REACTIONS INVOLVING SILICON HALIDES

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COMPUTERISED

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BY

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DECEMBER 1983

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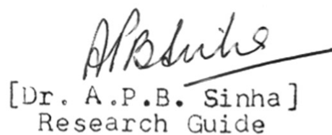
नित्यानन्दं परमसुखदं केवलं ज्ञानमूर्तिम्
द्वन्द्वातीतं गगनसदृशं तत्त्वमस्यादिलक्ष्यम् ।
एकं नित्यं विमलमचलं सर्वधीसाक्षिभूतम्
भावातीतं त्रिगुणरहितं सद्गुरुं तं नमामि ॥

DEDICATED TO MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled 'Reactions Involving Silicon Halides' describes the original work done by Shri Anant C. Choube under my supervision for the Degree of Doctor of Philosophy in Chemistry of the University of Poona, Pune.



[Dr. A.P.B. Sinha]
Research Guide

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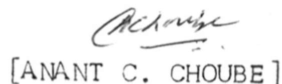

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CHAPTER-I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

1. This thesis presents the investigations of the reactions involving silicon halides especially silicon-trichloride and silicon tetrachloride. These compounds are vitally important in preparation of semiconductor grade silicon.

1.1 Background

Silicon is the most important material in modern semiconductor industry. The general features which favour its key role in semiconductor as well as in photovoltaic industry are : (i) the energy gap of silicon (e_g = 1.12 eV) which permits silicon devices to operate at high ambient temperatures (130°C) with very small leakage current, (ii) the long life-time of charge carriers, (iii) the relatively high mobility of charge carriers, (iv) the knowledge of most of the basic physical properties of silicon including radiation damage effect, (v) the knowledge of the effect of electrically inactive impurities on carrier lifetime and optical properties of silicon and (vi) its abundant availability, its mature technology and its low toxicity.

The number of surface states which can be realized at the SiO_2-Si interface is surprisingly small. This is the basis of all metal-oxide semiconductors (MOS) type

transition structure and of surface passivation of other devices.

The diffusion coefficient of almost all impurity atoms in SiO_2 is small and hence SiO_2 layers are eminently suitable as a masking layer[1]. Minute SiO_2 layers can be produced and can be removed by simple chemical reaction. SiO_2 layers which are formed are well suited to mask material for the fabrication of all types of integrated circuits. This has led to the success of photolithographic techniques for masking very large scale integrated circuits of phenomenal capability and complexity. However, the most important features which have been responsible for the tremendous success of silicon technology relate to the properties of SiO_2 and $Si-SiO_2$ interface.

Solar cells seem more and more likely to supply part of the world's future energy needs. Single crystal silicon solar cells are the most advanced of all photovoltaic devices. Nearly all the commercial solar cells sold to date have been silicon cells. This dominance has resulted from the availability of techniques for growing the large defect free silicon single crystals required by the electronic industry. High quality single crystal silicon with moderate resistivity (about 1 to 10 ohm cm) and an adequate diffusion

length is readily available. The p-n junction cells with efficiencies higher than 10% have been routinely reported since the late 1950[2]. Progress during the past decade demonstrates that silicon can be fabricated into devices with efficiencies approaching 19%[3].

However certain elements (Ti, Zr, Mo, V, Cr, Fe, P, B etc.) have been found to be detrimental to the operation of solar silicon cell by acting as recombination trap when present in concentration of as little as 1 ppba[4,5]. Furthermore, the cost of silicon solar cell is still too high for economic energy production and the cost of pure elemental silicon is itself a major problem in achieving the cost objective of $ 100 to $ 300 per KW by 2000 AD[6]. Low cost silicon of high purity is therefore required to hasten the continued development of solar photovoltaic system.

Elemental ultrapure silicon used in transistors, rectifiers, ICs and electronic components require even higher purity. For many applications boron content has to be less than 0.1 ppba. Zone refining cannot be used for removing boron from silicon due to the unfavourable segregation coefficient (0.8), hence one has to resort to chemical purification method.

Any chemical purification process involves conversion of silicon to some intermediate material which can be easily purified upto some desired purity and which can be reduced to elemental silicon without contamination.

1.2 Intermediate Silicon Compounds

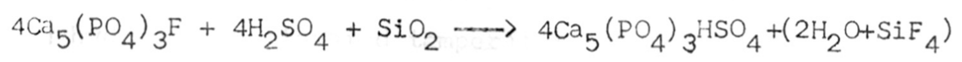
The various silicon intermediate compounds which have been tried for the preparation of high purity silicon are as follows:

1.2.1 Silicon tetrafluoride (SiF_4)

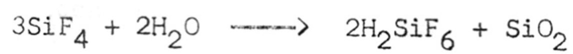
SiF_4 can be prepared by the action of moisture free hydrofluoric acid on silica. Moisture free HF is first prepared by reacting calcium fluoride with concentrated sulphuric acid. This then reacts with silica as

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O.$$

SiF_4 is also obtained as a byproduct in the wet process manufacture of phosphoric acid from fluorapatite $Ca_5(PO_4)_3F$ which is present in phosphate rocks:

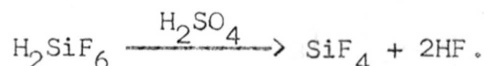


$$4Ca_5(PO_4)_3F + 4H_2SO_4 + SiO_2 \longrightarrow 4Ca_5(PO_4)_3HSO_4 + (2H_2O + SiF_4)$$



$$3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_2$$

The decomposition of H_2SiF_6 with sulphuric acid gives SiF_4,



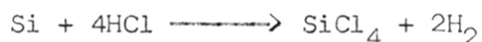
$$H_2SiF_6 \xrightarrow{H_2SO_4} SiF_4 + 2HF.$$

This compound is a colourless gas at room temperature. Its vapours are pungent, fuming and with moist air it forms a dense white mist and hydrolyses to hydrofluorosilicic acid and silica.

1.2.2 Silicon tetrachloride ($SiCl_4$)

When silicon is heated in chlorine gas it ignites and burns forming $SiCl_4$. This condenses to liquid on cooling. $SiCl_4$ can also be prepared by reacting dry HCl gas with ferrosilicon in presence of catalyst at about 400-500°C. The reactions that take place are:

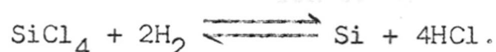
$$Si + 2Cl_2 \longrightarrow SiCl_4$$



$$Si + 4HCl \longrightarrow SiCl_4 + 2H_2$$

These reactions are highly exothermic.

$SiCl_4$ is a transparent, colourless, fuming liquid at room temperature. When exposed to moist air the liquid fumes with a white cloud of SiO_2. The reduction of $SiCl_4$ with hydrogen at elevated temperatures ($\approx$ 1200°C) gives silicon:



$$SiCl_4 + 2H_2 \rightleftharpoons Si + 4HCl.$$

1.2.3 Trichlorosilane ($SiHCl_3$)

This compound is also known as silicochloroform. It can be prepared by the reaction of dry HCl gas with ferro-silicon in presence of copper catalyst at temperatures around 180–230°C. At room temperature, $SiHCl_3$ is a colourless volatile liquid with a smell like that of silicon tetra-chloride. It immediately hydrolyses in presence of moisture giving SiO_2 and HCl. On heating with hydrogen at about 900–1100°C it gives elemental silicon:

$$SiHCl_3 + H_2 \rightleftharpoons Si + 3HCl.$$

1.2.4 Dichlorosilane (SiH_2Cl_2)

It is a byproduct obtained in the preparation of $SiHCl_3$. It is also prepared by disproportionating $SiHCl_3$ as

$$2SiHCl_3 \longrightarrow SiCl_4 + SiH_2Cl_2.$$

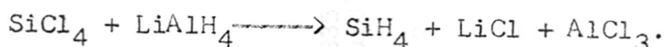
However, its technology for large scale production is still under development.

This is also a colourless mobile liquid which boils at 12°C. It decomposes immediately on coming in contact with H_2O forming silica and HCl. With alkali it forms sodium salt with evolution of hydrogen.

1.2.5 Silane (SiH_4)

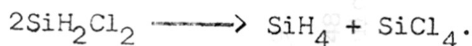
Silane may be prepared by (a) the action of hydrochloric acid on metal silicides like Mg_2Si, (b) reaction of $SiCl_4$ with $LiAlH_4$ in tetrahydrofuran. The reactions that take place are:

$$Mg_2Si + 4HCl \longrightarrow 2MgCl_2 + SiH_4$$



$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + LiCl + AlCl_3.$$

(c) disproportionating SiH_2Cl_2 on a suitable catalyst:



$$2SiH_2Cl_2 \longrightarrow SiH_4 + SiCl_4.$$

SiH_4 is also a colourless gas, having repulsive smell. The dry gas decomposes on exposure to light. When it comes in contact with oxygen or chlorine it bursts explosively and catches fire. It is insoluble in distilled deionized water but if the water contains traces of impurities it decomposes to SiO_2.

The physical properties of all the above compounds are given in Table-1.

1.3 Processes for Preparation of Silicon

The processes successfully used for the preparation of silicon are:

Table - 1 : Physical properties of some silicon compounds.

Sr. No.	Properties	SiH_4	SiF_4	$SiCl_4$	$SiHCl_3$	SiH_2Cl_2	SiH_3Cl
1.	Melting point °C	-185.00	- 90.30	- 70.40	-126.50	-122.00	-118.10
2.	Boiling point °C	-119.90	- 95.70	57.00	31.70	8.30	- 30.40
3.	Molecular weight	32.09	104.06	169.92	135.47	101.01	66.56
4.	Density	16.32 (gas)	4.69 (gas)	1.48 (liquid)	1.335 (liquid)	4.60 (gas)	3.03 (gas)
5.	Bond distance Å	1.48	1.54	2.01	2.02 Si-X 1.47 Si-H	2.02 Si-X 1.46 Si-H	2.05 Si-X 1.45 Si-H
6.	Bond energy Kcal.	77.70	135.00	91.00	-	-	-
7.	Δ Hf Kcal/mole	7.3 ± 0.5	-370.00	-157.10 ± 2.0	-119.60	- 80.00 ± 15.0	- 48.00 ± 15.0
8.	ΔS Cal deg^{-1} mol^{-1}	48.70	24.40	21.00	20.00	21.40	19.80

(a) reduction of $SiCl_4$ by metal like Zn or H_2[7],

(b) reduction of trichlorosilane ($SiHCl_3$) with hydrogen[8],

(c) pyrolytic decomposition of SiH_4, SiI_4, $SiBr_4$, $SiHCl_3$[9,10]

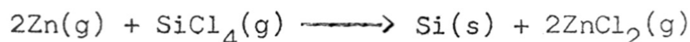
(d) reduction of SiI_4 and $SiBr_4$ with H_2[11,12], and

(e) reduction of $SiCl_4$ with Na[13].

In the process where SiH_4 or chlorosilane e.g. $SiCl_4$, $SiHCl_3$, etc. are used, upgraded ferrosilicon is first chlorinated either by chlorine or by dry HCl using Cu as a catalyst (5%)[14] at about 200-300°C. The products are collected at about -70°C by solid-CO_2 and acetone mixture and then purified by fractional distillation.

1.3.1 Zinc reduction of $SiCl_4$

The earlier method of reducing $SiCl_4$ with Zn was re-examined by Blotcher and Browning[15]. Both solid and vapour Zn feeding systems were utilized in the fluidized bed reactor with solid Zn granules. No silicon was deposited on the seed particles but silicon needles were formed in the down stream of the bed.[16] When Zn was fed as a vapour at a temperature from 900°-1027°C, Si was deposited on the seed particle. Si and $ZnCl_2$ were obtained as :

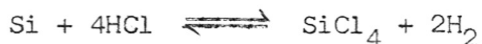


$$2Zn(g) + SiCl_4(g) \longrightarrow Si(s) + 2ZnCl_2(g)$$

Zn and chlorine can be recovered from $ZnCl_2$ by electrolysis and then recycled. The efficiency of this reaction is about 75%.[17] This work was done at Battelle-Columbus Laboratory and the investigations claim a good possibility of meeting the target of $ 10 per Kg.[18]

1.3.2 Hydrogen reduction of $SiHCl_3$

Ultrapure $SiHCl_3$ and H_2 are fed in a reactor tube generally made of quartz which is heated to 1000°–1050°C. The reaction $SiHCl_3 + H_2 \rightleftharpoons Si + 3HCl$ occurs and Si gets deposited on the tube. This reaction is reversible i.e. at this temperature the generated HCl reacts with Si as follows:



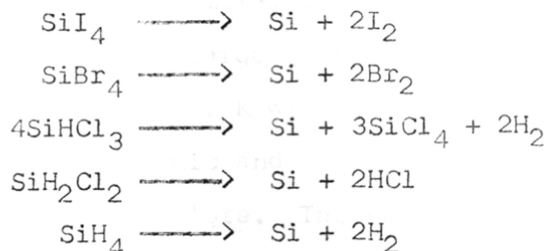
$$Si + 4HCl \rightleftharpoons SiCl_4 + 2H_2$$

In Siemens process, the deposition of Si is done on electrically heated silicon rods. This is a batch process that consumes large amount of energy and hence is energy intensive and therefore expensive.[19]

This reaction can be carried out in a fluidized bed, however, $SiCl_4$ is an undesired by-product which comes out along with unreacted H_2 and $SiHCl_3$.

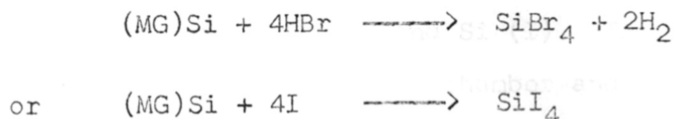
1.3.3 Pyrolytic decomposition

High purity Si can be obtained by thermal decomposition of SiI_4, $SiBr_4$, $SiHCl_3$, SiH_2Cl_2 or SiH_4[20-26] as follows:



$$SiI_4 \longrightarrow Si + 2I_2$$
$$SiBr_4 \longrightarrow Si + 2Br_2$$
$$4SiHCl_3 \longrightarrow Si + 3SiCl_4 + 2H_2$$
$$SiH_2Cl_2 \longrightarrow Si + 2HCl$$
$$SiH_4 \longrightarrow Si + 2H_2$$

SiI_4 can be obtained by heating high quality ferrosilicon with iodine at about 600°C while $SiBr_4$ can be obtained by reacting MG-silicon with HBr at about 400°C. The chemical reactions involved are :



$$(MG)Si + 4HBr \longrightarrow SiBr_4 + 2H_2$$

or $$(MG)Si + 4I \longrightarrow SiI_4$$

Because of the high cost of iodine it is essential to recover it after cracking. However, there is always some loss of I_2 during the recovery. Secondly the cracking of SiI_4 requires low pressure. Hence, the process has not become commercially feasible.

1.3.4 Reduction of halo silanes with Na or K

[a] Reduction of $SiCl_4$: Dickson et al.[27] and Olson et al.[28] have taken the advantage of continuous high temperature reaction of alkali metal and silicon halides especially $SiCl_4$ to produce Si in large quantities. It is known that reaction of gaseous Na or K with Si-halides like $SiCl_4$ or SiF_4 is highly exothermic and luminiscent and produces high adiabatic flame temperature. The reactions are :

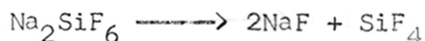
$$SiCl_4 + 4Na \longrightarrow Si + 4NaCl$$

$$SiF_4 + 4Na \longrightarrow Si + 4NaF$$

The flame temperature produced by the reaction is a function of pressure in the system which goes to about $3000^{o}K$. The reaction products are NaCl (g) and Si (l). The sodium salt exists as a gas from the reaction chamber and silicon is present as a condensed phase. The method is adopted by Westinghouse.[29,30] The company claims that the process achieves the target of $ 10 per Kg. However there are difficulties in selecting the material of construction. Hence it is at present in a laboratory scale.

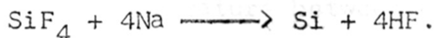
[b] Reduction of Na_2SiF_6 : Nanis et al.[31] have developed a method to produce low cost silicon by reducing SiF_4 with Na. The basic principle is as narrated above.

SiF_4 is obtained from Na_2SiF_6 which is obtained from H_2SiF_6. This is a by-product of fertilizer industry. Na_2SiF_6 is obtained by the reaction $H_2SiF_6 + 2NaF \longrightarrow 2HF + Na_2SiF_6$. When Na_2SiF_6 is decomposed at about 700°C, SiF_4 is obtained:



$$Na_2SiF_6 \longrightarrow 2NaF + SiF_4$$

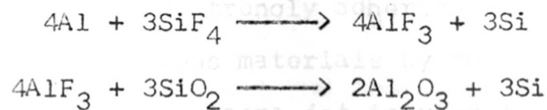
Reduction of SiF_4 starts as soon as sodium chips are dropped into the reactor,



$$SiF_4 + 4Na \longrightarrow Si + 4HF.$$

The reaction is highly exothermic and self-igniting above 150°C. The reaction products are Si, NaF and some Na_2SiF_6 which are collected at the bottom of the reactor. This product is then removed and heated to above 1420°C in a graphite crucible. Molten Si is collected at the bottom of the crucible and the NaF separates as the upper layer. After cooling two separate phases of solids are obtained with Si at the bottom and NaF at the top. The NaF is separated by acid leaching. The Si produced is of enough purity for solar cell. The cost of the Si produced is about $ 5 per Kg.[32] The difficulty is in the separation and disposal of the by-product i.e. NaF which is sparingly soluble in hot water. Hence the separation is difficult. This is called SRI process (Stanford Research Institute).

Ingle and Thomson[33] have developed a process to produce high purity Si from SiF_4, (MG)Si and SiO_2. These are heated upto 1100°C to form SiF_2. The SiO_2 is found essential for purification as for example for removal of aluminium,



$$4Al + 3SiF_4 \longrightarrow 4AlF_3 + 3Si$$

$$4AlF_3 + 3SiO_2 \longrightarrow 2Al_2O_3 + 3Si$$

For a continuous process a small amount of SiF_2 is first prepolymerized at a temperature between -45°C to 200°C to remove most of the impurities present in the gas and then the bulk of SiF_2 is polymerized at -45° and -196°C. The $(SiF_2)_n$ polymer is then heated to 100-300°C to form a stable binary silicon fluoride homologue as $SiXF_y$ which on distillation is converted to pure Si by heating to 400-950°C for a sufficient length of time. The Si obtained can be amorphous, polycrystalline or single crystal depending on the substrate material and temperature.

1.4 Other Methods of Preparing Silicon

1.4.1 Epitaxial growth on MG or polycrystalline silicon substrate

It is known that better performance Si solar cell can be fabricated using 25-15 μm epitaxial structure grown on Si single crystal silicon.[34] This concept has been extended

to improve the efficiency of polycrystalline material such as EFG ribbon[35-39]. The substrates are cleaned and then epitaxial solar cell structures are grown by reducing SiH_2Cl_2 by H_2 at about 1100°C in a horizontal reactor. Calcote[40] has prepared strongly adhering film of amorphous or polysilicon on various materials by reacting H/H_2 jet with $SiCl_4$, $SiHCl_3$. A plasma jet is used to provide the source of $H^{\cdot}$ atoms by dissociating H_2 in electrical discharge. The jet is operated at a temperature 125-325°C with a discharge pressure ranging from $6.7\text{-}20 \times 10^3$ Pa (50-150 torr). The silicon deposits are obtained by placing the substrate material near the bottom of reactor. However a refinement of this process is needed in order to dope the film controllably and prepare photovoltaic amorphous silicon. The impurities present in these materials are Cl, Br and Ni.

1.4.2 <u>Electrodeposition</u>

Deville[41] first investigated the electrolysis of SiO_2 in NaF/KF. Oslon and Carleton[42] have electrolysed pure Si from LiF, KF and SiF_4 in presence of Cu as electrolyte. Elwell[43] also demonstrated that Si can be electro-deposited from saturated solution of SiO_2 in NaF/CaF_2 and KF/CaF_2. Eutectic salts yielding fine elemental Si particles at cathode were obtained in this process.

1.4.3 Fractional crystallization

Solar grade Si can be produced from MG silicon by this method[44,45]. The MG grade Si alloy is transferred to crystallizer kept at a temperature above the liquid. The temperature is then reduced to eutectic temperature and consequently Si is precipitated from the crystallizer and the process is repeated to remove additional quantities of metal from the crystal bed. The crystal bed is cooled and residual metal is removed by acid leaching procedure. Further purification is done by directional solidification technique.

In electronic grade silicon, used for ICs, transistors etc., both polycrystalline or single crystal, the impurities allowable are at ppba level or even less while slightly higher levels are tolerable in case of solar grade silicon used for photocells. If Zn is used in reduction of chlorosilane especially of $SiCl_4$,[28] the material obtained is of poor quality and in the form of dendrites or powder if fluidized bed is used[46]. Zn being a strong reducing agent than H_2 at about 900-950°C, it reduces even traces of boron halides which are present along with $SiCl_4$ and deposits elemental boron with silicon. Thus Zn has low rejection rate for boron and other impurities as compared to H_2. H_2 is a poor reducing agent as compared to Zn or other metals.

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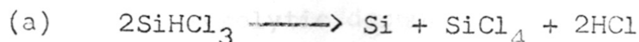
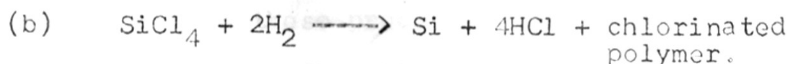
It leaves boron halides unreacted in gaseous mixture[47]. On the other hand $SiCl_4$ which can be produced by various ways like chlorination of ferrosilicon[48], silicon carbide[49] or by heating silica coke and chlorine in arc furnace[50] is cheaper than $SiHCl_3$ but can contain some impurities of boron, P, along with metallic impurities as compared to $SiHCl_3$. Secondly $SiCl_4$ distills at a higher temperature 56°C as compared to $SiHCl_3$. $SiHCl_3$ can be produced by reacting MG-Si with dry HCl gas in presence of Cu as a catalyst in the temperature range of 200 to 250°C. The reaction occurs with the formation of the mixture containing 80-90% $SiHCl_3$ and 10-20% $SiCl_4$ which can be separated by fractional distillation under reflux conditions and exchange resin absorptions. This $SiHCl_3$ when reduced by CVD technique with H_2 gives Si, the predominant reaction being:

$$SiHCl_3 + H_2 \rightleftharpoons Si + 3HCl$$

It is a heterogeneous equilibrium reaction which occurs on hot silicon surface. This is a two step reaction, as



(a) $2SiHCl_3 \longrightarrow Si + SiCl_4 + 2HCl$



(b) $SiCl_4 + 2H_2 \longrightarrow Si + 4HCl$ + chlorinated polymer.

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1.5 Critical Estimates of Silicon Processes

In the case of the zinc reduction of $SiCl_4$ in which $ZnCl_2$ is formed, it is necessary that zinc value should be recovered from $ZnCl_2$. This requires an electrolytic plant which is capital intensive. Therefore this process has not been commercialized.

In case of sodium reduction of $SiCl_4$, the reduction is carried out at a very high temperature like $3000^{\circ}K$ which poses the problems of both materials of construction and operation. As such this process is at present in the laboratory stage.

In case of silicofluoride/silicon tetrafluoride reduction by sodium metal at 600 to $800^{\circ}C$, the difficulty is the separation of silicon metal from the reaction product and the disposal or utilisation of the byproduct NaF.

The commercial methods of producing silicon are :

(i) H_2 reduction of $SiHCl_3$

(ii) Pyrolytic decomposition of SiH_4

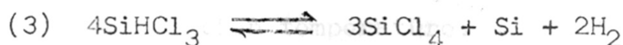
Although both these processes have been commercialized the preparation of SiH_4 from $SiCl_4$ is very difficult and gives very poor yield. However the cracking of SiH_4 is highly efficient.

The H_2 reduction of $SiHCl_3$ has the drawback that in preparation and also in H_2 reduction, a lot of $SiCl_4$ is formed as an undesirable byproduct as per the following reactions:

(1) $Si + 3HCl \rightleftharpoons SiHCl_3 + H_2$

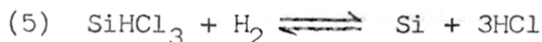
(2) $Si + 4HCl \rightleftharpoons SiCl_4 + 2H_2$

While in the reduction of $SiHCl_3$ the reactions are:



(3) $4SiHCl_3 \rightleftharpoons 3SiCl_4 + Si + 2H_2$

(4) $2SiHCl_3 \rightleftharpoons SiCl_4 + Si + H_2$



(5) $SiHCl_3 + H_2 \rightleftharpoons Si + 3HCl$

In the case of preparation of $SiHCl_3$ reaction (2) predominates, while in the reduction of $SiHCl_3$ reaction (3) prevails over the reactions (4) and (5). Thus in the overall process $SiCl_4$ is formed in large excess.

If the formation of $SiCl_4$ can be suppressed in the preparation of $SiHCl_3$ and if the $SiCl_4$ formed during cracking of $SiHCl_3$ can be converted back to $SiHCl_3$ which can be recycled, then the overall process can compare with silane process.

1.6 Aims and Objectives of the Present Investigations

[1] To minimise the formation of $SiCl_4$ during the preparation of $SiHCl_3$ at 230°C by passing H_2

along with HCl on ferrosilicon. This study has also been extended to higher temperatures upto $800^\circ C$.

[2] Conversion of $SiCl_4$ to $SiHCl_3$ by hydrogenation at 650° to $800^\circ C$ on ferrosilicon bed and also to study the effect of some hydrogenating catalyst such as platinum, palladium, titanium, copper and magnesium silicide at 100° to $500^\circ C$ in reducing the reaction temperature.

During the study of conversion of $SiCl_4$ to $SiHCl_3$ in presence of various catalysts, it was observed that the reaction of $SiCl_4$, Mg_2Si and H_2 takes place presumably via formation of SiH_4. The study has therefore been extended to investigate this reaction. It was also observed that during the conversion of $SiCl_4$ to $SiHCl_3$ in presence of catalysts like Pt, Ti, Pd and Cu, some impurities were getting deposited on the surface of catalysts which were reducing the conversion efficiency. Therefore the surfaces of the metal catalysts were studied before and after the reaction by X-ray photoelectron spectroscopy. The morphology of catalyst surface was investigated by Scanning Electron Microscope.

[3] Silicon deposition by H_2 reduction of $SiHCl_3$ on electrically heated silicon rods is highly energy intensive. Efforts have been made to deposit silicon on silicon particles by H_2 reduction of $SiHCl_3$ in a fluidized bed reactor.

The results of these investigations are described in the following Chapters.

Chapter-II describes the preparation of $SiHCl_3$ by reacting dry HCl gas with ferrosilicon in presence and absence of H_2. The study has been extended to higher temperatures upto 800°C.

In the absence of hydrogen the formation of $SiHCl_3$ decreases with increase in temperature i.e. at 650 and 800°C the $SiHCl_3$ was 23% and 21% respectively in the absence of H_2. This increased to 64% and 46% with increase in H_2/HCl to about 12 and 14 respectively.

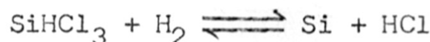
Copper which acts as a positive catalyst at low temperature for the formation of $SiHCl_3$ behaves as a negative catalyst at higher temperatures and this reduces the formation of $SiHCl_3$. Thus at 800°C in presence of copper the $SiHCl_3$ was 19% in absence of H_2 which then increased to only 28% when H_2/HCl ratio was 14.5.

Furthermore, the conversion of $SiCl_4$ to $SiHCl_3$ by hydrogenation was also studied using some hydrogenating

catalysts like Pt, Pd, Ti and Cu to reduce the reaction temperature from 800°C. However it was observed that the conversion was poor at low temperature inspite of the use of the catalyst. In order to gain an insight into the behaviour of these catalysts, the catalyst surface was studied by X-ray photoelectron spectroscopy before and after the reaction. It was observed that the catalyst surface was getting poisoned by deposition of foreign materials which reduced the conversion of $SiCl_4$ to $SiHCl_3$.

The third chapter describes the preparation of magnesium silicide and its reaction with $SiCl_4$ in presence of hydrogen. There is a strong indication of the intermediate formation of SiH_4 and its subsequent decomposition to Si. The highest efficiency in terms of Si/Mg_2Si was obtained at 500°C with molar ratio of $H_2/SiCl_4 = 5$.

The fourth chapter describes the preparation of Si by reduction of $SiHCl_3$ in a fluidized bed. The reduction of $SiHCl_3$ in fluidized bed increases the yield per pass and hence is likely to give economy in energy and raw material consumption. The efficiency of the reaction



$$SiHCl_3 + H_2 \rightleftharpoons Si + HCl$$

is 24% when $H_2/SiHCl_3 = 19$, and efficiency increases with increase in $H_2/SiHCl_3$ ratio.

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CHAPTER-II

PREPARATION OF TRICHLOROSILANE

PREPARATION OF TRICHLOROSILANE

2.1 Introduction

In this section we briefly review only that portion of the literature on the preparation of trichlorosilane which has a direct relevance to our work. The review is therefore mainly confined to (a) the preparation of $SiHCl_3$ by the reaction of HCl with elemental Si in presence of H_2 and (b) preparation by the reduction of $SiCl_4$ to $SiHCl_3$.

It is well-known that the direct reduction of SiO_2 with metals like Al or Mg, does not give silicon of the required semiconductor grade purity. The commercial silicon is therefore converted into its low boiling volatile compounds like SiH_4, $SiHCl_3$, $SiCl_4$ etc. which can be purified by complexation, distillation or by appropriate fractionation. High purity silicon is obtained by the thermal decomposition or by hydrogen reduction of these high purity silicon compounds. Trichlorosilane ($SiHCl_3$) seems to be an attractive intermediate because

(i) it can be easily prepared and is less hazardous as compared to SiH_4,

(ii) its boiling point is lower (32°C) as compared to that of $SiCl_4$ (56°C) so that the higher boiling impurities like metal halides and lower boiling impurities like boron halide and phosphorous chlorides can be easily separated,

(iii) it can be reduced at lower temperatures (900 to $1100^{\circ}C$) as compared to $SiCl_4$ which is reduced by hydrogen at $1200-1300^{\circ}C$ so impurities such as boron whose halides get reduced at the higher temperatures do not get codeposited, and

(iv) the reduction efficiency of $SiHCl_3$ is better than that of $SiCl_4$.

Geo H. Wagner[51] prepared $SiHCl_3$ by reacting ferro-silicon with HCl gas at 250 to $450^{\circ}C$ in presence of copper catalyst. Pierre Chaussaing and Felix Callomb[52] prepared high purity $SiHCl_3$ with an yield of 95 % by reacting HCl gas with ferrosilicon using copper catalyst. The reaction of ferrosilicon and HCl which gives silicon tetrachloride and trichlorosilane is temperature dependent. At low temperature more of $SiHCl_3$ is formed while at higher temperature higher percentage of $SiCl_4$ is favoured[53,54].

In regard to the preparation in presence of hydrogen there are actually only few references. G. Pauls[55] reacted HCl with ferrosilicon at $220-240^{\circ}C$ in presence of hydrogen and obtained 95% of $SiHCl_3$ in the condensate. Fritz Robert[56] reacted HCl with ferrosilicon at 250 to $500^{\circ}C$ in presence of $SiCl_4$ varying $HCl/SiCl_4$ mole ratio from 0.2 to 10 and obtained a mixture of $SiHCl_3$ and $SiCl_4$. Diamanta Laudoniu[53,57] reacted HCl with ferrosilicon in presence of

hydrogen and obtained 88% $SiHCl_3$ with H_2:HCl ratio 1:1. The $SiHCl_3$ was above 90% when HCl:H_2 was in the range 1:3 to 5.

Schwarz Rudolf and Meyer Simon[58] manufactured $SiHCl_3$ by the reaction of ferrosilicon and dry gas HCl at 400--800°C in presence of hydrogen. At 400°C with H_2:HCl = 30:1, the condensate consisted of 95% $SiHCl_3$, 4.5% $SiCl_4$ and 0.6% SiH_2Cl_2. While in absence of H_2 the composition was 33.7% $SiHCl_3$, 65.6% $SiCl_4$ and 0.49% SiH_2Cl_2. At 800°C he got 41.4% $SiHCl_3$, 55.7% $SiCl_4$ and 3.17% SiH_2Cl_2 when HCl:H_2 was 1:30.

During hydrogen reduction of $SiHCl_3$ to silicon, either in fluidized bed or in rod reactor, major bulk of $SiHCl_3$ gets converted to silicon tetrachloride (STC) which is an undesirable byproduct. This adversely affects the cost of silicon produced. The formation of $SiCl_4$ should therefore be minimised or it should be reconverted to $SiHCl_3$.

Haldor et al.[59] reacted STC and H_2 in a ratio 1:10 on a pure silicon wire at 1100°C and observed that 11.5% of $SiCl_4$ was deposited on the wire as Si and 15% was reduced to $SiHCl_3$ which was coming out from reduction chamber.

Bradely Howard[60] prepared $SiHCl_3$ by passing a water-free mixture of 15 mole % $SiCl_4$ and 50:50 gaseous mixture of hydrogen and hydrochloric acid, through a quartz tube at 1200°C and converted 52 mole % of $SiCl_4$ to $SiHCl_3$.

Bawa Mohendras et al.[61] prepared $SiHCl_3$ by passing a gas mixture of HCl, N_2 as a carrier gas and SiH_2Cl_2 and $SiCl_4$ through a fluidized bed of Si particles held at 620-640°F. In this case the residence time of the vapourised reactants in the reaction zone was 5 to 20 seconds.

Noda Toshio et al.[62] passed a preheated mixture of $SiCl_4$ and hydrogen in mole ratio 0.8:1 on silicon in a fluidized bed at temperatures greater than 500°C. The preheating was done by passing the mixture through an inert bed of 4-10 mesh of SiO_2 and reduced STC to 24% $SiHCl_3$ and 76% SiH_4.

Weigert Wofgang et al.[63] manufactured $SiHCl_3$ by passing (1 to 5 mole ratio) $SiCl_4$:H_2 over charcoal as a catalyst at 1100°C keeping a residence time 1.5 seconds and obtained a mixture which contained 37.1 mole % of $SiHCl_3$, 0.6 mole % of SiH_2Cl_2 and 62.3 mole % of $SiCl_4$.

Kodaka Aklo et al.[64] reduced $SiCl_4$ to $SiHCl_3$ with hydrogen using a platinum group element as a catalyst and $SiCl_4$:H_2 ratio from 1:1-40 with residence time from 1 to 300 seconds. Kuratomi Tatsuo[65] hydrogenated $SiCl_4$ at 200-550°C by treating a gaseous stream, containing $SiCl_4$ 3% and H_2 17% by volume with titanium hydride.

Rodgers Michael[66] hydrogenated $SiCl_4$ to $SiHCl_3$ without using any catalyst by passing a mixture of $SiCl_4$ and H_2

through a tube furnace at 900-1100°C at such a rate that the dwell time was a few seconds. Blocher John et al.[67] hydrogenated $SiCl_4$ with hydrogen in presence of Si which gave $SiHCl_3$ and SiH_2Cl_2, the latter then reacted with HCl and gave $SiHCl_3$. Seyferth[68] studied reaction of $SiCl_4$ with Si metal and hydrogen in presence of copper catalyst. The study was carried out at different temperatures (upto 500°C), pressures (upto 550 psi) and $H_2/SiCl_4$ feed ratios. The same route is followed by the Union Carbide Company, U.S.A. in preparing silane from $SiCl_4$ where $SiHCl_3$ is further disproportionated to SiH_2Cl_2 and finally to SiH_4.

$SiCl_4$ can be hydrogenated in radio frequency plasma[69] at 100°K Pa leading to the formation of a mixture of $SiHCl_3$ and SiH_2Cl_2. Okuwaki[70] hydrogenated $SiCl_4$ at 1100-1600°C by feeding hydrogen around $SiCl_4$ and converted a major fraction of $SiCl_4$ to $SiHCl_3$.

As most of the literature is in patented form and not much experimental data is available either on preparation of $SiHCl_3$ or on conversion of $SiCl_4$ to $SiHCl_3$, it was proposed to study the reaction of ferrosilicon and HCl leading to the formation of $SiHCl_3$ and $SiCl_4$ at various temperatures. It was also proposed to study the effect of hydrogen in presence and absence of copper catalyst since it is known that H_2 suppresses the formation of $SiCl_4$. Study of hydrogenation

of $SiCl_4$ to $SiHCl_3$ has also been undertaken at various temperatures in presence and in absence of different catalysts.

2.2 Experimental

A silica reactor tube of 20 cm length and 25 mm (ID), as shown in Fig.1 was filled with an inert material like silica beads for about 2 cm to 3 cm till it touched the base of the thermowell. Metallurgical grade silicon of the following assay in the form of granules of (-7 to +20 mesh) size was then placed over the inert bed. The composition of metallurgical grade silicon was 98.5% Si, 0.60% Fe, 0.40% Ca, 0.05% Al, 0.05% S and 0.05% P. The height of the silicon column was about 6 to 7 inches. When a catalyst was to be used, the same was mixed with the silicon granules. The catalysts used were Pd on charcoal, Pt-asbestos, titanium granules or copper powder (-200 to +300 mesh). The catalyst was always activated by heating for two hours at 500°C in presence of hydrogen before starting the run. The heating was done in a tubular silica furnace which was wound with Kanthal A (20 SWG) wire. Chromel-alumel thermocouple was used in a silica sheath for measuring the temperature as shown in Fig.1. The furnace temperature was controlled within $\pm$ 5°C by a temperature controller and a high current capacity relay.

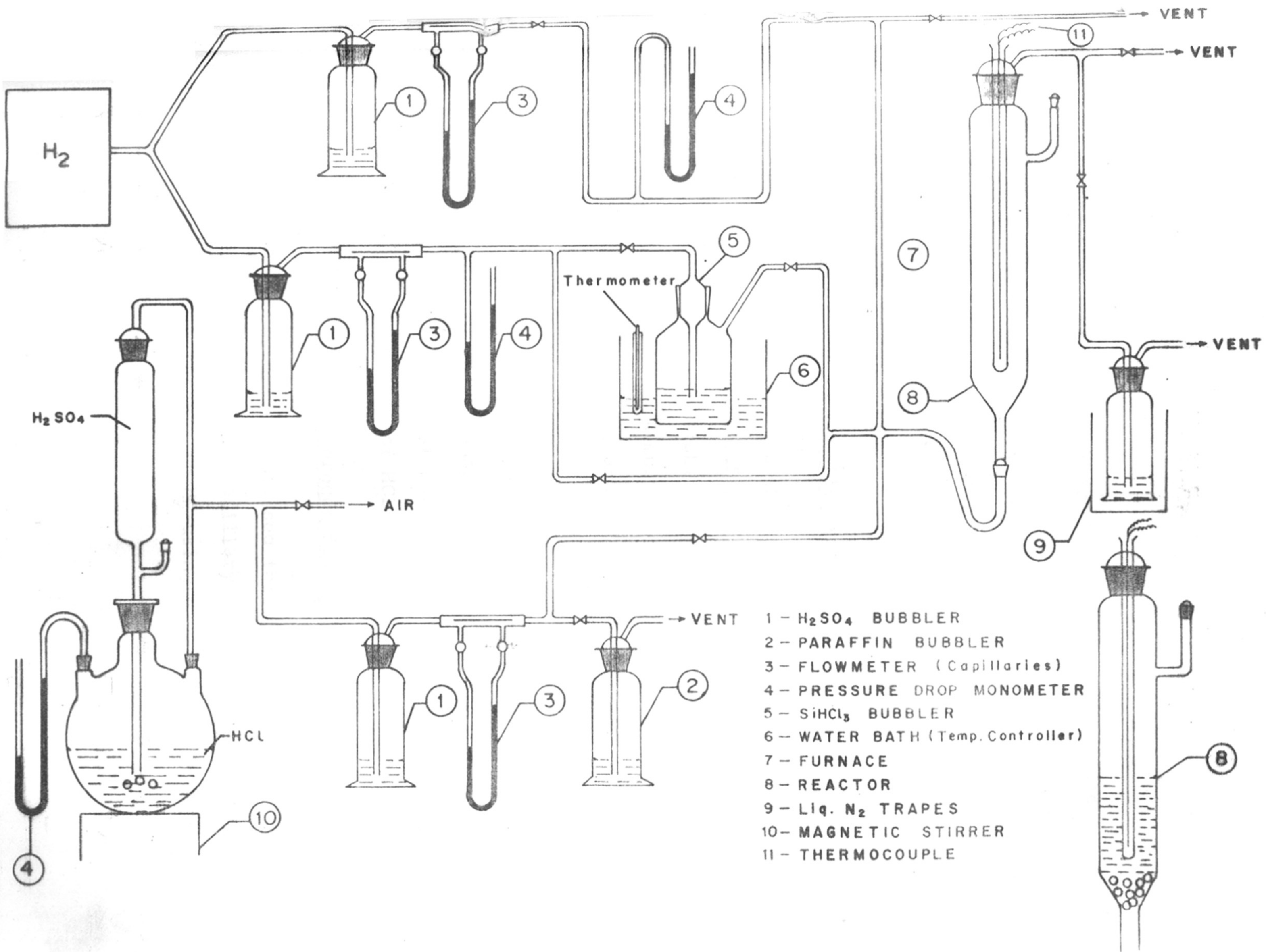


FIG.1- EXPERIMENTAL SET-UP FOR $SiHCl_3$ PREPERATION.

2.2.1 HCl gas generation

Hydrogen chloride gas was generated by drop-wise addition of concentrated sulphuric acid from a reservoir to hydrochloric acid in a flat bottom flask. The whole mixture was stirred using a teflon coated magnetic needle using a magnetic stirrer. Dry HCl gas was obtained after passing the gas through a series of sulphuric acid bubblers.

2.2.2 Calibration of HCl flow rate

The dry HCl gas was then passed through a sulphuric acid manometer having a 0.5 mm (ID) capillary. The capillary was precalibrated by establishing a constant flow rate, measuring the H and simultaneously absorbing the HCl in a series of NaOH absorbers and estimating the reacted NaOH by titration difference.

About 6 to 7 readings were recorded for each ΔH value, and this procedure was adopted for different ΔH values in the required range. A graphical plot was made with ΔH on the ordinate and flow rate of HCl on the abscissa.

2.2.3 Calibration of hydrogen flow rate

Hydrogen (dry) was passed through a sulphuric acid manometer consisting of a capillary. The capillary was calibrated with respect to H_2 using a wet-gas flow meter.

This method was used for high flow rates of H_2. For lower flow rates, the capillary was calibrated by directly measuring the volume of H_2 in a given time using water displacement. A graph of ΔH *vs* the flow rate of H_2 was plotted.

2.3 Study of HCl reaction with MG Si (98.5%) up to 800°C

2.3.1 In absence of H_2

In absence of copper : The reactor was filled with MG silicon as mentioned earlier and heated at first to 650°C. A known quantity of HCl gas was then passed through it for 30 minutes in absence of H_2. The evolved vapours were condensed in liquid nitrogen cooled traps. The condensed liquid was then mixed with dehydrated CCl_4 and then analysed on an off-line gas chromatograph. The column used for analysis was SE-52.

In presence of copper : In another set of experiments, HCl gas was passed through MG silicon containing copper catalyst (5%).

2.3.2 In presence of H_2

In absence of copper : In these experiments the HCl flow rate was constant and was supplemented by H_2 gas, with the flow rates varying from 8 cc/sec. to 56 cc/sec. In every experiment the evolved vapours were condensed in

liquid nitrogen cooled traps and brought to liquid stage, mixed with CCl_4 and then analysed on the off-line gas chromatograph.

In presence of copper : In another set of experiments HCl gas was passed through MG silicon containing copper catalyst (5%).

In another set of experiments the above HCl-MG silicon reaction was repeated at 800°C, at first without Cu catalyst and then in presence of 5% Cu-catalyst, at first in absence of H_2 and then in presence of H_2 gas with the flow rates varying from 8 cc/sec. to 56 cc/sec.

2.3.3 Thermodynamic discussion

The thermodynamic values for the reactions involved in reduction of $SiCl_4$ and $SiHCl_3$ are given in Table-2.

From Table-2 it is observed that the free energy change for the forward reaction in 1-3 is not favourable but it is favourable in case of backward reaction leading to the formation of $SiCl_4$. The free energy change is slightly favourable for forward reaction in case of reactions (6) upto 900°K. This becomes unfavourable with increase in temperature. The free energy changes are highly negative in reactions (4), (5) and (9), in which

Table - 2 : Heats of reactions and standard free energy changes at various temperatures.

Sr. No.	Reaction	ΔH_{298} Kcal. $mole^{-1}$	ΔF Kcal. $mole^{-1}$							
			400°K	500°K	600°K	700°K	800°K	900°K	1000°K	1100°K
1	$SiCl_4+H_2 \rightleftharpoons SiHCl_3+HCl$	15.50	24.36	18.56	17.81	17.12	16.47	15.77	15.08	14.50
2	$SiCl_4+H_2+Si \rightleftharpoons SiHCl_3 + HCl$	15.50	24.36	18.56	17.81	17.12	16.47	15.77	15.08	14.50
3	$3SiCl_4+Si+2H_2 \rightleftharpoons 4SiHCl_3$	-8.90	40.18	25.98	26.94	27.79	29.22	30.17	31.16	32.45
4	$SiCl_4+2H \rightleftharpoons SiHCl_3 + HCl$	-89.10	-70.36	-73.68	-71.89	-70.51	-68.05	-66.05	-64.04	-61.89
5	$SiHCl_3+2H \rightleftharpoons Si + 3HCl$	-50.60	-61.82	-62.55	-63.20	-63.76	-64.23	-64.68	-65.02	-65.34
6.	$SiCl_4+2HCl+Si \overset{H_2}{\rightleftharpoons} 2SiHCl_3$	-37.98	- 8.54	-11.13	- 8.86	- 6.24	- 3.81	- 1.38	0.99	3.45
7.	$Si+3HCl \rightleftharpoons SiHCl_3+H_2$	-46.00	-32.90	-29.68	-26.50	-23.35	-20.23	-17.15	-14.08	-11.05
8.	$Si+4HCl \rightleftharpoons SiCl_4+2H_2$	-69.10	-57.26	-48.24	-44.31	-40.46	-36.67	-32.92	-29.17	-25.55
9.	$SiHCl_3+2H \rightleftharpoons SiH_2Cl_2 + HCl$	-86.77 ±15	-82.55	-80.65	-78.65	-76.56	-74.38	-72.17	-69.91	-67.61

The values of ΔH_f and ΔF_f are taken from JANAF THERMOCHEMICAL TABLE[88]

atomic hydrogen is formed, therefore the reaction takes place even at low temperatures. Reaction (5) also takes place along with reactions (4) and (9) which affects the formation of $SiHCl_3$. Reactions (7) and (8) are both thermodynamically favourable, however, reaction (8) prevails over reaction (7).

The forward reactions (1) and (2) are endothermic while all other reactions are exothermic.

Reactions (1), (2) and (5) are pressure independent as there is no change in volume, while the remaining reactions i.e. (3), (4), (6), (7), (8) and (9) are all pressure dependent as there is a reduction in volume in the forward reaction.

2.3.4 Results and discussion

When dry HCl gas is passed over silicon (-20 to +30 mesh) formation of $SiHCl_3$ and $SiCl_4$ occurs. From Table-3, Fig.2 it is evident that in presence of 5 to 6% copper catalyst, the formation of trichlorosilane is favoured at lower temperatures (about 180°-$200^{\circ}C$). The mixture is 75% $SiHCl_3$ and 25% $SiCl_4$. As the temperature is increased, the formation of $SiCl_4$ is favoured[53,54]. At $650^{\circ}C$ when HCl gas is reacted with silicon the exit gases contain 23.5% $SiHCl_3$ and 76.5% $SiCl_4$. The reactions are as follows:

Table - 3 : Effect of temperature on reaction of dry HCl(g) with ferrosilicon in presence of 5% copper catalyst

[i] Weight of MG silicon ... 125 gms.
[ii] Bed height ... 17 cms.

Sr. No.	Temperature °C	Exit gas composition	
		% $SiHCl_3$	% $SiCl_4$
1.	150	55.0	45.0
2.	180	75.0	25.0
3.	220	75.0	25.0
4.	270	40.0	60.0
5.	400	30.0	70.0
6.	650	23.5	76.5
7.	800	19.0	81.0

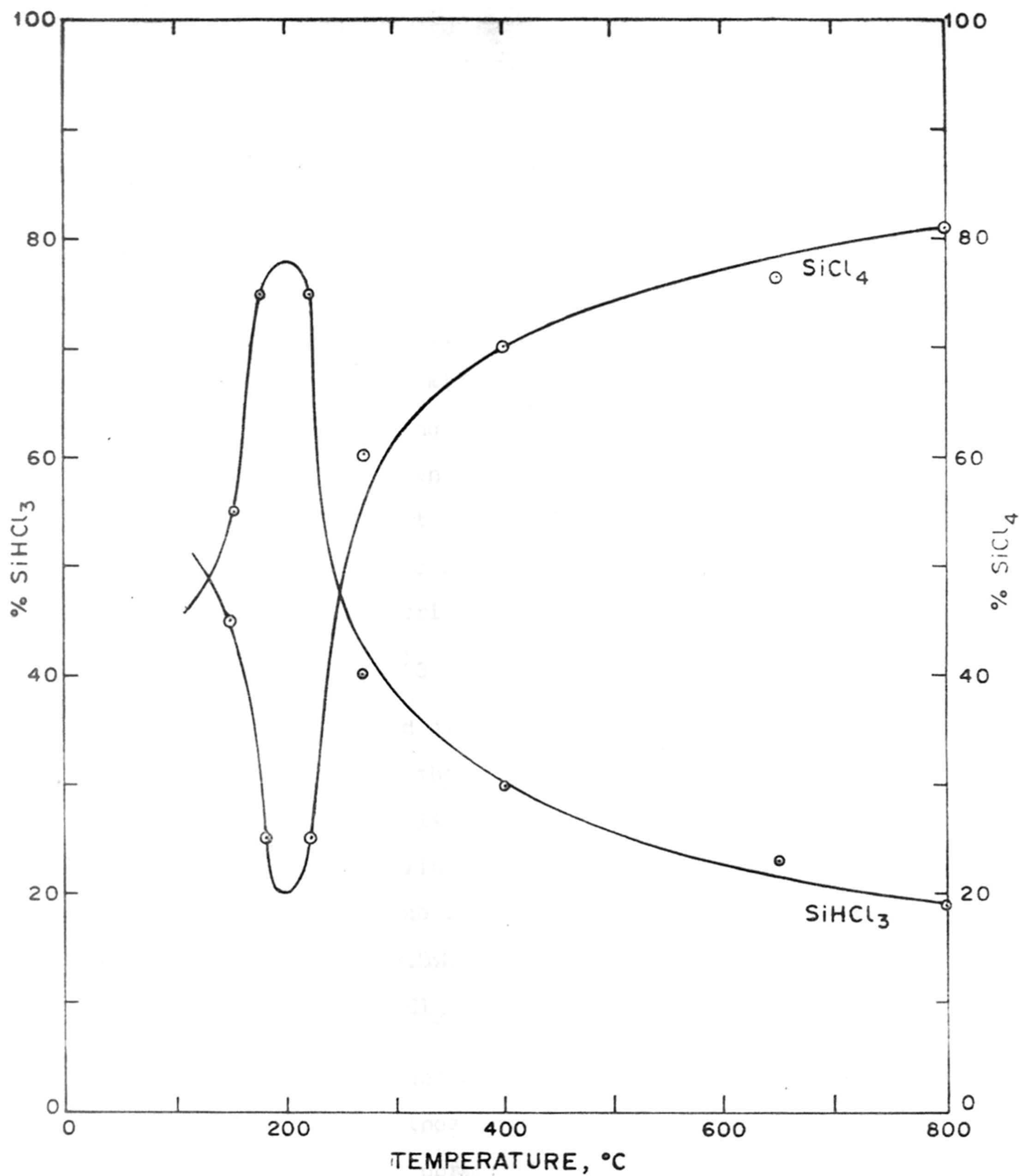
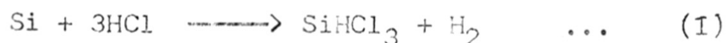
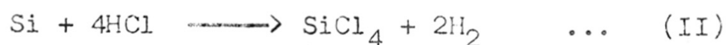


FIG. 2. TEMPERATURE Vs. PERCENTAGE OF $SiHCl_3$ AND $SiCl_4$



$$Si + 3HCl \longrightarrow SiHCl_3 + H_2 \quad \ldots \quad (I)$$



$$Si + 4HCl \longrightarrow SiCl_4 + 2H_2 \quad \ldots \quad (II)$$

From the table of thermodynamic parameters reaction (II) appears to be more favourable as compared to reaction (I) at all temperatures, but still one observes that at low temperature (200-300°C) the formation of $SiHCl_3$ is favoured. This could be due to the kinetic factors e.g. the free energy of activation being smaller for $SiHCl_3$ formation than that for $SiCl_4$. When temperature is increased the molecules have sufficient energy which reduces the formation of $SiHCl_3$ and favours the formation of $SiCl_4$. The same reaction, when it is carried out at 800°C, the exit gas composition is 19% $SiHCl_3$ and 81% $SiCl_4$.

When H_2 is passed along with HCl, the formation of $SiCl_4$ is suppressed and the formation of $SiHCl_3$ is favoured. From the Table-4, Fig.3 it is observed that at 650°C the formation of $SiHCl_3$ is linearly proportional to the ratio of hydrogen to HCl in the feed. Thus when no hydrogen is passed the $SiHCl_3$ is 23.5%, while when mole ratio of H_2/HCl is 14.5, the $SiHCl_3$ is 63.8%.

While at 800°C the addition of H_2 with HCl favours $SiHCl_3$ formation, the linear relationship of H_2/HCl to $SiHCl_3$ formation is not observed as seen in Table-5, Fig. 4.

Table - 4 : Effect of H_2 in preparation of chlorosilane from HCl(g) and ferrosilicon in presence of 5% copper catalyst at 650°C

[i] Bed height ... 10 to 17 cms.

[ii] Weight of MG silicon ... 125 gms.

Sr. No.	Duration of experiment	Mole ratio H_2/HCl	Exit gas composition			Remark
			% $SiHCl_3$	% $SiCl_4$	% SiH_2Cl_2	
1	30 minutes	-	23.50	76.50	-	H_2 = 0 only HCl passed
2	30 minutes	3.44	35.50	64.50	-	-
3	30 minutes	3.96	44.80	55.20	negligible	-
4	30 minutes	5.44	52.00	47.00	1.00	-
5	30 minutes	9.39	60.20	37.80	2.00	-
6	30 minutes	10.24	64.80	33.00	2.20	-
7	30 minutes	14.47	63.80	34.70	2.50	-

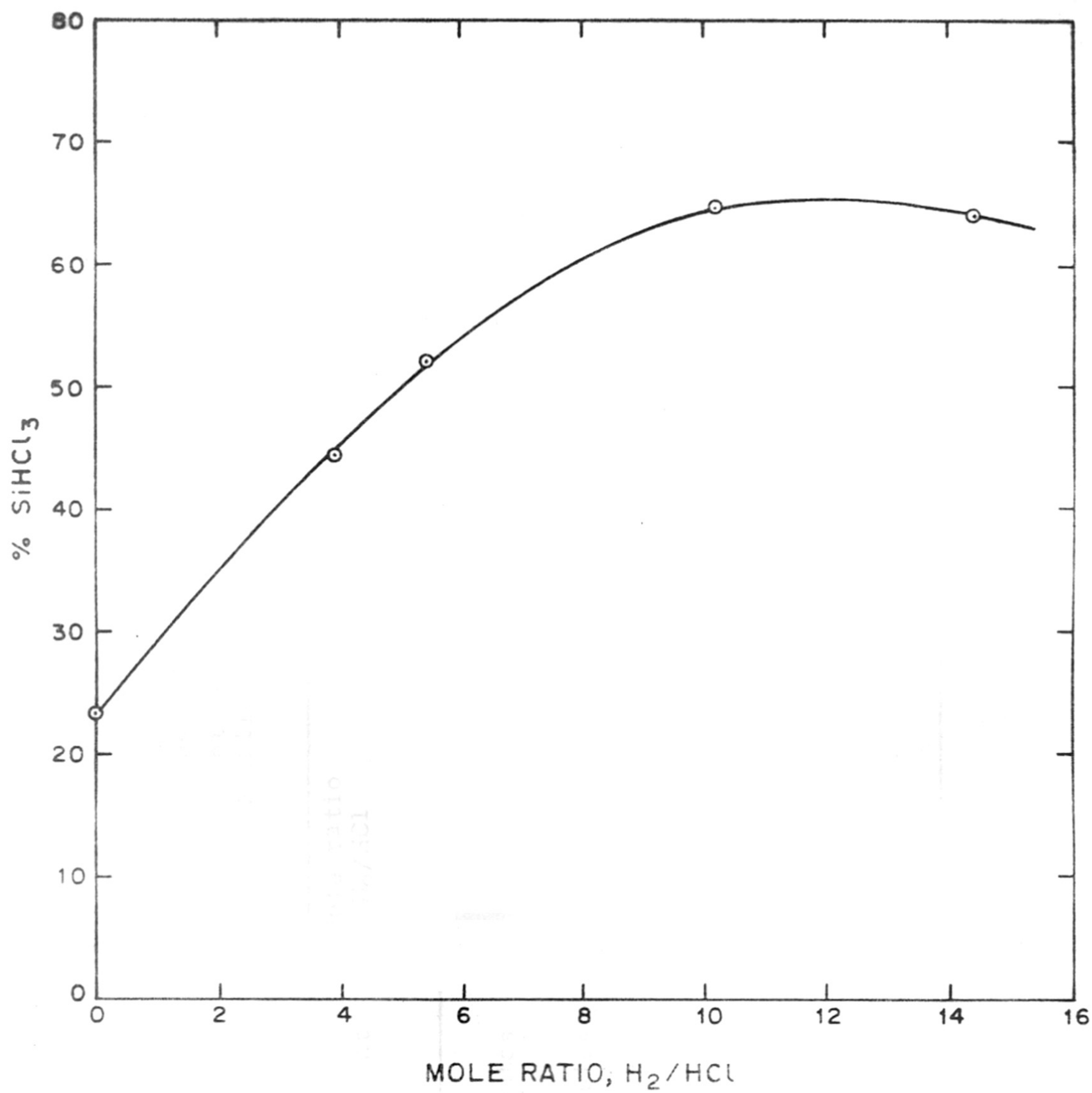


FIG. 3. MOLE RATIO OF H_2/HCl Vs. PERCENTAGE OF $SiHCl_3$ OBTAINED AT 650 °C.

Table – 5 : Effect of H_2 in preparation of chlorosilane from HCl(g) and ferrosilicon in absence of catalyst at 800°C

[i] Bed height ... 10 to 17 cms.

[ii] Weight of MG silicon ... 125 gms.

Sr. No.	Duration of experiment	Mole ratio H_2/HCl	Exit gas composition		Remark
			% $SiHCl_3$	% $SiCl_4$	
1	30 minutes	-	21.00	79.00	$H_2 = 0$ only HCl passed
2	30 minutes	2.60	29.70	70.30	-
3	30 minutes	4.46	32.25	67.75	-
4	30 minutes	5.97	39.57	60.43	-
5	30 minutes	8.28	39.73	60.27	-
6	30 minutes	9.16	45.45	54.55	-
7	30 minutes	11.55	46.33	53.67	-

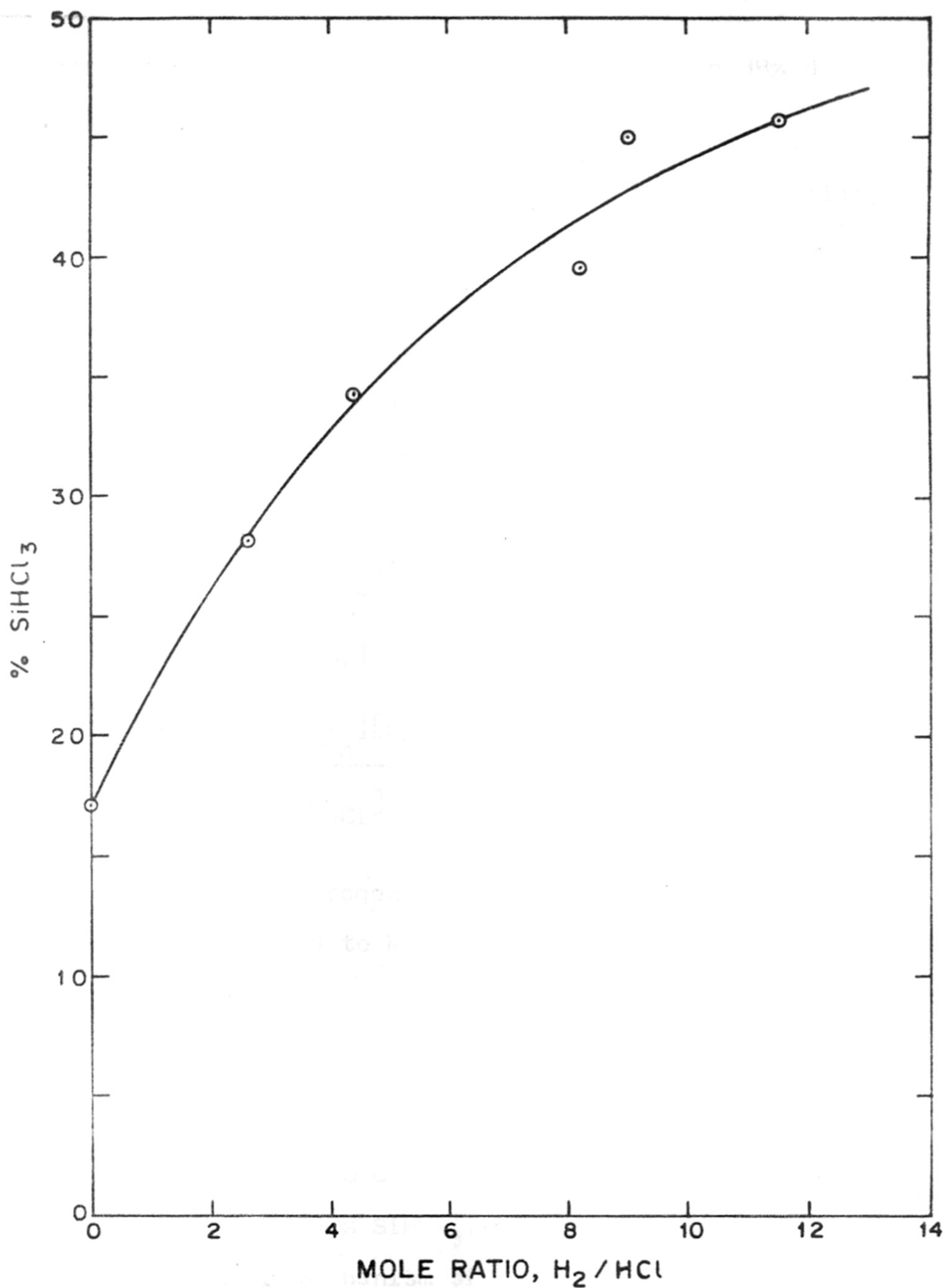


FIG. 4. MOLE RATIO OF H_2/HCl Vs. PERCENTAGE OF $SiHCl_3$ OBTAINED AT 800 °C

It changes from 19% in the absence of hydrogen to 38% $SiHCl_3$ at H_2:HCl = 14.5.

The formation of $SiHCl_3$ is favoured by the addition of hydrogen. This can be explained as follows. In the reactions (I) and (II) hydrogen is liberated along with $SiCl_4$ and $SiHCl_3$. Hence by the Le-Chatelier's principle when hydrogen is passed along with HCl the equilibrium shifts to the left hand side. Considering the equilibrium constants of the reactions

$$K_1 = \frac{[p_{SiHCl_3}][p_{H_2}]}{[p_{HCl}]^3}$$

$$K_2 = \frac{[p_{SiCl_4}][p_{H_2}]^2}{[p_{HCl}]^4}$$

it can be seen that hydrogen dependence in K_2 is in the square term as compared to K_1. Hence the formation of $SiCl_4$ is suppressed with respect to $SiHCl_3$. Also, hydrogen maintains a reducing atmosphere.

Paul[55] prepared $SiHCl_3$ by reacting dry HCl with ferrosilicon at about 240°C in presence of nitrogen and hydrogen and obtained 90% $SiHCl_3$. Joklik and Bazant[54] suggested a probable mechanism of catalyst like Cu, in

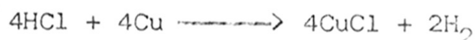
preparation of $SiHCl_3$ from HCl and Si. The HCl is adsorbed on the surface of catalyst with the dissociation into H and Cl atoms, the adsorbed hydrogen recombines into molecular hydrogen instantaneously, which is desorbed. The remaining adsorbed chlorine atoms react with Si, which first leads to the surface formation of $SiCl_2$. This then reacts further with chlorine to form $SiHCl_3$ or $SiCl_4$.

Slobodan et al.[71] proposed that the synthesis of chlorosilane like $SiHCl_3$ or $SiCl_4$ at low temperature is possible due to the presence of CuCl as per the reaction

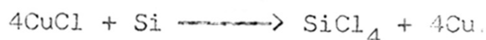
$$Si + 4CuCl \longrightarrow SiCl_4 + 4Cu$$

resulting in a large number of new centres of Cu for further reaction. Brown[72] reports that the formation of $SiHCl_3$ can be increased by decreasing the formation of $SiCl_4$. By a proper choice of experimental conditions, he claims to have increased the formation of $SiHCl_3$ upto 400°C without increasing the formation of $SiCl_4$. Schwarz, Rudolf[58] did the reaction of HCl in presence of hydrogen in ratio 1:30 at 800°C and collected 41.4% $SiHCl_3$. In our case we have collected 46% $SiHCl_3$ with 1:14 ratio at the same temperature.

The reaction of HCl in presence of Cu as a catalyst can be explained as follows. First HCl reacts with Cu forming CuCl, which reacts with Si, giving $SiCl_4$ as :



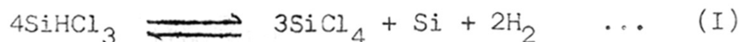
$$4HCl + 4Cu \longrightarrow 4CuCl + 2H_2$$



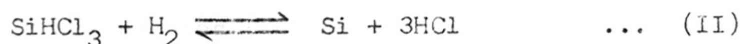
$$4CuCl + Si \longrightarrow SiCl_4 + 4Cu$$

When these reactions occur, the H_2 which is desorbed from Cu in atomic form, can also react with $SiCl_2$ forming $HSiCl_2$ which on further reaction with CuCl gives $SiHCl_3$. Hence, in absence of external hydrogen, at 650-800°C, the formation of $SiHCl_3$ is observed as 23 and 18 % respectively. When hydrogen is passed along with HCl the quantity of hydrogen in contact with Cu increases which increases the free radical hydrogen that will favour the formation of $SiHCl_3$ than $SiCl_4$. At 650°C when there is no hydrogen, the $SiHCl_3$ is 23% which increases to 63.8% with $H_2/HCl = 14$.

The yield of $SiHCl_3$ decreases at 800°C. This is possibly due to the partial thermal cracking or by hydrogen reduction of $SiHCl_3$ as



$$4SiHCl_3 \rightleftharpoons 3SiCl_4 + Si + 2H_2 \quad \ldots \quad (I)$$

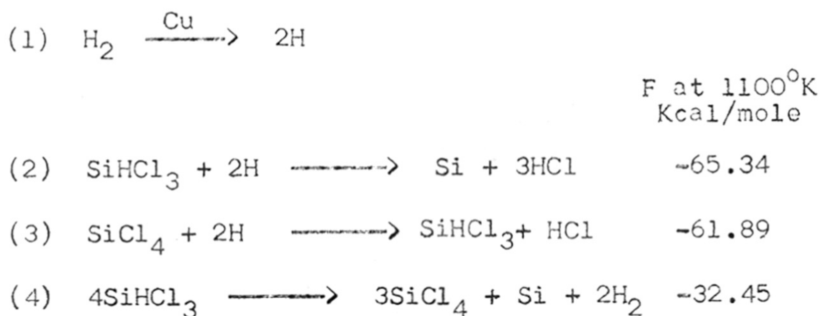


$$SiHCl_3 + H_2 \rightleftharpoons Si + 3HCl \quad \ldots \quad (II)$$

as reaction (I) is thermodynamically more favourable, $SiHCl_3$ is decomposed by this route even in presence of hydrogen.

It is interesting to find that at 800°C the role of copper is reversed. The yield of $SiHCl_3$ is less when

Cu is present as seen in Table--6, Fig.5 than when it is absent. This can be explained by the following reactions:



(1) $H_2 \xrightarrow{Cu} 2H$

		F at $1100^{o}K$ Kcal/mole
(2)	$SiHCl_3 + 2H \longrightarrow Si + 3HCl$	-65.34
(3)	$SiCl_4 + 2H \longrightarrow SiHCl_3 + HCl$	-61.89
(4)	$4SiHCl_3 \longrightarrow 3SiCl_4 + Si + 2H_2$	-32.45

Copper activates hydrogen which can react with $SiCl_4$ as well as $SiHCl_3$ as per above equations (2) and (3). Since reaction (2) is equally favourable thermodynamically but more favourable kinetically this leads to the decomposition of $SiHCl_3$. The final yield of $SiHCl_3$ is therefore reduced considerably at $800^{o}C$, even in presence of hydrogen. From thermodynamic consideration the reaction of HCl with silicon is exothermic. The heat generation depends upon the quantity of HCl reacting with silicon. The mixing of hydrogen with HCl reduces its feed rate and also maintains reducing atmosphere. This lowers the rate of reaction and controls the heat generation. Thereby formation of local hot spots is reduced and the temperature is not allowed to increase. Hence the formation of $SiCl_4$ is reduced in presence of hydrogen.

Table - 6 : Effect of H_2 in preparation of chlorosilane from HCl(g) and ferrosilicon in presence of 5% copper catalyst at 800^oC

[i] Bed height ... 10 to 17 cms.

[ii] Weight of MS silicon ... 125 gms.

Sr. No.	Duration of experiment	Mole ratio H_2/HCl	Exit gas composition		Remark
			% $SiHCl_3$	% $SiCl_4$	
1	30 minutes	-	19.00	81.00	$H_2 = 0$ only HCl passed
2	30 minutes	2.58	28.00	72.00	-
3	30 minutes	4.74	31.00	69.00	-
4	30 minutes	6.51	32.00	68.00	-
5	30 minutes	9.23	32.00	68.00	-
6	30 minutes	9.38	35.00	65.00	-
7	30 minutes	14.52	38.00	62.00	-

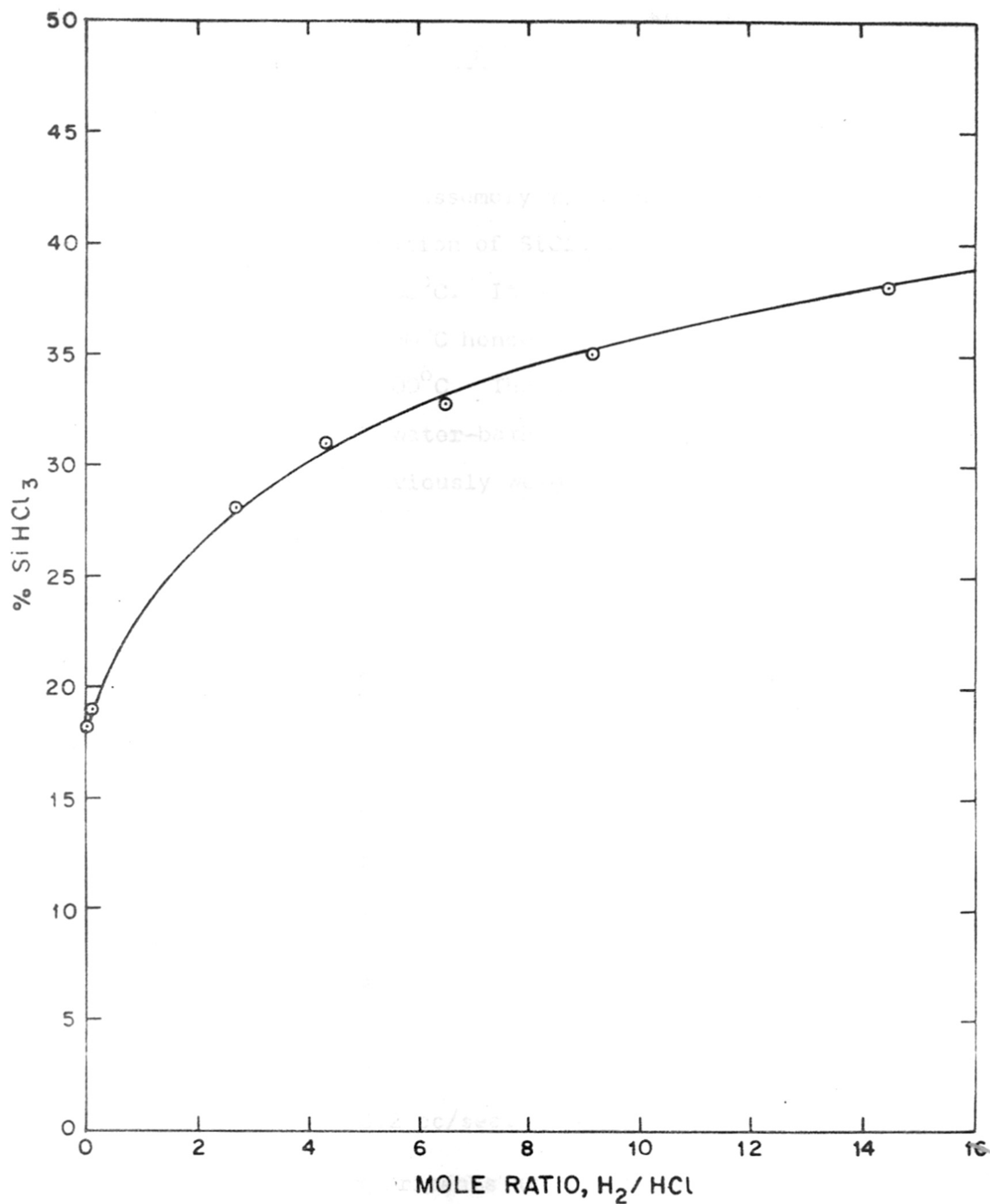


FIG. 5. MOLE RATIO OF H_2/HCl Vs. PERCENTAGE OF $SiHCl_3$ OBTAINED AT 800 °C IN PRESENCE OF COPPER CATALYST

2.4 Study of Hydrogenation of $SiCl_4$

2.4.1 In absence of copper catalyst

The same reaction assembly mentioned in Section 2.3 was used. The hydrogenation of $SiCl_4$ was carried out from 200-800°C in steps of 100°C. It was observed that the reduction starts from 650°C hence the study was confined to the range 650°C to 800°C. The $SiCl_4$ bubbler was kept in a constant temperature water-bath for adjusting its vapour pressure. This was previously weighed. A known amount of hydrogen gas was then bubbled through this $SiCl_4$ bubbler and the entire gas mixture with an additional hydrogen was passed through the reactor. The H_2 inlet was bifurcated prior to the $SiCl_4$ bubbler, one going through the $SiCl_4$ bubbler to the reactor, the other going directly to the reactor in known quantities. The out-going gases in each case were condensed in liquid N_2 cooled traps, mixed with CCl_4 and then analysed using a gas chromatograph. A summary of the experimental conditions is as follows:

Temp. °C	$SiCl_4$ flow rate	H_2 flow rate	Bed
650	0.2 cc/sec.	8-56 cc/sec.	MG Si
800	0.2 cc/sec.	8-56 cc/sec.	MG Si

The results of the experiments are given in Tables 7 to 10.

In presence of copper catalyst :

In another set of experiments the temperature was kept at 650 and 800°C and the gas mixture was passed through MG silicon which contained 5% copper as catalyst, the H_2 being varied from 8-56 cc/sec.

In absence of MG Si and Cu :

In another set of experiments the reactor tube was packed with SiO_2 beads, instead of MG silicon or (MG silicon + Cu catalyst) and was heated to 800°C. The $SiCl_4$ and hydrogen was passed over it.

In all these cases the effluent vapours were condensed in liquid N_2 cooled traps and analysed on a gas chromatograph using dehydrated CCl_4 as solvent.

2.4.2 Results and discussion

These results indicate that a simple process for conversion of $SiCl_4$ to $SiHCl_3$ can be developed. This could make a recycling of $SiCl_4$, a by-product in the Siemens process, possible. This would have a definite beneficial impact on the overall economics of the process. There are some literature references indicating that $SiCl_4$ can be converted to $SiHCl_3$, but many of them have not been supported by subsequent investigation. The available

description reveals that some of the reported conversions are carried out at a very high temperature[59,60,63,66,70] in the range of 800-1600°C without using any catalyst. The conversion at such a high temperature is again energy intensive. In that context the present results on the hydrogenation of $SiCl_4$ at lower temperature with and without hydrogenating catalyst are interesting.

When $SiCl_4$ and H_2 are passed over MG silicon from room temperature to various temperatures like 100°C to 800°C it has been observed from Table-7 and Table-8 that the reaction starts from 650°C where about 1 to 2% formation of $SiHCl_3$ occurs. This increases with increase in temperature and decreases with increase in $H_2/SiCl_4$ ratio. From the result (Table-9, Fig.6), it is observed that 31% $SiHCl_3$ is formed with $H_2/SiCl_4$ = 16.33 and 22.6% of $SiHCl_3$ is formed with $H_2/SiCl_4$ = 32.41. The formation of $SiHCl_3$ occurs as:

$$2H_2 + 3SiCl_4 + Si \rightleftharpoons 4SiHCl_3 \qquad \ldots \qquad (III)$$

In the silane process developed by the Union Carbide Corporation, USA, when hydrogen and $SiCl_4$ in the mole ratio of 5.04 are reacted with silicon at 500°C and 515 psi pressure with residence time of 45.5 seconds, 22.6% $SiHCl_3$ is formed. This yield decreases with decrease in temperature and residence time. However our results show better performance at 800°C without catalyst and at atmospheric pressures.

Table - 7 : Hydrogenation of $SiCl_4$ on ferrosilicon bed in absence of catalyst at 650°C

[i] Bed height ... 10 to 17 cms.

[ii] Weight of MG silicon ... 125 gms.

[iii] $SiCl_4$ passed per hour ... 55 gms.

Sr. No.	Duration of experiment	Moles of $H_2/SiCl_4$	Exit gas composition	
			$SiHCl_3$ %	$SiCl_4$ %
1	30 minutes	6.28	2.82	97.18
2	30 minutes	9.69	2.50	97.50
3	30 minutes	11.10	2.00	98.00
4	30 minutes	16.02	1.00	99.00
5	30 minutes	19.68	negligible	100.00
6	30 minutes	33.23	-	100.00

Table - 8 : Hydrogenation of $SiCl_4$ on ferrosilicon bed in presence of 5% copper catalyst at 650°C

[i] Bed height ... 10 to 17 gms.

[ii] Weight of MG silicon ... 125 gms.

[iii] $SiCl_4$ passed per hour ... 55 gms.

Sr. No.	Duration of experiment	Moles of $H_2/SiCl_4$	Exit gas composition	
			% $SiHCl_3$	% $SiCl_4$
1	30 minutes	6.76	1.60	98.40
2	30 minutes	11.04	2.30	97.70
3	30 minutes	14.13	2.00	98.00
4	30 minutes	20.32	1.00	99.00
5	30 minutes	20.33	negligible	100.00
6	30 minutes	23.41	-	100.00

Table - 9 : Hydrogenation of $SiCl_4$ on ferrosilicon bed in absence of catalyst at 800°C

[i] Bed height ... 10 to 17 cms.

[ii] Weight of MG silicon ... 125 gms.

[iii] $SiCl_4$ passed per hour ... 55 gms.

Sr. No.	Duration of experiment	Mole ratio $H_2/SiCl_4$	Exit gas composition	
			% $SiHCl_3$	% $SiCl_4$
1	30 minutes	10.20	35.00	65.00
2	30 minutes	16.33	31.30	68.70
3	30 minutes	19.49	24.40	75.60
4	30 minutes	21.88	28.75	71.25
5	30 minutes	31.54	26.00	74.00
6	30 minutes	32.41	22.00	78.00

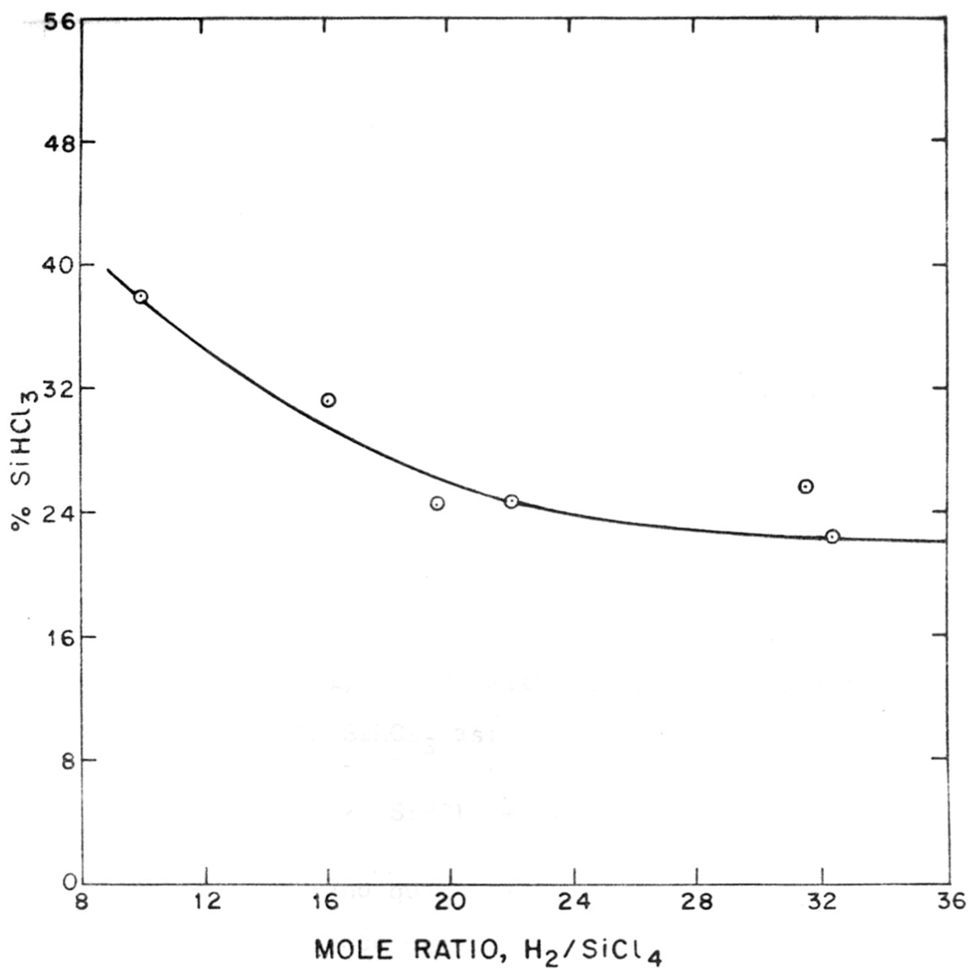
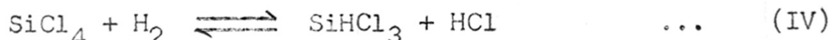


FIG. 6. MOLE RATIO OF $H_2/SiCl_4$ Vs. PERCENTAGE OF $SiHCl_3$ OBTAINED AT 800 °C

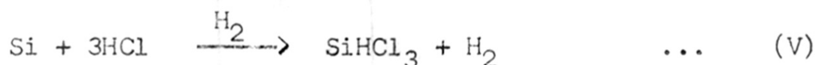
Kinetics of the reaction

The mechanism of the reaction involves the gas phase reaction between $SiCl_4$ and H_2 to form $SiHCl_3$ and HCl as



$$SiCl_4 + H_2 \rightleftharpoons SiHCl_3 + HCl \qquad \ldots \qquad (IV)$$

This is confirmed from Section 2.4.1 by passing $SiCl_4$ and H_2 through a tube packed with silica beads at 800°C. The condensed effluents contain 16% $SiHCl_3$ and HCl along with $SiCl_4$. The same has been confirmed by Union Carbide Corporation where they get 1% $SiHCl_3$ when $SiCl_4$ and H_2 were passed through a heated empty tube at 500°C and 515 psi pressure. Thus the $SiCl_4$ and H_2 react and give $SiHCl_3$ and HCl. The HCl immediately reacts with silicon in presence of H_2 giving additional $SiHCl_3$ as:



$$Si + 3HCl \xrightarrow{H_2} SiHCl_3 + H_2 \qquad \ldots \qquad (V)$$

This reaction is rapid and quantitative. Though the reaction of H_2 and $SiCl_4$ in presence of silicon could well be a sequence of reactions (IV) and (V) in which silicon acts to scavenge the HCl generated, shifting the equilibrium of reaction (IV) to the higher yield of $SiHCl_3$.

If 5% Cu is added in silicon, it is observed that the formation of $SiHCl_3$ is suppressed (Table-10, Fig. 7) as observed in case of Si with hydrogen chloride with H_2 in

Table – 10 : Hydrogenation of $SiCl_4$ on ferrosilicon bed in presence of 5% copper catalyst at 800°C

[i] Residence time is kept constant

[ii] Weight of MG silicon ... 125 gms.

[iii] $SiCl_4$ passed per hour ... 55 gms.

Sr. No.	Duration of experiment	Mole ratio $H_2/SiCl_4$	Exit gas composition	
			% $SiHCl_3$	% $SiCl_4$
1	30 minutes	7.20	24.10	75.90
2	30 minutes	12.30	28.70	71.30
3	30 minutes	15.40	22.90	77.10
4	30 minutes	19.00	20.00	80.00
5	30 minutes	21.10	20.40	79.60
6	30 minutes	26.70	17.65	82.35

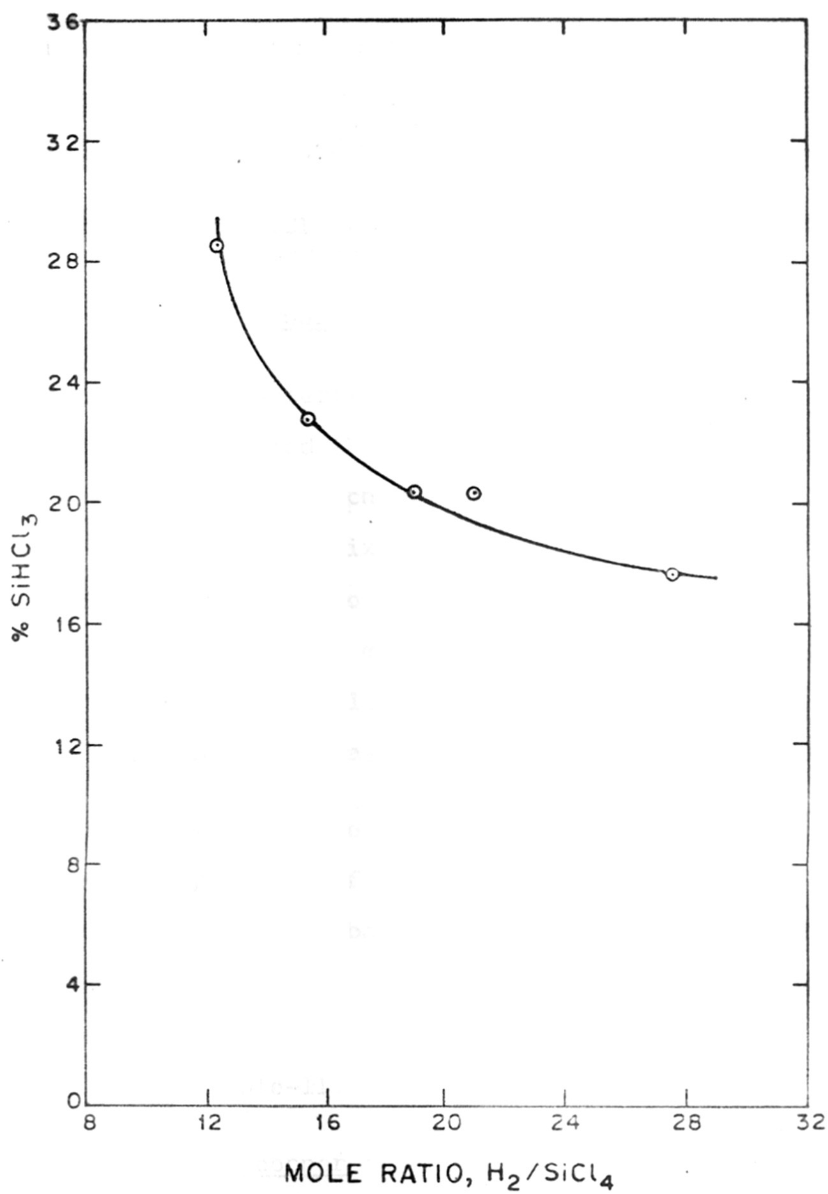


FIG. 7. MOLE RATIO OF $H_2/SiCl_4$ Vs. PERCENTAGE OF $SiHCl_3$ OBTAINED AT 800 °C IN PRESENCE OF COPPER CATALYST.

presence of Cu. This confirms that the presence of Cu at high temperature does not favour the formation of $SiHCl_3$, the reason of which is mentioned earlier in Section 2.3.4.

2.5 Hydrogenation of $SiCl_4$ in Presence of HCl

2.5.1 In absence of copper :

Initially a predetermined flow-rate of H_2 was established. This was bubbled through a previously weighed bubbler containing $SiCl_4$ which was kept at a constant temperature in a thermostat. A fixed amount of HCl gas at a controlled flow-rate was also let in along with H_2-$SiCl_4$ mixture. The entire gaseous mixture was passed through a reactor containing the metallurgical grade silicon. The duration of the experiment was kept as 30 minutes.

The temperature of the reactor was varied from 250° to 800°C. At every change of temperature the experiment was stopped and the $SiCl_4$ bubbler was reweighed to know the quantity of $SiCl_4$ passed. The exit gases of the reactor were analysed by the procedure mentioned earlier. The result is given in Table-11.

2.5.2 In presence of copper :

In another set of experiments, the fixed amount of HCl gas along with hydrogen was mixed with $SiCl_4$ vapours

Table - 11 : Effect of temperature on hydrogenation of $SiCl_4$ in presence of HCl(g) and H_2 on ferrosilicon bed in absence of any catalyst

[i] Bed height ... 10 to 17 cms.

[ii] Duration of each experiment ... 30 minutes

Sr. No.	Temp. °C	$SiCl_4$ passed (gms.)	H_2 Lit./hr.	HCl/hr. (gms.)	Weight of condensed gases (gms.)	% $SiHCl_3$	% $SiCl_4$	Weight of $SiCl_4$ (gms.)	Weight of $SiHCl_3$ (gms.)
1	200	31.5	151	23	30.5	1.00	99.00	30.5	-
2	300	24.0	155	15	23.5	1.00	99.00	23.5	-
3	400	27.5	151	25	25.5	2.00	98.00	25.5	-
4	500	28.0	155	20	46.0	19.00	81.00	36.34	9.66
5	600	31.0	155	18	43.0	26.12	73.88	33.48	9.52
6	800	29.0	155	20	44.0	39.50	60.50	27.7	16.30

Table - 12 : Effect of temperature on hydrogenation of $SiCl_4$ in presence of HCl(g) and H_2 on ferrosilicon bed using 5% copper catalyst.

[i] Bed height ... 10 to 17 cms.

[ii] Duration of each experiment ... 30 minutes

Sr. No.	Temp. °C	$SiCl_4$ passed (gms.)	H_2 Lit./hr.	HCl/hr. (gms.)	Weight of condensed gases (gms.)	% $SiHCl_3$	% $SiCl_4$	Weight of $SiCl_4$ (gms.)	Weight of $SiHCl_3$ (gms.)
1	230	35.0	148	10	51.5	26.00	74.00	38.00	13.50
2	340	29.5	148	10	43.0	36.10	63.90	27.46	15.54
3	440	30.5	148	10	45.0	29.87	70.13	31.55	13.45
4	550	30.6	148	15	42.7	30.43	69.57	29.70	13.00
5	650	48.0	162	38	75.0	30.80	69.20	51.90	23.10
6	800	48.0	162	38	72.0	30.60	69.40	50.00	22.00

and the entire gaseous mixture was passed through a reactor containing ferrosilicon and 5% copper as a catalyst and the procedure was repeated as described earlier. The result is given in Table-12.

2.5.3 Results and discussion

When $SiCl_4$, HCl(g) and H_2 are passed over silicon at temperature from 200° to 800°C, it is observed from Table-11 that no reaction occurs upto 400°C, and all the $SiCl_4$ that has passed condenses as it is without reacting with Si in presence of HCl and H_2. At 600°C the amount of $SiCl_4$ condensed in the exit gases is the same as that which is passed with HCl through the reactor. However, at this temperature the exit gas is found to contain some amount of $SiHCl_3$. This shows that the HCl, which has reacted with silicon, gives exclusively $SiHCl_3$ in presence of $SiCl_4$ and H_2. The same reaction when carried out at 800°C shows reduction in weight of $SiCl_4$ that has passed. This supports the $SiCl_4$ and H_2 reaction on silicon as described earlier in Section 2.4.2.

It is observed from Table-12 that the presence of Cu at high temperature favours the formation of $SiCl_4$ e.g. at 800°C, the $SiCl_4$ passed was 48 gms. while in condensed liquid it was 50 gms. This proves that Cu reduces the formation of $SiHCl_3$ at high temperature. At

lower temperature 200-600°C in presence of Cu, the $SiCl_4$ condensed is slightly greater than $SiCl_4$ passed because additional $SiCl_4$ is generated by HCl reaction with Si.

2.6 Hydrogenation of $SiCl_4$ in Presence of Catalysts

The hydrogenation of $SiCl_4$ to $SiHCl_3$ was also carried out in presence of catalysts other than Cu in an attempt to lower the reaction temperature from 800°C. The catalysts used were (a) Pd on charcoal, (b) Pt-asbestos and (c) Ti-granules.

5% palladium on charcoal[73] was prepared as follows:- A solution of 1.7 gm of palladium chloride was prepared in 1.7 ml of concentrated sulphuric acid and 20 ml of water by heating on a water bath. This solution was then added to a solution of 30 gms. of sodium acetate in 200 ml of water contained in a 500 ml hydrogenation flask. To this, 20 gms of activated charcoal (E.Merk quality) was added and the sample was hydrogenated in a hydrogenation apparatus until absorption ceased. The catalyst was filtered on a Buchner funnel and was washed 4-5 times with water. It was first dried in air at room temperature and then over anhydrous calcium chloride in a vacuum dessicator.

Pt-asbestos and Ti-granules were available and were used directly as catalyst.

2.6.1 Hydrogenation experiment

In these experiments the reactor of the setup in Section 2.2 was filled with catalyst alone, and in another set with metallurgical grade silicon powder and catalyst. Hydrogen was bubbled in $SiCl_4$, which was kept at the pre-determined temperature to adjust its vapour pressure, and a mixture of hydrogen and $SiCl_4$ along with additional hydrogen, if needed, was passed at atmospheric pressure through the bed. The exit gases were condensed in traps chilled with ~~with~~ liquid nitrogen. On completion of the experiment, heating was stopped and the bed was flushed for 15 minutes and cooled by passing hydrogen which was let out through a by-pass to avoid any carry over of the condensed gases. A sample of the product was dissolved in anhydrous distilled CCl_4 and the solution was analysed by G.C.

The conversion of $SiCl_4$ to $SiHCl_3$ was studied at atmospheric pressure at different (a) temperatures, (b) molar ratios of H_2:$SiCl_4$ and (c) residence time.

(a) Temperature :- The catalytic bed after activation was cooled to the desired temperature and then hydrogen and $SiCl_4$ vapours were passed. The temperature was

varied from 100°C to 400°C. At every temperature the molar ratio and residence time were kept constant. The residence time was kept constant by adjusting the bed height.

(b) Mole ratio $H_2:SiCl_4$:- This was varied by bubbling a pre-determined quantity of hydrogen through $SiCl_4$ which was kept at some fixed temperature. This was adjusted in such a way that the total volume of H_2 and $SiCl_4$ was nearly constant. This helped in maintaining the residence time constant. Thus when (a) molar ratio $H_2:SiCl_4$ varied, temperature and residence time were kept constant.

(c) Residence time :- This was varied by varying the bed height. At this time temperature and mole ratio were kept constant. Thus for a given catalyst the conditions for optimum conversion were determined.

When a mixture of $SiCl_4$ vapour and hydrogen gas was passed through titanium bed it was observed that the Ti powder was getting blackened. This was due to the deposition of silicon on Ti granules. Hence it was decided to pass hydrogen through the bed of Ti and mix it up with $SiCl_4$ at a point above the titanium bed. This was done in the reactor II as shown in Fig. 8 which consists of

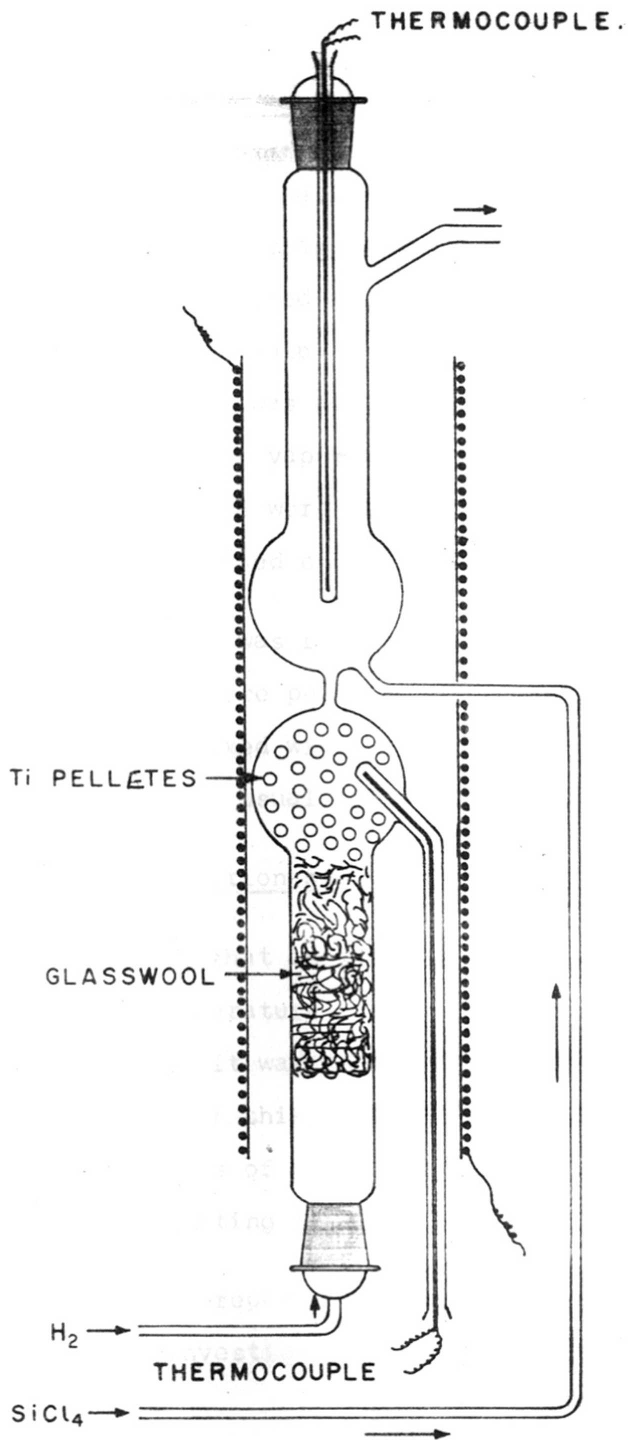


FIG. 8 - REACTOR II FOR REDUCTION OF $SiCl_4$ TO $SiHCl_3$

two bulbs separated by 0.1 mm dia. capillary of 2-3 mm length. Ti granules or pellets were kept in the lower bulb which was supported by glass wool packed from the lower side. Hydrogen was passed over titanium and $SiCl_4$ was injected in the upper bulb through another side tube. The rate of feed of $SiCl_4$ was adjusted, as usual, by controlling the temperature of the vapouriser. Both bulbs were kept at 500°C. The exit gases were condensed in liquid nitrogen traps and later analysed on the G.C.

This reaction was repeated in reactor II (Fig. 8) in absence of H_2. Here pure dry nitrogen gas was passed over titanium and mixed with $SiCl_4$. The gases were cooled in liquid N_2 and the usual analytical process was repeated.

2.6.2 X-ray diffraction study

It appeared that on passing hydrogen over Ti, the two react at a temperature of 500°C to give a soft and powdery material. It was therefore decided to undertake the investigation of this material by X-ray diffraction. X-ray diffractograms of original titanium powder and Ti powder after activating it in H_2 at 500°C were taken.

The earlier-reported blackened Ti powder (on passing $SiCl_4$) was also investigated by X-ray diffraction.

2.6.3 Results and discussion

In all the cases i.e. platinised asbestos, palladium on charcoal and titanium granules it is observed from Tables 15, 18 and 21 that the conversion of $SiCl_4$ to $SiHCl_3$ increases with increase in residence time. For example, in case of Ti it increases from 3.2% to 5.8%, while in case of Pt and Pd it increases from 0.8% to 5.2% and 1% to 4.5% respectively. In all the cases the residence time was increased by increasing the bed height from 10 cms. to 17 cms. The increase in conversion with increase in residence time can be attributed to the fact that $SiCl_4$ and H_2 remain in contact with the catalyst for a longer time. This decreases the associative desorption of hydrogen as $H^{\bullet} + H^{\bullet} = H_2$. The increase in conversion with higher $H_2/SiCl_4$ ratio as observed in Tables 13, 16 and 19 can be attributed to the probability of more H_2 coming in contact with catalyst as compared to $SiCl_4$ while in case of lower ratio of $H_2/SiCl_4$, more $SiCl_4$ molecules come in contact with the catalyst and this is of little use in the hydrogenation reaction. It is observed that copper has no effect on conversion of $SiCl_4$ to $SiHCl_3$ below 500°C as the reaction is carried out at atmospheric pressure. However the Union Carbide hydrogenates $SiCl_4$ to $SiHCl_3$ using copper as a catalyst at 500°C with 515 psi pressure.

Table - 13 : Effect of mole ratio on hydrogenation of $SiCl_4$ in presence of platinised asbestos as a catalyst

[i] Temperature ... $300^{o}C$

[ii] Residence time ... Constant (bed height - 15 cms.)

[iii] Duration of each experiment... 30 minutes

Sr. No.	$SiCl_4$ passed (gms.)	Mole ratio $H_2/SiCl_4$	Weight of condensed gases (gms.)	% Conversion of $SiCl_4$ to $SiHCl_3$
1.	7.00	24.00	6.00	3.74
2.	18.00	7.62	17.00	3.00
3.	26.00	5.24	24.50	2.60
4.	35.00	3.93	33.40	2.20
5.	39.00	3.15	37.40	1.83
6.	47.5	2.32	46.5	1.00

Table - 14 : Effect of temperature on hydrogenation of $SiCl_4$ in presence of platinised asbestos as catalyst[4]

[i] Residence time is constant
[ii] Mole ratio $H_2/SiCl_4 = 24$
[iii] $SiCl_4$ passed at each temperature ... 14.3 gms/hr
[iv] H_2 passed ... 45 lits/hr
[v] Duration of each experiment ... 30 minutes

Sr. No.	Temperature °C	Bed height cms.	% conversion $SiCl_4$ to $SiHCl_3$
1	200	12	2.00
2	250	13	3.50
3	300	14	4.30
4	350	15	4.10
5	400	16	4.00
6	450	17	3.80

Table - 15 : Effect of residence time on hydrogenation of $SiCl_4$ in presence of platinised asbestos as a catalyst.

[i] Temperature ... $300^{\circ}C$

[ii] Mole ratio $H_2/SiCl_4$ = 24

[iii] $SiCl_4$ passed at each experiment ... 14.3 gms/hr.

[iv] H_2 passed ... 45 lits /hr.

[v] Duration of each experiment ... 30 minutes

Sr. No.	Bed height cms.	% conversion $SiCl_4$ to $SiHCl_3$
1	17	5.8
2	16	5.0
3	15	4.7
4	14	4.2
5	13	3.8
6	12	3.8
7	11	3.5
8	10	3.0

Table - 16 : Effect of mole ratio on hydrogenation of $SiCl_4$ in presence of 5% palladium on charcoal as a catalyst.

[i] Temperature ... 150°C

[ii] Residence time is constant.

[iii] Duration of each experiment ... 30 minutes

Sr. No.	$SiCl_4$ passed (gms.)	Mole ratio $H_2/SiCl_4$	Weight of condensed gases (gms.)	% conversion $SiCl_4$ to $SiHCl_3$
1	7.5	24.00	6.00	3.00
2	17.5	7.63	16.00	2.00
3	26.0	5.24	25.00	1.50
4	35.5	3.92	34.50	1.50
5	39.0	3.15	37.50	0.50
6	48.0	2.31	47.00	0.40

Table - 17 : Effect of temperature on hydrogenation of $SiCl_4$ in presence of 5% Palladium on Charcoal as a catalyst.

[i] Residence time is constant.

[ii] Mole ratio $H_2/SiCl_4 = 24$

[iii] $SiCl_4$ passed at each temperature ... 14.3 gms./hr.

[iv] H_2 passed ... 45 litres/hr.

[v] Duration of each experiment ... 30 minutes

Sr. No.	Temperature °C	Bed height cms.	% conversion $SiCl_4$ to $SiHCl_3$
1.	100	10	2.0
2.	150	11	1.5
3.	200	12	1.0
4.	250	13	0.4
5.	300	14	0.4
6.	350	15	-
7.	400	16	-

Table - 18 : Effect of residence time on hydrogenation of $SiCl_4$ in presence of 5% Palladium on Charcoal as a catalyst.

[i] Temperature ... $150^{\circ}C$

[ii] Mole ratio $H_2/SiCl_4$ = 24

[iii] $SiCl_4$ passed at each experiment ... 14.3 gms./hr.

[iv] H_2 passed ... 45 litres/hr.

[v] Duration of each experiment ... 30 minutes

Sr. No.	Bed height cms.	% conversion $SiCl_4$ to $SiHCl_3$
1.	17	4.50
2.	16	4.00
3.	15	4.00
4.	14	3.20
5.	13	2.50
6.	12	1.80
7.	11	1.50
8.	10	1.00

Table - 19 : Effect of mole ratio on hydrogenation of $SiCl_4$ in presence of Titanium sponge as a catalyst.

[i] Temperature ... 150°C
[ii] Residence time is constant.
[iii] Duration of each experiment ... 30 minutes

Sr. No.	$SiCl_4$ passed (gms.)	Mole ratio $H_2/SiCl_4$	Weight of condensed gases (gms.)	% conversion $SiCl_4$ to $SiHCl_3$
1.	7.00	24.00	5.80	3.5
2.	18.50	7.62	17.00	2.0
3.	27.00	5.21	26.00	1.5
4.	34.00	3.91	32.50	0.87
5.	39.00	3.15	37.20	0.55
6.	48.00	2.31	46.75	0.35

Table - 20 : Effect of temperature on hydrogenation of $SiCl_4$ in presence of Titanium sponge as a catalyst.

[i] Residence time is constant.

[ii] Mole ratio $H_2/SiCl_4 = 24$

[iii] $SiCl_4$ passed at each temperature ... 14.3 gms./hr.

[iv] H_2 passed ... 45 litres/hr.

[v] Duration of each experiment ... 30 minutes

Sr. No.	Temperature ^{o}C	Bed height cms.	% conversion $SiCl_4$ to $SiHCl_3$
1.	100	10	3.0
2.	150	11	2.8
3.	200	12	2.1
4.	250	13	0.5
5.	300	14	0.3
6.	350	15	--

Above 350°C the reaction of TiH_2 and $SiCl_4$ is vigorous and silicon gets deposited on TiH_2.

Table - 21 : Effect of residence time on hydrogenation of $SiCl_4$ in presence of Titanium sponge as a catalyst.

[i] Temperature ... 150°C

[ii] Mole ratio $H_2/SiCl_4$ = 24

[iii] $SiCl_4$ passed at each experiment ... 14.3 gms./hr.

[iv] H_2 passed ... 45 litres/hr.

[v] Duration of each experiment ... 30 minutes

Sr. No.	Bed height cms.	% conversion $SiCl_4$ to $SiHCl_3$
1.	17	5.8
2.	16	5.2
3.	15	4.7
4.	14	4.2
5.	13	3.8
6.	12	3.6
7.	11	3.5
8.	10	3.0

From the Table-14 it is observed that Pt in the form of platinised asbestos at a temperature range 350-400°C gives about 4% conversion. While palladium at a temperature 100-150°C as seen in Table-17 gives about 2% conversion. The titanium gives above 3% conversion at the temperature 100-150°C as seen in Table-20.

The activated titanium catalyst was found to be soft and in powdery form. Therefore, it was subjected to X-ray diffraction study. The 'd' values of X-ray diffractogram of hydrogen activated titanium shows that the 'd' values of the powder matches with the 'd' values of TiH_2 (Table-2[illegible] Figs. 9, 10) and thus Ti when activated in hydrogen at 500°C forms TiH_2. This is in agreement with the reports of Whitten et al.[74], Upton et al.[75] and others[76-79]. According to them Ti forms TiH_2 above 419°C.

X-ray diffractogram of activated titanium, after the reaction, i.e. after passing $SiCl_4$ and H_2, matches with the previous diffractogram obtained before reaction i.e. with TiH_2. This indicates that the TiH_2 does not decompose during the reaction. The visual observation of the Ti powder after reactions leads to the conclusion that some fine material presumably Si gets deposited on the catalyst in the form of a fine layer which could not be detected by X-ray. There were no additional lines of 'd' values matching with Si in the diffractogram.

Table - 22 : X-ray diffractogram of pure Titanium metal.

Sr. No.	Observed dA values	Reported dA values	I/I_1	hkl
1.	2.55	2.56	30	010
2.	2.33	2.34	26	002
3.	2.24	2.24	100	011
4.	1.72	1.72	19	012

X-ray diffractogram of TiH_2

Sr. No.	Observed dA values	Reported dA values	I/I_1	hkl
1.	2.54	2.55	100	111
2.	2.22	2.21	40	002
3.	1.56	1.56	60	022
4.	1.33	1.33	60	113
5.	1.23	1.27	60	222

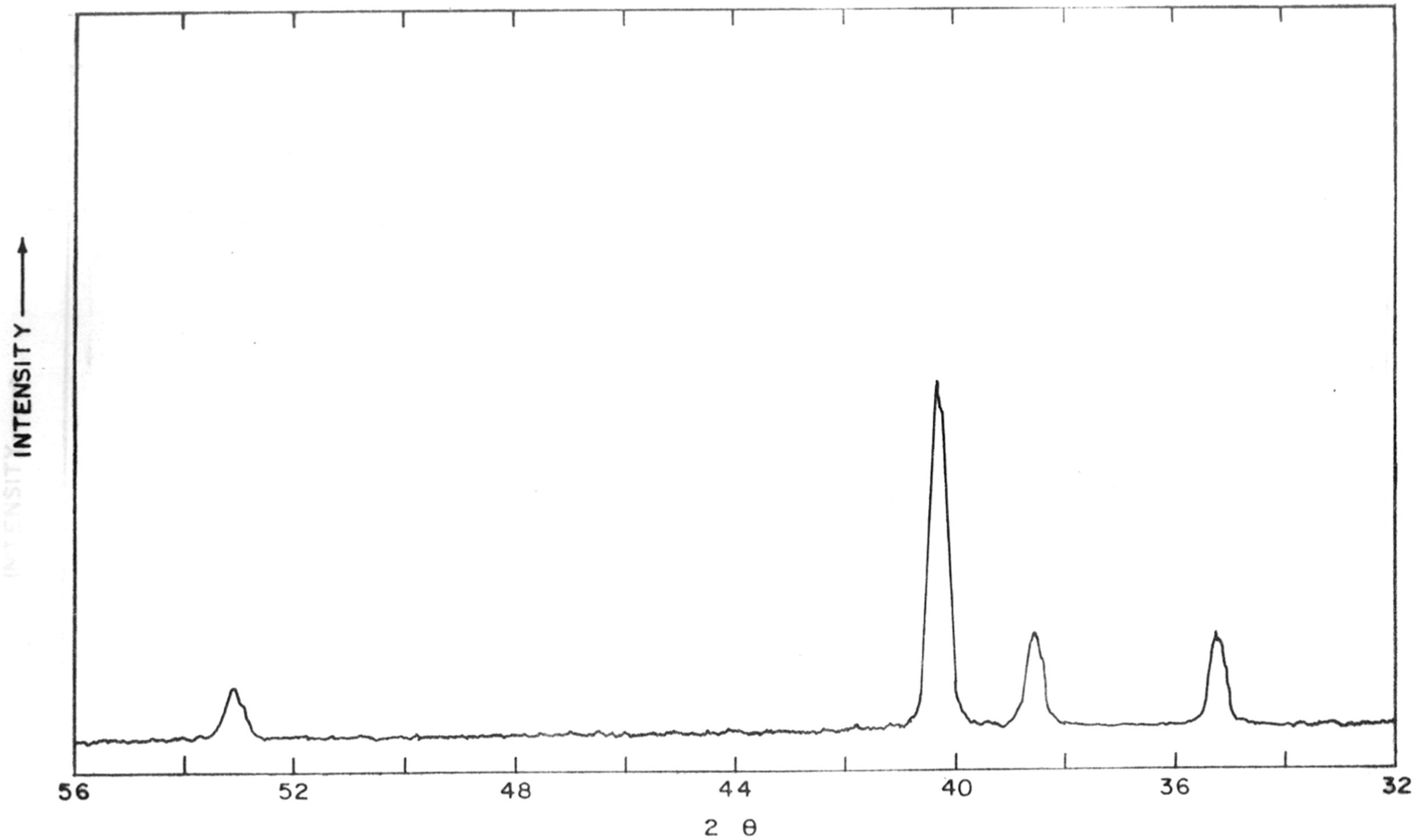


FIG. 9. X-RAY DIFFRACTOGRAM OF PURE TITANIUM

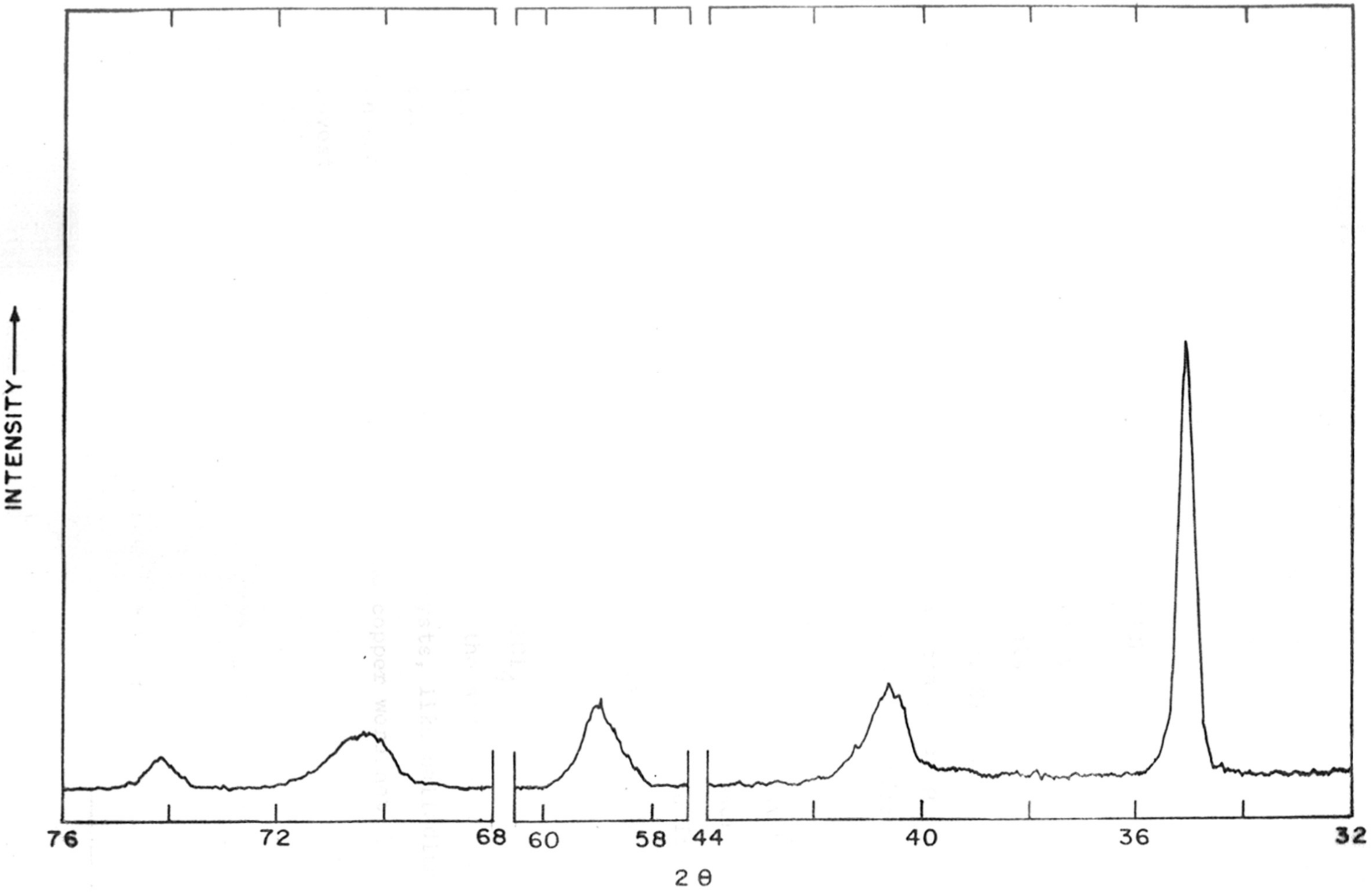


FIG. 10. X-RAY DIFFRACTOGRAM OF TiH_2

From the result tables it is seen that the conversion of $SiCl_4$ to $SiHCl_3$ does not improve significantly. This is due to the following reaction:

$$SiHCl_3 + 2H \longrightarrow Si + 3HCl$$

From the thermodynamic Table-2 the reactions (IV) and (V) both are highly favourable and this can be the reason which reduces the effective yield of $SiHCl_3$. Because of the second reaction the catalyst gets coated or passivated which makes the catalyst functionless with passage of time.

When the hydrogen was passed through Ti bed at 500°C kept in the lower bulb and $SiCl_4$ was injected in upper bulb, it was observed that no silicon was deposited on the Ti-pellet. The G.C. analysis of the exit gases showed 2% formation of $SiHCl_3$.

The conversion efficiencies of $SiCl_4$ to $SiHCl_3$ were low with all the catalysts used, hence the structural and other detailed studies of other catalysts, like palladium on charcoal, platinised asbestos and copper were not investigated.

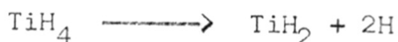
The reactor tube containing Ti granules was coated from inside with a mirror like deposition above 200°C and the deposition was increasing with increase in temperature. This proves the rapid rate of decomposition of intermediate with increase in temperature.

When H_2 diffuses through TiH_2, the dissociative adsorption takes place. The dissociation of H_2 occurs above the surface at 1.3 Å.[74] In case when H_2 gets dissolved then formation of H^+ or H^- takes place[80].

According to Breisacher et al.[81] TiH_2 combines with hydrogen as

$$TiH_2 + H_2 \longrightarrow TiH_4$$

This is very unstable and immediately decomposes to



$$TiH_4 \longrightarrow TiH_2 + 2H$$

Therefore, we propose that according to this mechanism the atomic hydrogen reacts with $SiCl_4$ as

$$SiCl_4 + 2H \longrightarrow SiHCl_3 + HCl$$

or alternately when H_2 comes in contact with this hydrogenating catalyst like Pt, Pd, Ti either by diffusion or by adsorption-desorption the molecular hydrogen splits into atomic hydrogen. This activated hydrogen reacts with $SiCl_4$ giving $SiHCl_3$ or the lower chlorosilane to silane.

2.7 X-ray Photoelectron Spectroscopic Study of the Catalyst

During the hydrogenation reaction of $SiCl_4$ to $SiHCl_3$ using various catalyst like Ti, Pd, Cu and Pt, it was observed that the catalysts were loosing their activity with passage of time. The efficiency of the conversion of $SiCl_4$ to $SiHCl_3$ was not reproducible if the same catalyst was used for the second time. It was, therefore, thought that either the catalyst might be reacting during the reaction giving some other compound or it might be getting covered by some other compound and getting poisoned or passivated so that the reacting species were prevented from coming into contact with the catalyst. Hence it was thought desireable to investigate the surface of the catalyst by X-ray photoelectron spectroscopy.

2.7.1 Experimental

2. Preparation of substrate :

Single crystal silicon wafers of semiconductor purity were used for these studies. Wafers of 4 x 4 x 0.2 mm were cleaned first by A.R.-HCl and then by A.R.-HF. These wafers were then kept immersed in boiling deionised water for some time and then in boiling trichloroethelene for five minutes to remove any organic matter. Finally the wafers

were washed by distilled acetone and then dried. The following catalysts were deposited on different wafers: (i) Ti, (ii) Pd, (iii) Cu and (iv) Pt.

Deposition of metal catalyst on silicon substrates :

An array of dots of above metals (about 2 mm dia) were deposited on the silicon wafers by electron beam evaporation using a mask of stainless steel. The source of electron beam was a heated tungsten filament. The metal, which was to be deposited was placed in a graphite crucible and evaporated under the following conditions

(a) Power supplied	2 KV and 100 milliamps D.C.
(b) Vacuum	(3 to 6) x 10^{-5} torr
(c) Duration of deposition	45 minutes

Reaction of $SiCl_4$ and H_2 on surface of the catalyst

Prior to the experiment the deposited wafers were activated at 500°C in H_2 for 3 hours. The temperature was then reduced to the optimised reaction temperature (as described in earlier Section) at which maximum efficiency of conversion from $SiCl_4$ to $SiHCl_3$ was observed. For different catalysts, this temperature was as given below:

Catalyst	Temperature °C
Ti	150
Pd	150
Pt	350
Cu	500

The $SiCl_4$ vapour was passed along with H_2 in the ratio $H_2/SiCl_4 = 12$, for 45 minutes. On completion of the experiment the furnace was switched off and the samples were cooled (out of contact with air) and taken out from the reactor tube.

2.7.2 ESCA study

The ESCA study was carried out on a V.G. Scientific ESCA-3-MK.II spectrometer. The wafers before and after the reaction were mounted on a suitable holder used for recording the photoelectron spectra. XPS spectra were recorded on the spectrometer provided with Al and Mg anodes as well as He source. Al-K_α radiation (1486.6 eV) and He radiation (21.2 eV) were used for excitation and the kinetic energy of the photoelectron was measured. All the XPS spectra were recorded under similar conditions such as 50 eV pass energy, 4 mm entry slit and vacuum better than 10^{-9} torr. The calibration of the spectrometer was checked by determining the binding energy of Au $4f_{7/2}$ (84.0 eV), C 1S (285.0 eV),

Ag $3d_{5/2}$ (368.3 eV) and Cu $2p_{3/2}$ (932.4 eV) levels using spectroscopically pure metals obtained from M/s Johnson and Matthey, U.K. The B.E. values were in good agreement with literature values[82]. The instrumental resolution obtained under these conditions for the Au $4f_{7/2}$ levels was 1.6 eV (FWHM). All the XPS spectra were recorded before and after the cleaning of the sample by argon ion etching till the spectra did not show any O 1S, C 1S lines.

2.7.3 Results and discussion

Pd on Si :

From Table-23, Fig-11 it is observed that the measured binding energy before the reaction was 335.2 eV for $3d_{5/2}$ and 340.2 eV for $3d_{3/2}$. This matches with the binding energy of metallic palladium[83]. After the reaction it was observed that carbon, silicon and SiO_2 were deposited on the Pd spots. It was therefore essential to clean the sample by Ar ion bombardment. The binding energies as measured after argon ion etching were 336.2 for $3d_{5/2}$ and 341.2 for $3d_{3/2}$. These match with PdO.[83] The positive line shifts in case of $3d_{5/2}$ and $3d_{3/2}$ with respect to Pd metal were due to the oxidation of Pd to PdO. Contamination with carbon and oxygen was surprising because there was no known source of these contaminants.

Table - 23 : Binding energies of core level of Pd

Treatment	Pd		τ	Oxygen	Si
	$3d_{5/2}$	$3d_{3/2}$	eV	1s	
Literature value*	335.2	340.2			
Before reaction	335.2	340.2	2.0	532.4	SiO_2
After reaction	336.2	341.2	2.4	532.6	SiO_2
After reaction (first cleaning)	336.2	341.2	1.8	532.8	SiO_2

* Reference 83

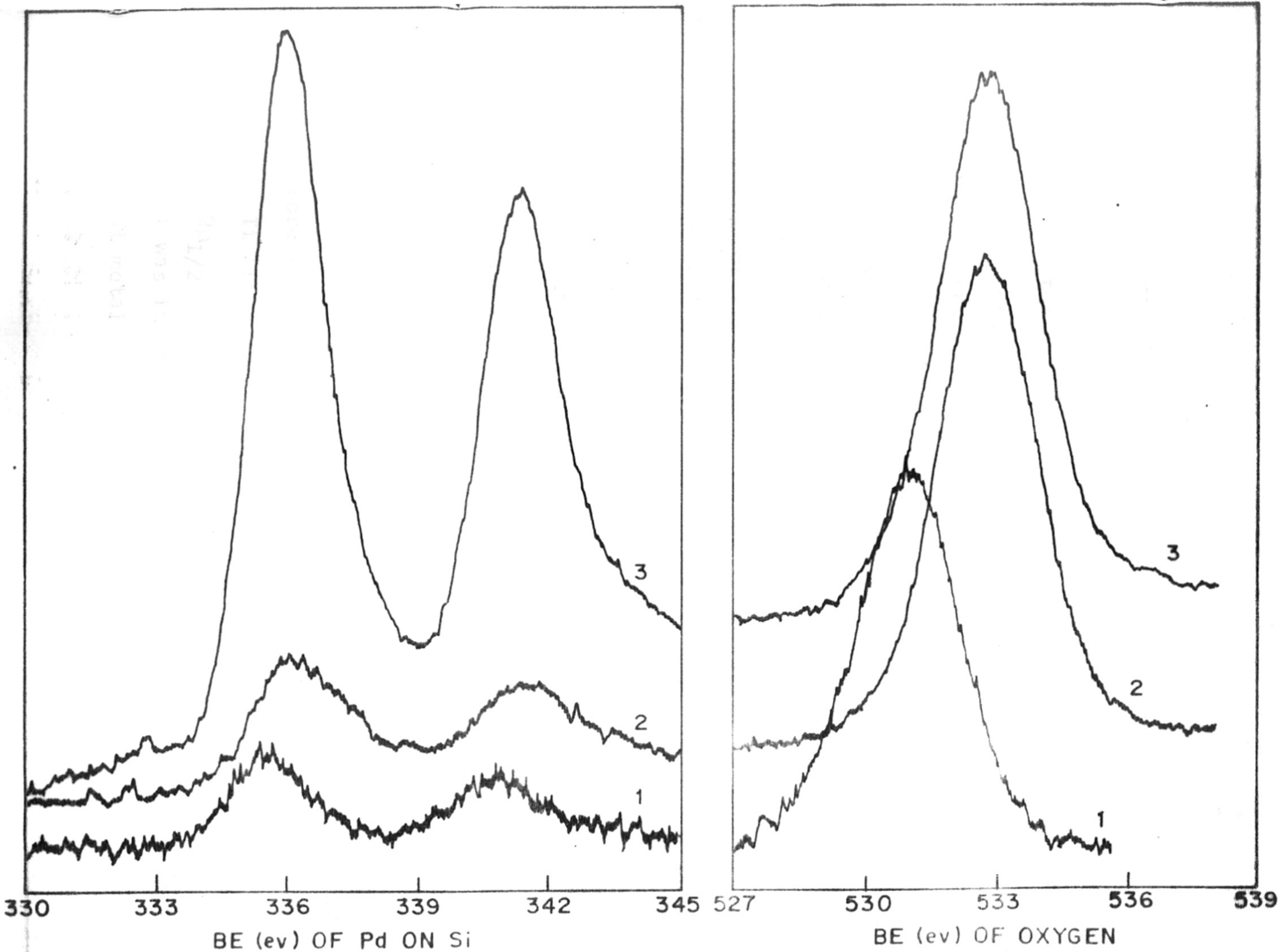


FIG. 11. BINDING ENERGY CURVES OF Pd ON Si (1) BEFORE REACTION (2) AFTER REACTION (3) AFTER REACTION 1st CLEANING

Cu on Si :

From Table-24 Fig-12 it is observed that the binding energies of the metal catalyst before the reaction were 932.4 and 934.6 for $2p_{3/2}$ and 952.4, 954.6 eV for $2p_{1/2}$. The peak at 532 eV corresponds to 1s oxygen peak. After the reaction it was observed that carbon, silicon and SiO_2 were deposited on copper metal. Therefore, the metal spot was cleaned by Ar ion bombardment for 3 minutes. After removing C, Si and SiO_2 the binding energies were observed to be 932.4 and 934.6 for $2p_{3/2}$ and 952.4 and 954.6 eV for $2p_{1/2}$ which matched with the B.E. values of CuO. In addition, there was a satellite, which confirmed the formation of CuO.[84] After the second cleaning, the satellite disappeared and the negative line shifts of binding energies 932.6, 933.2 for $2p_{3/2}$ and 952.6, 953.2 eV for $2p_{1/2}$ confirm the presence of Cu and CuO.

Ti on Si :

A silicon wafer with titanium deposit was scanned before the experiment. From Table 25 Fig-13 it is observed that the Ti lines $2p_{3/2}$ were at 458 eV and the binding energy for $2p_{1/2}$ was 464.6 eV.[85] This indicates that the deposited metal was in the form of titanium oxide as the B.E. value for Ti metal is 455.0 eV for $2p_{3/2}$ and 461.0 for $2p_{1/2}$.

Table - 24 : Binding energies of core level of Cu

Treatment	Cu $2p_{3/2}$	$2p_{1/2}$	Γ eV	Oxygen 1s	Si
Before reaction	932.4	952.4	Broad	532.0	No Si
	934.6	954.6	Broad	532.0	No Si
First cleaning	Carbon, Si and SiO_2 were removed.				
After reaction	932.4	952.4	Broad	532.0	$Si+SiO_2$
	934.6	954.6	Broad	532.0	$Si+SiO_2$
After second cleaning	932.6	952.6	Broad	532.6	SiO_2
	933.2	953.2	Broad	533.6	SiO_2
Theoretical value*	932.4	952.4			

* Reference 84

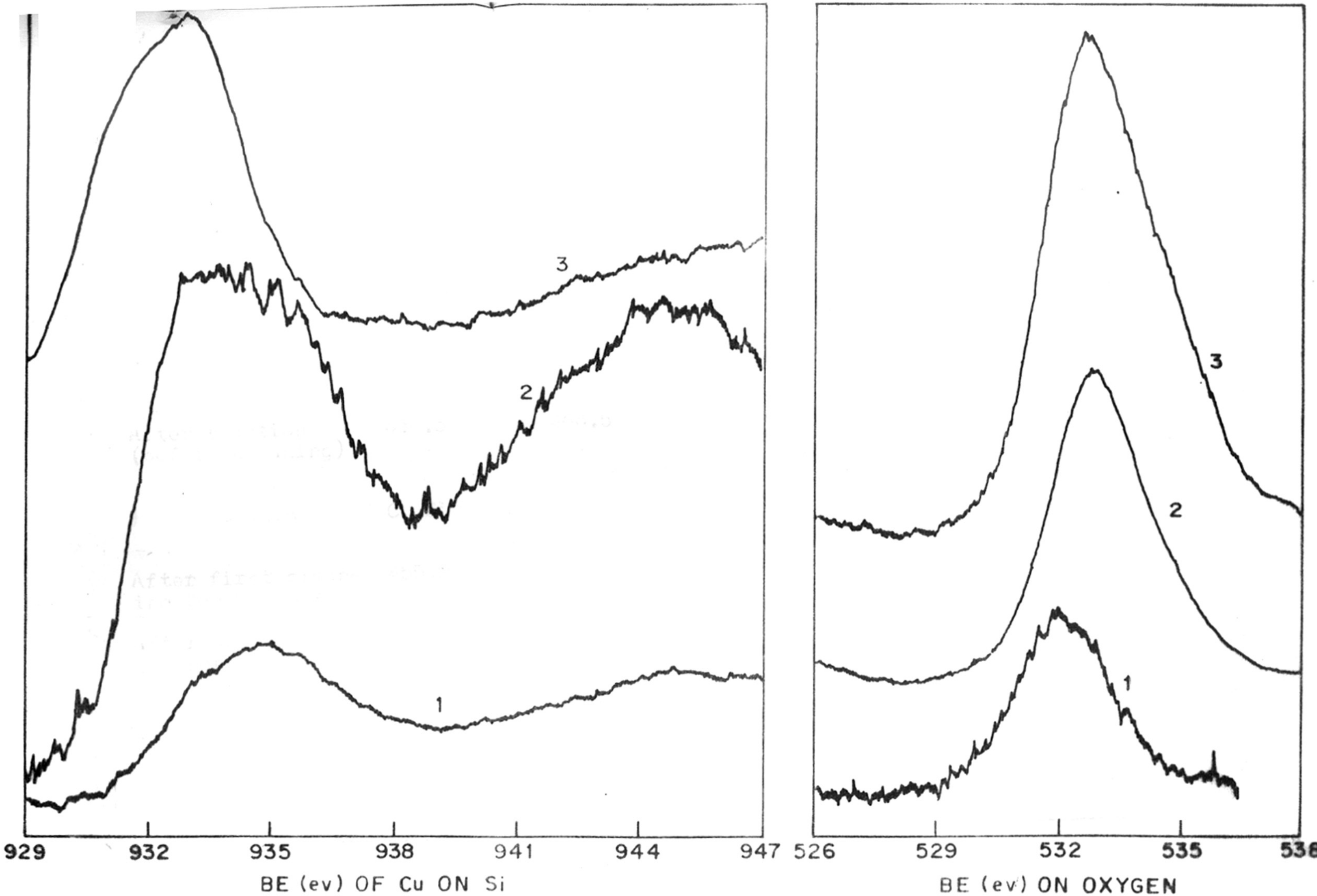


FIG. 12. BINDING ENERGY CURVES OF Cu ON Si (1) BEFORE REACTION (2) AFTER REACTION (3) AFTER REACTION 1st CLEANING

Table - 25 : Binding energies of core level of Ti

Treatment	Ti		Γ	Oxygen 1s	Si
	$2p_{3/2}$	$2p_{1/2}$	eV		
Before reaction	459.0	464.6	2.0	530.6, 532.6	No Si
After reaction (before cleaning)	459.5	464.5	Broad	532.8	SiO_2
First cleaning	C, SiO_2 and Si were present on the metal surface.				
After first cleaning for 5 minutes	455.2	461.0	1.8	532.6	SiO_2
After second cleaning for 3 minutes	458.2	464.3	2.4	532.6	SiO_2
After third cleaning for 5 minutes	458.2	464.2	1.8	534.4	SiO_2
After fourth cleaning for 3 minutes	459.0	464.3	1.8	-	-

Reference 85.

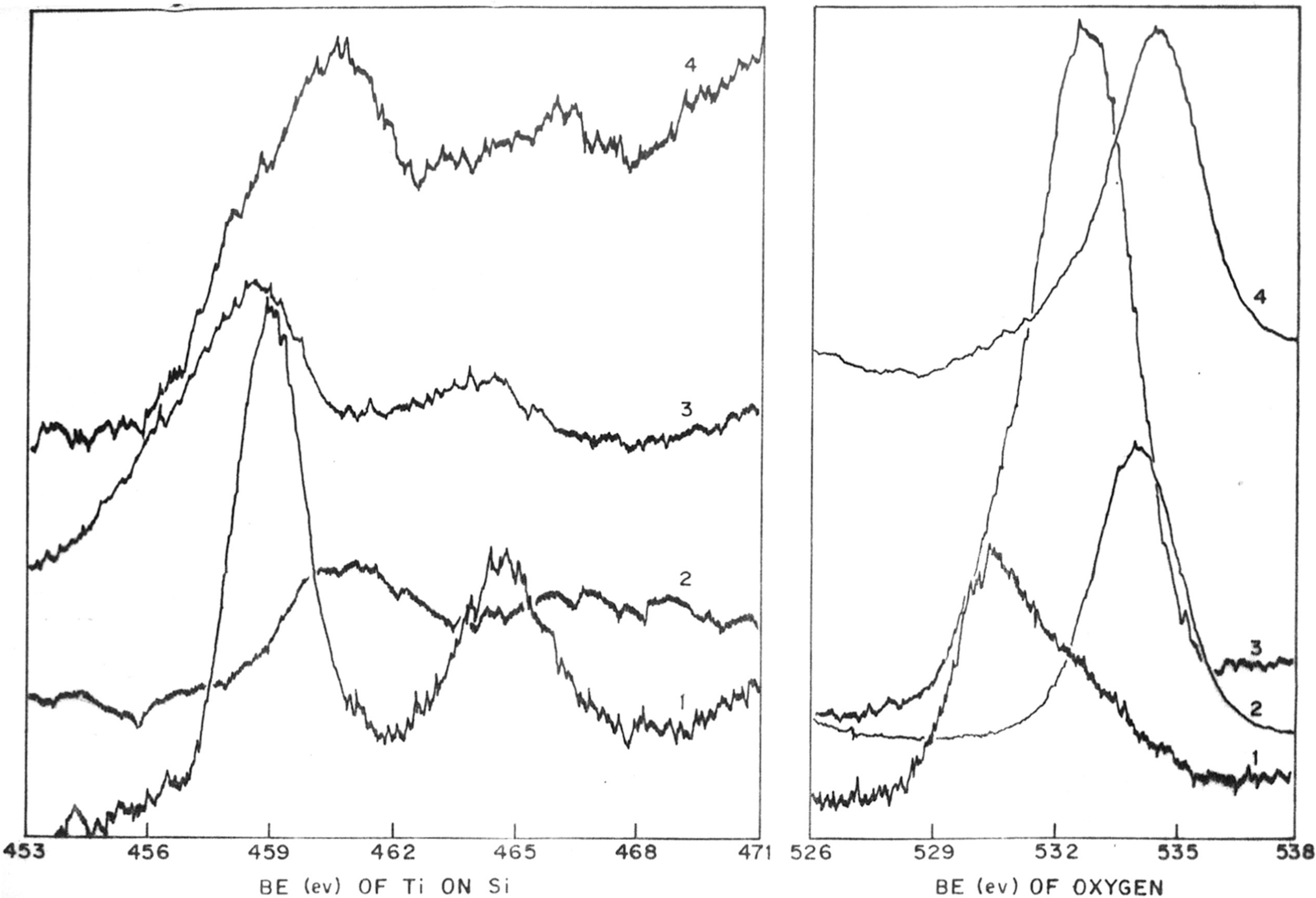


FIG. 13. BINDING ENERGY CURVES OF Ti ON Si (1) BEFORE REACTION (2) AFTER REACTION (3) AFTER REACTION 1st CLEAING (4) AFTER REACTION 2nd CLEANING

This might be due to insufficient vacuum. When the reaction was carried out metal was activated at 500°C in presence of H_2 and later $SiCl_4$ and H_2 was passed for 30 minutes. The XPS analysis shows the B.E. values of 455.2 and 461.0 eV, matching with those of Ti^0 metal. It indicates that the titanium oxide changed to Ti metal during the process of activation. The first cleaning for three minutes indicates a considerable deposition of C, Si and SiO_2. After second cleaning B.E. shift is again towards positive side with respect to the B.E. after first cleaning i.e. 458.2, 459.0 for $2p_{3/2}$ and 464.2, 464.3 for $2p_{1/2}$. This indicates that deposited metal which was in the powdery form, was in the form of titanium oxide. The silicon is always coated by SiO_2 layer.

The formation of oxide of palladium and copper viz. PdO and $CuO+Cu_2O$ can be attributed to the reaction of metal with oxide from the surface of silicon wafer. Therefore, it can be said that the metal surface changes its composition as seen in case of copper and palladium. Secondly, during the reaction, catalyst is covered by carbon, silicon and SiO_2 which does not allow the reacting species $SiCl_4$ and H_2 to come in contact with the catalyst. The catalyst loses its activity and the conversion of $SiCl_4$ to $SiHCl_3$ ceases.

2.8 Surface Morphology Study

2.8.1 Experimental

To study the surface change the catalyst deposited silicon wafers (as given in 2.7.1) of all the catalysts were photographed before and after the reaction by scanning electron microscope (Model Cambridge Stereoscan S-150) with magnification of 500 to 2000 and accelerating voltage 20 KV. The photographs are shown on pages 83, 84 and 85.

2.8.2 Results and discussion

The photographs of the metal catalysts like Pt, Pd, Ti and Cu before and after the reaction show the deposition of impurities like carbon, silicon and SiO_2. This affects the conversion of $SiCl_4$ to $SiHCl_3$. However, more work is needed to understand the precise surface reaction mechanism.

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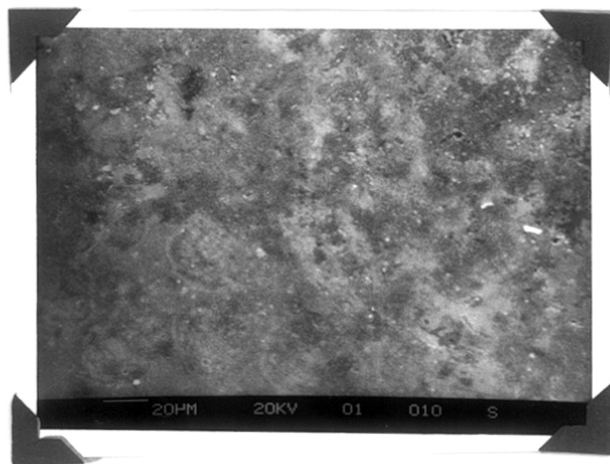
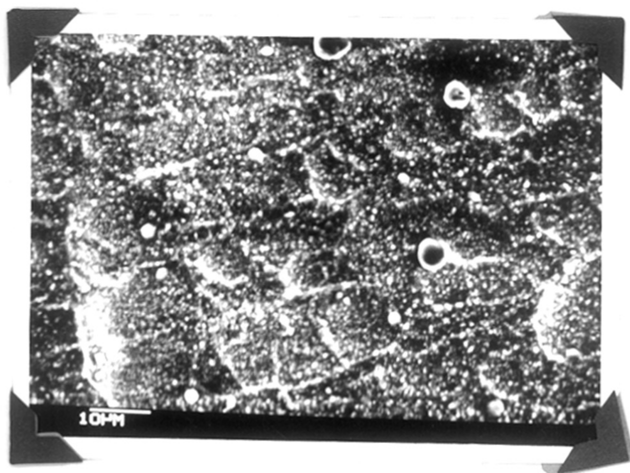
SEM Of Palladium Catalyst On Silicon



A

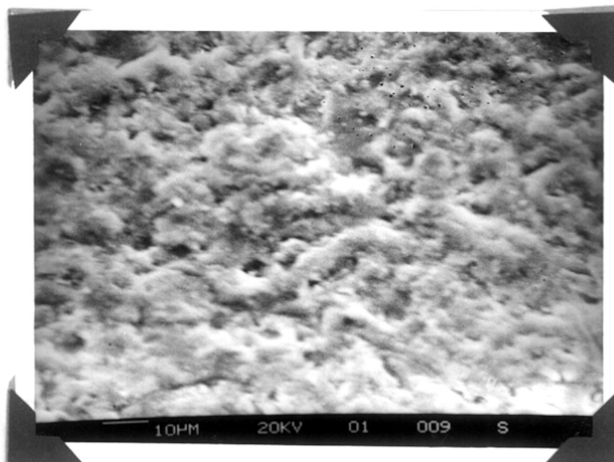
Before reaction



B

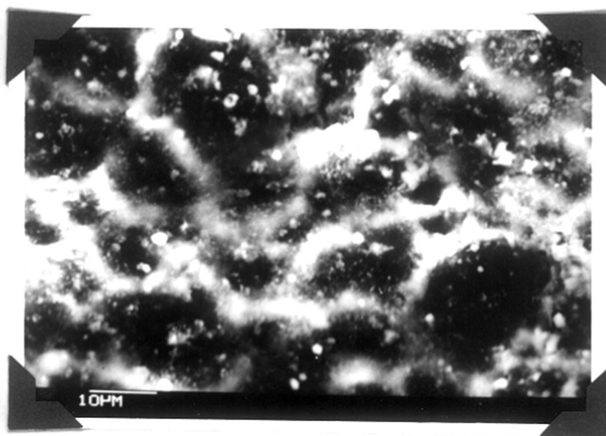
After reaction

S E M of copper catalyst on Silicon



(A)

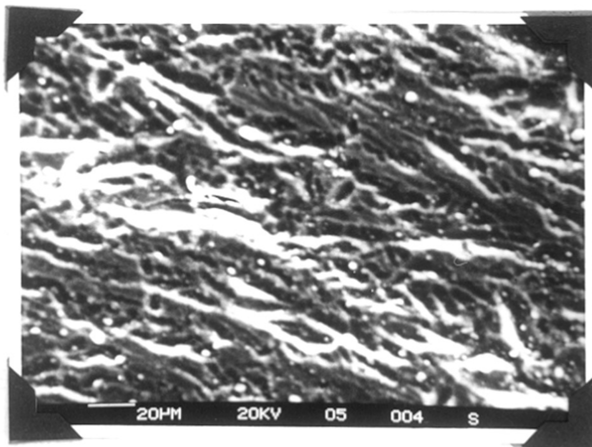
Before reaction



(B)

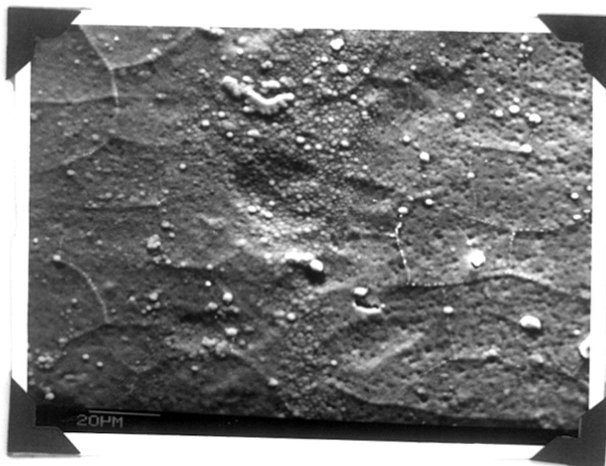
After reaction

S E M of titanium catalyst on Silicon



(A)

Before reaction



(B)

After reaction

CHAPTER–III

REACTION OF SILICON TETRACHLORIDE AND HYDROGEN IN PRESENCE OF MAGNESSIUM SILICIDE

REACTION OF SILICON TETRACHLORIDE AND HYDROGEN IN PRESENCE OF MAGNESIUM SILICIDE

3.1 Introduction

As mentioned earlier, pyrolytic decomposition of silane is one of the methods of producing silicon and has the advantage of (i) higher efficiency, (ii) low decomposition temperature and (iii) higher purity of silicon obtained.

During the course of our studies on the reaction of $SiCl_4$ and H_2 in presence of several catalysts, we observed a reaction taking place between Mg_2Si, $SiCl_4$ and H_2 leading to to the formation of free silicon. Literature survey indicated that this reaction had not been reported. We therefore investigated this reaction in more details to find the effect of changes in temperature and H_2:$SiCl_4$ ratio. We also attempted to find out the possible chemical pathway leading to this ultimate product.

3.2 Experimental

The experimental set-up was arranged as shown in Fig. 1. A silica reactor tube, shown in Fig. 14, 15 cms long and 20 mm ID with M and F-19 joints at both ends, was chosen. Inside the tube, a sintered silica disk was fixed which acted as support to the powder and functioned as the distributor. A thermowell of silica tube 0.6 mm ID closed

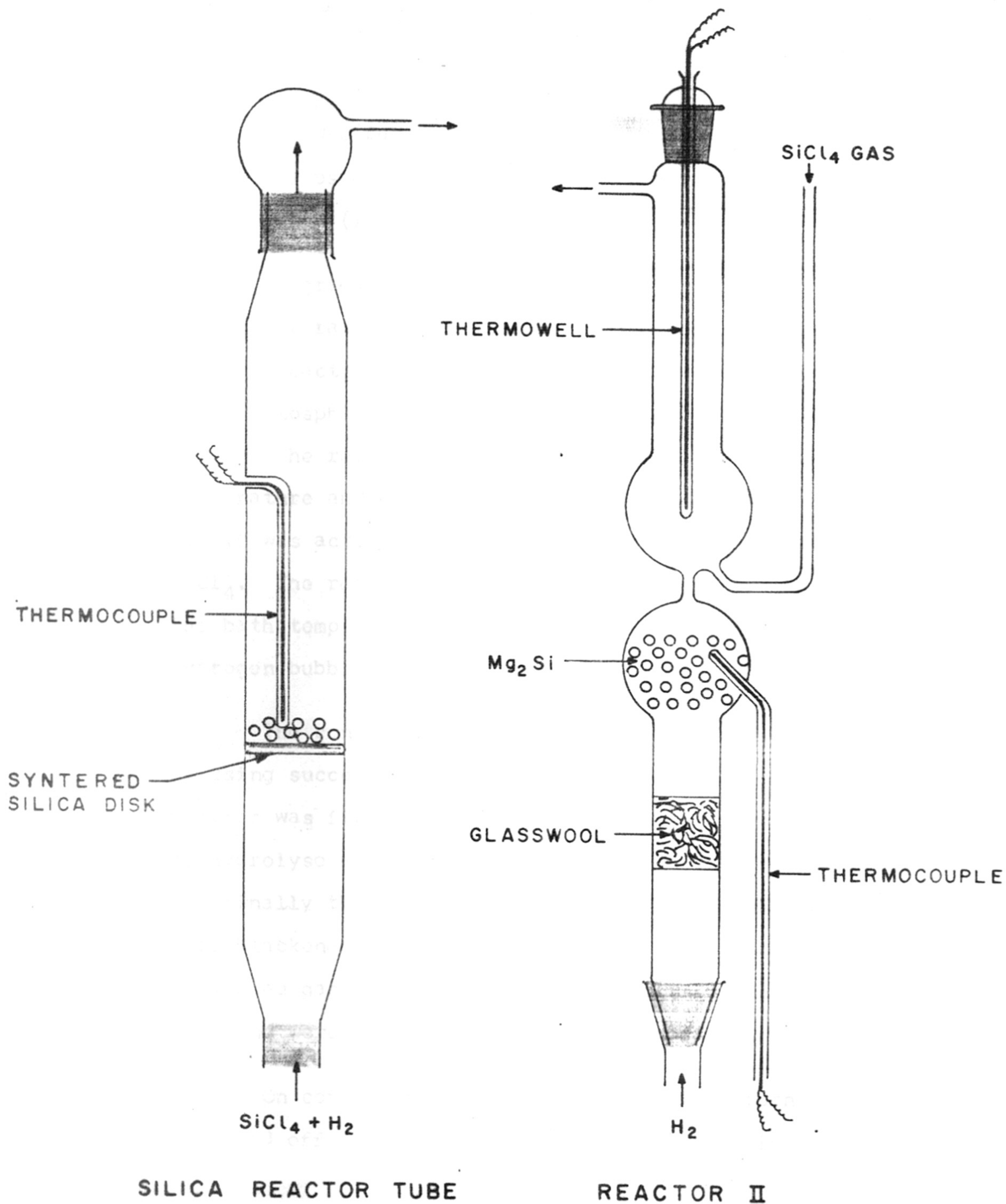


FIGURE. 14.

at one end was fused in the reactor tube. A Cr-Al thermocouple was used to measure the reaction temperature. Mg_2Si was prepared (1 to 1.5 g.) as follows:

AR grade Mg powder and MG grade silicon powder in the weight ratio 64:36 were mixed and kept in a previously weighed reactor. This mixture was heated for about six hours in an atmosphere of hydrogen at 480 to 500°C. The temperature of the reactor was then reduced to the desired reaction temperature and a mixture of $SiCl_4$ and H_2 was passed. H_2 itself was acting as a carrier gas to carry the vapours of $SiCl_4$. The ratio of $H_2/SiCl_4$ was adjusted by (i) adjusting the bath temperature of $SiCl_4$ and (ii) the quantity of hydrogen bubbled through $SiCl_4$.

The condensable portion of exit gases was condensed by using successively three liquid N_2 traps. The uncondensed portion was first scrubbed through distilled deionised water to hydrolyse any chlorosilane which had escaped condensation and finally through $AgNO_3$ solution[86]. The $AgNO_3$ bubblers were blackened from outside to avoid photo-reaction. The condensed gases were dissolved in distilled dehydrated CCl_4 and were analysed by gas chromatography.

On completion of the experiment, the furnace was switched off and the reactor tube was cooled in a current of

hydrogen without bubbling through $SiCl_4$. The reactor was taken out from the furnace and was weighed immediately. The experimental result showed that the reaction did not take place at 350°C while at 400°C it was barely perceptible. This was indicated by the observation that at 350°C the reactor tube showed no increase in weight while at 400°C the increase in weight was to an extent of 100-200 mg only. At higher temperatures, a mirror like silicon deposition was observed on the walls of the reactor tube a little away from the position of Mg_2Si. The results of these experiments are given in Tables 26,27. The powder was boiled with distilled deionized water to dissolve $MgCl_2$ and filtered through previously weighed Gooch crucible G_4. The residue was washed several times with distilled water. The whole filtrate was collected and diluted to 250 cc. From this filtrate the $MgCl_2$ was estimated quantitatively using 0.1 M EDTA and Erichrome Black T as an indicator[87]. The residue of the unreacted Mg_2Si was decomposed by AR HCl (1:1) and filtered, the residue was washed several times and again Mg was estimated as described above. The residue was dried in oven at about 120°C in Gooch crucible. The difference of weight gave the weight of Si. The traces of SiO_2 were removed before estimating silicon. A known weight of Si powder was taken in an initially weighed platinum crucible. This was treated by 1:1 HF and evaporated to dryness. Thus

Table-26 : Effect of variation of mole ratio $H_2/SiCl_4$ on the reaction of Mg_2Si at 440°C

Sr. No.	Weight of Mg_2Si gms.	Increase in weight gms.	Total weight gms.	Initial Si gm.	Final Si gms.	Increase in Si gm.	Mole ratio $H_2/SiCl_4$	Si/Mg_2Si
1.	1.584	0.352	1.936	0.569	0.920	0.352	2.580	0.220
2.	1.531	2.448	3.979	0.549	1.365	0.815	5.880	0.533
3.	1.440	2.101	3.541	0.517	1.210	0.693	6.740	0.481
4.	1.519	2.145	3.663	0.545	1.251	0.706	11.130	0.465
5.	1.693	2.886	4.579	0.608	1.257	0.650	14.880	0.384

Table-27 : Effect of variation of mole ratio $H_2/SiCl_4$ on the reaction of Mg_2Si at 500^oC

Sr. No.	Weight of Mg_2Si gms.	Increase in weight gms.	Total weight gms.	Initial wt. of Si gm.	Final wt. of Si gms.	Increase in wt. of Si gms.	Mole ratio $H_2/SiCl_4$	Si/Mg_2Si
1.	1.571	0.501	2.073	0.564	0.733	0.169	0.65	0.108
2.	1.425	1.6019	3.026	0.511	0.869	0.358	1.38	0.251
3.	1.324	2.334	3.658	0.475	1.412	0.986	1.77	0.530
4.	2.122	1.702	3.824	0.762	1.490	0.728	1.81	0.343
5.	1.503	2.331	3.835	0.540	1.903	1.364	5.13	0.837
6.	1.524	2.557	4.08	0.547	1.05	0.502	11.49	0.328
7.	1.427	2.557	3.984	0.512	1.185	0.679	29.31	0.298

SiO_2 was removed and finally pure free Si was weighed. By this way the total pure Si obtained was determined.

To study the effect of temperature on the efficiency of reduction, the reaction was carried out at 350, 400, 450 and 500°C and the efficiency of the reduction ($SiCl_4$ to Si) was studied. As H_2 is one of the constituent reactant, it was desirable to study its effect on the conversion efficiency of $SiCl_4$ to Si. This was studied by varying the ratio $H_2/SiCl_4$ at each temperature.

To study the reaction mechanism and the role of h hydrogen, Mg_2Si was prepared as above. $SiCl_4$ was passed over it, in absence of hydrogen, using pure dry N_2 as a carrier gas for $SiCl_4$. In this case also, the gases were condensed in liquid nitrogen and analytical processes were repeated as described earlier.

To study the possibility of H_2 getting dissociated or getting activated by Mg_2Si an experiment was arranged in another reactor shown diagramatically in Fig. 8. This reactor consists of two bulbs connected by a capillary 2-3 mm in length and 0.1 mm ID. The temperature in both bulbs could be measured by thermocouples through thermo-wells. Mg_2Si powder or pellets initially formed by compres-sing the Mg_2Si at 10,000 psi) was kept in the lower bulb.

Glass-wool was packed in the tube near the bulb to support the material. In the upper bulb, $SiCl_4$ was injected by adjusting its vapour pressure without using H_2 as a carrier gas. In this reactor the experiments were repeated keeping two bulbs at 500^oC in one set of experiments and at 350^oC in another.

3.2.1 Particle size study of Mg_2Si

It was observed that Mg_2Si left unreacted was in a powdery form. We, therefore, studied the effect of hydrogen on the morphology of Mg_2Si. For this, Mg_2Si was prepared in presence of pure dry N_2 and in another set Mg_2Si was prepared in current of hydrogen. Both samples of Mg_2Si were photographed and their particle size was measured using the Scanning Electron Microscope, Model Cambridge Stereoscan 150.

3.2.2 X-ray diffraction study of Mg_2Si

To study the structure and composition of Mg_2Si prepared in H_2 and N_2, both types of Mg_2Si powders were studied by X-ray diffraction (XRD) technique (with X-ray Diffractometer Model Philips PW 1730).

3.3 Results and Discussion

The observation that a mirror like deposition of silicon had been formed on the walls of the reactor tube

in all those cases where hydrogen had been used is indicative of the formation of a volatile compound of Si presumably SiH_4. This SiH_4 decomposed in that temperature range depositing silicon on the walls of the reactor. The experimental results show that the reaction does not take place at 350°C while at 400°C it is barely perceptible. However, at 500°C the reaction is practically complete (Table 27).

The gas chromatographic analysis of the exit gas samples indicates the formation of $SiHCl_3$, SiH_2Cl_2 etc. in the reaction. Inspite of the protection of $AgNO_3$ bubblers from sunlight blackening of $AgNO_3$ solution was observed. The blackening of this $AgNO_3$ solution due to traces of free silicon and deposition of free silver was indicative of the presence of free silane. The free silicon and metallic silver in the $AgNO_3$ trap were in traces which were difficult to weigh quantitatively.

The various possible primary reactions that could be taking place in the reactor are :

Reaction	ΔH Kcal/mole	ΔF Kcal/mole	
		600°K	800°K
1. $Mg_2Si+SiCl_4 = 2MgCl_2+2Si$	-114.25	-97.00	-92.00
2. $Mg_2Si+SiCl_4+H_2 = 2MgCl_2+Si+SiH_4$	-106.95	-74.00	-71.00
3. $Mg_2Si+SiCl_4+2H_2 = 2MgCl_2+2SiH_4$	- 99.65	-56.00	-47.00
The secondary possible reactions are:			
4. $SiH_4+SiCl_4 = SiHCl_3+SiH_3Cl$	- 17.9	-14.84	-16.08
5. $SiH_4+SiCl_4 = 2SiH_2Cl_2$	- 10.3	- 6.06	- 7.74

(The free energy changes and the heat of reactions are calculated from the thermodynamic values given in JANAF THERMOCHEMICAL TABLE)[88].

Out of the reactions (1, 2, 3), reaction (1) is thermodynamically highly favourable. However, our experiment in N_2 atmosphere showed neither silicon deposition on the wall of the reactor nor the formation of $MgCl_2$ and therefore this reaction (1) does not seem to be taking place. Hence the reaction is considered to take place as per equations (2) or (3). The result of the study made in the

reaction with different $H_2/SiCl_4$ ratio is shown in Fig. 15. It can be seen from Fig. 15 that the yield of silicon increases with increase in mole ratio of $H_2/SiCl_4$, reaches to maximum at about $H_2/SiCl_4 = 5$ and then decreases further with increase in mole ratio of $H_2/SiCl_4$. The best yield in the range of mole ratio of 4 to 5 supports the equation (3). The formation of $SiHCl_3$, SiH_2Cl_2 etc. is due to the secondary reactions (4) and (5)[89] which are also thermodynamically favourable. The reaction (4) competes with reaction (5). This is observed in G.C. analysis which indicates 5 to 6 % $SiHCl_3$ as compared to SiH_2Cl_2 which is less than 1%.

It has already been shown that the reaction between Mg_2Si and $SiCl_4$ to give $MgCl_2$ + Si does not take place. Furthermore direct reduction of $SiCl_4$ with H_2 is not possible so it is clear that the reduction has been facilitated by the presence of Mg_2Si; presumably Mg_2Si is responsible for the activation of molecular hydrogen to reactive atomic hydrogen. To study the formation of activated hydrogen, hydrogen was passed through Mg_2Si kept in the lower bulb and $SiCl_4$ was injected in upper bulb to exclude any possibility of $SiCl_4$ + Mg_2Si direct reaction. When both bulbs were kept at 500°C, some silicon was deposited on the wall of upper bulb and considerable amount of HCl gas was condensed in liquid nitrogen traps. The quantity of HCl

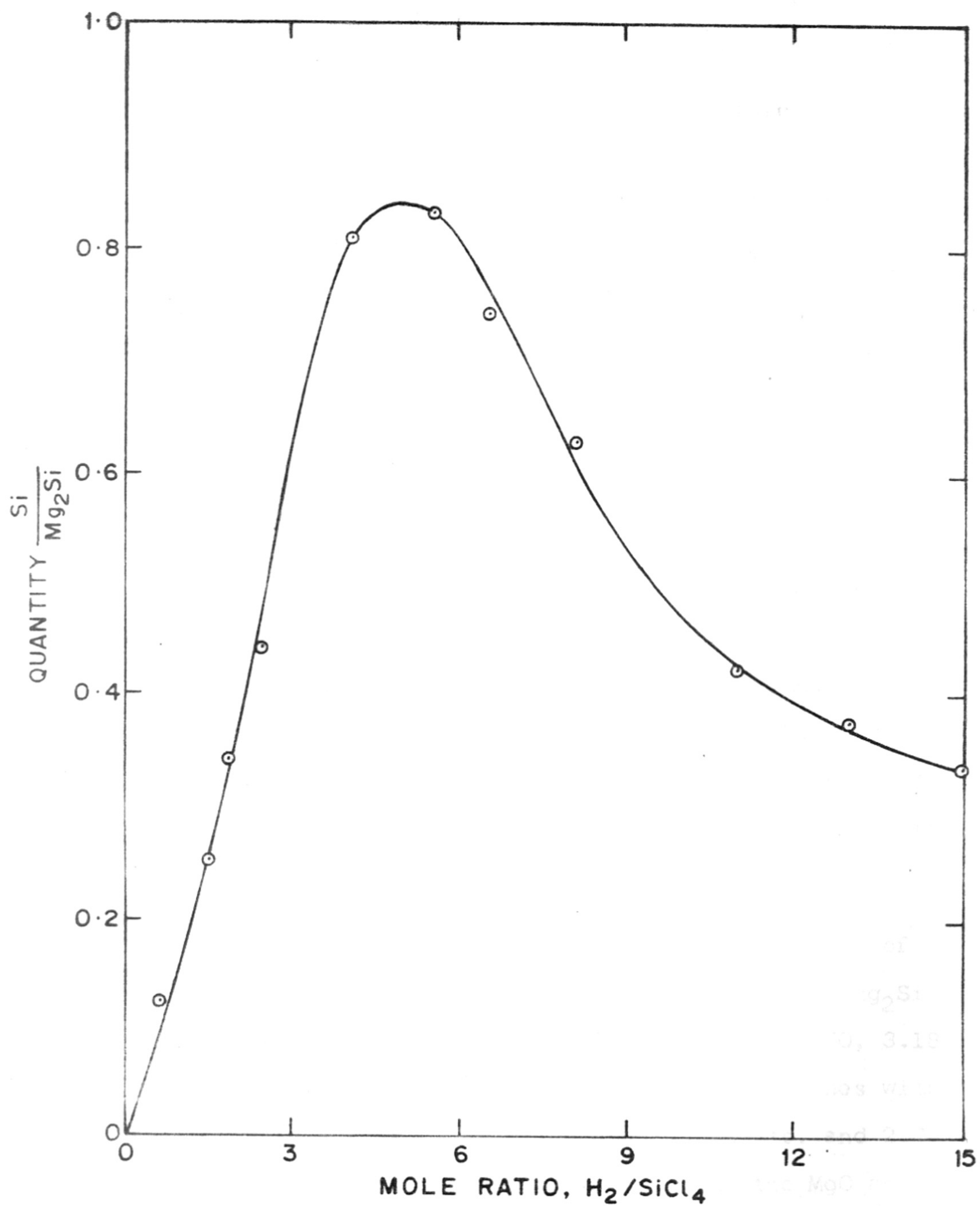


FIG. 15. A GRAPH OF MOLE RATIO $H_2/SiCl_4$ Vs. Si/Mg_2Si QUANTITY

TEMPERATURE: 500 °C; REACTION TIME: 60 min

condensed was very little when the temperature of the bulbs was 350°C. This proves the presence of activated hydrogen and the catalytic activity exhibited by Mg_2Si. When the pellets of Mg_2Si were kept in lower bulb and hydrogen was passed at 500°C, it was observed, at the end of the experiment, that the pellets of Mg_2Si were crumbled to fine powdery form. This indicates the diffusion of hydrogen through Mg_2Si.

3.3.1 Composition study

It was felt that the Mg_2Si prepared in different atmospheres, either hydrogen or nitrogen, might have different structure. It was also thought that the Mg_2Si prepared in H_2 atmosphere might have less magnesium oxide. The Mg_2Si samples prepared in H_2 and N_2 current were therefore studied with x-ray diffraction. The diffractograms are shown in Figs. 16 and 17.

The 'd' values calculated from various peaks of diffractogram (Fig. 16) indicate the formation of Mg_2Si which is shown in Table 28 with 'd' values of 3.70, 3.18, 3.25, 1.92, 1.84 Å etc. There are weak extra lines with the 'd' values 2.11, 1.49, 1.46 and 1.45 Å etc. and 2.79, 2.46 and 1.58 Å which can be attributed to the MgO and Mg respectively. The other lines with 'd' values 3.15, 1.64 and 1.36 are attributed to the Si. The diffraction patterns

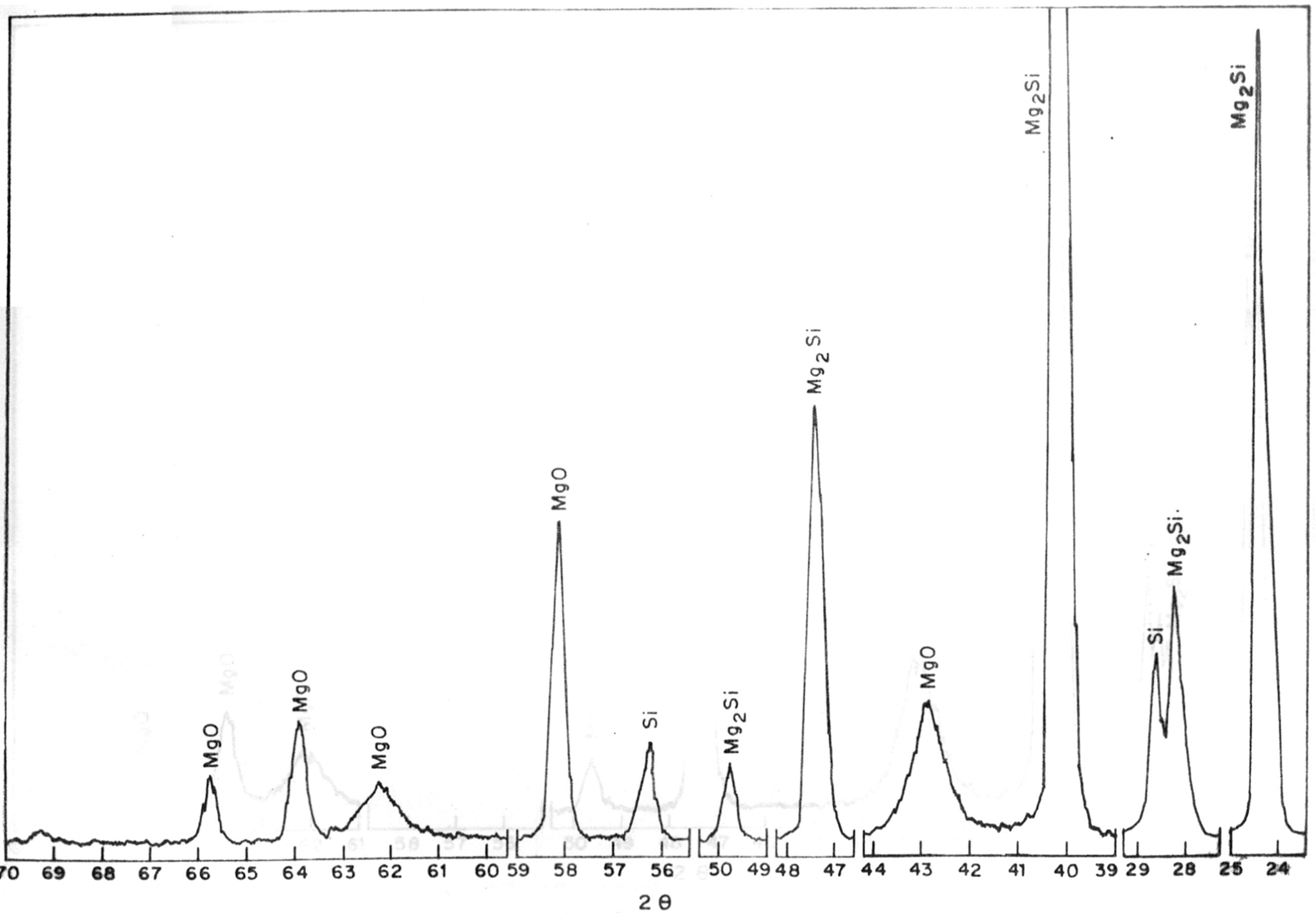


FIG. 16. X-RAY DIFFRACTROGRAM OF Mg_2Si PREPARED IN H_2

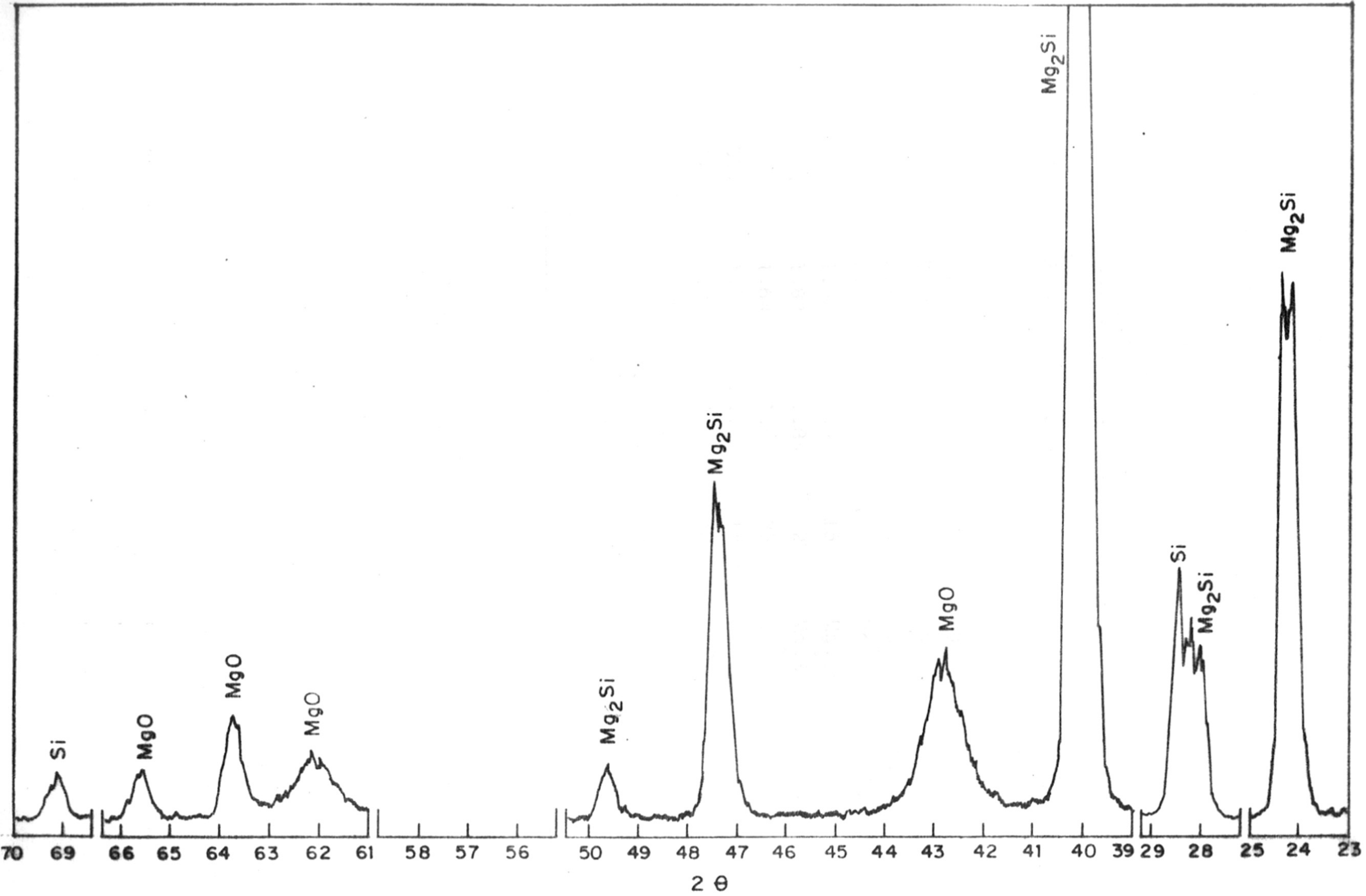


FIG. 17. X-RAY DIFFRACTROGRAM OF Mg_2Si PREPARED IN N_2

Table-28 : X-ray analysis of Mg_2Si

Sr. No.	2θ values	dA values observed	dA values standard	I/I_1	Attri-buted to	Intensity of the peak
1.	24	3.70	3.70	40	Mg_2Si	V.S.
2.	28	3.18	3.20	10	Mg_2Si	M.S.
3.	28.3	3.15	3.14	100	Si	M.S.
4.	32	2.79	2.78	35	Mg	V.W.
5.	36.5	2.46	2.45	100	Mg	V.W.
6.	40	2.25	2.25	100	Mg_2Si	V.S.
7.	42.8	2.11	2.11	100	MgO	V.S.
8.	47.3	1.92	1.92	15	Mg_2Si	V.S.
9.	49.5	1.84	1.84	2	Mg_2Si	M.S.
10.	56	1.64	1.64	35	Si	M.S.
11.	57.9	1.58	1.60	18	Mg	V.S.
12.	62	1.49	1.49	52	MgO	M.S.
13.	63.7	1.46	1.49	52	MgO	M.S.
14.	63.9	1.45	1.49	52	MgO	M.S.
15.	69.2	1.36	1.36	8	Si	V.W.

V.S. - very strong
M.S. - medium strong
V.W. - very weak

of both Mg_2Si prepared in hydrogen and nitrogen atmosphere are the same. The strong peaks of MgO and Mg and weak lines of Si show the impurities of MgO, Mg and free Si are present in Mg_2Si. MgO inherently present in Mg as Mg metal in contact with oxygen forms MgO even at room temperature forming a surface coating. This is not reduced by hydrogen. This shows that Mg_2Si contains MgO, Mg and a little Si as an impurity.

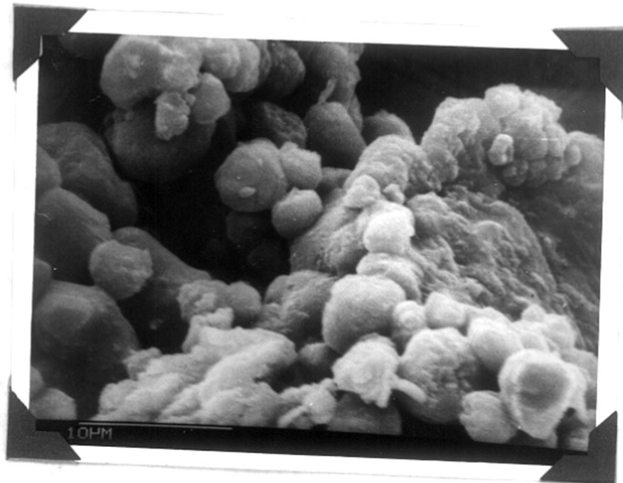
Furthermore when Mg_2Si prepared in H_2 and N_2 atmospheres were seen under Scanning Electron Microscope, it was observed that the particle size of Mg_2Si prepared in N_2 atmosphere was 6 to 8 μm while that of other was 2 to 4 μm (see photograph on page 99). This indicates the smaller particle size of Mg_2Si, if prepared in H_2 atmosphere.

At the moment we do not have enough information about the behaviour of H_2 in presence of Mg_2Si at 500°C, hence we are not in a position to explain how various chlorosilanes leading to silane are formed when Mg_2Si formed in situ acts as a catalyst. However, the probable mechanism can be as follows which is based on various experimental observations.

In presence of Mg powder or Si powder, H_2 does not react with $SiCl_4$. Also $SiCl_4$ is not reduced or decomposed at 400-500°C by hydrogen when H_2 is a reactant.

S E M of Mg_2Si

A) Prepared in H_2



B) Prepared in N_2

We would like to refer to Boulet et al.[90] and Ono[91] for the observations of dissociation of molecular H_2 to atomic H_2 by diffusion mechanism through Mg_2Ni. Since our explanation is based on the formation of atomic hydrogen from molecular H_2 on Mg_2Si we would like to propose the same mechanism as in the paper mentioned above.

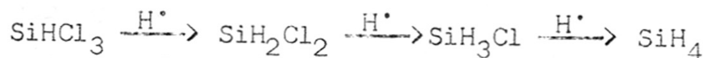
According to Schefer et al.[92] and Ono[93] the Mg_2Ni is monoclinic below 234°C and becomes cubic above that temperature. Bjørn Vigeholm et al.[94] report that in Mg_2Ni absorption, dissociation and desorption of H_2 occurs above 400°C. Charlot and Kohn[95] have studied the hydrogen chemisorption on Ni and suggested that a charge transfer from Ni to hydrogen in which sp orbitals of Ni are involved instead of 'd' orbitals. This weakens the H-H bond and favours chemisorption. Parallel to this Mg_2Si is cubic and the reaction of $SiCl_4$ and H_2 starts above 400°C in presence of Mg_2Si. The covalent radii of Si and Ni are 1.11 and 1.15 Å respectively. The space group of Mg_2Si and Mg_2Ni are same as cubic Fm 3m and the cell volumes are 256.16 and 270 $Å^3$ respectively. These are fairly near to each other. Therefore like Mg_2Ni when hydrogen diffuses through Mg_2Si the molecular H_2 gets split into atomic hydrogen which reacts further with $SiCl_4$ giving silane, lower chlorosilane or silicon as:

(i) $H_2 \rightleftharpoons 2H^{\cdot}$ catalytically on Mg_2Si.

This $H^{\cdot}$ reacts with $SiCl_4$ giving

(ii) $SiCl_4 + 2H^{\cdot} \longrightarrow SiHCl_3 + HCl$

and



$SiHCl_3 \xrightarrow{H^{\cdot}} SiH_2Cl_2 \xrightarrow{H^{\cdot}} SiH_3Cl \xrightarrow{H^{\cdot}} SiH_4$

Polizzotti and Ehrlich[96] have shown that the defects such as lattice steps can significantly affect the rate of H_2 desorption. Absorption-desorption of hydrogen by Mg in presence of various metals has been studied[90,91]. It has been shown that adsorption-desorption of hydrogen has a hysterisis when some metal alloys of Mg is present along with Mg. Mg appears to react more readily with H_2 forming MgH_2 in presence of MgO. Ito et al.[97] have recently reported that Mg is capable of dissociatively chemisorbing hydrogen. The MgO is present in Mg_2Si as seen from X-ray study. The preferential oxidation produces metallic clusters in Mg alloys may be responsible for high catalytic activity for dissociation of H_2. Therefore the other possibility may be -

$Mg(MgO) + H_2 \longrightarrow MgH_2 \longrightarrow Mg + 2H^{\cdot}$

This $2H^{\cdot}$ reacts with $SiCl_4$ as mentioned above.

Considering the recent work on the metal silicides in the literature which supports the diffusion mechanism,

we feel that the first mechanism is plausible in which dissociation of H_2 takes place on Mg_2Si which reacts with $SiCl_4$ giving silane and lower chlorosilane. Furthermore, the HCl produced during the reaction may also combine with Mg_2Si if they come in contact to give $MgCl_2$ and a further amount of SiH_4. However, we feel that the question of exact catalytic mechanism of Mg_2Si is still open for further work.

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CHAPTER - IV

CRACKING OF $SiHCl_3$ ON FLUIDIZED BED

CRACKING OF $SiHCl_3$ ON FLUIDIZED BED

4.1 Conventional Process for the Preparation of Ultra Pure Si

Conventionally ultrapure silicon is prepared by H_2 reduction of $SiHCl_3$ (Trichlorosilane - TCS) at about 1000°C. This reaction is carried out in a quartz belljar as shown in Fig. 18. The deposition of silicon takes place on electrically heated silicon slim rods, which grow in size after deposition. The power required to maintain these rods at required temperature (1000°C) has to be increased as the diameter of rods goes on increasing since the radiation losses from bare quartz belljar goes on increasing because of increase in surface area of rods.

4.2 Introduction to fluidization

Currently, several improvements in the silicon manufacture process are being thought of. One of the promising improvements seems to be the deposition of silicon on silicon particles in a fluidized bed. This approach has several advantages :

(1) The temperature and solid distribution are much more uniform than in the fixed bed due to the fast agitation in a well fluidizing dense phase bed.

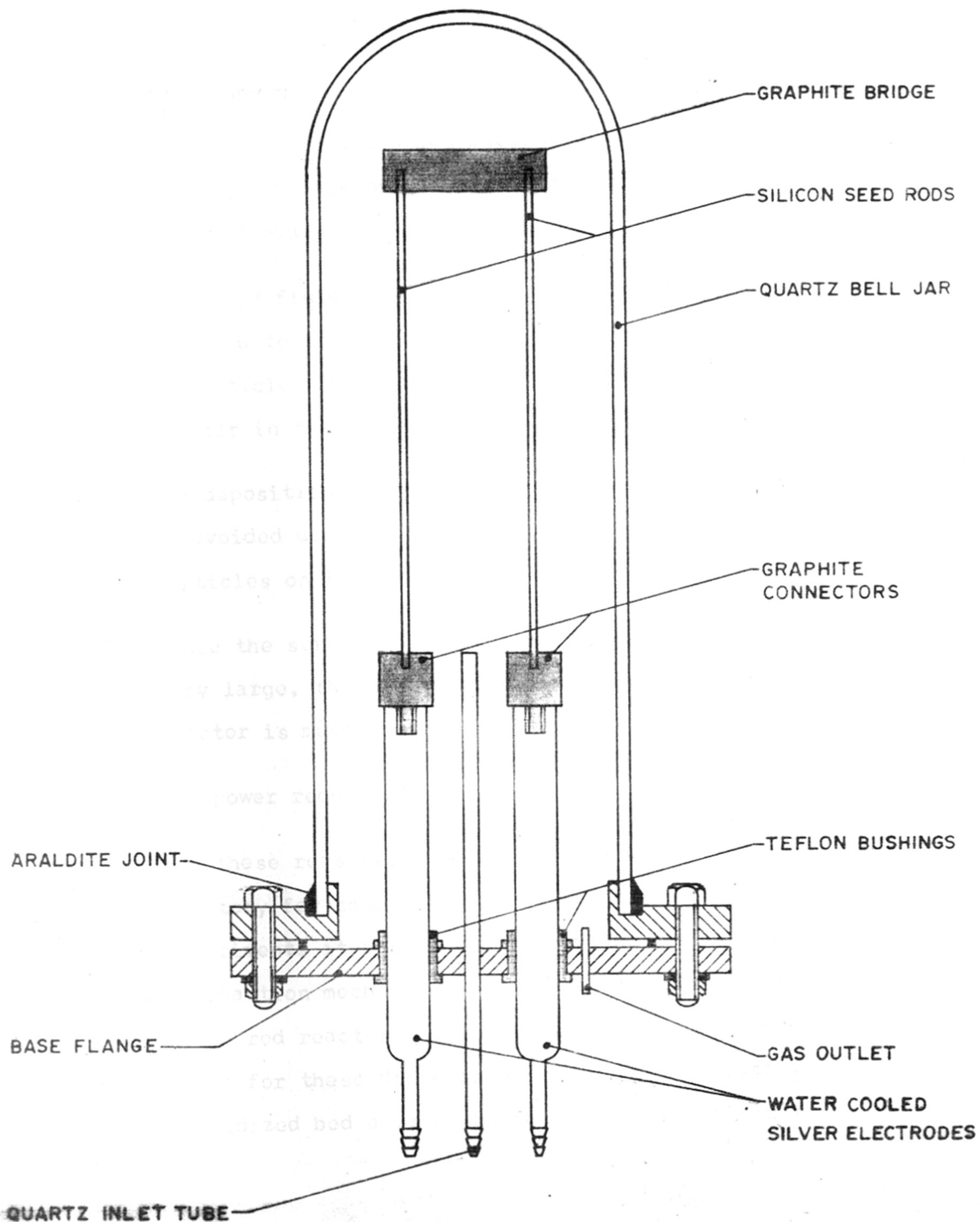


FIG. 18. TWO ROD REACTOR (PROTOTYPE 1)

(2) The resistance to diffusion through the particle is smaller in fluidized bed because of the fact that the particle size is of a smaller order of magnitude than in fixed bed.

(3) The solid fluid heat transfer is much greater as compared to static bed due to the state of subdivision of particle. The heat transfer surfaces are much greater in fluidizing bed.

(4) The deposition of silicon on the wall of the reactor is avoided due to the brushing action of the silicon particles on the wall.

(5) Since the surface area available for deposition is very large, the output of silicon in a fluid bed reactor is much higher than the rod reactor.

(6) The power requirement is known to be less.

For these reasons, this process is being developed in our laboratory for commercial preparation of silicon. During these experiments it became clear from the product pattern that the reaction mechanism and the pathway are not the same in the rod reactor and in fluidized bed, presumably the reasons for these differences reside in the fact that in the fluidized bed a large surface area of silicon is

exposed for deposition as compared to a rod reactor. It therefore appeared interesting to study the effect of variations in various parameters on the kinetics, efficiency and the product pattern and to understand the mechanism, reaction pathway and the factors controlling the reaction.

In silicon preparation by chemical vapour deposition (CVD) technique, various types of reactors are used for depositing silicon. When chlorosilanes are used as a starting material, they are reduced by either H_2, or by metals like Zn, at about 1000°-$1200^{o}C$. In case of quartz tubular reactor, silicon gets deposited on the inner wall of the tube which results in the cracking of the tube while cooling due to the unequal coefficient of expansion of silica and silicon. Thus in every experiment there is a loss of quartz reactor tube. Also, some oxygen at SiO_2-Si interface reacts with Si and forms SiO and contaminates the silicon. The use of tantalum tube for deposition reduces the cost and the contamination but tantalum gives some impurities, the removal of which is essential. Bradley Howard[60] deposited silicon on electrically heated graphite rod, but the formation of SiC was observed and desired purity could not be achieved. Kurotomy Tatsuo[65] deposited silicon on electrically heated metal wire like Ta, Ti, Hf, Zr but removal of metallic impurities was essential. Yatsuri Yoshibumi et al.[98] deposited Si from SiH_4 on electrically heated Si rod.

However, they observed that SiH_4 decomposed before reaching the rods resulting in a fluffy powder-like deposition. Handling of SiH_4 also poses a problem and hence this route to prepare silicon is not widely accepted. Siemens and Halske[99] deposited silicon by the reaction of trichlorosilane and H_2 on electrically heated silicon rod. Recently, Union Carbide Corporation (U.C.C.), U.S.A. and Komatsu, Japan, in collaboration have developed a technique in which Si is deposited from SiH_4 to get polysilicon.

The deposition of Si from $SiCl_4$(STC)/$SiHCl_3$(TCS), depends upon the surface area available for deposition, contact time, flow rate, temperature of substrate, mole ratio of H/Cl, hydrodynamics of the system, process of mass and heat transfer from surface to gas[60,100-104].

In Siemens reactor, surface area available for deposition is small and heat transferred from rod to the gas is also small. Wakefield et al.[105] and other investigators[46,106-109] in silicon field, then tried the Si deposition in fluidized bed, where Si is deposited on Si particles.

4.2.1 Fluidization

When a solid bed of appropriate particle size is supported by buoyancy force of a fluidizing medium,

the solid starts behaving like a fluid. This process is referred to as fluidization.

4.3 Experimental

Initially, cold fluidization trials were taken to determine the parameters such as pressure drop, bed expansion etc. as shown in Fig. 19. To begin with, 200 gms. of MG silicon powder -72 +100 mesh was filled in a silica reactor tube of 25 mm ID and 100 cm in length. A porous silica gas distributor plate was fixed in the reactor. The bed was 29.5 cm. The reactor was heated to the required temperature of about 1000°-$1100^{o}C$ in a tubular silica furnace which was wound with Kanthal A (16 SWG) element. Chromel-Alumel thermocouple was used for sensing the temperature, in a silica sheath (8 mm ID), which was controlled within $\pm 5^{o}C$ at $1000^{o}C$ by a temperature controller and a high current capacity relay. The vertical length of the silica tube was 75 cm with 30 mm diameter (ID) and 38 mm (OD). Input power to the heating element was varied by using a 30 A/230 V variac. The voltage and current were measured on the meters on the panel.

The onset of fluidization started with pressure drop of 8 cms of H_2SO_4 column and better fluidization was observed with pressure drop of 11.7 cm (in cold) - when the bed was heated to $1000^{o}C$, sintering was observed. This might be

due to strong cohesion due to fine particles. Other particle size was also studied like (-50 + 100) and finally (-30 +50) was found suitable for fluidization at 1000°C. When trichlorosilane was passed in fluidized bed through a porous silica distributor plate, it was observed that silicon deposition had occurred on the distributor plate itself. Hence in subsequent experiments sintered silica gas distributor plate was replaced by about 10 cm high static bed of -7 +16 mesh silicon particles with a layer of -16 +20 mesh silicon powder of about 1 cm. height which also serves for gas distribution. In order to avoid any deposition of silicon in static bed, it was kept out of the furnace in such a way that the temperature of the top of the static bed did not exceed 500°C.

In the subsequent experiment, the silicon deposition was observed in the free board region of the reactor tube along with the deposition on fluidized bed region. Hence fluidized bed was changed to slug bed.

4.3.1 Advantages of slug bed

As compared to fluid bed, the advantages of the slug bed are:

(1) In slug bed, l/d (l = length, d = diameter) of reactor is higher.

(2) The bubbles of the gas in slug bed coalesce to a diameter approaching that of the confining vessel. The particle layers, or slug of granular solid, between such large gas pockets will move upwards, attain a certain height and then disintegrate. The granular matter will then rain through the ascending gas pocket either in the form of smaller aggregates or as individual particles.

(3) Due to friction between solid slugs and wall of the reactor tube, deposition of Si on the reactor wall is avoided.

(4) In view of the movement of gas in the slug and interslug regions in plug flow the concentration of the gas species is kept high. This is desirable since higher cracking rates of the TCS to silicon can now be achieved. Also in view of a larger concentration of solids in the bed, this material quickly gets deposited without any problem of sintering and choking. A higher efficiency of operation can then be achieved.

4.3.2 Particle size reduction

200 gms. of Si powder (-30 +50) mesh, 29.5 cms. in height was slugged in N_2 at 900°C for 12 hours with superficial velocity of 28.06 cm/sec. 0.6% of powder passed through 50 mesh. This shows that the material gets powdered due to attrition.

The feeding of trichlorosilane ($SiHCl_3$) was done initially by flash evaporation in which case the TCS was allowed to drop from reservoir into a bubbler which was heated electrically by a furnace to about 150°C. The hydrogen was acting as a carrier gas to carry vapours of $SiHCl_3$, but by this method, the feeding was not uniform and secondly at high feed rate the cooling of $SiHCl_3$ used to occur while going to the reactor. The feeding of trichlorosilane was therefore modified by bubbling of H_2 gas through $SiHCl_3$. The feed rate of $SiHCl_3$ was controlled by :

(i) the bath temperature of the bubbler
(ii) the amount of H_2 gas bubbled.

The amount of $SiHCl_3$ vapourized can be calculated from the vapour-pressure data and the flow-rate of hydrogen, assuming the complete saturation of the gas. The rates observed in our experiments were in good agreement with those reported in the literature upto 2 moles of H_2/hour as with increase in quantity of H_2, partial saturation of H_2 occurs.

Thus a known volume of H_2 was bubbled through $SiHCl_3$ and a mixture of $SiHCl_3$ + H_2 was fed to the reactor. The additional H_2 required was passed through another manometer and whole of $SiHCl_3$ and H_2 were mixed before feeding to the reactor. The calibrated capillary manometers were used for

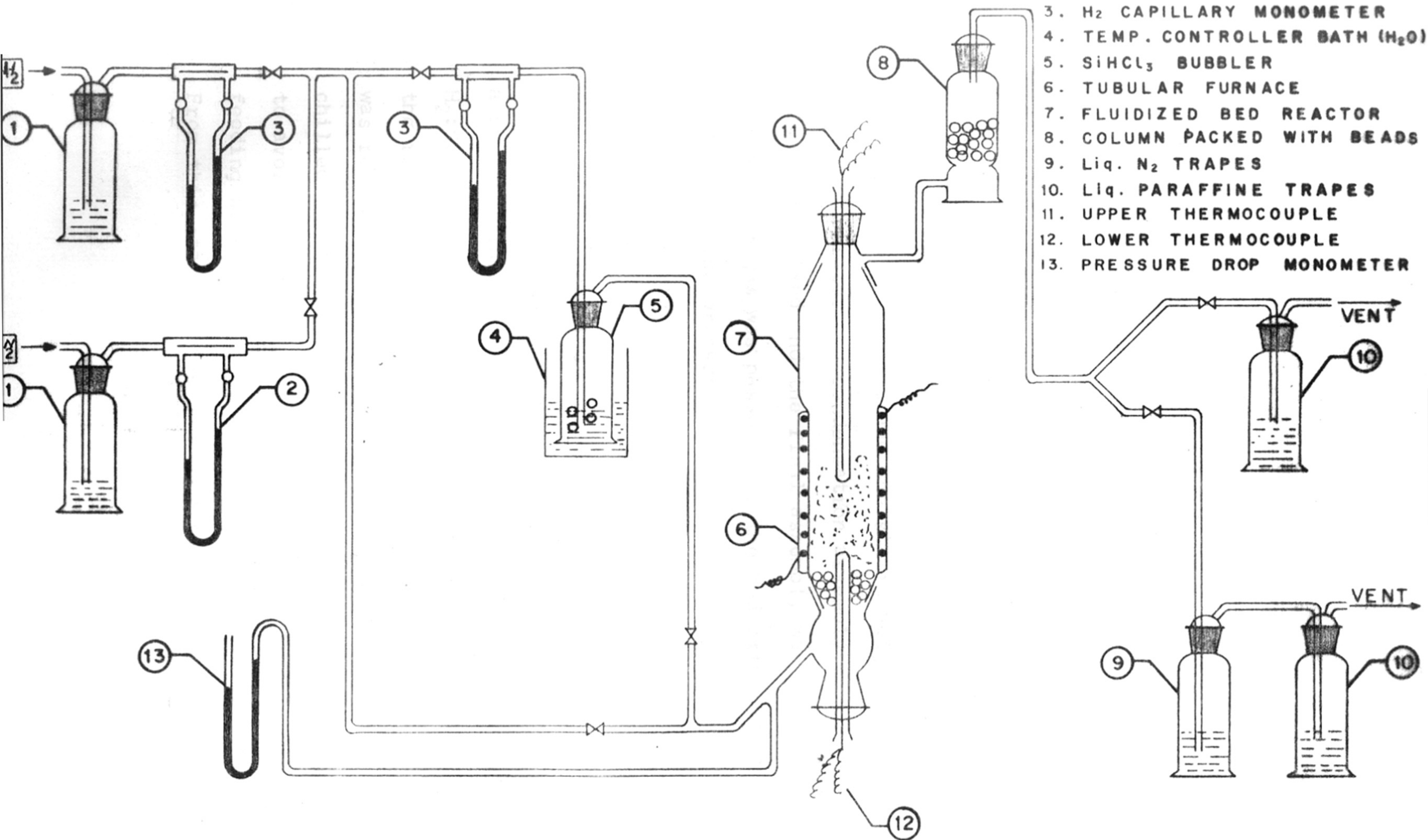


FIG. 19 - EXPERIMENTAL SET-UP OF FLUIDIZED BED REACTOR.

volume measurements of hydrogen. A pressure drop-manometer containing sulphuric acid connected to the system was used for indicating the bed movement and also if bed was getting plugged or choked during the experiment. Two thermocouples, one at the top and the other at the bottom of the slug bed were used to measure the temperature. A known weight of silicon powder (-7 +16 mesh) was packed in a static bed and the height was noted. Then about 160 gms. of fine particles (-30 +50 mesh) was packed and the static height was recorded. Cyclone-seperator and condensation assembly as shown in Fig. 19 was fixed and the final assembly was made leak-proof. The hydrogen gas was passed till the bed attained slugging condition. The pressure drop was noted. This automatically flushed the system. The reactor was then heated electrically. Hydrogen gas was passed constantly to maintain slugging throughout. The $SiHCl_3$ bubbler was flushed with H_2 when attached to system. When the desired temperature was attained a predetermined amount of H_2 corresponding to the desired H_2:$SiHCl_3$ ratio was bubbled through $SiHCl_3$ and finally fed to the reactor along with make-up hydrogen. The pressure drop was recorded throughout the experiment. The exit gases were chilled and condensed in liquid nitrogen condenser, adjusted to avoid choking. At the end of the experiment, $SiHCl_3$ feeding was stopped and the power supply was also put off. From this stage only H_2 was passed to avoid sintering till

the bed attained room temperature. When feeding of $SiHCl_3$ was stopped, the hydrogen was passed through other bypass outlet to avoid the carryover of condensed volatile silicon compounds. The condensed gases were then analysed using carbontetrachloride (CCl_4) as solvent, on VPC having a TCD detector. The VPC column was composed of SE-52. silicon oil (DC 200/350) and Kiselguhr (optimum weight ratio 3:1:5 at 70°C). The carrier gas was H_2.

After attaining room temperature the whole bed was removed from the reactor and weighed again. The increase in weight of Si was noted. Experiments were repeated by varying the molar ratio $H_2/SiHCl_3$ at constant temperature.

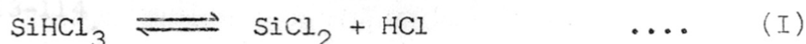
4.4 Results and Discussion

According to Bylander[110], although there is some controversy as to whether $SiHCl_3$ decomposes on silicon surface or just near it[111], it will be convenient to discuss the result in terms of heterogeneous reaction theory. A classical reaction takes place with following steps.

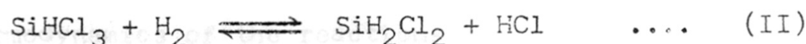
1. Mass transfer of the reactants to the surface
2. Adsorption on to the surface
3. The reaction or a series of reactions which take place on the surface
4. Desorption of product molecules
5. Mass transfer of the product molecules to the main gas stream, and for growing crystal
6. Addition of atoms to growth steps.

If one of the above steps is much slower than the others, it will control the growth rate. In addition, the mass transfer step will be influenced by gas flow rate, yet relatively temperature and flow rate independent. In the temperature region of 950°C to 1100°C the reduction of $SiHCl_3$ is temperature dependent but relatively flow rate independent. The surface of silicon deposited in this region is observed to be quite rough and uneven. This may be due to surface rate control.

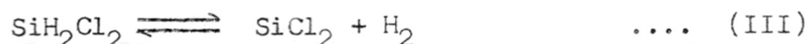
The mechanism proposed by Nishizawa[112] for hydrogen reduction of $SiHCl_3$ the various reactions are :



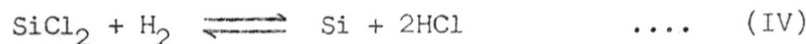
$$SiHCl_3 \rightleftharpoons SiCl_2 + HCl \quad .... \quad (I)$$



$$SiHCl_3 + H_2 \rightleftharpoons SiH_2Cl_2 + HCl \quad .... \quad (II)$$



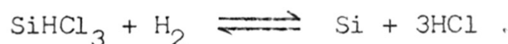
$$SiH_2Cl_2 \rightleftharpoons SiCl_2 + H_2 \quad .... \quad (III)$$



$$SiCl_2 + H_2 \rightleftharpoons Si + 2HCl \quad .... \quad (IV)$$

At higher temperature reactions (III) and (IV) prevail. The observed reactant species are $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, HCl, $SiCl_3$, $SiCl_2$. Much SiH_2Cl_2 is produced in the deposition.

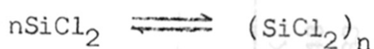
In the preparation of ultrapure silicon by hydrogen reduction of $SiHCl_3$ on heated silicon substrate, the overall reaction (at about 1000°C) is



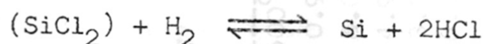
$$SiHCl_3 + H_2 \rightleftharpoons Si + 3HCl .$$

In this reaction only a certain percentage of conversion can be reached because at high temperature $SiCl_4$ and $SiCl_2$ are formed as,

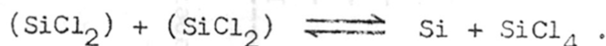
$$SiHCl_3 \rightleftharpoons SiCl_2 + HCl$$



$$nSiCl_2 \rightleftharpoons (SiCl_2)_n$$



$$(SiCl_2) + H_2 \rightleftharpoons Si + 2HCl$$

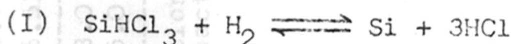


$$(SiCl_2) + (SiCl_2) \rightleftharpoons Si + SiCl_4 .$$

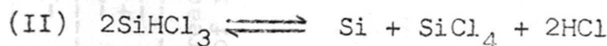
The theoretical yield depends upon the reaction temperature and the mole ratio $H_2/SiHCl_3$. The effective yield is also influenced by the gas flow pattern and the time of residence[113-114].

4.4.1 <u>Thermodynamics of the reactions</u>

From Table-29 the probable reactions are as follows:

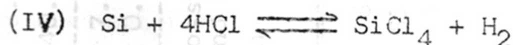


$$\text{(I)} \quad SiHCl_3 + H_2 \rightleftharpoons Si + 3HCl$$



$$\text{(II)} \quad 2SiHCl_3 \rightleftharpoons Si + SiCl_4 + 2HCl$$

$$\text{(III)} \quad 4SiHCl_3 \rightleftharpoons Si + 3SiCl_4 + 2H_2$$



$$\text{(IV)} \quad Si + 4HCl \rightleftharpoons SiCl_4 + H_2$$

In hydrogen reduction of $SiHCl_3$ silicon and HCl are obtained as in equation (I) but as the reaction is reversible the generated HCl reacts immediately with silicon producing $SiCl_4$ and H_2. The overall reaction becomes,

Table - 29 : Standard free energies of formation of compounds (Kcal/mole).

Temperature °K	SiH_4	SiH_3Cl	SiH_2Cl_2	$SiHCl_3$	$SiCl_4$	HCl	$SiCl_2$
1300	35.934	-20.968	-46.133	-78.624	-116.449	-24.534	-50.825
1400	38.302	-18.741	-43.836	-76.058	-113.409	-24.675	-51.604
1500	40.663	-16.519	-41.543	-73.496	-110.375	-24.813	-52.370
$H_{f_{298}}$	7.3 $\pm$ 0.3	-48.0 $\pm$15.0	-80.0	-119.6	-157.1 $\pm$ 2.0	-22.02 $\pm$ 0.05	-37.66

Possible reactions and their standard free energy changes and heat of reaction in Kcal/mole.

No.	Reaction	ΔF 1300°K	ΔF 1400°K	ΔF 1500°K	ΔH_r
1.	$SiHCl_3 + H_2 \rightleftharpoons Si + 3HCl$	5.022	2.033	- 0.943	53.543
2.	$SiH_2Cl_2 \rightleftharpoons Si + 2HCl$	-2.935	-5.514	- 8.083	35.962
3.	$2SiHCl_3 \rightleftharpoons SiCl_4 + SiH_2Cl_2$	-5.334	-5.129	- 4.926	2.100
4.	$2SiHCl_3 \rightleftharpoons Si + SiCl_4 + 2HCl$	-8.269	-10.643	-13.009	38.062
5.	$3SiHCl_3 \rightleftharpoons 2SiCl_4 + SiH_3Cl$	-17.994	-17.385	-16.781	- 3.400
6.	$4SiHCl_3 \rightleftharpoons 3SiCl_4 + Si + 2H_2$	-34.851	-35.995	-37.141	7.100
7.	$SiHCl_3 \rightleftharpoons SiCl_2 + HCl$	3.265	- 0.221	- 3.687	59.920
8.	$SiCl_2 + H_2 \rightleftharpoons Si + 2HCl$	1.757	2.254	2.744	- 6.378
9.	$SiH_3Cl \rightleftharpoons Si + H_2 + HCl$	- 3.566	- 5.934	- 8.294	25.981
10.	$SiCl_4 + 2H_2 \rightleftharpoons Si + 4HCl$	18.313	14.709	11.123	69.060
11.	$SiCl_4 + H_2 \rightleftharpoons SiCl_2 + 2HCl$	16.556	12.455	8.379	75.402

The values of $\Delta H_{f_{298}}$ and ΔF_f are taken from JANAF THERMOCHEMICAL TABLE[88]

$$4SiHCl_3 \rightleftharpoons 3SiCl_4 + Si + 2H_2.$$

Therefore silicon obtained in reaction (I) gets converted to $SiCl_4$.

According to Yasuda et al.[115] if molar ratio of $H_2/SiHCl_3$ is less than 10, silicon is produced principally by the reaction (III) and when the molar ratio is above 20, silicon is produced by reaction (I).

If the mode of reaction is as per equation (III) then the reaction is marginally endothermic as heat of reaction is 7 Kcal/mole, but if the reaction proceeds by equation (I) then the reaction is highly endothermic as heat of reaction is 53.54 Kcal/mole and the overall reaction becomes energy intensive.

According to Nishizawa[116] silicon deposition from $SiHCl_3$ is a two step reaction. The first step in which $SiHCl_3$ changes to SiH_2Cl_2 and $SiCl_2$, which is a gas phase reaction. The reaction of hydrogen and $SiCl_2$ leading to Si and HCl is a surface reaction. Thus the overall reaction becomes surface dependent.

In case of rod reactor, silicon is deposited by C.V.D. on electrically heated silicon rod by resistive heating. The reaction

takes place partially and in exit gases a lot of undecomposed $SiHCl_3$ comes out along with $SiCl_4$, HCl and H_2 (60:40 % of $SiHCl_3$ and $SiCl_4$)[117]. The efficiency of the reaction is about 25% up to $H_2/SiHCl_3 \approx 20$. The efficiency increases with increase in $H_2/SiHCl_3$ mole ratio as seen from Table 30, Fig. 20, but higher the ratio the yield of silicon per unit time decreases. Whatever the ratio of $H_2/SiHCl_3$, the surface area available on the rod reactor is limited and only such molecules which come in contact with the rods are in position to react. As a result a lot of $SiHCl_3$ goes unreacted. With this view therefore it was thought that this reaction could be carried out in a fluidized bed where the contacting surface is very large. However, the overall reaction efficiency could not be made very much higher although the throughput could be made fairly high due to the higher flow rates required in fluidized bed. Furthermore, it was observed that a large proportion of $SiHCl_3$ was still getting converted to the undesirable $SiCl_4$ (Fig. 21), probably due to the autothermal nature of cracking of $SiHCl_3$ as per equation (III). If the reaction is carried out in a slugging regime of the fluidized bed the advantage can be taken of the fact that the concentration of the reacting gases is very high due to the plug flow nature of the slug bed and there is no back mixing of the solid as in the conventional fluid bed, as a result a high concentration of solid offering the necessary contacting

Table - 30 : Effect of variation of mole ratio $H_2/SiHCl_3$ on the efficiency of $SiHCl_3$ reduction to silicon.

[i] Residence time is constant.

[ii] Particle size is same.

Sr. No.	Mole of $SiHCl_3$ passed per hour	Mole of H_2 passed per hour	Total mole per hour of $SiHCl_3+H_2$	Mole ratio $H_2/SiHCl_3$	Silicon obtained (gms.)	Weight of exit gas (gms.)	% efficiency	Composition of exit gas $SiHCl_3$: $SiCl_4$	Duration of experiment (minutes)
1.	1.483	5.80	7.28	3.91	3.7	120	14	8:92	40
2.	0.992	5.80	6.79	5.85	3.9	90	18	8:92	50
3.	0.565	5.80	6.30	10.26	5.0	102	18.6	5:95	105
4.	0.515	6.24	6.75	12.12	6.0	110	20	6:94	150
5.	0.330	6.24	6.57	18.90	2.1	33	23.5	0:100	60
6.	1.0	-	$SiHCl_3+N_2$	-	4.8	70	17	0:100	30

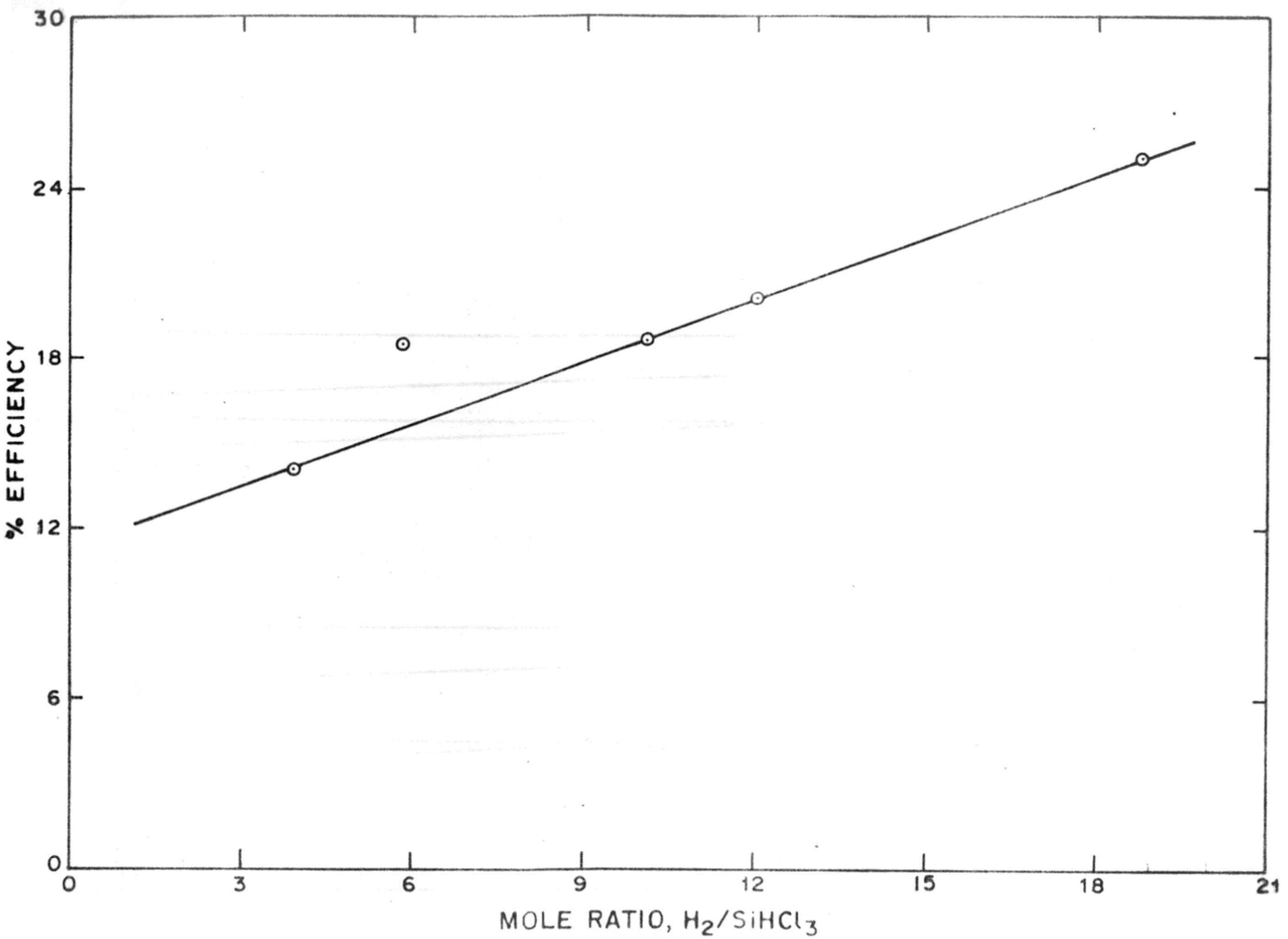


FIG. 20. A GRAPH OF % EFFICIENCY OF Si OBTAINED Vs. MOLER RATIO $H_2/SiHCl_3$

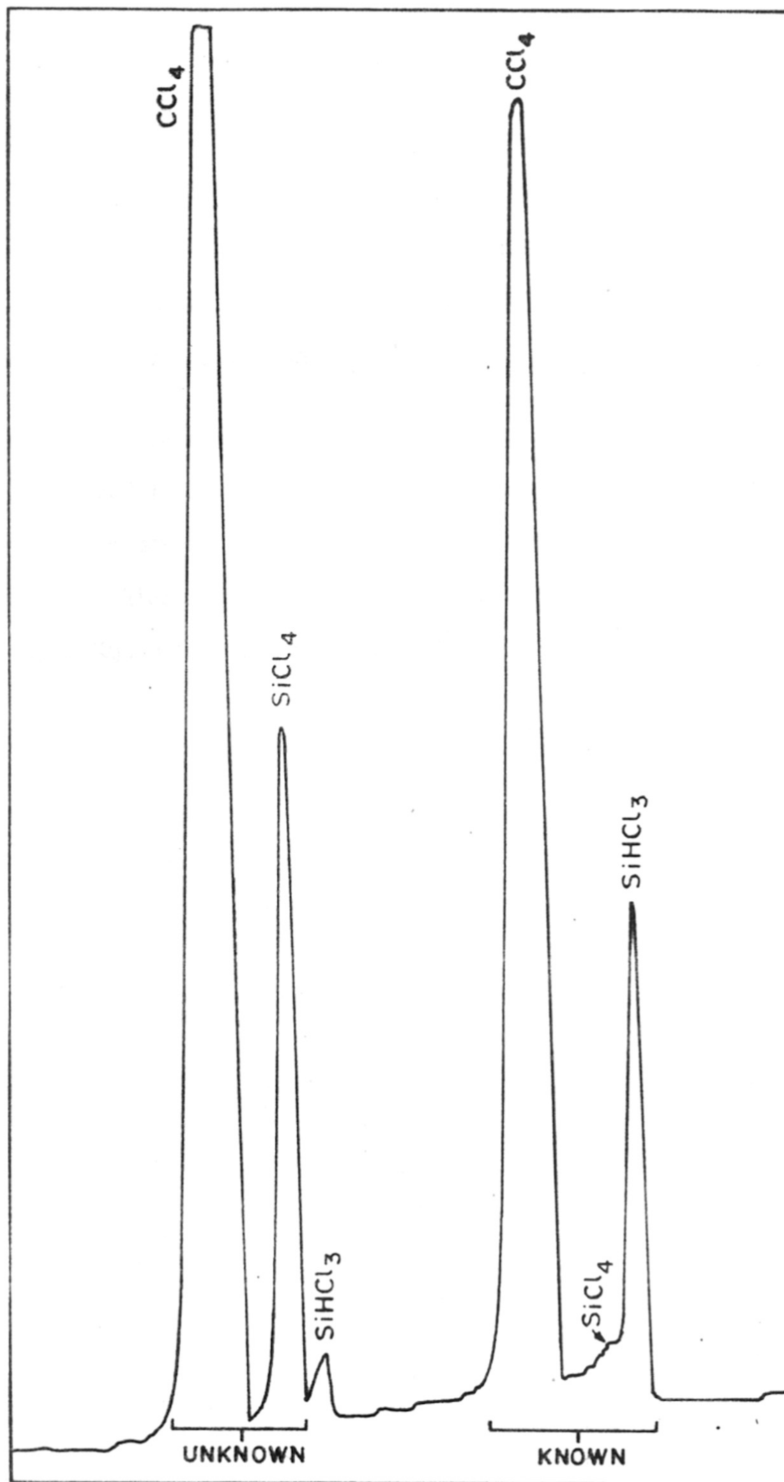


FIG. 21. GAS CHROMATOGRAPHIC SEPERATION OF CHLOROSILANE

surface for the two reactants to react is available. Therefore a higher rate of deposition is achieved in slug bed. The back reaction of HCl with the solid appears to get minimised by increasing the superficial velocity.

From the point of view of energy, the cracking of $SiHCl_3$ in fluid bed or slug bed is economical as the power requirement is smaller as compared to that required in the rod reactor. Thus the contribution of energy to the cost of silicon per Kg. can be appreciably reduced.

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