
<td>150 - 175</td>
<td>0.029</td>
</tr>
<tr>
<td>175 - 210</td>
<td>0.023</td>
</tr>
</tbody>
</table>

Two series of measurements for the effect of temperature are shown in Figures 25 and 26. The data given in Figure 25 apply to silicon of sieve fraction 60 - 75 microns, whereas Figure 26 shows the results for a sieve fraction of 50 - 75 microns. There is practically no difference between the two curves. In both cases the amounts of chlorine are fairly constant below 200 °C. Above this temperature both show a sharp increase in the amounts of chlorine with increasing temperature.

The same procedure has been followed in a series of experiments, where methylchloride is kept in contact with silicon for 15 minutes. In Figure...
27 the chlorine content expressed in mg methylchloride per g of silicon has been as function of the temperature. As in the case of hydrogen chloride adsorption, only a minor variation is observed below 200 °C. In the higher temperature range, again a sharp increase of the chlorine amount adsorbed is observed with increasing temperature.

3.4. Discussion of the results

In the reaction of silicon with cuprous chloride, equation (VII.1), which proceeds readily at temperatures above 260 °C some of the chlorine remains adsorbed on the contact mixture after heating for 1 hour at 380 °C. The amount of chlorine is proportional to the amount of silicon and not to the quantity of cuprous chloride that was introduced originally. Although a small fraction of the chlorine may still be in the form of unreacted cuprous chloride, the larger part must be bound to the surface. This explains why the amount of residual chlorine is proportional to the amount of the contact mixture, and thus to the available surface area. For the conditions chosen, i.e. after
heating for 1 hour at 380 °C, the contact mixture contains 0.065 (+ 0.022) wt % of chlorine. The inaccuracy of the result may be caused by the lack of homogeneity of the original mixtures of silicon and cuprous chloride. If it is assumed that 1 m² of a contact mixture surface exposes as many atoms as 1 m² of a silicon (1 1 1) plane, i.e. 7.9x10¹⁸ atoms (79), and that each surface atom will bind one chlorine atom, the specific surface area of the contact mixture obtained in the above manner is 1.4 (+ 0.5) m²/g. B.E.T. adsorption measurements reveal for silicon of the same sieve fraction (90 - 120 microns), but pre-treated with hydrochloric acid, values between 0.2 and 0.5 m²/g. The figures indicate that the contact mixtures contain at least one mono-atomic layer of chlorine and have been subject to a considerable increase of the surface area. The latter would provide a satisfactory explanation for the observed increase of reactivity upon addition of cuprous chloride to a reacting contact mixture (45).

The influence of temperature upon the adsorption of hydrogen chloride, and of methylchloride, on silicon shows a remarkable resemblance to each other. Two forms of sorption can be clearly distinguished. The low temperature form tends to decrease with amount adsorbed only up to 100 °C. It indicates an exothermic physical adsorption (see also VII-2-3 and VII-4-3). The high temperature form shows an increase of adsorption with temperature. The explanation can presumably be found in terms of an activated adsorption followed by increase of the surface area by etching. If the increase of the residual chlorine with temperature is proportional to the increase of the surface area, an activation energy of the etching process can be determined from a plot of the logarithm of the adsorbed

![Figure 28](image)

Arrhenius-plot of HCl-adsorption
amount versus the inverse of temperature (Figure 28). The value for the activation energy of etching of silicon by hydrogen chloride, as well as by methylchloride calculated in this manner is 10 (+ 2) kcal/mol.

From the adsorbed amount of chlorine at 300 °C (0.07 mg/g Si), it follows that \(1.2 \times 10^{18}\) chlorine atoms are bound to the surface. Thus a surface area of 0.15 m\(^2\) is occupied by chlorine atoms if the silicon surface exists in the (1 1 1) plane and if each silicon atom binds one chlorine atom. The specific surface area of the silicon specimen is estimated at 0.3 - 0.7 m\(^2\)/g. Therefore, complete coverage does not yet seem to be obtained.

VII-4. Adsorption of methylchloride on silicon (III-3)

The heat of adsorption methylchloride on silicon is \(-6.4\) kcal/mol. The isotherms reveal a single site adsorption up to 170 °C.

-4-1. Equipment

The adsorption equilibrium constant \(K_{MeCl}\) of methylchloride on silicon-copper contact mixtures can be determined indirectly from kinetic data when the reaction rate equation is known. In the temperature range of the direct synthesis the adsorption is immediately followed by chemical reaction so that the obtained \(K_{MeCl}\) values are merely of theoretical importance. Below the reaction temperatures it is possible to determine the \(K\)-value from the adsorption isotherms. With this aim, equipment was constructed, which is shown schematically in Figure 29.

A sample holder in the form of a U-tube may contain about 20 g of silicon and can be heated or cooled respectively by insertion in a heated bath of Wood's alloy or in a Dewar vessel with liquid nitrogen. The latter enables the determination of the specific surface area of the samples, when the equipment is used as a micro-B.E.T. instrument. The "dead" volume of the equipment - the volume between the sample holder - R -, the manometer - M -, and the dosing system - D - is 1.53 ml because of the connecting capillaries. It is small compared to the void volume in the sample holder (16 - 17 ml). The system is suitable for determination of the specific surface area with an accuracy of better than 0.01 m\(^2\)/g.
The conduction of an adsorption measurement is as follows. The sample is etched with hydrogen chloride at 300 °C and is degassed subsequently for 24 hours with a vacuum better than $10^{-5}$ torr.

With the cock -6- closed an amount of adsorbent gas is introduced in the system and the mercury level in the dosing system is adjusted to the mark labelled -S-. The quantity is determined from the pressure and the known volume of the system. After opening of the cock -6- the adsorption can take place, and the pressure can be determined when equilibrium is reached. By filling the known dosing volume -4- with mercury to the mark -D- the pressure can be increased. The reverse manipulation causes a desorption. A new quantity of adsorbent gas can be introduced after closure of the cock -6-. When a chemical reaction is expected to have taken place, the content of the sample holder can be introduced directly into a gaschromatograph by turning the four-way valve -2- with cock -6- closed.

The equipment had several disadvantages:
- Equilibration will take 10 to 60 minutes, which makes the experiments extremely time-consuming.
- Both methylchloride and hydrogen chloride appeared to react noticeably with mercury at 20 °C. Thereby the accuracy of the experiments suffers, although corrections have been applied.

- Filling of the sample holder with a solid specimen is hampered by the narrow access, necessary to keep the volume small.

- Due to the complexity the equipment gave rise to eventual leakages, which would make continuation of an experiment useless.

Some results, however, have been obtained.

In a preliminary experiment, hydrogen chloride was adsorbed on 18.4 g of silicon with specific surface area of 0.12 m²/g. After three times of introduction of hydrogen chloride, 8.5 mmol was adsorbed, leaving a pressure of 0.6 mm mercury. The remaining gas, upon introduction in the gaschromatograph appeared to consist only of hydrogen, so all of the hydrogen chloride had been adsorbed, and only a small part (3%) of the hydrogen had been freed. Heating at 380 °C starting with a vacuum of 10⁻⁵ torr freed most of the hydrogen in a very slow desorption process. In 1 hour, 3.1 mmol hydrogen and no hydrogen chloride desorbed from the silicon.

The experiment reveals that hydrogen chloride adsorbs irreversibly on silicon at temperatures above 250 °C.

-4-2 Adsorption rate of methylchloride on silicon (III-3)

The amount of methylchloride adsorbed is plotted versus time for 235 and 291 °C in Figure 30. The adsorptions are not corrected for the loss of methylchloride by its reaction with mercury of the manometer. The plot for 235 °C shows a linear course after 12 minutes. Extrapolation of the dotted line to zero adsorption time yields the equilibrium amount adsorbed.

For temperatures below 200 °C this method has been accepted for determination of adsorption isotherms (see VII-4-3). Above this temperature the time required to reach equilibrium increases substantially, making extrapolation very inaccurate. This shows the curve for 291 °C. From the gaschromatogram it can be concluded that reaction had taken place. The product contained 16% H₂, 7% CH₄, 0.7% C₂H₄ or C₂H₆ and 76.3% CH₃Cl.
An unidentified product appeared at the end of the chromatogram. Similar experiments in this temperature-range revealed more or less the same composition of the gas sample. It is obvious that cracking of methylchloride is responsible for the continuing decrease of pressure, so that no equilibrium pressure will be established before methylchloride is decomposed completely.

---

**Adsorption isotherms of methylchloride on silicon (III-3)**

In Figure 31 the observed adsorption isotherms of methylchloride on silicon of specific surface area 0.12 m²/g are drawn. Tabulated data may be found in (724). For a surface of this magnitude the monolayer coverage will require 27 x 10⁻³ ml of methylchloride, calculated from the density of liquid methylchloride at 20 °C. The isotherm measured at 20 °C exceeds this value already at 50 mm mercury pressure. If this value is adopted as the maximum coverage for methylchloride at any temperature, an interesting test is possible on the equations for the adsorption equilibrium constant. The Langmuir-type adsorption equilibrium is described with (VII.11) in case of single site adsorption. Upon substitution of the coverage fraction by \( \frac{V_{\text{ads}}}{V_{\text{max}}}, \) i.e. the ratio of the adsorbed amount to the maximum adsorbable amount, and rearranging, equation (VII.12) is obtained.

\[
K = \frac{\theta}{(1 - \theta) \cdot \rho} \quad \text{(VII.11)}
\]

\[
\frac{V_{\text{ads}}}{V_{\text{max}} - V_{\text{ads}}} = K \cdot \rho \quad \text{(VII.12)}
\]
Plotting the first term of equation (VII.12) against the pressure will yield a straight line through the origin. In Figure 32 this has been done for the two higher temperature isotherms. Although rather spread, the agreement is within the experimental error. This is however, not the case when the same procedure is followed assuming dual site adsorption. The relation (VII.13) now should give a straight line through the origin when the assumption was valid. Figure 33 shows that that the plots lie on a parabolic curve.

\[
\frac{v_{\text{ads}}^2}{(V_{\text{max}} - v_{\text{ads}})^2} = Kp \quad \text{(VII.13)}
\]
The slopes in Figure 32 give the values of $K_{\text{MeCl}}$ which are 3.1 atm$^{-1}$ at 101 °C and 0.84 atm$^{-1}$ at 169 °C. Because of the probable large error (50 %) the data may not have much significance, but for the calculation of the heat of adsorption of methylchloride on silicon, the systematic error in the data is of no importance. The adsorption equilibrium constants lead to: 

$$\Delta H_{\text{ads}} (\text{MeCl}) = -6.4 \text{ kcal/mol}$$

VII-5. Methylchlorosilanes synthesis in fluid-bed (IV)

Improvements in the direct synthesis of methylchlorosilanes can be obtained by complete removal of oxygen from the feed, etching at 200 °C with a chlorine-source and intermittent fluidization with inert gas.

-5-1. Introduction

Many experiments under the above heading have been performed and are described in detail in the literature (28, 127, 128). Selectivity and reactivity have been shown to be influenced by the type of reactor, the quality of reactants and catalyst, the addition of promoters and the temperature (e.g. 28, 48, 147). It seems hardly sensible to furnish kinetic data for a given set of process parameters as the number of combinations seems infinite. An empirical approach for a selected conduction of the synthesis seems in fact the only alternative for the rough prediction that is possible with the present insight. On the process with the technical silicon and the contact mixture which can be prepared from it, applied in the experiments described in this work a great deal of experimental results has been published (28, 127). Yet, with unchanged specification of the reactants it is possible to obtain results, which may differ slightly from this earlier work. In this section some experiments will be described performed to investigate the following:

- the influence of the removal of oxygen from methylchloride,
- reproducibility compared to experiments reported earlier (127),
- the effect of intermittent fluidization by inert gas,
- the promoting effect of zinc chloride.

Analysis of the products obtained in the experiments to be described in VII-5 and VII-6 was performed by means of gas-liquid chromatography.
Separation of the compounds is possible with a column containing 20 wt % nitrobenzene on Chromosorb W (80 - 120 mesh). Details of the analytic method may be found in (127, p. 12).

-5-2. The effect of removal of oxygen from methylchloride (IV-8, -9)

Purification of methylchloride allows a higher convertibility of the silicon and a higher selectivity.

Technical methylchloride may contain impurities, introduced during preparation or during transport. Table 29 gives the analysis of one sample.

Table 29

<table>
<thead>
<tr>
<th>Compound</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>0.2</td>
</tr>
<tr>
<td>C$_2$H$_3$Cl</td>
<td>0.07</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>0.03</td>
</tr>
<tr>
<td>C$_2$H$_5$Cl</td>
<td>0.006</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>0.006</td>
</tr>
<tr>
<td>O$_2$, N$_2$</td>
<td>0.003</td>
</tr>
</tbody>
</table>

A systematic investigation of the effect of moisture, methanol and oxygen in methylchloride has been performed by Lobusevich c.s. (78). The general effect of any of these impurities is a decrease in both selectivity and reactivity. For instance admixture of 0.2% of water to methylchloride resulted in a mixture of silicon compounds containing only 40% of dimethyldichlorosilane and a reactivity of half that of the experiment without moisture added. About the same effect is caused by admixture of 0.5% of methanol. Upon addition of 0.74 volume % of oxygen the reactivity falls to about one third of the reactivity in the blank experiment, while the selectivity does not exceed 47 %. In all cases the product contains substantial amounts of high-boiling substances, presumably siloxanes.

In the laboratory performance of the direct synthesis attempts can be made to purify methylchloride. By instalment of a column containing highly active copper (BTS-catalyst, from BASF) the amount of oxidizing gases can be decreased. By means of introduction of a column containing a 3A- or 4A-type molecular sieve the content of moisture can be reduced. Yet, when in the connection between the purification section and the reactor (see Figure 34) plastic tubes (polyvinylchloride or polyethylene) are used, it is still possible to detect high concentrations of oxygen in the reactor feed, strongly dependent upon the gas rate. An extremely high oxygen content of 0.15% has been observed when a current
of 20 ml/min of oxygen-free nitrogen is led through 0.5 m of polyethylene tube with inner and outer diameter of 0.8 and 1.2 cm respectively. To avoid this contamination by diffusion of air through the walls of plastic tubes, all-glass connections are prefered. The oxygen content is then lowered to 0.01 volume % in a current of 20 ml/min. As the usual feed rate of methylchloride amounts to about 3,000 ml/min in the fluid-bed experiments, the influence of uncontrolled oxygen contamination can be neglected. The results in fixed bed experiments may very well be influenced by this effect, due to the much smaller feed rates of about 100 ml/min. Some experiments have been conducted to investigate the effect of purification of methylchloride. The assembly of the equipment is given in Figure 34.

![Figure 34. Laboratory equipment for fluid-bed synthesis.](image)

1- and 2- cylinders with methylchloride and argon, 3- column containing BTS-catalyst for oxygen removal; volume 3 liter, temperature 100 °C, 4- columns containing Linde molecular sieve, type 4A as drying agent, 5- flowmeters, 6- waste line, 7- fluid-bed with silicon for heating of the reactor, 8- fluid-bed reactor with contact mixture, 9- dust trap containing glass wool, 10- distillation column for continuous separation of unconverted methylchloride, 11- container for condensed methylchloride, 12- waste line for uncondensable gases, 13- discharge of unreacted methylchloride, 14- discharge of methylchlorosilanes.
The contact mixture comprised technical silicon of particle size distribution as was usually applied in fluid-bed experiments (11.7 wt %, 36.9 wt %, 41.4 wt % and 10.0 wt % of sieve fractions 50-75, 75-105, 105-150 and 150-210 microns respectively). The content of iron was reduced magnetically (VII-1). The contact mixture was prepared in the reactor from a mixture of silicon, cuprous chloride (10 wt % related to metallic copper), 0.05 wt % aluminium and 0.1 wt % of zinc. There has been no contact with air between the preparation and the reaction with methylchloride.

The plots in Figures 35, 36 and 37 are the representation of the product composition in mol % of the collected condensate samples and of the reactivity as function of the converted silicon. The latter is calculated from the weight and composition of the condensate. Tabulated data may be found in (28).

Figure 35. Experiment (MCS-1) with unpurified methylchloride
- introduction of a pulse of air,
- Me$_2$SiCl$_2$, T- MeSiCl$_3$, M- Me$_3$SiCl

Figure 36. Experiment (MCS-2) with purified methylchloride
Temperature 335 °C. Dotted line after F25 (127)
Figure 35 (MCS-1) represents an experiment where the column with BTS-catalyst is not included in the feed line. The methylchloride feed is then expected to be contaminated by at least 30 ppm of oxygen. It serves as a blank experiment and it is comparable with experiments conducted by Voorhove. The dotted line is drawn after experiment F23 (127, p. 46), which was conducted at 327 °C. The small temperature difference accounts for the small deviation of the reactivity but the course of the selectivity agrees very well. The effect of an extra pulse of air which was introduced after 17% of silicon conversion is a temporary decrease in selectivity but an increase in reactivity.

Experiments MCS-2 and -3 (Figures 36 and 37) have been conducted with 100 and 200 grams of contact mixture respectively and with temperatures of 335 and 340 °C. In MCS-3 the temperature of the reactor was increased to 355 °C after 40% of silicon conversion. At this stage a fall in reactivity was frequently observed (127). The essential difference with MCS-1 is the removal of oxygen from the methylchloride feed by the BTS. MCS-2 resembles very much experiment F25 (127, p. 59), conducted at 333 °C with acontact mixture which was pre-heated for 16 hours in an inert gas stream.

![Graph](image-url)

**Figure 37.** Experiment (MCS-3) with purified methylchloride; temperature 340 °C and after -a- 355 °C; dotted line from experiment VS-4 (128)
at 400 °C. The dotted line in Figure 36 is drawn after this experiment. It reveals that the beneficial effect of pre-heating resembles that of purification of methylchloride. MCS-3, conducted at even higher temperature shows a selectivity which is already high in the beginning, i.e. over 90 mol % of dimethyldichlorosilane after 1.3% of silicon conversion. Even after 85% of silicon conversion the selectivity remains about 90 mol %. The result is comparable with the performance of a contact mixture promoted with cadmium chloride (739). In Figure 37 the dotted lines represent experimental results at 330 °C with a contact mixture prepared from the same silicon as was used in MCS-1, -2 and -3 containing 9.6 wt % copper and 2 wt % of cadmium chloride (728). Results of the analysis of the spent contact mixtures and of the entrained dust are given in Tables 30 and 31.

It can be concluded, that the use of oxygen-free methylchloride is of importance for a favourable selectivity over a considerably prolonged conversion of the silicon charge.

-5-3. The effect of intermittent fluidization with inert gas (IV-8, -9)

When promoters are absent, the contact mixture performs poorly. Copper- and coke-rich dust can be removed by a period of fluidization with inert gas. The effect is a recovery of selectivity and a lowering of reactivity.

When the contact mixture does not contain the promoters aluminium and zinc, the course of a direct synthesis of methylchlorosilanes is characterized by a fast de-activation of the contact mixture. Figure 38 shows such an experiment (MCS-4), which was conducted at 345 °C and which, except for the absence of the promoters, is comparable with MCS-2 (Figure 36). In spite of the somewhat higher temperature, the reactivity remains less than half of that of a promoted contact mixture. After 6% of silicon is converted the selectivity falls from an initial value of 80% to about 50%. It is remarkable that the combined contents of dimethyldichlorosilane and methyl­dichlorosilane remain rather constant at an average of more than 70 mol %. To check whether the traces of oxygen present in the methylchloride feed might be related with the unfavourable performance of this type of contact mixture the experiment was repeated with methylchloride now flowing through the BTS-column. As is shown in Figure 39 (MCS-5), no significant differences with the former experiment can be observed.
Both experiments were stopped for an intermittent period of fluidization with argon for three hours, while the reaction temperature was maintained. The gas rate was chosen to provide 5 times the rate required for minimum fluidization. After the fluidization, methylchloride was introduced again. In both experiments the significant results are a recovery of selectivity as well as a halving of reactivity.

From analysis of the dust collected during the treatment with inert gas, it is clear that the positive effect is caused by an abrasion of copper- and coke-rich particles. In Tables 30 and 31 the results of analysis of the contact mixture after the experiments and of various fractions of the entrained dust are given.

<table>
<thead>
<tr>
<th>Table 30. Composition of contact mixture after reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>MCS-1</td>
</tr>
<tr>
<td>-2</td>
</tr>
<tr>
<td>-3</td>
</tr>
<tr>
<td>-4</td>
</tr>
<tr>
<td>-5</td>
</tr>
</tbody>
</table>
It is evident from the data in Table 31 that the entrained dust from the unpromoted contact mixtures contains more carbon than that of the promoted ones, while the hydrogen content does not differ substantially. The copper content of all dust samples varies around 50 wt%.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Amount (g)</th>
<th>% Cu</th>
<th>% C</th>
<th>% H</th>
<th>% Al</th>
<th>% Zn</th>
<th>Collected after:</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCS-1</td>
<td>5.3</td>
<td>63.5</td>
<td>7.0</td>
<td>1.3</td>
<td>0.26</td>
<td>&lt;0.05</td>
<td>37.1% Si conv.</td>
</tr>
<tr>
<td>4.2</td>
<td>46.0</td>
<td>6.5</td>
<td>2.2</td>
<td>1.25</td>
<td>0.83</td>
<td>57.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>3.5</td>
<td>40.6</td>
<td>5.4</td>
<td>5.5</td>
<td>1.26</td>
<td>0.87</td>
<td>66.9</td>
<td>&quot;</td>
</tr>
<tr>
<td>-2</td>
<td>0.9</td>
<td>30.0</td>
<td>4.4</td>
<td>3.7</td>
<td>2.3</td>
<td>0.06</td>
<td>27.2</td>
</tr>
<tr>
<td>2.9</td>
<td>37.8</td>
<td>9.2</td>
<td>4.8</td>
<td>1.3</td>
<td>0.88</td>
<td>65.7</td>
<td>&quot;</td>
</tr>
<tr>
<td>-3</td>
<td>3.2</td>
<td>47.5</td>
<td>7.2</td>
<td>2.2</td>
<td></td>
<td>57.9</td>
<td>&quot;</td>
</tr>
<tr>
<td>5.4</td>
<td>62.5</td>
<td>9.1</td>
<td>3.0</td>
<td></td>
<td></td>
<td>88.3</td>
<td>&quot;</td>
</tr>
<tr>
<td>-4</td>
<td>1.5</td>
<td>49.8</td>
<td>13.0</td>
<td>3.1</td>
<td></td>
<td></td>
<td>22.0</td>
</tr>
<tr>
<td>2.6</td>
<td>37.0</td>
<td>21.0</td>
<td>3.4</td>
<td></td>
<td></td>
<td>3 hrs argon fluid</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>39.0</td>
<td>14.8</td>
<td>2.0</td>
<td></td>
<td></td>
<td>23.9% Si conv.</td>
<td></td>
</tr>
<tr>
<td>-5</td>
<td>0.4</td>
<td>49.5</td>
<td>8.8</td>
<td>2.1</td>
<td></td>
<td>13.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>1.7</td>
<td>49.5</td>
<td>11.2</td>
<td>1.5</td>
<td></td>
<td></td>
<td>3 hrs argon fluid</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>53.0</td>
<td>6.6</td>
<td>1.5</td>
<td></td>
<td></td>
<td>15.9% Si conv.</td>
<td></td>
</tr>
</tbody>
</table>

-5-4. Uncatalyzed reaction of methylchloride with fluidized silicon

Methylchloride reacts very slowly with silicon at 380 °C when no copper is present. The selectivity is about 10%.

A misinterpretation of a paper from Bazant (58) originated the idea that silicon was able to react with methylchloride already at 300 °C and with 90% selectivity (147). Although not explicitly stated, the result which is extremely conflicting with earlier observations (67) made the presence of copper obvious. Still, when the author of a review article adopts the idea (147), it leads to confusion and the investigator in the field of
interest is tempted to reproduce either result. In Table 32 the composition of the reaction product is given for a temperature of 380 °C. The experiment was conducted in a fluid-bed reactor in an assembly as discussed in VII-5-2. To cause extra attrition of the silicon particles in order to create an oxygen-free surface, 100 g of technical silicon of particle size between 50 and 210 microns was mixed with 100 g of silicon carbide of the same size distribution.

Table 32
Product composition of uncatalyzed reaction of MeCl and Si (mol %).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Est.Si conv. (%)</th>
<th>SiHCl3</th>
<th>SiCl4</th>
<th>Me3SiCl</th>
<th>MeSiCl3</th>
<th>MeSiHCl2</th>
<th>Me2SiCl2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>4.0</td>
<td>0.6</td>
<td>9</td>
<td>74</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>1.3</td>
<td>18</td>
<td>3</td>
<td>67</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>5</td>
<td>10</td>
<td>2</td>
<td>72</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>4</td>
<td>62</td>
<td>17</td>
<td>9</td>
</tr>
</tbody>
</table>

The table shows that about 10 mol % of dimethylidichlorosilane is formed. The reactivity decreases very fast, so that no more silanes are formed after some hours of reaction. The conclusion seems justified that an uncatalyzed reaction is only possible at high temperature, mainly forming methyltrichlorosilane.
VII-6. Fixed bed experiments in methylchlorosilanes synthesis (IV)

In a fixed bed reactor, results comparable with the fluid-bed process can be obtained if high gas rates are applied in order to avoid local hot spots. Thus, over 20% of the silicon can be converted with high reactivity and 90% selectivity. Continuous addition of zinc chloride in the form of vapour exerts the same beneficial effect as intermittent addition of metallic zinc.

6-1. Introduction

A series of experiments to acquire kinetic or mechanistic information under varying conditions must be conducted with great care because of the poor reproducibility of direct synthesis experiments. One of the main sources of irreproducibility lies in the preparation of the contact mixture, the reason why Voorhoeve suggested and applied standard methods for the preparation of cuprous chloride and contact mixtures (727). When a large series of tests is required with only short duration, the preparation of a contact mixture for each test is very time-consuming and may lead to results, differing because of minor variations in the preparation. For this reason preparation of a quantity of contact mixture in advance was adopted, and for each test a portion of the mixture has been used. To enable a large number of tests with the same contact mixture, the portions must be small, which implies the use of a small reactor. The use of a fixed bed reactor has the following advantages:
- A narrow sieve fraction of the contact mixture may be used.
- No attrition and subsequent entrainment of dust will cause uncontrollable effects.
- Small and widely varying residence times are easily obtained.

Some problems remain to be solved when a fixed bed reactor is charged with, for example, 7 g of contact mixture. For an expected reactivity between 20 and 100 g methylchloride/kg Si.hr the silanes production lies roughly in the order of 0.5 g per hour. If this amount is collected by condensation, with continuous removal of the larger part of the unreacted methylchloride by distillation, the errors in analysis (injection with hypodermic syringe into a gaschromatograph) and in the determination of the produced amounts become unacceptable. For this reason, samples
Figure 40. Assembly of equipment for fixed bed experiments

1- cylinders with CH$_3$Cl and argon (or nitrogen), 2- cylinder with hydrogen chloride, 3- columns with BTS-catalyst and 4A - type molecular sieve -, 4- flowmeters, 5- fixed bed reactor, 6- fluidized bed for immersion of the reactor, 7- Eight-way valve, 8- sample tube in U-form to allow immersion in dry ice/ethanol Dewar flask or hot water, 9- circuit of gaschromatograph.

Of the reaction gases are led through an eight-way valve to be collected in a sample tube which can be cooled to increase the amount sampled. If the eight-way valve is included in the circuit of the gaschromatograph, introduction of the sample is possible without contact with air. By heating of the sample tube with hot water, a rapid evaporation of the sample guarantees a narrow sample pulse. By accurately weighing the contact mixture before and after the test, the converted amount of silicon can be determined, but variation of reactivity during the test remains unobserved in this way. When the reactivity is quoted for the tests, it is the average value over the experiment, calculated from the silicon conversion and the duration. The changes of the reactivity in a qualitative way can be obtained from the sum of the peak areas of the products in the chromatogram, provided that sampling time and temperature, and the sensitivity of the katharometer and the recording system are constant. It must, however, be realized that analysis data from collected condensate samples are average values over the period of condensation, usually
amounting to one hour. Analysis of pulses of the reaction gases, however, are more or less "snap shots", and usually give the composition of less than 1% of the product.

Figure 40 is a representation of the equipment used in nearly all fixed bed experiments. The reactor is a glass tube in U-form, for some of the experiments in double-U-form, the latter to enable better pre-heating or transport of a volatile compound from the first to the second U (see also Figure 55). The tube which forms the reactor has an internal diameter of 10 mm and is provided with a coaxial tube with outer diameter of 6 mm for thermocouples. The length of a contact mixture layer of 8 g is about 20 cm; it is supported by a sintered glass filter of 10 - 40 microns pore-size. The outer bed contains silicon, which is fluidized with air and which is heated electrically on the outside. A platinum resistance thermometer is used to control a thermostat, which keeps the temperature of the outer bed constant within 2 degrees Celsius.

-6-2. Influence of contact time (IV-2, -7)

Methylchlorosilanes are formed in parallel reactions, as variation of the contact time does not influence the product composition significantly. The high gas velocities accompanying small contact times avoid local hot spots and allow a selectivity of over 90%, provided the feed is free of oxygen.

That methylchlorosilanes are formed in parallel reactions is quite acceptable because of the fact that dimethyldichlorosilane can not be disproportionated when led over an active contact mixture at 370 °C and with contact times of less than some minutes (132). Methylidichlorosilane, however, is convertible to some degree into methyltrichlorosilane over a bed of copper powder at 360 °C (62). From the molar ratios of the products formed the overall reaction must somehow proceed according to equation (VII.14). With excess of methylchloride present this disproportionation appears greatly retarded, which diminishes its importance under direct synthesis conditions.

\[
4 \text{CH}_3\text{SiHCl}_2 \rightarrow 2 \text{CH}_3\text{SiCl}_3 + (\text{CH}_3)_2\text{SiCl}_2 + \text{Si} + 2 \text{H}_2 \quad \text{(VII.14)}
\]

Vague indication exists that increase of the average contact time in a fluidized bed from 3 to 30 seconds causes a decrease in selectivity of about 5% (127, p. 83). Owing to the properties of a fluidized bed a
rather broad residence time distribution can be expected which hampers a conclusion about the relation between selectivity and contact time. In a suitable fixed bed reactor contact times below one second can be reached easily, while the residence time distribution is much smaller.

In a series of tests with very short residence times a contact mixture was applied which contained 5 wt % copper and 0.5 wt % zinc. The silicon used was of sieve fraction 105 - 150 microns, had been washed with water to remove fine dust and had been dried at 150 °C. This contact mixture was expected to be highly reactive because a similar one performed well in a fluidized bed. In preliminary tests, however, attempts to conduct the synthesis with high gas rates to create short contact times, and in the temperature range of 280 - 320 °C failed completely. The explanation was sought in the deactivation of the contact mixture during transport from the reactor, in which it was previously prepared, to the exsiccator and from there to the fixed bed reactor. In such a procedure contact with air could not be avoided. The remedy seemed to be etching with hydrogen chloride during heating of the reactor to the desired temperature. When the temperature reached a value of 130 °C, hydrogen chloride was introduced for some minutes. Yet, the reaction would not start below 350 °C and upon lowering of the temperature from 350 to 300 °C the reaction ceased completely. It was then decided to carry out the experiments at a temperature of 360 °C although substantial cracking and consequently a fast deactivation had to be expected. Amazingly, it was observed that at this temperature a high and rather constant selectivity over at least 20% of the silicon conversion could

Table 33. Fixed bed experiments with high gas velocities at 360 °C
Contact mixture: 5% Cu, 0.5% Zn; vibrated reactor.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Cont.time (sec)</th>
<th>Duration (min)</th>
<th>Si-conv. (%)</th>
<th>Av. Reactivity (g MeCl/kg Si.hr)</th>
<th>Av. Selectivity (mol % Me₂SiCl₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCS-6</td>
<td>0.33-4.04</td>
<td>300</td>
<td>18.0</td>
<td>125</td>
<td>92.2</td>
</tr>
<tr>
<td>-7</td>
<td>0.27-0.67</td>
<td>360</td>
<td>14.0</td>
<td>80</td>
<td>91.7</td>
</tr>
<tr>
<td>-8</td>
<td>0.32-1.18</td>
<td>405</td>
<td>17.5</td>
<td>88</td>
<td>88.7</td>
</tr>
<tr>
<td>-9</td>
<td>0.29-1.15</td>
<td>435</td>
<td>25.6</td>
<td>120</td>
<td>94.3</td>
</tr>
<tr>
<td>-10</td>
<td>0.47-9.19</td>
<td>360</td>
<td>20.6</td>
<td>117</td>
<td>91.1</td>
</tr>
</tbody>
</table>
be reached. In order to assure a compact packing of the contact mixture, the bed was vibrated. No local voids which could disturb the flow pattern in the reactor could be observed after the tests, which is otherwise often the case. All contact mixtures had a homogeneous reddish colour after the tests, indicating that reaction had taken place over the whole bed.

Figure 41

Fixed bed experiments with small contact times, temperature 360 °C

![Graphs showing product composition over contact time for different contact mixtures](image-url)
Table 33 lists the overall results of some tests. During the tests the rates of methylchloride and nitrogen were varied to study the influence of the contact time while the partial pressure of methylchloride was kept constant. Figures 41-a through -d show the composition of the silanes product for subsequent samples, taken at roughly one hour intervals. The lower part of the figures show the contact time, calculated from the methylchloride feed and the estimated amount of contact mixture in the reactor. If the feed rate was changed, it was done immediately after a sample was taken, so that about 45 minutes would pass at the desired time of contact before the corresponding sample was taken. Tabulated data may be found in (27).

The plots allow no distinct conclusion about the influence of the residence time. MCS-6 and -10 show increase of selectivity with shortening of contact time, MCS-7 and -9 show no influence and MCS-8 shows decrease of selectivity with contact time. The study reveals some interesting facts:

- No other compounds, usually present in the silanes product occur with a higher content than 1 - 2%.
- It is possible to reach 90% selectivity in a fixed bed when high gas-velocities are employed to avoid local overheating.
- At least 20% of the silicon charge can be converted, without the usual initial cracking and changing selectivity when the test is conducted with great care.
- With a bulk temperature below 320 °C the direct synthesis reaction will not start, and it even ceases when the temperature is lowered to 300 °C.

The extremely good behaviour of the contact mixture is caused by the combination of the following circumstances:

- Methylchloride is free of oxygen and moisture.
- The contact mixture contains 0.5% zinc and 5% copper.
- High gas rates together with a narrow reactor provide high linear gas velocities and may account for proper cooling of "hot particles".
- The reactor is subject to a 50 cycles vibration, which may induce a better heat transport between particles and between particles and gas.
-6-3. Intermittent addition of zinc chloride (IV-8, -9)

Periodical admixture of zinc or continuous supply of zinc chloride makes up for the losses of zinc chloride by evaporation. A higher convertibility of silicon and higher selectivity results from the supply.

Enough evidence has been produced that the presence of small amounts of zinc or zinc chloride provides a high and constant selectivity and allows a high conversion of the silicon in a batch process. Generally the silicon fraction which is converted into a product containing an average of 85 mol % of dimethyldichlorosilane is twice as high, while reaction rates remain on a higher level. Because of evaporation the zinc chloride content in the contact mixture will gradually decrease in the course of the process. Table 30 (VII-5) shows that the zinc content of a contact mixture decreases during a fluid-bed experiment from the original 0.1 wt % to an amount below the limit of quantitative detection (<0.05 wt %). Supply in the form of zinc powder or zinc chloride is then required in order to make up for the losses. The entrained dust, which is collected in a colder part downstream of the reactor will contain part of the zinc chloride (see Table 31 in VII-5).

In a fixed bed experiment the effect of zinc addition has been shown to improve the performance substantially, until after some hours both reactivity and selectivity decrease, due to evaporation of zinc chloride. Figure 42 shows the course of such a fixed bed experiment. The contact mixture consisted of silicon, of sieve fraction 105 - 150 microns,

Figure 42.
Fixed bed experiment (MCS-11)
methylchloride not purified,
contact mixture with 0.1 % zinc

Figure 43
Fixed bed experiment (MCS-12)
methylchloride not purified,
no promoters added to contact mixture
containing 10 wt % copper, 0.1 wt % zinc and 0.05 wt % aluminium. For comparison, Figure 43 shows an experiment where no zinc and aluminium were added to the contact mixture, although more than 0.04% of aluminium is always present in the silicon as impurity (see VII-1). Both experiments were conducted at about 355 °C.

In Figure 44 a series of experiments at 355 °C with one batch of contact mixture is represented. At intervals, when the reaction slowed down, the reactor was cooled under a stream of nitrogen and 8 - 10 mg of zinc powder was mixed with the contact mixture. Then the mixture was introduced in the reactor again and heated to the reaction temperature under a stream of methylchloride. The time on the abscissa represents the real

**Figure 44**

Intermittent addition of zinc (MCS-13)
arrows indicate addition of 9 mg zinc
time of reaction. Because of the long duration of the experiment the time scale is frequently broken, but the synthesis was performed continuously except when zinc had to be added. The experiment shows that both reactivity and selectivity retook normal values shortly after the addition of zinc. The constancy of the combined content of dimethyldichlorosilane and methyldichlorosilane is remarkable. It is only slightly influenced by the intermittent zinc addition and lies, on the average, at a value of 75 mol %. Also the amount of methyltrichlorosilane was rather constant and remained around 15 mol % during the whole experiment. The average content of trimethylchlorosilane was 2 mol %, the rest was made up from 4 - 10 mol % of trichlorosilane and tetrachlorosilane.

Figure 45
Continuous addition of zinc chloride (MCS-14)

That it is zinc chloride and not zinc in metallic form that acts as the promoter is shown by an experiment (MCS-14) where zinc chloride vapour is continuously fed to the reactor. For this purpose the first U-tube of the fixed bed reactor contained 1 gram of zinc chloride, so that the feed, consisting of methylchloride and nitrogen, was able to entrain some zinc chloride vapour. The course of the experiment is given in Figure 45. The difference between experiments MCS-13 and -14 is striking. The latter shows a reactivity which remains constant within the observational error and a selectivity of about 42 mol % dimethyldichlorosilane. Again the sum of the contents of dimethyldichlorosilane and methyl-
Dichlorosilane is constantly 75 mol %. It should be mentioned that after the experiment the inner wall of the glass tube between the molten zinc chloride in the first "U" and the layer of contact mixture in the second "U" had a black coating, probably due to some cracking of methyl chloride. This amount of tar is rather small for the long duration (148 hrs) of the experiment; it could not be collected for analysis.

In Table 34 additional information of MCS-11 through -14 is listed. The experiments show that zinc chloride has a positive effect on reactivity and selectivity. If zinc is added in metallic form its effect commences a short time after the addition, indicating that it has to be transformed into zinc chloride before it performs beneficially. Because the content of zinc chloride decreases with time due to evaporation, supply is required to maintain the optimum performance. Mention should be made of the fact that MCS-11 through -14 have not been conducted with properly purified methyl chloride. Another difference with respect to the experiments described in VII-6-2 is that the reactor was not subjected to vibration.

<table>
<thead>
<tr>
<th>Expt Nr</th>
<th>Temp (°C)</th>
<th>Duration (hours)</th>
<th>Si-conv. (%)</th>
<th>react. (g CH₃Cl/kg Si.h)</th>
<th>In.charge (g)</th>
<th>Spent mixt. % C % H</th>
<th>see</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCS-11</td>
<td>355</td>
<td>29</td>
<td>26.7</td>
<td>32</td>
<td>7.57</td>
<td>1.45 0.06</td>
<td>42</td>
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<tr>
<td>-12</td>
<td>357</td>
<td>29</td>
<td>5.5</td>
<td>7</td>
<td>7.50</td>
<td>0.65 0.08</td>
<td>43</td>
</tr>
<tr>
<td>-13a</td>
<td>355</td>
<td>26</td>
<td>21.4</td>
<td>30</td>
<td>7.47</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>28</td>
<td>32.5</td>
<td></td>
<td>18</td>
<td>6.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>21</td>
<td>40.9</td>
<td></td>
<td>22</td>
<td>5.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>35</td>
<td>52.0</td>
<td></td>
<td>19</td>
<td>4.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>31</td>
<td>62.8</td>
<td></td>
<td>26</td>
<td>3.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>6</td>
<td>66.5</td>
<td></td>
<td>60</td>
<td>3.25 13.9 0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-14</td>
<td>355</td>
<td>71</td>
<td>31.6</td>
<td>16</td>
<td>7.03 3.6 0.3</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>
The occurrence of methyl radicals in the gas phase could not be demonstrated. The cracked product methane presumably forms in the adsorbed layer.

In the first mechanism proposed for the reaction of methylchloride with silicon, under catalytic action of copper, the methylation of silicon was thought to proceed via gaseous methylcopper \( (98) \). Attempts to prove the existence of this compound have failed, but showed that methyl radicals may be formed already from methylchloride and metallic copper at 270 °C \( (87) \). If methyl radicals do occur in the gas phase during methylchlorosilanes formation, the presence of some co-products is explainable, as was concluded from experiments where decomposing dimethylmercury was reacted with some silanes \( (9) \). Direct evidence for the existence of methyl radicals in the course of a direct synthesis has, however, not yet been given. Experiments with nitrous oxide \( (102) \), iodine and azomethane \( (127) \) showed the influence of the admixtures but the experiments were not fully conclusive. They did confirm the fact that methyl radicals play no rôle in the formation of methylchlorosilanes. Additional indication of absence of methyl radicals is furnished by an experiment where toluene is added to the methylchloride feed. If methyl radicals are present in the gas phase they are expected to react with toluene according to equation (VII.15) \( (110) \):

\[
\text{C}_6\text{H}_5\text{CH}_3 \ + \ \text{CH}_3. \ \rightarrow \ \text{C}_6\text{H}_5\text{CH}_2. \ + \ \text{CH}_4 \quad (\text{VII.15})
\]

The benzyl radicals are more stable than methyl radicals, invoke no chain reactions and will dimerize forming dibenzyl \( (110, 115) \).

The effect of toluene is accordingly expected to be an increase in the amount of methane formed. As formation of hydrogen is the probable result of a continued decomposition of methyl radicals, the increase of the amount of methane will be accompanied by a decrease in the amount of hydrogen formed.

In a fixed bed experiment the effect of toluene admixture has been investigated. The experimental equipment is a modification of that represented in Figure 40. A small reactor with rectangular cross-section of
inner measures 0.4x1.2 cm² and length 20 cm is charged with 6.4 g of contact mixture containing 10 wt % copper and 0.1 wt % zinc. Analysis of the uncondensable gases is possible by freezing out the products, unconverted methylchloride and toluene. To create a gasflow between the cold trap and the sample holder of the gaschromatographic equipment, the methylchloride feed is diluted with nitrogen. With an average methylchloride rate of 15.5 Nml/min and nitrogen rate of 10 Nml/min, the residence time in the contact mixture bed can be estimated at 3 sec for the applied temperature of 315 °C. Figure 46 shows the production of methane and hydrogen, calculated from peak-heights in the chromatograms, versus the elapsed time since the start of the reaction. Tabulated data may be found in (133). The figure shows the period of silicon conversion between 15 and 25%, estimated from the totally converted silicon. The introduction of toluene (average molar ratio CH₃Cl:C₆H₅CH₃ = 2:1) is started when the production of methane and hydrogen are fairly constant. The amounts of hydrogen show an increase by about 30%, which diminishes later on. For this effect no explanation is obvious. Apart from small fluctuations in the amounts of methane no significant change is evident. Gaschromatographic analysis of the condensed toluene revealed no detectable amounts of dibenzyl.

In conclusion it may be stated that the produced methane originated from cracking in the adsorbed layer, because once more the detection of methyl radicals in the gas phase has failed.
The fast exothermic reaction of hydrogen chloride with a contact mixture obstructs simple experimenting. At 260 °C the maximum dichlorosilane yield appeared to be 24 mol % at a contact time of 0.1 s.

-7-1. Introduction

Hydrogen chloride reacts readily with silicon-copper contact mixtures at temperatures higher than 170 °C (VII-10). The main product formed is trichlorosilane, but dichlorosilane and tetrachlorosilane usually occur in the reaction product (Table 15, p. 77). In analogy with the alkylchlorosilanes synthesis it could be expected that the copper-catalyzed process would mainly yield dichlorosilane:

\[ 2 \text{HCl} + \text{Si} \text{(Cu)} \rightarrow \text{H}_2\text{SiCl}_2 \] (VII.16)

This seems not at all the case, as trichlorosilane is formed with high selectivity:

\[ 3 \text{HCl} + \text{Si} \rightarrow \text{HSiCl}_3 + \text{H}_2 \] (VII.17)

Gas phase kinetics on reactions of chlorosilanes give the indication that dichlorosilane can be converted with hydrogen chloride into trichlorosilane:

\[ \text{H}_2\text{SiCl}_2 + \text{HCl} \rightarrow \text{HSiCl}_3 + \text{H}_2 \] (VII.18)

The activation energy for this reaction is rather high (33.2 kcal/mol, see V-3), but the contact mixture surface is undoubtedly able to lower this value substantially. It thus seemed of interest to investigate the product composition with much smaller contact times, for example down to 0.1 s and at different temperatures.

-7-2. Experimental conditions

To conduct experiments where the influence of the contact time upon the product composition is investigated, a fixed bed type reactor is required, as was discussed in VII-6-1. Some measures were taken to conduct the experiments reproducibly, which followed from preliminary tests.

At the reaction temperature of 260 °C the reaction rate is so high that
hydrogen chloride had to be diluted more than 10 times with an inert gas, e.g. nitrogen. When using pure hydrogen chloride, local overheating occurred even in reactors with a diameter of 0.2 cm. The temperature might rise several hundreds of degrees C locally.

The chlorosilanes were condensed out of the product stream by means of a cold trap containing Chromosorb-W, and which was cooled with liquid nitrogen. The sample was brought immediately in the circuit of the gas-chromatograph, after a pre-separation between condensable and not-condensable gases. After the collection of a proper amount of product, the sample could be evaporated rapidly by replacing the Dewar vessel with liquid nitrogen by a vessel containing hot water.

The experimental arrangement fulfilling the above requirements resembles the equipment described in VII-6-1 for the methylchlorosilanes experiments in fixed bed. In Figure 40 (p. 132) the assembly is schematized, with only a few minor differences applied in the chlorosilanes experiments.

The contact mixture, prepared in advance, was kept under vacuum above concentrated sulfuric acid. For each experiment a part of the mixture was used, to obtain a contact mixture as much reproducible as possible. In the transport from exsiccator to reactor, contact with air could not be avoided. The hydrogen chloride used had a purity of better than 99.9%, and contained hydrogen as main impurity.

Evaluation of the chromatogram in order to obtain the product composition was performed with a planimeter. In absence of calibration data for the chlorosilanes, it was assumed that the ratios of the peak-areas in the chromatograms represent molar ratios in the sample.

The conversion rates are determined from the differences in weight of the contact mixture charge before and after the test and the time of reaction. Such average values have an estimated accuracy of ± 0.003 mmol Si/g Si.min.

-7-3. Results and discussion

In Table 35 a summary is given of the experiments with data regarding temperature, copper content, reactor load, sieve fraction of the used silicon, duration of the experiment, conversion rates of silicon and with reference to the graphic representations of the details. Tabulated data may be found in (20). No use has been made of the product analysis of
It is probable from some of the values for the conversion rates of silicon (Table 35) that slow diffusion in the gas-film around the particles may have obstructed the complete reaction of the introduced hydrogen chloride in a number of experiments. This can also be concluded from the value of the activation energy, estimated from an Arrhenius graph after CS-3, -11 and -13. The value of 16 ± 7 lies lower than the value obtained in a much lower temperature range: 24 ± 2 kcal/mol at 172 - 198 °C, which applies for the same contact mixture (see also Table 19, p. 85). Because of a small reactor load and a high linear gas velocity in the reactor of 2.4 m/s, the best value for the reaction rate at 260 °C will be found in CS-3. Complete absence of limitation by film-diffusion is not to be expected in most of the performed experiments.

For the silicon consumption, the average value of CS-2, -5, -8, -9 and -10, being 0.126 (+ 0.012) mmol.g⁻¹.min⁻¹ will be taken as the best representation of the experiments at 260 °C. The value applies to contact mixtures with 1 - 10 wt % copper.

In the Figures 47 - 49 the product composition observed during experiments at temperatures 220, 240 and 260 °C is plotted versus the contact time. In all three
experiments, the dichlorosilane content can be seen to increase with decreasing contact time. Also with increase of temperature the dichlorosilane content tends to increase.

Only in CS-1 and -2, monochlorosilane ($\text{H}_3\text{SiCl}$) occurred in sufficient quantity to be measurable (Figures 49 and 51). The average content in both experiments is $4 \text{ mol} \%$ and does not seem to vary with the contact time. In the other experiments the tailing of the hydrogen chloride peak in the gas chromatogram obscured its presence, although sometimes a "shoulder" was observed, indicating some tenths of a percent.

Tetrachlorosilane has only occasionally been detected. CS-5, conducted with a contact mixture containing only $1 \text{ wt} \%$ of copper showed an amount of about $3 \text{ mol} \%$ of silicontetrachloride (Figure 50). No significant influence of the copper content can be demonstrated in CS-5, -2 and -8 (Figures 50, 51 and 52).

An example of the reproducibility is obtained when the Figures 49, 51 and 53 are compared, resulting from experiments under the same conditions.

It can be concluded, that it is possible to obtain a chlorosilanes mixture containing $24 \text{ mol} \%$ of dichlorosilane when very short contact times are applied, for example $0.1 \text{ s}$. With longer contact times, a secondary reaction will decrease the content of dichlorosilane. With the contact
mixtures applied in the above experiments, the temperature where the highest selectivity is obtained, appeared to be 260 °C. When hydrogen chloride is not diluted with an inert gas or when the reaction temperature exceeds 260 °C, the exothermic reaction disturbs the isothermic performance.

Figure 53
Tests at 260 °C; 5% Cu (CS-10)

Figure 54
Tests at 240 °C; 5% Cu (CS-11)

Table 35. Conditions and results of experiments

<table>
<thead>
<tr>
<th>Nr</th>
<th>Temp (°C)</th>
<th>% Cu</th>
<th>Charge (g)</th>
<th>Fraction (microns)</th>
<th>Duration (min)</th>
<th>Rate (mmol.g⁻¹.min⁻¹)</th>
<th>p⁰_HCl (atm)</th>
<th>see Fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-1</td>
<td>260</td>
<td>5</td>
<td>9.00</td>
<td>175-210</td>
<td>200</td>
<td>0.069</td>
<td>0.20-0.30</td>
<td>49</td>
</tr>
<tr>
<td>-2</td>
<td>260</td>
<td>5</td>
<td>9.00</td>
<td>175-210</td>
<td>134</td>
<td>0.131</td>
<td>0.22-0.36</td>
<td>51</td>
</tr>
<tr>
<td>-3</td>
<td>260</td>
<td>5</td>
<td>3.00</td>
<td>175-210</td>
<td>31</td>
<td>0.238</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-4</td>
<td>260</td>
<td>1</td>
<td>8.00</td>
<td>125-150</td>
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<td>0.38-0.77</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>10</td>
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<td>125-150</td>
<td>89</td>
<td>0.133</td>
<td>0.18-0.27</td>
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</tr>
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<td>-10</td>
<td>260</td>
<td>5</td>
<td>9.22</td>
<td>175-210</td>
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<td>0.103</td>
<td>0.18-0.33</td>
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<tr>
<td>-11</td>
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<td>5</td>
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<td>5</td>
<td>8.00</td>
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<td>260</td>
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<td>8.10</td>
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<td>150</td>
<td>0.088</td>
<td>0.17-0.52</td>
<td>18</td>
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</tbody>
</table>
VII-8. Direct synthesis of ethylchlorosilanes (VI)

Details of the gaschromatographic analysis are given. Investigation of the ethylchlorosilanes synthesis is hampered by the often poor reproducibility of experiments, caused by the heterogeneity of the contact mixture.

-8-1. Introduction.

Experiments in ethylchlorosilanes synthesis are of importance because of possible future interest in diethyldichlorosilane and ethyldichlorosilane (VI-1). A high yield in the dichloro-compounds should be the aim in the conduction of the synthesis. The main product in the copper catalyzed reaction of ethylchloride and silicon is diethyldichlorosilane, if the conditions and the quality of the reactants are chosen carefully. The attempt to produce ethyldichlorosilane from a mixture of hydrogen chlo-

Figure 55. Arrangement of equipment in ethylchlorosilanes experiments. 1- container with ethylchloride, 2- thermostat bath, 3- cylinder with nitrogen, 4- flowmeter, 5- purification columns, 6- reactor heating, 7- air inlet for fluidization of outer bed, 8- double-U reactor, 9- eight-way valve, 10- cooling or heating of sample tube, 11- GLC-system.
ride and ethylchloride have failed:

\[ \text{C}_2\text{H}_5\text{Cl} + \text{HCl} + \text{Si} \rightarrow \text{C}_2\text{H}_5\text{SiHCl}_2 \]  

(VII.19)

For each molecule of ethyldichlorosilane, two molecules of ethylchloride proved necessary. The hydrogen chloride added, mainly formed chlorosilanes and increased the content of ethyltrichlorosilane. This reveals that formation of ethyldichlorosilane is accompanied by formation of ethylene or other products of the cracking of an ethyl group. The highest combined content of diethyldichlorosilane and ethyldichlorosilane mentioned in the literature was 75 wt %, and it was obtained with an alloy containing 5% of copper (5).

In this section some experiments will be described which may furnish more information on the process. The experiments were conducted with contact mixtures prepared from technical silicon (specification see VII-1) and cuprous chloride in fixed bed reactors. The equipment used in the experiments resembles closely that used in experiments with methylchlorosilanes (VII-6-1). Figure 55 shows the schematic arrangement.

-8-2. Gaschromatographic analysis of ethylchlorosilanes (VI-4)

Separation of the products obtained from reaction of ethylchloride with silicon-copper proceeds well with a stationary phase of o-nitrobiphenyl. Separation of ethyltrichlorosilane from diethyltrichlorosilane by means of gaschromatography seems impossible.

To determine the composition of a mixture of ethylchlorosilanes, use has been made of gaschromatographic analysis with katharometer detection. Table 36 lists the relative retention of a number of compounds that can be expected in the product of a direct synthesis of ethylchlorosilanes. The relative retention of a compound is given as the ratio of its retention time and the retention time of diethyldichlorosilane, both measured from the moment of injection. In all cases hydrogen was used as carrier gas. The fastest analysis was obtained under the conditions as given in column 6, with a sufficient separation of the main products. With none of the tested liquid phases separation of ethyltrichlorosilane and diethylchlorosilane appeared possible. These compounds form an azeotropic mixture with boiling point 99 °C and they presumably possess dipole moments of the same magnitude, because even with the very polar
Table 36. Relative retention for various packings

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling pt. (°C)</th>
<th>a)</th>
<th>b)</th>
<th>c)</th>
<th>d)</th>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>-83.7</td>
<td>115</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>EtCl</td>
<td>12.3</td>
<td>125</td>
<td>57</td>
<td>63</td>
<td>204</td>
<td>60</td>
</tr>
<tr>
<td>SiCl₄</td>
<td>57.4</td>
<td>130</td>
<td>72</td>
<td>96</td>
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<tr>
<td>SiHCl₃</td>
<td>31.8</td>
<td>165</td>
<td>51</td>
<td>63</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Me₂SiCl</td>
<td>57.6</td>
<td>170</td>
<td></td>
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<tr>
<td>Me₃SiCl</td>
<td>66.1</td>
<td>232</td>
<td></td>
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</tr>
<tr>
<td>Me₂SiCl₂</td>
<td>70.2</td>
<td>250</td>
<td></td>
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<tr>
<td>Et₂SiHCl₂</td>
<td>74.9</td>
<td>265</td>
<td>178</td>
<td>223</td>
<td>385</td>
<td>250</td>
</tr>
<tr>
<td>SiCl₆</td>
<td>153</td>
<td>275</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Et₃SiH</td>
<td>107</td>
<td>340</td>
<td>193</td>
<td>225</td>
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<tr>
<td>Et₃SiCl₃</td>
<td>99.5</td>
<td>425</td>
<td>361</td>
<td>412</td>
<td>565</td>
<td>460</td>
</tr>
<tr>
<td>Et₂SiHCl</td>
<td>99.7</td>
<td>425</td>
<td>361</td>
<td>412</td>
<td>565</td>
<td>460</td>
</tr>
<tr>
<td>Et₄Si</td>
<td>153.0</td>
<td>622</td>
<td>708</td>
<td>1920</td>
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<td></td>
</tr>
<tr>
<td>Et₂SiCl₂</td>
<td>129.0</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Et₃SiCl</td>
<td>143.5</td>
<td>1250</td>
<td>1055</td>
<td>1300</td>
<td>1540</td>
<td>1630</td>
</tr>
<tr>
<td>Column-temp. (°C)</td>
<td>120</td>
<td>95</td>
<td>110</td>
<td>110</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Gas rate (NmL/min)</td>
<td>30</td>
<td>25</td>
<td>24</td>
<td>30</td>
<td>74.5</td>
<td></td>
</tr>
<tr>
<td>Retention time of Et₂SiCl₂ (min)</td>
<td>28</td>
<td>45</td>
<td>18</td>
<td>15</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>

a) column of length 2.5 m, charged with Chromosorb W (80 - 100 mesh), containing 26 wt % of o-nitro biphenyl. Hydrogen is used as carrier gas.

b) same as a) with different temperature and gas rate.

c) same as a) but adsorbate contained 30 wt % of o-nitro biphenyl.

d) column of length 4 m, charged with Chromosorb W (60 - 70 mesh), containing 20 wt % of silicone-gum GE-SE 30.

e) after (57); column contains 55.5 g of ground brick with 9 wt % of methyl-silicone oil MSO 150. Nitrogen was used as carrier gas.
o-nitrobiphenyl the separation failed. Column packings containing p-nitrobiphenyl, nitrilsilicone oil, Carbowax 1500 (polyethylene-glycol), Porapak Q (polystyrene), dinonylphthalate, and a phenylchlorosilanes mixture have been tested with the same aim, but none of them with success. In all analyses performed on ethylchlorosilanes mixtures, the peak appearing at the relative retention of the azeotropic mixture has been interpreted as belonging to ethyltrichlorosilane. This implicates the presumably not very speculative assumption that diethylchlorosilane occurs only in negligible amounts in the samples.

For conversion of the peak areas to the weight or molar percentages of the components of a product sample, the calibration factors have been determined by injecting mixtures of known composition. In Table 37 the calibration factors relative to diethyldichlorosilane for the main compounds appearing in the samples to be analyzed are given. The data have an accuracy of about 1%, except the one for ethylchloride. A rather large error was made during weighing and injection of the samples, caused by evaporation of ethylchloride. The value for ethylchloride may be in error for \( \pm 10\% \).

Table 37.

Calibration factors for gaschromatographic analysis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calibration factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtCl</td>
<td>0.62 ( \pm 0.07 )</td>
</tr>
<tr>
<td>SiCl(_4)</td>
<td>1.24 ( \pm 0.02 )</td>
</tr>
<tr>
<td>EtSiHCl(_2)</td>
<td>0.96 ( \pm 0.01 )</td>
</tr>
<tr>
<td>EtSiCl(_3)</td>
<td>1.02 ( \pm 0.01 )</td>
</tr>
<tr>
<td>Et(_2)SiCl(_2)</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Analysis of the reaction products was performed partly by injection of a sample of the collected condensate. This was done in cases where the synthesis was conducted with 50 - 100 g of contact mixture. When a smaller charge was tested, a sample of the product gas was introduced in the gaschromatographic system by means of an eight-way valve.
Strong indication is obtained that formation of an alkytrichlorosilane proceeds by subsequent interaction of cuprous chloride and alkylchloride with silicon.

An active contact mixture is prepared by heating silicon and cuprous chloride for some time in a small current of inert gas, in order to remove tetrachlorosilane (III-1). After reduction of cuprous chloride, the mixture is heated for some time, to allow Cu$_3$Si to be formed. Most direct synthesis experiments therefore start with a contact mixture of which the surface is only slightly or not at all chlorinated. In the latter case, an induction period is frequently observed, during which cracking of the reacting chloride produces the chlorinated surface.

In this paragraph some experiments will be discussed where ethylchloride was introduced in the reactor before all of the cuprous chloride had reacted with silicon. For this purpose, the reactor was heated to the reaction temperature, without waiting for complete reduction of cuprous chloride, and ethylchloride was introduced at once. The contact mixture in the first test comprised 94.4 g of silicon of sieve fraction 150 - 210 microns and 6.0 g of cuprous chloride. No promoters were added. 16 g/hr of ethylchloride was introduced, diluted with nitrogen to give a partial pressure of 0.14 atm and a contact time of 1.6 s. The reactor had an internal diameter of 20 mm and was provided with a central tube of 6 mm diameter for thermocouples. In Figure 56 the course of the product composition in the first hours of this experiment (ECS-28) is given. At zero time the introduction of ethylchloride had begun and the first product sample was already taken after 5 minutes. This consisted only of tetrachlorosilane and ethyltrichlorosilane. Already 15 minutes after the ethylchloride feed had been started, no more tetrachlorosilane was formed. The amount of diethyl dichlorosilane increased steadily until after 1.5 hours the maximum value was reached. When the course of the product composition is compared with that in an experiment where the reduction of cuprous chloride is completed before introduction of the alkylchloride, it is obvious that the formation of ethyltrichlorosilane is related with the presence of cuprous chloride. For instance, in ECS-10 the mixture of cuprous chloride and silicon had been heated for 2 hours at 420 °C. Right from the beginning the product
The effect of cuprous chloride is even more pronounced in ECS-21 where ethylchloride was introduced when the temperature reached the value 280 °C. While this temperature was maintained, a mixture of 1 Nl/hr of ethylchloride (3 g/hr) and 8 Nl/hr of ethylene was fed to the reactor. The contact time was about 7 s. Because of the lower temperature, the phenomena proceeded much slower. It took about 10 hours before the content of ethyltrichlorosilane approached an average value of 15 wt % and before the total reactivity became constant. The lower line in Figure 57 shows the reactivity and the upper line represents the cumulative amount of ethyltrichlorosilane formed. Extrapolation of the linear part of the line leads to a value of 4.50 g of ethyltrichlorosilane. Of this amount, 4.2 g could be formed from the cuprous chloride, which shows a simple calculation. From 9 g of cuprous chloride initially present, 1.7 g tetrachlorosilane, collected before the start of the test consumed 1.4 g of chlorine. The remaining 1.8 g chlorine now may yield 4.2 g of ethyltrichlorosilane, if two of its three chlorine atoms come from cuprous chloride. That not the expected 4.2, but 4.5 g results from the extrapolation in the figure may be caused by extra cracking of ethylchloride from the presence of free copper.

It appears that the formation of alkyltrichlorosilane proceeds in two stages. First a silicon atom is chlorinated by cuprous chloride,
forming surface bound SiCl₂. When the alkylchloride interacts with this intermediate, an alkyltrichlorosilane molecule in adsorbed state will be formed, which may desorb. Schematically the reactions may be given as:

\[
\begin{align*}
\text{Si} + 2 \text{CuCl} & \rightarrow \text{SiCl}_2 + 2 \text{Cu} \\
\text{SiCl}_2 + \text{RCl} & \rightarrow \text{RSiCl}_3
\end{align*}
\] (VII.20)
(VII.21)

The scheme resembles the one suggested by Golubtsov c.s (45), except for the state of the silicon dichloride, which was assumed to exist in the gas phase (see also IV-3, V-2). The hypothesis that silicon dichloride is the precursor of dialkyldichlorosilane is not supported by the present evidence and not by the experimental results given in (45) either.

-8-4. Experiments in fixed bed reactors (VI-2)

The content of ethyltrichlorosilane decreases when ethylene is added to the feed. The activation energy of the reaction of ethylchloride with silicon-copper is 20 kcal/mol.
ethylchloride appears to decompose and to form cuprous chloride.
Schematically:

\[ 2 \text{Cu} + 2 \text{C}_2\text{H}_5\text{Cl} \rightarrow 2 \text{CuCl} + 2 \text{C}_2\text{H}_4 + \text{H}_2 \]  \hspace{1cm} \text{(VII.22)}

The content of ethyldichlorosilane supplements that of diethyldichlorosilane to 72 wt %. Its nearly random variation seems independent from any process parameter, which suggests that an unnoticed effect causes the decomposition of an ethyl group about to form diethyldichlorosilane. This unnoticed effect is in all probability the local particle temperature, which can not be controlled under the experimental circumstances applied.

Figure 59 is a plot of the formation of cracked gases in the course of ECS-11. To check the mass-balance, the gas production, calculated from the formation of ethyltrichlorosilane and ethyldichlorosilane, is also plotted. The values are obtained, assuming that equations (VII.23) and
Production of gases in ECS-11
1- observed, 2- calculated from EtSiCl$_3$-formation, 3- calculated from EtSiHCl$_2$-production; (Nl/hr)

Figure 59

Table 38
Average rates of formation and selectivity at different temperatures

<table>
<thead>
<tr>
<th>Expt (nr)</th>
<th>Temp. (°C)</th>
<th>Rate</th>
<th>% Et$_2$SiCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECS-10 a</td>
<td>260</td>
<td>19</td>
<td>17</td>
</tr>
<tr>
<td>b</td>
<td>280</td>
<td>30.5</td>
<td>25</td>
</tr>
<tr>
<td>c</td>
<td>300</td>
<td>49.2</td>
<td>34</td>
</tr>
<tr>
<td>-11 a</td>
<td>300</td>
<td>63.7</td>
<td>31</td>
</tr>
<tr>
<td>b</td>
<td>325</td>
<td>117</td>
<td>35</td>
</tr>
<tr>
<td>-12 a</td>
<td>300</td>
<td>79</td>
<td>37</td>
</tr>
<tr>
<td>b</td>
<td>280</td>
<td>36</td>
<td>31</td>
</tr>
<tr>
<td>c</td>
<td>350</td>
<td>254</td>
<td>46</td>
</tr>
</tbody>
</table>

a) g silanes/kg Si.hr

(VII.24) represent the overall reactions in the formation of the cracked gases.

\[
\begin{align*}
3 \text{C}_2\text{H}_5\text{Cl} + \text{Si} & \rightarrow \text{C}_2\text{H}_5\text{SiCl}_3 + 2 \text{C}_2\text{H}_4 + \text{H}_2 \quad \text{(VII.23)} \\
2 \text{C}_2\text{H}_5\text{Cl} + \text{Si} & \rightarrow \text{C}_2\text{H}_5\text{SiHCl}_2 + \text{C}_2\text{H}_4 \quad \text{(VII.24)}
\end{align*}
\]

It is not surprising that the actual formation of cracked gases is proportional to the formation of ethyltrichlorosilane and ethyldichlorosilane, although the mass-balance is poorly satisfied.

ECS-10, -11 and -12 have been conducted over a temperature range of 90 degrees C and under the same circumstances. In all cases, undiluted ethylchloride was introduced with a feed rate of 2 Nml/s at atmospheric pressure in a steel reactor containing 90 g contact mixture. From the rates of formation of the ethylchlorosilanes, given in Table 38, when plotted in an Arrhenius-graph (Figure 60), a value of the activation energy of 20 + 3 kcal/mol follows. The value applies to the reaction of ethylchloride with a contact mixture containing 4 - 6%
copper and 1% cadmium chloride, and it agrees satisfactorily with data from the literature (VI-2). For the formation of cracked gases such a calculation fails, due to the spread of the data.

About the content of ethyltrichlorosilane in relation with some of the process parameters, the overall results of a number of experiments listed in Table 39 may furnish some elucidation. The average contents of ethyltrichlorosilane fall in two groups, with values respectively around 20% when ethylene was used to dilute the ethylchloride and around 28% when nitrogen was used as a diluent or without any diluent. The phenomenon has been illustrated in Figure 20 (p. 98), a plot of the content of ethyltrichlorosilane versus the temperature of the reaction. In spite of a considerable spread, the difference between the two series can be clearly recognized. The presence of cadmium chloride, the contact time and the temperature seem not at all related with the content of ethyltrichlorosilane in the product mixture.

Table 39

The influence of some process parameters on the content of EtSiCl₃

<table>
<thead>
<tr>
<th>Expt (nr)</th>
<th>Diluent</th>
<th>Av. wt % EtSiCl₃</th>
<th>Temp (°C)</th>
<th>τ (s)</th>
<th>Promoted with</th>
<th>Fig. (nr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECS-10</td>
<td>-</td>
<td>30</td>
<td>260-300</td>
<td>9.5</td>
<td>CdCl₂</td>
<td>19</td>
</tr>
<tr>
<td>-11</td>
<td>-</td>
<td>30</td>
<td>300-325</td>
<td>9</td>
<td>CdCl₂</td>
<td>59</td>
</tr>
<tr>
<td>-12</td>
<td>-</td>
<td>29</td>
<td>280-350</td>
<td>9</td>
<td>CdCl₂</td>
<td>58</td>
</tr>
<tr>
<td>-14 a</td>
<td>C₂H₄</td>
<td>18</td>
<td>350</td>
<td>18</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>-</td>
<td>28</td>
<td>350</td>
<td>24</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>-15</td>
<td>C₂H₄</td>
<td>20</td>
<td>360</td>
<td>5</td>
<td>CdCl₂</td>
<td></td>
</tr>
<tr>
<td>-16</td>
<td>C₂H₄</td>
<td>19</td>
<td>360</td>
<td>3.1</td>
<td>CdCl₂</td>
<td></td>
</tr>
<tr>
<td>-17 a</td>
<td>C₂H₄</td>
<td>20</td>
<td>325</td>
<td>2.2</td>
<td>CdCl₂</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>C₂H₄</td>
<td>14</td>
<td>350</td>
<td>1.2</td>
<td>CdCl₂</td>
<td></td>
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<tr>
<td>-18</td>
<td>C₂H₄</td>
<td>21</td>
<td>325</td>
<td>2.2</td>
<td>CdCl₂</td>
<td></td>
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<tr>
<td>-19</td>
<td>C₂H₄</td>
<td>14</td>
<td>310</td>
<td>2.2</td>
<td>CdCl₂</td>
<td></td>
</tr>
<tr>
<td>-21</td>
<td>C₂H₄</td>
<td>16</td>
<td>300</td>
<td>7</td>
<td>-</td>
<td>57</td>
</tr>
<tr>
<td>-24</td>
<td>N₂</td>
<td>26</td>
<td>306</td>
<td>7</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>-25</td>
<td>N₂</td>
<td>24</td>
<td>333</td>
<td>4.6</td>
<td>CdCl₂</td>
<td></td>
</tr>
<tr>
<td>-28</td>
<td>N₂</td>
<td>30</td>
<td>340</td>
<td>1.6</td>
<td>-</td>
<td>56</td>
</tr>
<tr>
<td>-30 a</td>
<td>N₂</td>
<td>26</td>
<td>340</td>
<td>2.8</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>C₂H₄</td>
<td>22</td>
<td>340</td>
<td>2.8</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>-34 a</td>
<td>C₂H₄</td>
<td>22</td>
<td>340</td>
<td>3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>N₂</td>
<td>29</td>
<td>340</td>
<td>3</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Over 50% of silicon conversion into a product containing 76 mol % diethyldichlorosilane is obtained when ethylchloride is free of oxygen and when contact times are below 0.6 seconds.

When a chemical process yields several reaction products, attempts will be made to determine the conditions under which the most favourable product composition will be obtained. One of the parameters to be varied in order to distinguish between primary and secondary reactions, is the contact time. In the direct synthesis of ethylchlorosilanes, the main products formed are diethyldichlorosilane, ethyltrichlorosilane and ethylchlorosilane, and it is not fully clear, whether these compounds are formed in parallel reactions (17) or that possible secondary reactions are of importance (VI-3). The relation between the contents of diethyldichlorosilane and ethyldichlorosilane raise especially the question whether the formation of the latter compound is connected with decomposition of the former one.

In order to obtain more information on this topic, some experiments with short contact times have been conducted. In the methylchlorosilanes system, the phenomenon could be observed, that high gas rates, which accompany the small contact times applied, exert a beneficial effect upon the selectivity (VII-6-2). Presumably the prevention of local hot spots was connected with this effect, and it can thus be expected that the same applies to the reaction of ethylchloride with a contact mixture.

The tests to be discussed have been conducted similarly to the ones described in VII-6, i.e. with portions of 8 g of a pre-prepared contact mixture in a reactor of small diameter. The high gas rates caused a considerable pressure drop over the reactor, which used to increase during the experiments, due to tar deposition in the glass-filter of the reactor. To be able to maintain a constant partial pressure of ethylchloride, nitrogen was used as a diluent gas, and the flows of the gases were adjusted when a pressure-rise demanded such. Both gases were purified from oxygen by means of a BTS-catalyst (see VII-5-2).
In Tables 40 and 41 the overall results of some tests with small contact times are given. The first series was performed with a contact mixture containing 5% copper and 0.1% zinc.

### Table 40. Tests with small contact times

<table>
<thead>
<tr>
<th>Expt (nr)</th>
<th>Average rate (g Si/kg Si.hr)</th>
<th>Duration (hrs)</th>
<th>Si conv. (%)</th>
<th>Product composition a)</th>
<th>( p_{\text{EtCl}} ) (atm)</th>
<th>Feed (g/s)</th>
<th>( \tau ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECS-37</td>
<td>33</td>
<td>6</td>
<td>20.1</td>
<td>D 65; DH 15; T 20</td>
<td>0.11</td>
<td>0.16</td>
<td>0.23</td>
</tr>
<tr>
<td>-38</td>
<td>21</td>
<td>12.6</td>
<td>23.4</td>
<td>D 80; DH 5; T 15</td>
<td>0.11</td>
<td>0.16</td>
<td>0.23</td>
</tr>
<tr>
<td>-39</td>
<td>28</td>
<td>5</td>
<td>12.9</td>
<td>D 60; DH 20; T 20</td>
<td>0.20</td>
<td>0.16</td>
<td>0.27</td>
</tr>
<tr>
<td>-40</td>
<td>19</td>
<td>9.5</td>
<td>16.7</td>
<td>D 55; DH 25; T 20</td>
<td>0.13</td>
<td>0.29</td>
<td>0.28</td>
</tr>
<tr>
<td>-41</td>
<td>23</td>
<td>14</td>
<td>27.1</td>
<td>D 75; DH 10; T 15</td>
<td>0.13 a 0.17</td>
<td>0.29 b</td>
<td>0.21 c</td>
</tr>
</tbody>
</table>

| ^a) composition in mol%, D- \( \text{Et}_2\text{SiCl}_2 \), DH- \( \text{EtSiHCl}_2 \), T- \( \text{EtSiCl}_3 \) |

Although the conditions of the experiments listed in Table 40 are the same, they appear rather irreproducible. Figure 61, which shows the product composition in the course of ECS-41, where the contact time was varied while the partial pressure of ethylchloride was kept constant, reveals the absence of a significant influence of the contact time.

In Table 41 the results are given of tests performed with a contact mixture containing 10% copper, 0.1% zinc and 0.05% aluminium. The Figures 62...
through 65 illustrate the course of these experiments. In ECS-44 (Figure 64) the ethylchloride feed was stopped after 6.5 hours of reaction. While the temperature was maintained at 330 °C, a small current of nitrogen was led through the reactor for 17 hours and then ethylchloride was introduced again. It can be seen that the content of ethyltrichlorosilane starts on a high level but soon retakes its original value. It does not seem very speculative to explain this phenomenon by extra cracking of ethylchloride, required to re-activate the silicon (IV-9,b).

In ECS-45 (Figure 65) the contact time was varied between 0.22 and 0.47 seconds. No influence of this variation was observed.

Characteristic in all experiments is the high content of ethyltrichlorosilane in the first three hours, gradually decreasing to a value of 15 - 20 mol %. It is the usual picture of the direct synthesis and it is to be associated with the distribution of copper over the particles of the mixture. Compared to tests where the contact times are considerably longer, the selectivity, between 60 and 80 mol %,
is high over a considerable silicon conversion. The influence of the copper content, which may follow from comparison of the two series, seems to lie only in the reactivity. The average reaction rates of the contact mixture with 10% copper are roughly twice as high as those of the mixtures with 5% copper. The selectivity seems unaffected by the difference in the copper content.

It can be concluded, that the contact mixtures as applied successfully in the direct synthesis of methylchlorosilanes, yield favourable results in the ethylchlorosilanes synthesis as well. With short contact times, mainly three compounds are formed, i.e. ethyltrichlorosilane, in amounts between 15 and 20%, diethyldichlorosilane in
maximum amounts of 80 mol % and ethyldichlorosilane supplementing 100%. Only minor amounts of other ethylchlorosilanes, hexachlorodisilane and other high-boiling substances are formed, their total content usually amounting to not more than a few percent. As the product composition is unaffected by variation of the contact time below 0.5 s, it is plausible that the three main products are formed in parallel reactions. That the content of ethyldichlorosilane is relatively low, although not very constant, in the experiments described, is presumably due to the high gis rates, which avoid the occurrence of local hot spots. The results closely resemble those described in VII-6-2, regarding the methylchlorosilanes.


A gas flow calorimeter is described which enables measurements of heat effects of a catalytic process over a temperature range of 20 to 400 °C. As the reactions are carried out in a glass tube, highly corrosive gases may be used.

-9-1. The calorimeter

In order to measure heat effects occurring in reactions of hydrogen chloride, methylchloride and ethylchloride with silicon or mixtures of silicon and copper, a gas flow calorimeter has been developed (Figure 66). The principle of this calorimeter is the measurement of the temperature difference between two places of a thin-walled glass tube with outer diameter of 5.0 mm. One part contains up to 0.3 ml of catalyst or solid reactant, the other serves as a reference. In both parts the glass tube is surrounded by silver tubes (3) on the outside of which four chromel-alumel thermocouples (4) are welded. The silver tubes are separated by 2 cm of asbestos-cement (5). Around the silver on the sample side (on the right in Figure 66) is a thin layer of baked soap-stone (6), which insulates somewhat from the concentric silver tube with heating coils (7). The calorimeter can be heated up to 400 °C. A thick layer of asbestos-cement (1) insulates the calorimeter from the outside. The axial insulation exists in two cover plates (8) of 3 cm. Connections for the electrical heating and the thermocouples (4) are led through a spacing between the two parts of the insulation.
Figure 66. Cross-section of gas flow calorimeter

1- radial insulation, 2- silver cylinders, 3- silver tube of 5.0 mm inner diameter and 7.0 mm outer diameter, 4- thermocouples, 5- insulation between sample part (right) and reference part (left), 6- insulating cylinder of baked soap-stone, 7- heating coils, 8- axial insulation.

The arrangement of the instruments is shown in Figure 67. Three thermocouples of the reaction side are connected opposite in series with three couples of the reference side. Now the three-fold of the thermo-electric potential difference is obtained and the effect of possible radial differences in thermal conduction from glass tube to its surroundings is somewhat avoided. The two remaining couples are also connected opposite; the signal is fed to a 50 micro-Volt recorder (Kipp BD-2). This recorder is equipped with an extra slide wire (2,000 ohm), which is connected parallel to the calorimeter heating. The slide contact of the recorder-resistance is connected to the shunt between the two parts of the heating coil. Thus an automatic balancing of the temperatures of the two calorimeter parts is obtained. This
device proved necessary because of the practical impossibility to get the two heating coils exactly equal in electrical resistance. In order to avoid extreme currents in the extra slide wire in case the slide is off-scale, the circuit is secured with two resistances of 1,000 ohm. When the required temperature for an experiment is reached and the temperature difference of the two calorimeter parts is sufficiently small and constant, the position of the slide on the slide wire is fixed by switching off the recorder. With one of the thermocouples, used in the balance, the temperature of the calorimeter can be measured.

The signal from the 6 main couples is fed to a micro-Volt recorder (Kipp BD-5). Peaks written by this recorder can be integrated electronically to obtain peak areas directly. When the temperature of the immediate surroundings of the calorimeter is kept constant within 0.1 °C, the base-line remains constant within 1/100 of the scale in the most sensitive position (20 micro-Volt) of the recorder. Direct integration of the signal has been found to yield more accurate results. The calorimeter is contained in a thick-walled copper box of which the bottom and the lid are double-walled to allow water of constant temperature to be pumped through.
-9-2. Measuring methods

In the glass tube in the calorimeter a quantity of not too finely powdered sample is held between quartz-wool plugs. The length of the sample in the tube should not exceed 25 mm. With a small stream of inert gas flowing through the tube, the calorimeter is heated until the desired temperature is reached and the temperature difference of the two sides is small enough. By means of a four-way valve a continuous stream, or a pulse of a gaseous reactant will be led through the sample and the reaction can take place. Simulation of a chemical heat effect for calibration can be arranged by instalment of an electrical heating coil in the glass tube. In the coil a known amount of heat can be produced. During the temperature rise of the reaction side the heat-loss into the calorimeter will increase until after a while a stationary state will be reached. When the heat production is stopped, the reaction side will cool, so the temperature difference of reaction part and reference part will decrease gradually until the "base-line" will be reached. A thermogram as shown in Figure 68 will be obtained. The shape of the thermogram and some theoretical considerations (VII-9-3) show the following quantities to be characteristic:

1. The initial slope of the thermogram, which is proportional to the heat production in the sample. This quantity is very appropriate for the measurement of activation energies and for comparative measurements. Calibration of the calorimeter will then in principle not be necessary. Application of this method is described in VII-10 through -12. In an Arrhenius-graph, the logarithm of the slope can be plotted against the inverse temperature. From the Arrhenius-equation it can

![Figure 68. Theoretical shape of a thermogram](image-url)
be seen that all multipliers which are constant, influence the absolute height in the graph, but they do not influence the slope, which gives the activation energy.

2. The temperature difference in the stationary state, which is in case of a constant heat production proportional to it. This state will, as a result of the geometry of the calorimeter, be reached in about 10 minutes. In cases where reaction products should be formed in some quantity for analytical purposes, the calorimeter may be calibrated for this method.

3. The peak area, which is proportional to the total heat effect. This quantity is obtained by integration of the thermogram. It may be used for adsorption and desorption measurement, where the heat effects take place in a short time. It is also the appropriate quantity to be used in cases when reaction rates are high, and small amounts of reactants are converted at a time, i.e. with pulses of reactants. An application is given in VII-9-4 and VII-13.

-9-3. Theoretical considerations

Expressions are derived for the meaning of the shape of the thermograms.

For a derivation of the equations, describing the form of the thermograms the model given in Figure 69 will be used. In the upper part a quadrant of the cross section of the calorimeter has been drawn. The temperature profile for various times after the beginning of the (constant) heat production has been sketched correspondingly below. The temperature difference of reaction side (variable T) and reference side (constant T\text{ref}) is given by:

\[ T - T_{\text{ref}} = \frac{\varnothing}{u} (1 - \alpha_1 \exp(-\beta_1 t) + \alpha_2 \exp(-\beta_2 t)) \quad (VII.24) \]

in which the symbols have the following meaning:

- \( \varnothing \) = heat production (cal.s\(^{-1}\))
- \( t \) = time (s)
- \( \alpha_1 = (p + q)/2q, \alpha_2 = (p - q)/2q \)
- \( \beta_1 = (p - q)/2r, \beta_2 = (p + q)/2r \)
- \( p = u' W_a + u W_m + u' W_m, q = ((u' W_a + u W_m + u' W_m)^2 - 4 u u' W_a W_m) \)
- \( r = W_a W_m \)
When the heat production stops after 'a' seconds, the sample part will cool according to:

\[ T - T_{\text{ref}} = \frac{\Theta}{u} (\alpha_1 \exp(-\beta_1(t-a)) - \alpha_1 \exp(-\beta_1 t) - \alpha_2 \exp(-\beta_2(t-a)) + \alpha_2 \exp(-\beta_2 t)) \]

for \( t > a \) \hspace{1cm} (VII.25)

The surface area of the peak formed by the curves given by the equations (VII-24) and (VII-25) and the time-axis, is proportional with the total heat (\( \Delta H \)) evolved in the sample:

\[ \int_{0}^{\infty} (T - T_{\text{ref}}) \, dt = \frac{1}{u} \cdot \Delta H \]

(VII.26)

From calibrations it was concluded that the constants have a magnitude as follows:

\[ \alpha_1 = 1 + 10^{-7}, \alpha_2 = 10^{-7}, \beta_1 = 10^{-3}, \beta_2 = 10^5 \]
The figures show that a good approximation is already obtained with an even simpler model. As the heat transfer coefficient in the glass-wall $(u)$ is much larger than the heat transfer coefficient from the silver-tube into the calorimeter, the temperature of silver (+ thermocouples) can be taken equal to the temperature of the sample. The equations (VII.24) and (VII.25) can then be replaced by (VII.27) and (VII.28) respectively:

$$T - T_{ref} = \frac{\vartheta}{u} (1 - \exp(-u \cdot t/(W_a + W_m)))$$  \hspace{1cm} (VII.27)

$$T - T_{ref} = (T_a - T_{ref}) \cdot \exp(-u \cdot (t-a)/(W_a + W_m)) \quad t \geq a$$  \hspace{1cm} (VII.28)

$T_a$ is the temperature of the sample reached in "t=a" seconds. It follows for the initial slope of the thermogram that:

$$tg = \frac{\vartheta}{W_a + W_m} (t \to 0)$$  \hspace{1cm} (VII.29)

For the stationary temperature difference when the heat production has been constant for a long time (about 10 minutes), equation (VII.30) can be obtained, by setting $t$ infinite in equation (VII.27):

$$T_{stat} - T_{ref} = \frac{1}{u} \vartheta$$  \hspace{1cm} (VII.30)

In the derivation of the equations (VII.24) and (VII.25) it is assumed that no temperature gradient exists in the sample and in the silver tube, and that there is no loss of heat by axial transport in the glass tube. The heat-loss by increase of temperature of the gas stream has been neglected, which is justified for the small gas flows applied here, in the order of 10 Nm³/min.

**Derivation of equation (VII.24)**

From the heat balance in the sample with temperature $T_m$ follows that:

$$\frac{dT_m}{dt} = (\vartheta - u'(T_m - T))/W_m$$  \hspace{1cm} (i)

The heat transfer coefficient $u'$ can be found according to:

$$u' = 2.1 \cdot \frac{\text{glass}}{\ln(R_2/R_1)}$$  \hspace{1cm} (ii)
In this relation 1 represents the length of the sample in the glass-tube, \( \lambda_{\text{glass}} \) is the thermal conductivity of glass and \( R_1 \) and \( R_2 \) are the inner and outer radius of the glass-tube respectively.

From the heat-balance in the silver tube it follows that:

\[
\frac{dT}{dt} = \frac{(u'(T_m-T) - u(T-T_{\text{ref}}))}{W_a}
\]  

(iii)

The heat capacity of the glass-wall is in this instance neglected, but is included in \( W_a \) in practice. The differential equations (i) and (iii) are of the type:

\[
\frac{dz}{dx} = a - b.z + b.y
\]

(iv)

\[
\frac{dy}{dx} = e + f.z - g.y
\]

(v)

If (v) is solved for \( z \), \( z = \frac{1}{f}\frac{dy}{dx} - \frac{e}{f} + \frac{g}{f}y \), differentiation with respect to \( x \) yields:

\[
\frac{dz}{dx} = \frac{1}{f}\frac{d^2y}{dx^2} + \frac{g}{f}\frac{dy}{dx}.
\]

When this is substituted in (iv), it follows that:

\[
\frac{d^2y}{dx^2} + (b+g)\frac{dy}{dx} + (b.g - b.f)y - (b.e + a.f) = 0
\]  

(vi)

Transformation of \( y \) via: \( w = (b.g - b.f)y - (b.e + a.f) \), yields a linear differential equation with constant coefficients:

\[
\frac{d^2w}{dx^2} + (b + g)\frac{dw}{dx} + (b.g - b.f)w = 0
\]  

(vii)

The solution of this equation is:

\[
w = A.\exp(c_1.x) + B.\exp(c_2.x),
\]

with \( A \) and \( B \) as integration-constants and with \( c_1 \) and \( c_2 \) as the real roots of the equation:

\[
c^2 + (b + g)c + (b.g - b.f) = 0
\]  

(viii)

Solving \( c_1 \) and \( c_2 \) and re-substitution of the original symbol leads to the expression:

\[
T-T_{\text{ref}} = \frac{\Theta}{u} + \left(W_a/W_m/u.u'\right)(A.\exp(-\beta_1.t) + B.\exp(-\beta_2.t))
\]  

(ix)
in which $\beta_1$ and $\beta_2$ stand for $-c_1$ and $-c_2$ respectively; the meaning of $\beta_1$ and $\beta_2$ has been given above. The constants $A$ and $B$ can be found using the boundary conditions:

For $t = 0$, $T = T_{ref}$, and equation (ix) simplifies to:

$$A + B = \frac{\Phi}{u'/w_a}w_m$$  \hspace{1cm} (x)

For $t = \infty$, $T$ reaches a stationary value so that $dT/dt = 0$. Differentiation of equation (ix) and setting the derivative to zero leads to:

$$-A\beta_1 \exp(-\beta_1 t) - B\beta_2 \exp(-\beta_2 t) = 0$$

and because $t$ is infinite:

$$A\beta_1 + B\beta_2 = 0$$  \hspace{1cm} (xi)

From equations (x) and (xi), $A$ and $B$ can be solved, leading to the desired equation (VII.23).

**Derivation of thermogram-equation (VII.25)**

$$T - T_{ref} = \frac{\Phi}{u'}\left(\alpha_1 \exp(-\beta_1 (t-a)) - \alpha_2 \exp(-\beta_2 (t-a)) - \alpha_2 \exp(-\beta_2 t)\right)$$  \hspace{1cm} \text{for } t \geq a  \hspace{1cm} (VII.25)

The differential equations representing the heat balances in the case of cooling can be written analogously to equations (i) and (iii). The heat production $\Phi$ has worked during "a" seconds and is zero now.

For the sample:  \hspace{1cm} $$dT/dt = (T - T_m) u'/w_m$$  \hspace{1cm} (xii)

For the silver tube:  \hspace{1cm} $$dT/dt = (u'(T_m - T) - u(T - T_{ref}))/w_a$$  \hspace{1cm} (xiii)

With the same procedure as given above the analogue of equation (ix) can be obtained:

$$T - T_{ref} = \alpha_3 \exp(-\beta_1 t') + \alpha_4 \exp(-\beta_2 t')$$  \hspace{1cm} (xiv)

in which $\alpha_3$ and $\alpha_4$ are integration constants, still to be found. At the moment that $\Phi$ becomes zero, $T = T_a$ and $t' = t - a (= 0)$, so:

$$T_a - T_{ref} = \alpha_3 + \alpha_4$$  \hspace{1cm} (xv)
and from equation (VII.24) it follows:

\[ T_a - T_{ref} = \frac{0}{u}(1 - \alpha_1 \cdot \exp(-\beta_1 \cdot a) + \alpha_2 \cdot \exp(-\beta_2 \cdot a)) \]  
(xvi)

The other boundary condition must be the known temperature of the sample at \( t = a \), \( T_m = T_m,a \), so first \( T_m \) has to be found during a constant heat production from equations (VII.24) and (iii):

\[ T_m - T_{ref} = \frac{0}{u}(1/u + 1/u')(1 - \alpha_1 \cdot \exp(-\beta_1 \cdot t) + \alpha_2 \cdot \exp(-\beta_2 \cdot t)) + \]  
\[ \frac{0 \cdot W_a (\exp(-\beta_1 \cdot t) - \exp(-\beta_2 \cdot t))/q}{q} \]  
(xvii)

\( T_m \) during the cooling period can be derived from equations (xiii) and (xiv):

\[ T_m - T_{ref} = \alpha_3((u+u'/W_a \cdot \beta_1/u') \cdot \exp(-\beta_1 \cdot t')) + \alpha_4((u+u'/W_a \cdot \beta_2/u') \cdot \exp(-\beta_2 \cdot t')) \]  
(xviii)

For \( t = a \), \( t' = 0 \) and both the equations (xvii) and xviii) offer \( T_m,a - T_{ref} \). After some manipulations it can be found that:

\[ -0 \cdot u'(\exp(-\beta_1 \cdot a) - \exp(-\beta_2 \cdot a))/q = \beta_1 \cdot \alpha_3 + \beta_2 \cdot \alpha_4 \]  
(xix)

Introduction of equations (xv) and (xvi) in equation (xix) will now lead to the solution of the integration constants \( \alpha_3 \) and \( \alpha_4 \). Substitution in equation (xiv) gives the required equation (VII.25).

-9-4. Some examples (III-3)

The heat of adsorption of hydrogen chloride on silicon-copper was determined at -4.4 kcal/mol.

The calorimeter has been applied in experiments described in VII-10 through -13. To test the sensitivity of the instrument, the heat effect of the adsorption of hydrogen chloride on a silicon copper contact mixture was determined. The glass-tube contained in these tests 252 mg of a 5 wt% copper containing contact mixture of which the specific surface area was determined to be 0.24 m²/g. At 20 °C the exothermic effect of adsorption of hydrogen chloride amounted to 58 (+ 6) mcals, the average value of 12 measurements. When complete coverage of the surface of the
particles by hydrogen chloride molecules is assumed, the heat of adsorption can be calculated at -4.4 (+0.5) kcal/mol.

In attempts to find a fast method to determine the specific surface area of powders, ethylchloride vapour was used as adsorbent. It turned out that the heat effects of adsorption or desorption were strongly dependent upon the nature of the adsorbate. A relative change of the surface of a contact mixture, however, can be determined very well. When a contact mixture (391 mg containing 5% copper) was reacted with hydrogen chloride so that 2.8% of the silicon was converted, the heat effect of the adsorption of ethylchloride had increased by 67%. It is probable that the increase was caused by an increase of the surface area of the contact mixture sample by 67%.

VII-10. The activation energy of the trichlorosilane formation (V-4)

The gasflow calorimeter is used for kinetic measurements. The formation of trichlorosilane from hydrogen chloride and silicon-copper requires an activation energy of 24 kcal/mol.

A fast determination of the activation energy of a reaction between a gas and a solid is possible with the use of the gas flow calorimeter, described in VII-9. To relate the initial heat production to the reaction rate it is necessary that the gas flow and the product composition are constant. When the gas flow influences the initial heat production, it means that reaction rates are fast compared to the rate of transport of the pulse through the layer of catalyst. The product composition should be constant because of the possibility that different compounds can have different heats of formation. For an imaginary reaction: \( A \rightarrow bB + cC \), the initial heat production on the surface of the catalyst sample will be given by:

\[
\Phi_0 = R(\Delta H_f(A) - b \cdot \Delta H_f(B) - c \cdot \Delta H_f(C)) \quad (VII.31)
\]

Variation of the reaction coefficients \( b \) and \( c \) along the sample or in the temperature range investigated will disturb the proportionality between the heat production \( \Phi_0 \) and the reaction rate \( R \).

The formation of trichlorosilane from hydrogen chloride and a contact
mixture is assumed to proceed according to:

\[
3 \text{HCl} + \text{Si (Cu)} \rightarrow \text{HSiCl}_3 + \text{H}_2 \quad (\text{VII.32})
\]

For this reaction, values for the activation energy have been found between 3 and 28 kcal/mol (V-4). The lower values, which were obtained at high temperatures, must be considered unreliable because of the possibility that gas film diffusion may have obscured the reaction rate. The gas flow calorimeter is sufficiently sensitive to allow the choice of a low temperature range, i.e. below 200 °C. At this temperature, diffusion limitation is less probable.

The experiments were conducted with 372 mg of a 5 wt % copper containing contact mixture of sieve fraction 175 - 210 microns. The mixture was identical to that used in the experiments described in VII-7. The initial thermogram slopes for subsequent hydrogen chloride pulses are plotted in Figure 70. The series were performed in the sequence 198 °C - 172 °C - 186 °C. If the average values are plotted in an Arrhenius-graph, the slope yields a value:

\[E_{\text{act}} = 24 (\pm 2) \text{ kcal/mol}\]

**VII-11. Comparison of the rates of reaction of hydrogen chloride and chlorine**  
(IV-2, -7, V-1)

Chlorine and hydrogen chloride do not react noticeably with silicon below 341 °C. With catalytic action of copper, chlorine reacts faster than hydrogen chloride at 215 °C.

**-11-1. Introduction**

It seems of interest to compare the rates of reaction of hydrogen chloride and chlorine with the same silicon or contact mixture specimen.

\[
\text{Si} + 3 \text{HCl} \rightarrow \text{SiHCl}_3 + \text{H}_2 \quad (\text{VII.32})
\]
Of both reactions it is known that copper acts as a catalyst (24). It was furthermore established, that the ability of chemisorption of chlorine on silicon-copper exceeds that of hydrogen chloride (154). This information indicates that the catalytic function of copper is to be found in the chlorination of silicon. Reaction steps of the type:

\[
\begin{align*}
2 \text{Cu} + \text{Cl}_2 & \rightarrow 2 \text{CuCl} \\
\text{Si} + 2 \text{CuCl} & \rightarrow \text{SiCl}_2 + 2 \text{Cu}
\end{align*}
\]

provide an easy explanation of the catalytic action of copper in the reaction of chlorine, although there is doubt about the minimum temperature of reaction of cuprous chloride and silicon (IV-7, p. 66).

A fast method to determine qualitative effects of possible catalysts in a heterogeneous reaction is to carry the reactions out in the gas flow calorimeter. As the principle of the method is to measure the production of heat during the reaction, the two reactions may only be compared after proper correction for the reaction enthalpies. The enthalpy change of the reactions (VII-32) and VII-33) have been taken as -160 and -53 kcal/mol of silicon respectively (Appendix 2), the ratio being about 3.

-11-2. Results and discussion

Carried by a stream of helium, pulses of 2.1 ml of the reactant have been led through samples of 100 - 150 mg of silicon or silicon-copper, charged in the calorimeter reactor (VII-9). Of the thermograms obtained, the initial slope and the peak-height will be given. The initial slope is expressed in the temperature-rise of the sample in degrees centigrade per minute. It is for a specific sample proportional to the heat production and accordingly with the rate of the chemical reaction. The peak-height is given in degrees centigrade. Its value indicates roughly the total amount of heat evolved in the reaction.

The experiments with chlorine and hydrogen chloride performed on silicon without copper, but containing 0.002% iron, gave no deviation from the baseline, indicating that no reaction occurred within the limits of detection at a temperature of 341 °C.
For a silicon-copper mixture with 9.9% copper some results are given in Table 42. Hydrogen chloride and chlorine pulses are alternatingly fed to the reactor in a frequency of about one pulse per ten minutes.

**Table 42**
Thermogram-characteristics of Si (9.9% Cu) at 342 °C.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Slope (°C/min)</th>
<th>ΔT(max) (°C)</th>
<th>Carrier flow (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1.16</td>
<td>.61</td>
<td>10</td>
</tr>
<tr>
<td>Cl₂</td>
<td>5.12</td>
<td>2.83</td>
<td>40</td>
</tr>
<tr>
<td>HCl</td>
<td>6.58</td>
<td>.92</td>
<td>40</td>
</tr>
<tr>
<td>Cl₂</td>
<td>27.7</td>
<td>4.19</td>
<td>40</td>
</tr>
<tr>
<td>HCl</td>
<td>6.25</td>
<td>.92</td>
<td>40</td>
</tr>
</tbody>
</table>

From the table it can be seen that the heat production of the reaction of chlorine with silicon-copper is about 4 times that of hydrogen chloride, for a given stream of inert gas. From the data it is also obvious that at this temperature the heat productions are proportional to the velocity of the inert gas that carries the reactant pulses.

The same contact mixture will perform somewhat differently at a lower temperature. The results for a series of measurements at 225 °C are in Table 43.

**Table 43**
Thermogram-characteristics of Si (9.9 %Cu) at 225 °C. Gas rate 10 Nml/min.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Slope (°C/min)</th>
<th>ΔT(max) (°C)</th>
<th>Pulse nr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>.092</td>
<td>.104</td>
<td>1</td>
</tr>
<tr>
<td>Cl₂</td>
<td>&gt;5</td>
<td>&gt;1</td>
<td>2</td>
</tr>
<tr>
<td>Cl₂</td>
<td>1.96</td>
<td>1.14</td>
<td>3</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.37</td>
<td>.29</td>
<td>4</td>
</tr>
<tr>
<td>HCl</td>
<td>.108</td>
<td>.071</td>
<td>5</td>
</tr>
<tr>
<td>HCl</td>
<td>.134</td>
<td>.131</td>
<td>6</td>
</tr>
<tr>
<td>HCl</td>
<td>.162</td>
<td>.177</td>
<td>7</td>
</tr>
<tr>
<td>HCl</td>
<td>.212</td>
<td>.227</td>
<td>8</td>
</tr>
<tr>
<td>HCl</td>
<td>.262</td>
<td>.252</td>
<td>9</td>
</tr>
<tr>
<td>HCl</td>
<td>.288</td>
<td>.294</td>
<td>10</td>
</tr>
<tr>
<td>HCl</td>
<td>.324</td>
<td>.319</td>
<td>11</td>
</tr>
<tr>
<td>HCl</td>
<td>.346</td>
<td>.333</td>
<td>12</td>
</tr>
</tbody>
</table>

It is remarkable that the rate of reaction of hydrogen chloride increases for subsequent pulses, which is not the case for chlorine. Yet, it can be
seen that chlorine reacts faster than hydrogen chloride.

The contact mixture with 9.9 wt % copper has been leached with nitric acid to lower the copper content drastically. After washing with water and drying in a vacuum the remaining copper content was 0.27 wt % (iron 0.06%). The results from the thermograms obtained by reaction of this mixture at 332 °C are given in Table 44. Again subsequent pulses of hydrogen chloride show an increasing reactivity, a pattern which seems undisturbed by a pulse of chlorine. The ratio between the heat productions by pulses of chlorine and hydrogen chloride for the highest response of the latter is 4.8

Table 44
Thermogram-characteristics of Si (0.27% Cu) at 332 °C. Gas rate 10 Nm³/min.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Slope (°C/min)</th>
<th>ΔT(max) (°C)</th>
<th>Pulse nr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>.40</td>
<td>.23</td>
<td>5</td>
</tr>
<tr>
<td>HCl</td>
<td>.67</td>
<td>.41</td>
<td>6</td>
</tr>
<tr>
<td>HCl</td>
<td>.83</td>
<td>.48</td>
<td>7</td>
</tr>
<tr>
<td>HCl</td>
<td>.87</td>
<td>.50</td>
<td>8</td>
</tr>
<tr>
<td>HCl</td>
<td>.92</td>
<td>.50</td>
<td>9</td>
</tr>
<tr>
<td>Cl₂</td>
<td>4.58</td>
<td>2.75</td>
<td>10</td>
</tr>
<tr>
<td>HCl</td>
<td>.94</td>
<td>.52</td>
<td>11</td>
</tr>
</tbody>
</table>

The contact mixture with the same low copper content has also been investigated at a much lower temperature (215 °C), of which the results are in Table 45.

For the chlorine pulses the peaks now diminish in height and initial slope for subsequent pulses until a fairly reproducible response is reached. Pulses of hydrogen chloride on the other hand, again show peaks which are increased in height and initial slope. When after reacting 40 minutes with pulses of hydrogen chloride, a pulse of chlorine is introduced, its response is rather high again, and more so when the contact mixture has been left for about 14 hours in a helium current at 215 °C.

It can be concluded, that copper is a catalyst in the reaction of chlorine as well as hydrogen chloride. At temperatures slightly above 200 °C the reaction of chlorine is about 10 to 30 times faster than that of hydrogen chloride, but this only applies to the first pulse of chlorine; the next pulse reacts much slower.
Table 45
Thermogram-characteristics of Si (0.3% Cu) at 215 °C. Gasrate 20 Nml/min.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Slope (°C/min)</th>
<th>ΔT(max) (°C)</th>
<th>Pulse nr.</th>
<th>Elapsed time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂</td>
<td>5.66</td>
<td>1.34</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.816</td>
<td>.20</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.400</td>
<td>.13</td>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.117</td>
<td>.04</td>
<td>4</td>
<td>32</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.112</td>
<td>.04</td>
<td>5</td>
<td>40</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.121</td>
<td>.04</td>
<td>6</td>
<td>48</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.133</td>
<td>.03</td>
<td>7</td>
<td>54</td>
</tr>
<tr>
<td>HCl</td>
<td>.025</td>
<td>.008</td>
<td>8</td>
<td>63</td>
</tr>
<tr>
<td>HCl</td>
<td>.042</td>
<td>.016</td>
<td>9</td>
<td>69</td>
</tr>
<tr>
<td>HCl</td>
<td>.071</td>
<td>.029</td>
<td>10</td>
<td>76</td>
</tr>
<tr>
<td>HCl</td>
<td>.071</td>
<td>.031</td>
<td>11</td>
<td>82</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.666</td>
<td>1.08</td>
<td>13</td>
<td>94</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.045</td>
<td>.016</td>
<td>14</td>
<td>105</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.433</td>
<td>.142</td>
<td>15</td>
<td>111</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.204</td>
<td>.031</td>
<td>16</td>
<td>116</td>
</tr>
<tr>
<td>Cl₂</td>
<td>8.33</td>
<td>.358</td>
<td>17</td>
<td>960</td>
</tr>
<tr>
<td>Cl₂</td>
<td>.516</td>
<td>.216</td>
<td>18</td>
<td>970</td>
</tr>
</tbody>
</table>

a) pulse volume .08 Nml instead of the usual 2.1 Nml

It is probable that the decrease in the rate of reaction of chlorine is caused by the slow silicon diffusion to the surface of the contact mixture particles. This is supported by the fact, that the response of the sample increased when the contact mixture could equilibrate for some time. The reaction of hydrogen chloride with the contact mixture seems not limited by the diffusion in the solid. That subsequent pulses of hydrogen chloride show an increasing response is due to etching, which increases the reactive surface (III-3).

VII-12. Influence of zinc chloride upon copper-catalyzed reaction of chlorine and silicon

Zinc chloride is a promoter in the formation of tetrachlorosilane from chlorine and silicon with copper as a catalyst. The promoting effect only holds at temperatures above the eutectic temperature of the mixture of zinc chloride and cuprous chloride.

-12-1. Introduction
Zinc chloride has been mentioned as a promoter in the direct synthesis of
methylchlorosilanes and ethylchlorosilanes, but its function has not been elucidated yet. There has been a suggestion that zinc chloride would chlorinate copper atoms, leaving zinc subchloride and cuprous chloride according to (47):

$$\text{ZnCl}_2 + \text{Cu} \rightarrow \text{ZnCl} + \text{CuCl} \quad (\text{VII.36})$$

or even giving metallic zinc. From the enthalpy change of reaction (VII.37), being + 33.8 kcal/mol at 298 K it seems thermodynamically unfavourable.

$$\text{ZnCl}_2 + 2 \text{Cu} \rightarrow \text{Zn} + 2 \text{CuCl} \quad (\text{VII.37})$$

If the heat of formation of zinc subchloride is estimated as half that of zinc chloride - which is rather optimistic - the enthalpy change of reaction (VII.36) can be calculated at + 17 kcal/mol and also this reaction is unlikely to proceed. It suggests itself that when the reactions of various gaseous chlorides with silicon are catalyzed by metallic copper, an analogy may be found in the promoting effect of zinc chloride. For this reason some calorimetric tests have been conducted to study the effect of zinc chloride on the reaction of chlorine with silicon:

$$2 \text{Cl}_2 + \text{Si (Cu)} \rightarrow \text{SiCl}_4 \quad (\text{VII.38})$$

-12-2. Experiments

The micro reactor inserted in the calorimeter (see VII-9) contained about 100 - 200 mg of a silicon copper contact mixture with 9.9 wt % copper. The contact mixture has been prepared from cuprous chloride and silicon of particle size 90 - 125 microns at 350 °C. In some experiments 0.5 or 1.0 wt % zinc chloride was mixed with the contact mixture by thorough shaking. Pulses of chlorine of 2.1 NmL are fed to the reactor using a stream of helium as carrier. The pulses were introduced at 8 minute intervals. The thermograms show a peak-shaped response to the chlorine pulses. Of the peaks the maximum height has been taken as a measure for the amount of heat produced by the chemical reaction in the calorimeter. This height will be expressed in degrees centigrade. In Table 46a the maximum temperature rise of the sample caused by subsequent chlorine pulses is given for contact mixtures containing different amounts of zinc chloride in the temperature range around 260 °C. The table shows clearly that the contact mixture performs a fairly constant and high reactivity in the presence of zinc chloride only.
Table 46a. 
Calorimeter response; peak height in degrees C.

<table>
<thead>
<tr>
<th>Weight % ZnCl₂</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>259</td>
<td>264</td>
<td>259</td>
</tr>
<tr>
<td>Elapsed time (min)</td>
<td>0</td>
<td>2.33</td>
<td>9.75</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2.19</td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>1.13</td>
<td>2.92</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>0.83</td>
<td>2.85</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>2.65</td>
<td>3.46</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.29</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>2.15</td>
<td>3.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.35</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.71</td>
<td>3.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.75</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.71</td>
<td>3.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.67</td>
<td>3.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.71</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.67</td>
<td>3.52</td>
</tr>
</tbody>
</table>

Table 46b 
Calorimeter response; peak height in degrees C.

<table>
<thead>
<tr>
<th>Weight % ZnCl₂</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0.5</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>233</td>
<td>232</td>
<td>231</td>
<td>239</td>
<td>238</td>
<td>238</td>
<td>242</td>
<td>243</td>
</tr>
<tr>
<td>Elapsed time (min)</td>
<td>0</td>
<td>2.46</td>
<td>2.39</td>
<td>1.54</td>
<td>0.721</td>
<td>0.600</td>
<td>0.855</td>
<td>0.500</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.50</td>
<td>0.75</td>
<td>1.08</td>
<td>0.858</td>
<td>0.800</td>
<td>0.625</td>
<td>0.479</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>0.44</td>
<td>0.37</td>
<td>0.62</td>
<td>0.217</td>
<td>0.266</td>
<td>0.533</td>
<td>0.354</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>0.23</td>
<td>0.31</td>
<td>0.46</td>
<td>0.150</td>
<td>0.191</td>
<td>0.350</td>
<td>0.275</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>0.275</td>
<td>0.279</td>
<td>0.571</td>
<td>0.529</td>
<td>0.600</td>
<td>0.613</td>
<td>0.511</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.233</td>
<td>0.258</td>
<td>0.542</td>
<td>0.571</td>
<td>0.529</td>
<td>0.600</td>
<td>0.613</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>0.237</td>
<td>0.504</td>
<td>0.571</td>
<td>0.529</td>
<td>0.600</td>
<td>0.613</td>
<td>0.511</td>
</tr>
</tbody>
</table>

The calorimeter temperatures in these experiments are just below and above the melting point of zinc chloride, which is 262 °C. It seemed interesting to repeat these series in the temperature range of 240 °C, the melting temperature of the eutectic mixture of cuprous chloride and zinc chloride (58), of which the results are in Table 46b. The effect of the zinc chloride addition in this temperature region is far less pronounced. At the temperature of about 232 °C the subsequent peaks diminish substantially in height, which is illustrated graphically in Figure 71. The contact mixture in this series of measurements differed from the one used in the other experiments in that it was pretreated with diluted nitric acid to remove at least part of the free copper from the mixture. An increase of the reactive surface area can be expected from this treatment, reason why the reactivity at high temperatures exceeds that of other contact mixtures.
-12-3. Discussion.

The peak heights obtained at various temperatures are plotted versus the time elapsed since the first pulse was given for the contact mixture without zinc chloride and with 0.5% zinc chloride, in Figures 72 and 73 respectively. The peak heights show a considerable decrease when no zinc chloride is present, but remain constant with 0.5% zinc chloride. The promoting effect of zinc chloride is distinct only at about 240 °C and higher. No effect of zinc chloride addition could be observed at a lower temperature (Figure 71). As the melting point of zinc chloride is 264 °C and the eutectic temperature of a mixture of zinc chloride and (7.5 wt %) cuprous chloride is 242 °C, it is probable that the latter temperature indicates the point where the promoting effect of zinc chloride begins. The explanation of this phenomenon must probably be sought in the enhanced transport of chlorine – and copper (I) ions in the molten mixture of the salts, as it is evident that the promoting effect of zinc chloride comes into effect when it is in the molten state.
VII-13. Direct measurement of the heat of formation of tetrachlorosilane (II-3)

The heat effect of the direct combination of chlorine and silicon has been determined by means of the gas flow calorimeter. The measurements lead to a heat of formation of tetrachlorosilane of $-160.3 \pm 1.6$ kcal/mol.

-13-1. Calibration of the calorimeter

To obtain the quantitative relation between the heat effect $\Delta H$ of a chemical reaction in the calorimeter and the response of the integrator ($X$) of the thermogram (VII-9), calibration is required. This can be performed with two methods.

By insertion of an electrical heating coil in the sample part of the calorimeter, a known amount of heat can be produced. Time, current and potential need be measured and the relation (VII.39) gives the heat production

$$\Delta H = 239 \times E.I.t \quad \text{(mcal)} \quad \text{(VII.39)}$$

A series of 19 calibrations revealed a value of the instrument constant:

$$A = 20.45 \pm 0.60 \text{ mcal/scale-unit \quad [329 }^\circ\text{C]}$$

The standard deviation and the largest error amounted to 0.80 and 1.20 mcal/sc.u. respectively. Tabulated data may be found in (157).

Chemical calibration requires a suitable model reaction, which should fulfill some requirements:
- it must be a reaction between a gas and a solid,
- the heat effect must be known accurately,
- the product formed should not hinder further reaction, i.e. should be gaseous,
- the reaction should be fast and the degree of conversion must be measurable accurately.

The reaction of chlorine with aluminium fulfils such conditions:

\[ \text{2 Al} + 3 \text{Cl}_2 \rightarrow \text{Al}_2\text{Cl}_6 \]  \hspace{1cm} \text{(VII.40)}

Due to some dissociation of aluminium hexachloride:

\[ \text{Al}_2\text{Cl}_6 \rightleftharpoons 2 \text{AlCl}_3 \]  \hspace{1cm} \text{(VII.41)}

the resulting product is a mixture of the two chlorides. The composition has been assumed to be the equilibrium composition and can then be calculated from (VII.42):

\[ \log \left( \frac{1 - x}{x} \right)^2 \cdot \frac{1}{p} = - \frac{29,000}{4.571 \cdot T} + 1.75 \times \log(T) - 9.414 \times 10^{-4} \cdot T + 3 \]  \hspace{1cm} \text{(VII.42)}

in which \( x \) represents the fraction of aluminium hexachloride and \( p \) the total pressure. The amount of heat produced by the reaction of 1 mol of chlorine with aluminium powder can be determined from:

\[ \Delta H_R = \frac{\Delta H(\text{AlCl}_3) + x \cdot (\Delta H(\text{Al}_2\text{Cl}_6) - \Delta H(\text{AlCl}_3))}{1.5 \cdot (1 + x)} \]  \hspace{1cm} \text{(VII.43)}

The heats of formation and the heat content data of the substances involved come from (753). When the volume of the chlorine pulses is the same in the reactions of chlorine with aluminium and with silicon, it need not be determined. To enable a comparison between the instrument constants from the electrical and the chemical calibration, it has been determined at 2.10 ml at 20 °C.

From 34 measurements of the heat effect of the reaction of chlorine and aluminium, in the temperature range between 217 and 335 °C, the instrument constant appeared to be:

\[ A = 11.82 + 1.444 \times 10^{-3} \cdot T \text{ \hspace{1cm} mcal/scale-unit} \]  \hspace{1cm} \text{(VII.44)}

The value of 20.51 mcal/sc.-u. at 329 °C agrees very well with that obtained from the electrical calibration.
The reaction of chlorine with silicon

Pulses of chlorine with a volume of 2.1 ml were led over silicon containing 0.3% copper. By means of gas chromatography, it was established that in the temperature range of the measurements (312 - 333 °C) the chlorine reacted quantitatively with silicon, forming no other products than tetrachlorosilane. The heat of formation was determined from the heat effect and the pulse volume (V), using the relation:

\[ \Delta H_f^0(298) = A \cdot X \cdot \frac{22.064}{\frac{1}{2} V} \cdot \frac{273 + t}{273} \cdot \frac{760}{B + 2.5} - \frac{T}{298} \int \Delta C_p \cdot d(T) \] (VII.45)

which contains the conversion of the pulse volume to the number of moles. The conversion comprises corrections for the temperature (t), the barometric pressure (B) and the over-pressure in the system (2.5 mm mercury).

The results of 13 measurements are listed in Table 47, and lead to an average value:

\[ \Delta H_f^0(\text{SiCl}_4) = -160.29 \pm 1.60 \text{ kcal/mol} \]

The value which emerges from the experiments, lies well within the range of values obtained from determination of the heat of hydrolysis (Table 5, p.26) of tetrachlorosilane.
MULTIPLE EQUILIBRIUM COMPUTATION

A system of ncomp compounds, containing ngas gases which are assumed ideal is in thermodynamic equilibrium if the following equations hold:

\[ \sum_{k=1}^{\text{nev}} N(k,1) \log(p_{eq}(l)) - v_{ren}(k) = u_{it}(k) = 0 \quad [k = 1...\text{nev}] \quad (1) \]

\[ \sum_{l=1}^{\text{ncomp}} c_{o}(l,j) \cdot \text{moleq}(l) / \text{strt}(j) - 1 = \text{bal}(j) = 0 \quad [j = 1...\text{nel}] \quad (2) \]

\[ \sum_{l=1}^{\text{ngas}} p_{eq}(l) / p_{tot} - 1 = \text{help} = 0 \quad (3) \]

in which \( \text{moleq}(l) = v_{t} \cdot p_{eq}(l) \) \quad (4)

There are ncomp + 1 (= ncmp) unknowns to be solved:

- \( p_{eq}(l) \) \quad [l = 1,...,\text{ngas}]  
- \( \text{moleq}(l) \) \quad [l = \text{ngas} + 1,...,\text{ncomp}]  
- \( v_{t} \)

which must all be positive. In order to define an unconstrained function to be minimized, we set:

\[ x(l) = \log(p_{eq}(l)) \quad [l = 1...\text{ngas}] \quad (5) \]

\[ x(l) = \log(\text{moleq}(l)) \quad [l = \text{ngas} + 1...\text{ncomp}] \]

\[ x(\text{ncmp}) = \log(v_{t}) \]

The function \( F \) with unknowns \( x \) now becomes

\[ F = \sum_{k=1}^{\text{nev}} (u_{it}(k))^2 + \sum_{j=1}^{\text{nel}} (a \cdot \text{bal}(j))^2 + (b \cdot \text{help})^2 \]

with a minimum value of zero in case of equilibrium.

Minimization may be obtained using a method suggested by Fletcher and Powell (Computer Journal, vol. 6, iss. 2 1963, 163-168), available as procedure FMFP in the scientific subroutine package in the PL/1 library of the IBM 360/65 (T.H., Delft). This procedure requires a calculation of the partial derivatives of the function with respect to \( x \).
\[
\frac{\partial F}{\partial x(l)} = \sum_{k=1}^{\text{nev}} u_{it(k)} \frac{\partial u_{it(k)}}{\partial x(l)} + \sum_{j=1}^{\text{ngas}} \alpha_{bal(j)} \frac{\partial \alpha_{bal(j)}}{\partial x(l)} + \beta \cdot \text{help} \frac{\partial \text{help}}{\partial x(l)}
\]  
\[l = 1 \ldots \text{ngas}\] (7)

\[
\frac{\partial F}{\partial x(l)} = \sum_{j=1}^{\text{ngas}} \alpha_{bal(j)} \frac{\partial \alpha_{bal(j)}}{\partial x(l)}
\]  
\[l = \text{ngas} + 1 \ldots \text{ncomp}\]

\[
\frac{\partial F}{\partial x(\text{ncomp})} = \sum_{j=1}^{\text{ngas}} \alpha_{bal(j)} \frac{\partial \alpha_{bal(j)}}{\partial x(\text{ncomp})}
\]

We introduce equation (5) in the equations (1-3):

\[
\begin{align*}
\text{uit}(k) &= \sum_{l=1}^{\text{ngas}} N(k,l) \cdot x(l) - v_{ren}(k) \\
\text{bal}(j) &= \sum_{l=1}^{\text{ngas}} \text{co}(l,j) \cdot \exp(x(l)) \cdot \exp(x(\text{ncomp})) / \text{strt}(j) + \sum_{l=\text{ngas}+1}^{\text{ncomp}} \text{co}(l,j) \cdot \exp(x(l)) / \text{strt}(j) - 1 \\
\text{help} &= \sum_{l=1}^{\text{ngas}} \exp(x(l)) / \text{ptotin} - 1
\end{align*}
\] (8-10)

The derivatives of (8-10) with respect to \(x(l)\), necessary in equations (7) become:

\[
\begin{align*}
\frac{\partial \text{uit}(k)}{\partial x(l)} &= N(k,l) \\
[&\quad l = 1 \ldots \text{ngas}] (11)
\end{align*}
\]

\[
\begin{align*}
\frac{\partial \text{bal}(j)}{\partial x(l)} &= \text{co}(l,j) \cdot \text{moleq}(l) / \text{strt}(j) \\
[&\quad l = 1 \ldots \text{ncomp}]
\end{align*}
\]

\[
\begin{align*}
\frac{\partial \text{bal}(j)}{\partial x(\text{ncomp})} &= \sum_{l=1}^{\text{ngas}} \text{co}(l,j) \cdot \text{moleq}(l) / \text{strt}(j) \\
[&\quad l = 1 \ldots \text{ngas}]
\end{align*}
\]

\[
\frac{\partial \text{help}}{\partial x(l)} = \frac{\text{peq}(l)}{\text{ptotin}}
\]  
\[l = 1 \ldots \text{ngas}\]

The program functions as follows:

using the mass-balance:

\[
\sum_{l=1}^{\text{ncomp}} \text{co}(l,j) \cdot N(k,l) = 0 
\]  
\[j = 1 \ldots \text{neq}, k = 1 \ldots \text{nev}\]

the program defines the matrix of reaction coefficients \(N\) from the atomic coefficients \(\text{co}\) by inversion.

For a large number of compounds, thermodynamic functions and formulae are stored...
APP. I cont.

in the background-memory of an IBM 360/65 computer (T.H., Delft). The data may be retrieved with the use of a code-number. With this conception, the input to the program reduces to a series of code-numbers, atomic coefficients, the starting composition, volume, pressure and the temperatures for which calculations are required.

List of symbols used in Appendix I

- ngas: number of gases
- ncomp: " compounds
- nev: " independent equilibria
- nel: " elements
- N(k,l): reaction coefficient of compound l in equilibrium k
- co(l,j): atomic coefficient of element j in compound l
- vren(k): log(nat) of K-value of equilibrium k
- molec(l): grammol of compound l at equilibrium
- peq(l): partial pressure of gas l at equilibrium
- strt(j): total amount of element j in gramatoms
- ptotin: total pressure, remains constant
- vt: conversion factor (= volume x 273/(22.4 x temperature))
- α, β: constants to vary the weight of mass-balance and deviation of total pressure.
## APPENDIX II

### Table 48. Some properties of silicon compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol.wt</th>
<th>Boil.pt</th>
<th>$\Delta H_{vap}$ (°C)</th>
<th>$\Delta H_{vap}$ (kcal/mol) b)</th>
<th>$\Delta C_{p}^{0}$ (e.u.) b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SiH}_4$</td>
<td>32</td>
<td>112</td>
<td>7.6</td>
<td>1.15</td>
<td>2.57</td>
</tr>
<tr>
<td>$\text{SiH}_2\text{Cl}$</td>
<td>66.5</td>
<td>30.4</td>
<td>5</td>
<td>-36.2</td>
<td>1.36</td>
</tr>
<tr>
<td>$\text{SiH}_3\text{Cl}_2$</td>
<td>102.1</td>
<td>8.3</td>
<td>6</td>
<td>-78.8</td>
<td>1.64</td>
</tr>
<tr>
<td>$\text{SiHCl}_3$</td>
<td>135.5</td>
<td>31.8</td>
<td>6.4</td>
<td>-120.2</td>
<td>1.95</td>
</tr>
<tr>
<td>$\text{SiCl}_4$</td>
<td>170</td>
<td>57.6</td>
<td>7.2</td>
<td>-160.4</td>
<td>2.28</td>
</tr>
<tr>
<td>$\text{MeSiCl}_2$</td>
<td>149.5</td>
<td>66.1</td>
<td>7.5</td>
<td>-129.3</td>
<td>2.66</td>
</tr>
<tr>
<td>$\text{Me}_2\text{SiCl}_2$</td>
<td>129</td>
<td>70.2</td>
<td>7.3</td>
<td>-114.2</td>
<td>3.04</td>
</tr>
<tr>
<td>$\text{Me}_3\text{SiCl}$</td>
<td>108.5</td>
<td>57.3</td>
<td>7.2</td>
<td>-85.1</td>
<td>3.44</td>
</tr>
<tr>
<td>$\text{Et}_2\text{SiCl}_2$</td>
<td>88</td>
<td>27</td>
<td>6.3</td>
<td>-52.0</td>
<td>3.84</td>
</tr>
<tr>
<td>$\text{Me}_2\text{SiH}$</td>
<td>74</td>
<td>6.7</td>
<td>5.8</td>
<td>-36.8</td>
<td>3.15</td>
</tr>
<tr>
<td>$\text{Et}_2\text{SiH}_2$</td>
<td>60</td>
<td>20</td>
<td>5.1</td>
<td>-21.8</td>
<td>2.47</td>
</tr>
<tr>
<td>$\text{Me}_3\text{SiH}$</td>
<td>46</td>
<td>56.8</td>
<td>4.4</td>
<td>-7.0</td>
<td>1.81</td>
</tr>
<tr>
<td>$\text{Me}_2\text{SiHCl}$</td>
<td>94.5</td>
<td>35.7</td>
<td>6.3</td>
<td>-68.6</td>
<td>2.74</td>
</tr>
<tr>
<td>$\text{Et}_2\text{SiHCl}$</td>
<td>80.5</td>
<td>8.0</td>
<td>5.5</td>
<td>-52.3</td>
<td>2.05</td>
</tr>
<tr>
<td>$\text{Me}_2\text{SiHCl}_2$</td>
<td>115</td>
<td>41.2</td>
<td>6.2</td>
<td>-96.4</td>
<td>2.34</td>
</tr>
</tbody>
</table>

**a)** A register of a large number of silicon compounds with physical and chemical properties and an extensive bibliography has been compiled by Bzant c.s. (76).

**b)** The larger part of the thermodynamic data are estimations (727, 728, Chapter II). Heats of vaporization are mainly estimated with equation (11.3).

---

\( ^{c)} \) Heats of vaporization are mainly estimated with equation (11.3).
APPENDIX III

List of symbols and notations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>$R_2SiCl_2$</td>
<td></td>
</tr>
<tr>
<td>DH</td>
<td>$RSiHCl_2$</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>$RSiCl_3$</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>$SiCl_4$</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>$R_3SiCl$</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
<td></td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>barometric pressure</td>
<td>mm mercury</td>
</tr>
<tr>
<td>$E_a$</td>
<td>activation energy</td>
<td>kcal.mol$^{-1}$</td>
</tr>
<tr>
<td>G</td>
<td>free enthalpy</td>
<td>kcal.mol$^{-1}$</td>
</tr>
<tr>
<td>H</td>
<td>enthalpy</td>
<td>kcal.mol$^{-1}$</td>
</tr>
<tr>
<td>k</td>
<td>rate constant</td>
<td>(dimension in text)</td>
</tr>
<tr>
<td>K</td>
<td>degrees Kelvin</td>
<td>atm$^{-1}$</td>
</tr>
<tr>
<td>$K_A$</td>
<td>adsorption equilibrium constant</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>molecular weight</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>pressure</td>
<td>atm</td>
</tr>
<tr>
<td>R</td>
<td>reaction rate</td>
<td>(dimension in text)</td>
</tr>
<tr>
<td>R, Rg</td>
<td>gas constant</td>
<td>kcal.mol$^{-1}$.degree$^{-1}$</td>
</tr>
<tr>
<td>S</td>
<td>entropy</td>
<td>cal.mol$^{-1}$.degree$^{-1}$</td>
</tr>
<tr>
<td>T</td>
<td>temperature (K)</td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>$u, u'$</td>
<td>heat transfer coefficient</td>
<td>(dimension in text)</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>change of ...</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>molecular symmetry constant</td>
<td></td>
</tr>
<tr>
<td>$\Theta$</td>
<td>fraction of surface coverage</td>
<td></td>
</tr>
<tr>
<td>$\tau$</td>
<td>contact time</td>
<td>s</td>
</tr>
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</table>
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1. Voor kinetische metingen aan katalytische reakties met een aanzienlijk warmte-effekt is het gebruik van een gefluidiseerd bed reaktor af te raden.

2. Het schrijven en lezen van wetenschappelijke geschriften kan worden veraangenaamd wanneer het gebruik van de eerste persoon enkelvoud of meervoud in ere wordt hersteld.


4. In het programma voor vwo en havo dient een belangrijk deel van de waterige chemie te worden vervangen door chemische technologie.

5. Een groen remlicht aan de voorzijde van motorrijtuigen draagt bij tot de volksgezondheid.

6. De keuze der kursussen van Teleac is onvoldoende gemotiveerd.

7. Doordat knal- en stinkproeven als demonstratie worden gebruikt bij scheikundelessen is het wenselijke verband tussen onderwijs en ervaringswereld afwezig.

M.J. van Dalen, Parkweg 229, Voorburg