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Mechanism and Kinetics of the Metal-Catalyzed Synthesis of Methylchlorosilanes

II. The Kinetics of the Copper-Catalyzed Reaction of Methyl Chloride and Silicon

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In this paper investigations are described in which the effects of the temperature, the pressure, and the preparation of the catalyst on the reaction of methyl chloride and silicon were studied by means of a tubular fixed-bed differential flow reactor. Initial reaction rates were measured. The composition of the silane products appeared to be substantially insensitive to variations of the mentioned variables. The over-all activation energy of the reaction at moderate pressures has been determined. The pressure dependence of the initial reaction rate supports the view that the reaction studied is a heterogeneous catalytic process in which initially a dissociative chemisorption of a methyl chloride molecule on two active centers of the surface occurs, followed by a rate-determining reaction in the chemisorbed layer.

1. INTRODUCTION

In the first paper of this series (*1*), the behavior was studied of a copper-silicon contact mass, prepared from copper(I) chloride and silicon, during reaction with methyl chloride. The conversion of the silicon and the temperature were the main variables considered there. The results supported the view, presented earlier (*2*, *3*), that free copper is not effective as a catalyst and that an intermetallic compound of silicon and copper needs to be present in order to synthesize dimethyldichlorosilane selectively. A forthcoming paper in the present series will further elaborate this point (*4*). It seemed thus logical to perform further kinetic work with contact masses consisting exclusively of silicon and the intermetallic silicon-copper phase. Hence, in the present investigation, silicon-copper *alloys* are used to study the relation of the reaction rate and the selectivity with the temperature and the pressure.

In ideal circumstances the synthesis of methylchlorosilanes might proceed according to reaction equation (1)

$$2\,CH_3Cl + Si \xrightarrow{Cu} Si(CH_3)_2Cl_2 + \text{about 80 kcal} \quad (1)$$

Dimethyldichlorosilane is produced. Actually, a mixture of methylchlorosilanes is obtained, containing at best about 90 wt % of the mentioned substance. The competitive and consecutive reactions leading to the formation of the side products could trouble the kinetic studies, but fortunately, in the course of the present work it was found that temperature and pressure do not influence the product composition, provided that hot spots are absent in the reactor. This facilitates the kinetic study appreciably, as consequently the reaction may, overall, be regarded as a simple one, without parallel or consecutive processes.*

A number of experimental methods are available for kinetic work. Several methods were applied in the study of the copper-catalyzed synthesis of methylchlorosilanes.† Generally, batch reactors and differential or

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* The same does not hold for the synthesis of ethylchlorosilanes (*5*).

† A detailed survey of these studies need not be given here, as it is published elsewhere (*3*).

integral flow reactors may be distinguished. The first type is not very suitable in the study of reaction (1), which is rather exothermic (about 80 kcal/mole), thus easily giving rise to hot spots in the contact mass. The differential flow reactor is characterized by a very small conversion of the feed per pass. Partial pressures, gas velocities, and conversions of the solid mass are nearly constant throughout the reactor. By maintaining high gas rates and employing a small-diameter reactor it is possible to control the reaction temperature very well, while a fixed bed may be used. The calculation of the reaction rate from the measurements and the correlation of the rate with the reaction conditions is very simple. From a mass balance it is easily derived that the reaction velocity r may simply be expressed in terms of conversion x, feed rate F, and catalyst (or contact mass) weight W

$$r = Fx/W \qquad (2)$$

A disadvantage of the differential reactor is that working at a reasonable partial pressure of silanes is possible only by introducing silanes with the methyl chloride feed. The analysis of the reactor effluent presents difficulties then, as a very small increase of the amount of silanes in the stream has to be detected. In the present work we have made use of a fixed-bed differential flow reactor, which permits proper temperature control by its very small diameter.

The kinetic investigations have a double purpose. They provide technically interesting data on the interrelation of the process parameters. As a second result an insight may be gained into the mechanism of the reaction, as is demonstrated by Hougen, Watson, and Yang (*7–9*). The kinetic relations may allow a choice between the possible mechanisms. It has been pointed out, that in heterogeneous catalytic processes five unit steps may play a role, namely the diffusion of the gaseous reagent to the surface of the catalyst, the adsorption of a reagent molecule on the surface, the surface reaction, the desorption of a product molecule from the surface, and the diffusion of the products into the gas phase. In the present case, where the solid is both catalyst and reagent, a sixth step is of importance, the solid-phase diffusion of silicon to an active site where it may react with methyl chloride. In the foregoing article (*1*) of the present series it was shown that probably the latter step is rate determining in the last stages of the process, after a good deal of the silicon has been converted. During the rest of the process this solid-phase diffusion is most probably not rate limiting (*2, 10*). The diffusion of gaseous reagents and products from and to the surface cannot be considered to be rate determining either.

Some major results of earlier kinetic work on the synthesis of methylchlorosilanes should be recorded here. Preliminary studies with a fluid-bed integral reactor, employing a contact mass prepared from copper(I) chloride and silicon, indicated that at atmospheric pressure and at relatively high temperatures (338° and 348°C) the reaction could approximately be considered as first order in methyl chloride (*11*), in accordance with results presented by Joklík and coworkers (*12*). In a fluid bed the selectivity of the process is hardly influenced by the methyl chloride conversion (*11*) and not at all by the temperature in the range of 300° to 350°C, as is shown in the first article of the present series (*1*).

Kinetic work by Joklík, Bažant, and coworkers (*12–14*) showed that the kinetic data on the synthesis of methylchlorosilanes and methylbromosilanes could be correlated best with an expression [Eq. (4)] derived by Yang and Hougen (*9*) for a heterogeneous catalytic process with a dissociative adsorption of a reagent molecule on two active sites of the surface as an initial step, the subsequent surface reaction in the chemisorbed state being rate determining.

$$r = \frac{kK_A p_A}{[1 + (K_A p_A)^{1/2} + K_R p_R]^2} \qquad (4)$$

Here, r stands for the reaction velocity, k is the velocity constant of the surface reaction, K_A and K_R are the adsorption equilibrium constants of methyl chloride and silanes respectively, and p_A and p_R are the partial pressures of methyl chloride and products.

A survey of the results of the authors mentioned is given in Table 1. If initial

TABLE 1

Kinetic Data[a] for the Reactions of Organohalides and Silicon-Copper[b]

Gas	Contact mass	Temp (°C)	k $\left(\frac{\text{mole } CH_3X}{\text{kg Cu·hr}}\right)$	K_A (atm^{-1} $\times 10^5$)	K_R (atm^{-1} $\times 10^3$)	E_a (kcal/mole)	ΔH_A (kcal/mole)	ΔH_R (kcal/mole)	E_0[c] (kcal/mole)
CH_3Cl	Pure[d] Si	280	240	760	530				
	11.9% Cu	300	600	680	400	25.3	4.7	11.2	20.6
		320	1170	570	280				
		300	625	900	—				
	Techn.[e] Si	280	1000[f]	800[f]	570[f]				
	10.0% Cu	300	2025	280[f]	520[f]	20.1	21.0	2.7	−0.9
		340	8000[f]	100[f]	460[f]				
CH_3Br	Pure Si	280	1620	800	1670	37.0	27.4	15.2	9.6
	10.9% Cu								
C_2H_5Cl	Techn. Si	240–320	—	—	—	—	—	—	18
	10.0% Cu								

[a] References (*12–14*).

[b] The copper was analyzed: 96.2% Cu, 3.16% O, 0.14% Sn, 0.10% Ni, 0.26% Co, 0.05% Pb, 0.04% Si, 0.03% Zn, traces of Fe.

[c] E_0 is the over-all activation energy of the initial reaction rate, calculated by: $E_0 = E_a - \Delta H_A$.

[d] Analysis: 0.07% Al, less than 0.01 Ca, Mg, and Ti.

[e] Analysis: 0.8% Al, 0.5% Fe, less than 0.1 Ca, Mg, and Ti.

[f] Estimated from the graphical representation of the results of ref. (*14*).

reaction rates are measured (at zero methyl chloride conversion and zero silane pressure), expression (4) reduces to (5)

$$r_0 = \frac{kK_Ap_A}{[1 + (K_Ap_A)^{1/2}]^2} \qquad (5)$$

From this equation it appears that from measurements of r_0 and p_A the constants k and K_A may be calculated.

2. Experimental Procedures

The kinetic investigations are carried out in a stainless steel (steel 316) fixed-bed reactor, depicted in Fig. 1. The internal diameter is 12 mm, the length being 750 mm. The central thermocouple well has an outside diameter of 5 mm. The last part of the methyl chloride feedline is spiralled around the reactor, thus serving as a preheater. By placing the reactor and the preheater in an electrically heated, air-fluidized bed of sand or some other good fluidizing powder, the reactor may be kept at any desired temperature. Control of the temperatures of the fluid bed and the reactor is possible by regulating the air feed rate. This is done automatically by means of a resistance thermometer directing, via an amplifier, a magnetic valve in the feedline of the pressurized air. The remainder of the apparatus is depicted schematically in Fig. 2. The methyl chloride feed is withdrawn from a heated bomb, the working pressure being fixed by the temperature of the bomb. The methyl chloride is fed into the preheater through a regulating valve. The effluent from the reactor, consisting of methyl chloride and some silanes, is expanded to atmospheric pressure and then fed into a continuous rectification column. The silanes are withdrawn from the electrically heated still at regular intervals. The still temperature is fixed at 25° to 30°C. The top condenser of the column is maintained at the boiling point of methyl chloride by means of a carbon dioxide-methanol mixture. The reflux ratio is about 10:1. The methyl chloride emerging from the column is passed through a flow meter and a gas meter. The temperatures of three points in the central thermocouple well in the reactor and of a thermocouple in the fluidized-bed heating mantle are continuously recorded.

In the performance of exothermic solid–gas reactions appreciable differences of temperature and pressure may exist between the gas and the solid surface. These differences

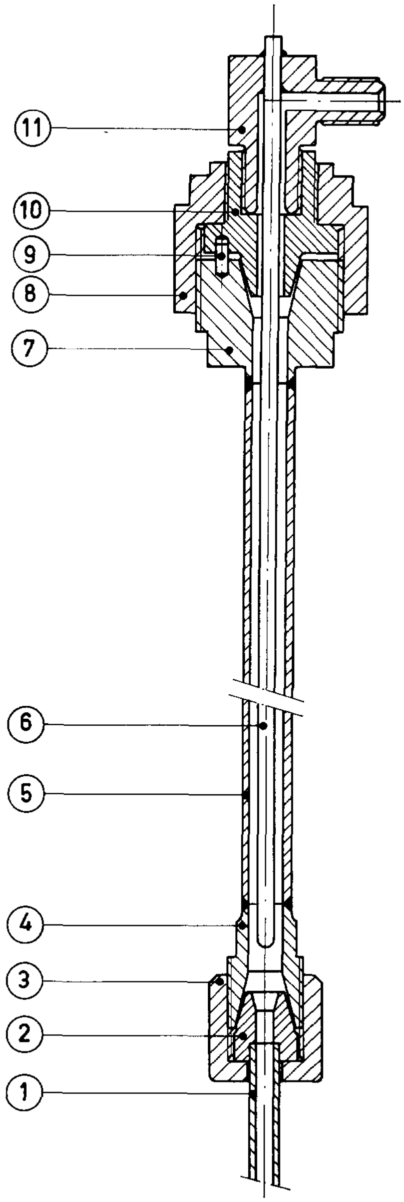

FIG. 1. The fixed-bed reactor applied in the kinetic studies. 1. End of spiralled preheater. 2. Conical collar. 3. Coupling nut. 4. Tapered end. 5. Reactor tube. 6. Thermocouple well. 7. Tapered end. 8. Coupling nut. 9. Safety pen. 10. Conical collar. 11. Angle piece.

are governed by the velocities of heat and mass transfer, and the rate and the exothermal effect of the reaction. The differences may be kept small by maintaining a high linear gas velocity. On the basis of the method presented by Yoshida, Ramaswami, and Hougen (*15*) the differences have been calculated for the circumstances encountered in our experiments. The temperature difference is calculated to be between 0.06° and 0.4°C, whereas the differences of the partial pressures are smaller than 0.0001 times the methyl chloride pressure. Besides the temperature differences between the gas and the surface of the solids, axial and radial temperature gradients in the reactor are important. In the axial direction the temperature differences were always smaller than 1°C. The same holds for the temperature differences between the central thermocouple well and the fluid heating bed.

The methyl chloride used in the experiments was gas chromatographically pure.

The purities of the metals employed for the contact masses were: Cu, 99.99%; Si, 99.98%; Zn, 99.99%; and Al, 99.99%. The contact masses used were prepared by melting silicon and copper together in the desired proportions and adding zinc and aluminum. The melting was carried out in an alumina-coated crucible. The melt was poured out in steel molds, internally coated with alumina, or eventually in a sand mold or in paraffin oil, and then allowed to solidify. The lumps thus obtained were polished to remove impurities and then stored. Just prior to use the lumps were ground and sieved and a fraction of 420 to 500 μm was used as a contact mass. In the grinding process some contamination of the alloys with iron occurred, due to the abrasion of the steel crushers.

Four types of contact masses are to be distinguished, resulting from alloys which were solidified in the sand molds, in steel molds of 8 cm diameter and 4 cm diameter or in paraffin oil, respectively. The alloys consist of big crystallites of primary silicon, separated by lamellae of the eutectic alloy containing 30 at.% silicon (Fig. 3). In Table 2 a survey is given of the employed contact masses with their main characteristics. In Fig. 4 some characteristic photographs of the alloys are given.*

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* We are indebted to Mr. P. F. Colijn of the Laboratory for Metallurgy of the Technological University, Delft, for the microphotographs.

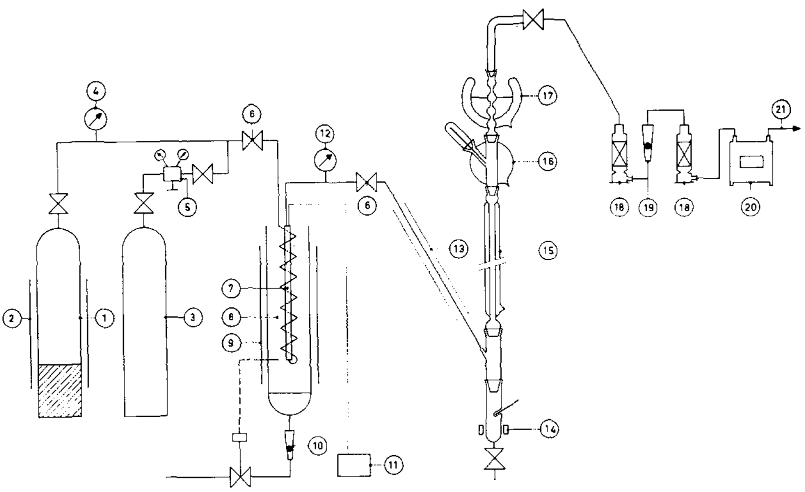

Fig. 2. The apparatus for fixed-bed kinetic measurements. 1. Methyl chloride bomb. 2. Heating mantle. 3. Nitrogen bomb. 4. Precision manometer. 5. Reducing valve with high outlet pressure. 6. Needle valves to control the working pressure and the flow. 7. Reactor and spiralled preheater tube. 8. Fluidized bed with sieve plate used to heat the reactor. 9. Resistance heating. 10. Control and measurement of the pressurized air, coupled with automatic temperature control. 11. Temperature recorder. 12. Precision manometer. 13. Connecting tube between the reactor and the rectification column. 14. Still of the distillation column, sampling stopcock. 15. Distillation column with vacuum jacket. 16. Measurement of the top temperature of the column. 17. Reflux cooler. 18. Drying tower with calcium chloride. 19. Flow meter. 20. Gas meter. 21. Vent.

3. Results

To study the effects of the temperature and the pressure on the rate and the selectivity of the reaction of methyl chloride and a silicon-copper contact mass it is necessary to check whether the properties of the contact mass remain constant throughout a series of experiments, as it has to be expected that the conversion of the silicon from the contact mass will affect the activity and the selectivity of the mass. Therefore, an experiment has been performed to study, at constant conditions, the variation of the properties of a contact mass with increasing conversion of the silicon. The experiment is carried out with a contact mass of Type 3 (Table 2). The results are recorded in Fig. 5 and in Table 3. It appears that after an initial period with increasing reactivity of the alloy the reaction velocity remains about constant. In the latter period the selectivity of the reaction does not alter much either.

TABLE 2
Contact Masses Employed in the Kinetic Study of the Direct Synthesis of Methylchlorosilanes

Type	Solidified in	Employed in expt	Analysis (%)		Size of silicon crystallites (μm)	Activity relative to Type 1
			Cu	Fe		
1	Oil (n.b.w.[a])	B8	9.3	0.5	60–150	1
2	Oil (b.w.[b])	B10	9.3	0.5	60–150	18
3	Sand mold	B11	8.8	0.4	200–400	14
4	Steel, 8 cm	B13 B14	8.0	0.3	200–400	7
5	Steel, 4 cm	B16	8.0	0.3	50–100	21

[a] n.b.w.: This alloy was not washed with benzene prior to grinding.
[b] b.w.: This alloy was washed with benzene prior to grinding.

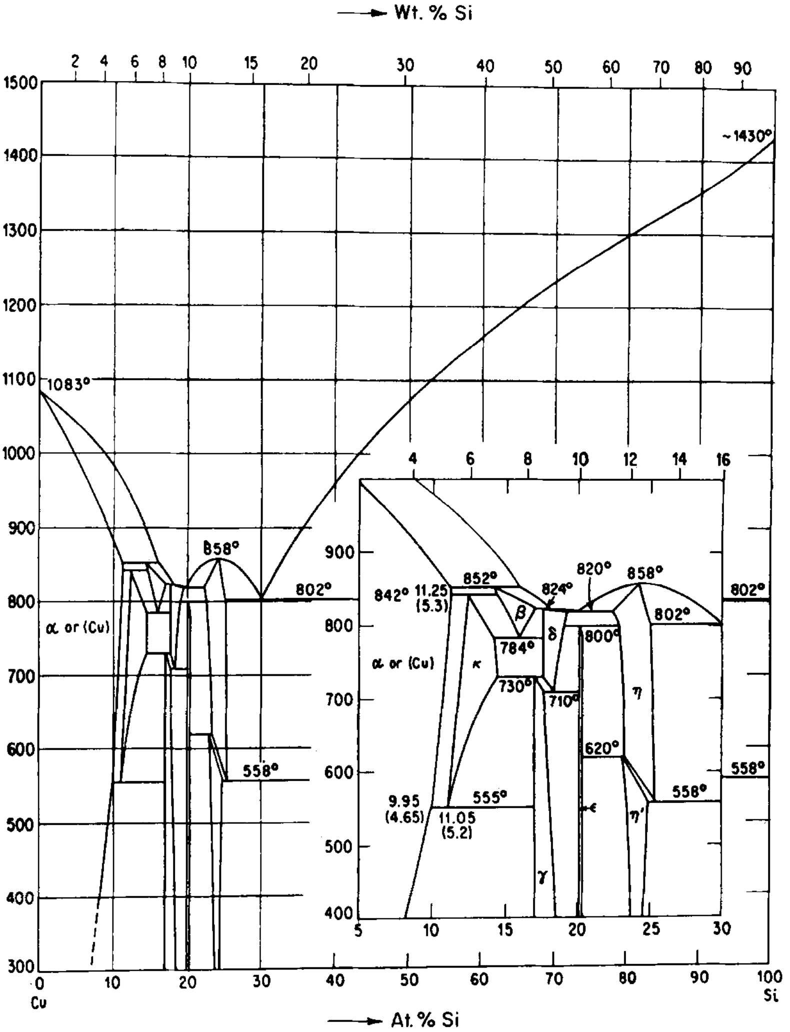

FIG. 3. The binary system Cu–Si according to M. Hansen "The Constitution of Binary Alloys," McGraw Hill, New York, 1958. (Used by permission.)

The selectivity of the process towards the formation of dimethyldichlorosilane is somewhat less than in the fluid-bed performance, which yields an average of 85 wt % dimethyldichlorosilane in the liquid products (*1*). To study the influence of the temperature and the pressure on the reaction parameters the period of constant reaction velocity in Fig. 5 may be employed.

The influence of the temperature of reaction on the rate and the selectivity of the process is studied, employing contact masses of the Types 4 and 5 (Table 2). The pressure is kept constant throughout a series of measurements and is fixed at 4.6 atm and 12.7 atm in experiments B13 and B16, respectively. The results are given in Figs. 6–8 and in Tables 4 and 5. Figures 6 and 8 show that the relation of the reaction rate to the temperature may be expressed by means of an Arrhenius equation for both pressures employed. At 4.6 atm an activation energy of 25.8 kcal/mole is determined, and at 12.7 atm the energy barrier is essentially the same, 25.4 kcal/mole. These values agree reasonably well with that obtained from fluid-bed experiments at atmospheric pressure, which yielded 26.6 kcal/mole (*1*).

FIG. 4. Microphotographs of copper-silicon alloys with about 10% copper. Large silicon-grains (grey) are separated by thin η-phase lamellae (bright): (a) Type 3. (b) Type 4. (c) Type 5. (see Table 2). Magnification: 100×.

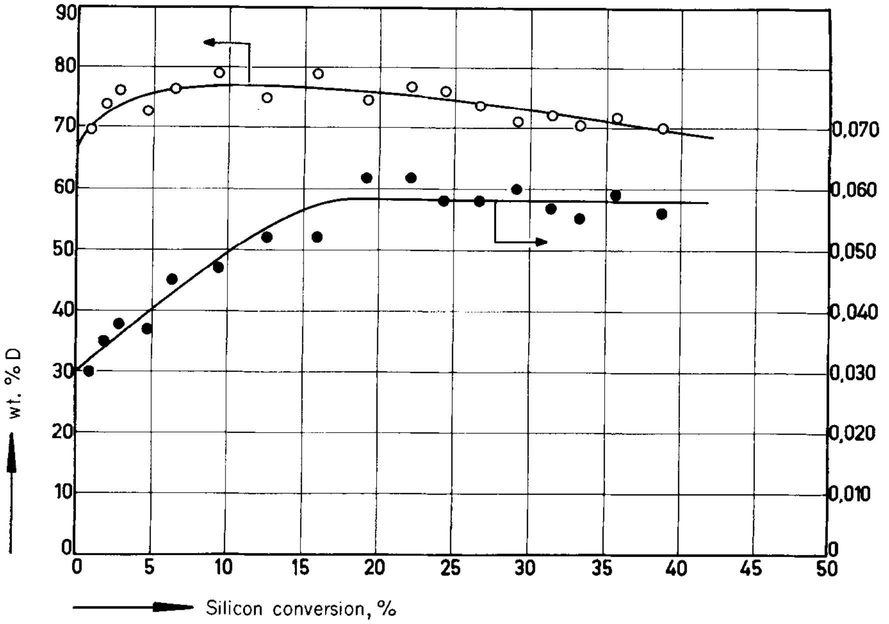

FIG. 5. The variation of the selectivity and the activity of a copper-silicon alloy during conversion in a fixed-bed reactor (B-11). Temp, 300°C; pressure, 2.4 atm; methyl chloride feed rate, 40 g/hr.

TABLE 3

THE CONVERSION OF A COPPER-SILICON ALLOY IN A FIXED-BED REACTOR

Measurement No. B11	Production of silanes (g/hr)	*W* (g Si)	Silicon conversion (%)	Reaction rate, $\left(\frac{\text{g } CH_3Cl}{\text{g Si·hr}}\right)$	Composition of the products (wt %)[a]				
					D	T	M	DH	Q + TH
1	1.50	39.6	1.0	0.030	69.7	16.0	2.3	7.8	3.2
2	1.76	39.2	1.9	0.035	73.8	12.2	1.9	8.0	4.4
3	1.88	38.9	2.8	0.038	76.2	11.0	1.8	7.7	3.3
4	1.82	38.4	4.6	0.037	72.6	10.1	2.6	10.9	3.8
5	2.15	37.6	6.5	0.045	76.4	9.7	2.3	8.8	2.5
6	2.22	36.7	9.4	0.047	79.0	8.0	1.5	8.9	2.6
7	2.38	35.4	12.6	0.052	74.8	7.7	1.3	13.2	3.0
8	2.30	34.1	15.9	0.052	79.0	6.9	1.4	11.5	1.2
9	2.60	32.8	19.3	0.062	74.6	8.6	1.4	14.4	1.0
10	2.50	31.6	22.1	0.062	76.8	9.3	1.4	11.2	1.3
11	2.28	30.6	24.4	0.058	76.2	8.3	1.5	13.4	0.6
12	2.25	30.1	26.8	0.058	73.6	9.2	1.6	13.2	2.4
13	2.22	29.1	29.2	0.060	70.9	8.9	1.6	15.8	2.8
14	2.05	28.2	31.5	0.057	71.8	10.1	1.5	14.1	2.5
15	1.94	27.4	33.4	0.055	70.2	9.5	1.3	16.0	3.0
16	2.01	26.5	35.8	0.059	71.6	10.5	1.4	14.2	2.3
17	1.85	25.6	38.8	0.056	69.9	8.7	1.6	17.1	2.7

[a] D, dimethyldichlorosilane; T, methyltrichlorosilane; M, trimethylchlorosilane; DH, methyldichlorosilane; TH, trichlorosilane; Q, tetrachlorosilane.

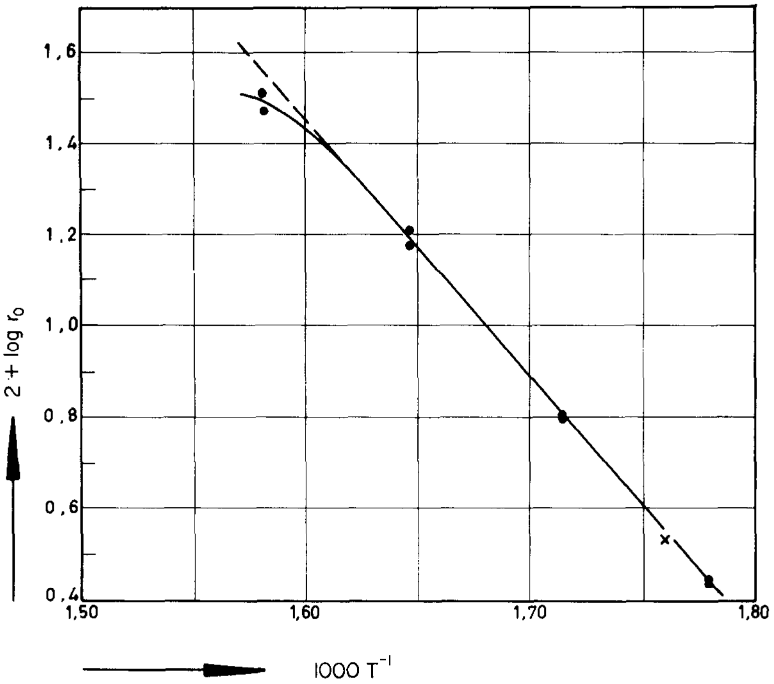

FIG. 6. Arrhenius graph for the reaction of methyl chloride and silicon-copper at 4.6 atm. Values from Table 4; ×, value from Fig. 9.

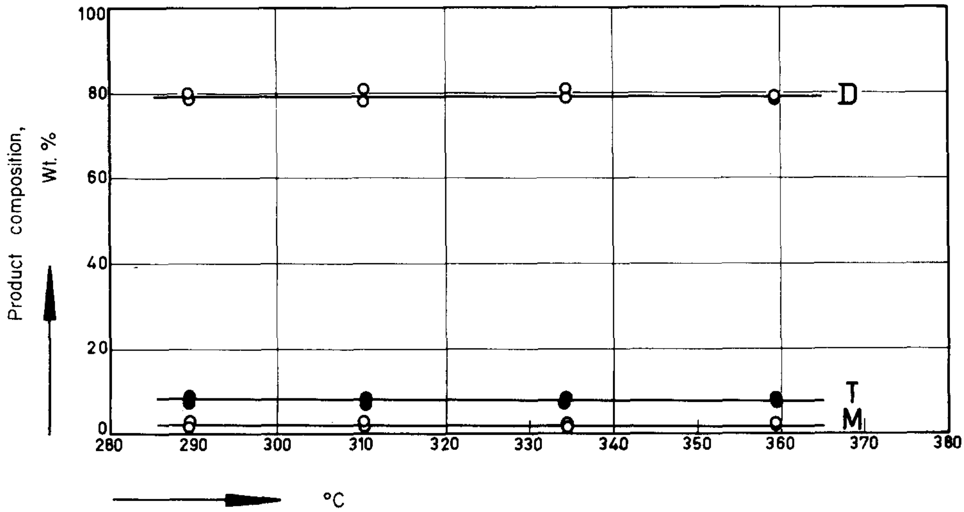

FIG. 7. The dependence of the composition of the products on the temperature at 4.6 atm; fixed-bed reactor. See Table 4.

The selectivity of the reaction is found to be hardly influenced by the temperature in the temperature range studied (Fig. 7 and Tables 4 and 5). These findings confirm the results of the fluid-bed experiments cited above.

The effect of the pressure on the reaction parameters is studied with a contact mass of Type 4 (Table 2). The temperature is kept constant at 295°C. Pressures up to 26 atm have been applied. Correlation of the resulting data, collected in Table 6, turned out

TABLE 4

THE TEMPERATURE DEPENDENCE OF THE REACTION OF METHYL CHLORIDE AND A SILICON-COPPER ALLOY IN A FIXED-BED REACTOR AT 4.6 ATM[a]

Expt. No.	Temp (°C)	W (g Si)	Silicon conversion (%)	CH_3Cl conversion (%)	Production of silanes, (g/hr)	r_0 $\left(\frac{\text{g } CH_3Cl}{\text{g Si·hr}}\right)$	Composition of the products[b] (wt %) D	T	M	DH	Q	TH
B13–1	359	59.7	10.7	8.4	22.1	0.296	78.2	7.8	2.0	9.7	1.9	0.4
2	359	58.4	12.6	9.2	23.7	0.324	77.8	7.9	1.9	9.7	2.4	0.3
3	334	54.0	19.3	4.0	10.3	0.150	78.6	7.7	2.4	7.6	2.8	0.9
4	334	52.7	21.2	4.6	10.8	0.162	80.7	7.2	1.8	7.6	2.2	0.5
5	310	51.0	23.7	1.8	4.08	0.063	78.7	7.9	3.0	6.5	2.5	1.4
6	310	50.6	24.3	2.1	4.14	0.064	80.3	7.9	2.9	5.8	2.1	1.0
7	289	50.0	25.3	0.7	1.78	0.028	78.0	8.6	3.1	4.8	2.4	3.1
8	289	49.6	25.9	0.8	1.72	0.027	80.1	9.1	2.6	4.2	1.8	2.2

[a] The initial weight of the silicon was 66.9 g. The particle sizes ranged from 420 to 500 μm. Pressure 4.6 atm. Methyl chloride feed rate about 200 g/hr. Prior to the experiments the contact mass was converted for about 10% at 4.6 atm and 330°C.

[b] See Footnote *a*, Table 3.

TABLE 5

THE TEMPERATURE DEPENDENCE OF THE REACTION OF METHYL CHLORIDE AND A SILICON-COPPER ALLOY IN A FIXED-BED REACTOR AT 12.7 ATM[a]

Expt. no.	Temp (°C)	W (g Si)	Silicon conversion (%)	Production of silanes (g/hr)	r_0 $\left(\frac{\text{g } CH_3Cl}{\text{g Si·hr}}\right)$	Composition of the products[b] (wt %) D	T	M	DH	Q	TH
B16-1	338	35.6	22.4	36.5	0.787	76.1	17.4	2.4	2.8	—	1.0
2	288	32.4	29.2	5.12	0.122	75.8	10.9	3.5	6.9	0.6	2.2
3	304	31.0	32.3	10.7	0.267	77.6	10.1	2.3	7.5	0.5	1.8
4	330	28.0	38.6	24.0	0.668	72.3	18.0	1.9	6.6	0.4	0.9

[a] The initial weight of the silicon was 45.7 g. The particle sizes ranged from 420 to 500 μm. Pressure 12.7 atm. Prior to the experiments the contact mass was converted for about 18%.

[b] See Footnote *a*, Table 3.

to be impossible by means of a simple first order rate equation. A satisfactory correlation of the results is obtained by employing the Eq. (5), used earlier by Bažant and co-workers in the interpretation of their kinetic results. From Eq. (5) the constants k and K_A were determined to be 1.60 g CH_3Cl/g Si·hr and 0.0065 atm^{-1}, respectively. With the aid of these values Eq. (5) is plotted in Fig. 9. The points in the figure represent the experimental values of Table 6. Judged from the figure the experimental points fit satisfactorily with the theoretical line, although at higher pressure some scatter of the experimental points is observed. The relation of the composition of the products to the operating pressure is given in Table 6. The variation of the selectivity with the pressure is only slight,

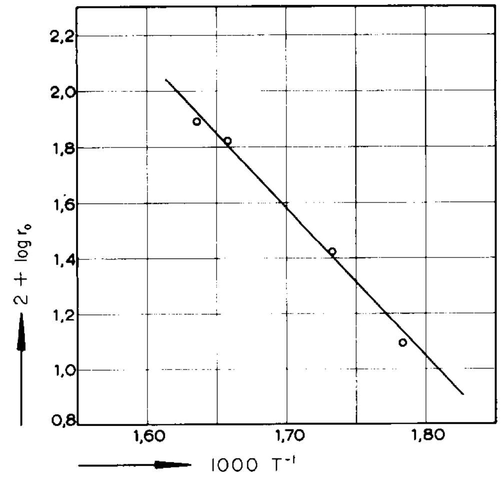

FIG. 8. Arrhenius graph for the reaction of methyl chloride and silicon-copper at 12.7 atm. See Table 5.

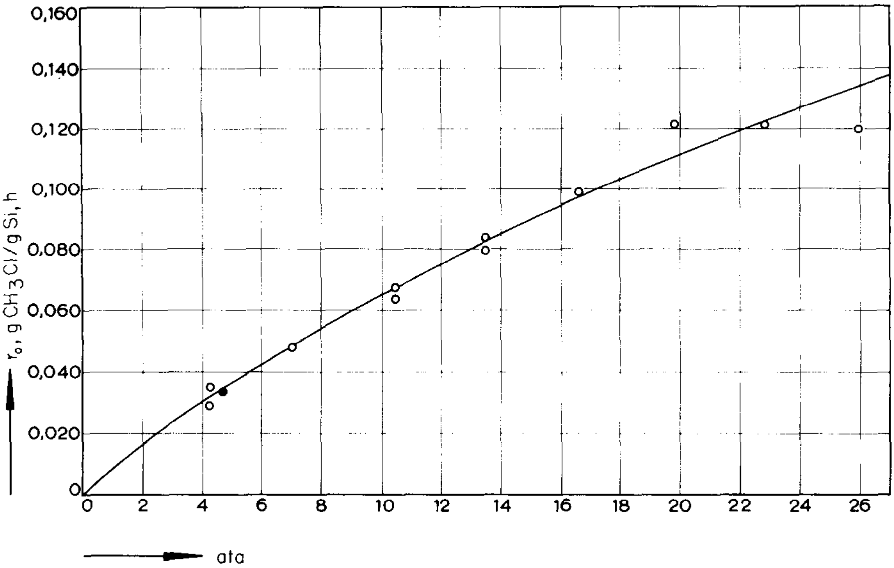

FIG. 9. The relation of the pressure and the initial reaction velocity. The curve has been calculated by Eq. (5). The experimental points have been taken from Table 6; ●, point from Fig. 6.

indicating a small drop in selectivity with rising pressure.

To estimate the third term in the denominator of expression (4), which is the term determined by the adsorption of the products on the surface of the contact mass, it is necessary to work with a measurable pressure of silanes. However, when a measurable partial pressure of silanes is maintained, the problem arises how to determine the small amounts of fresh silanes, produced in the differential reactor, in the presence of the large amounts of silanes which are introduced to maintain the desired partial

TABLE 6

THE PRESSURE DEPENDENCE OF THE REACTION[a]

Expt. no.	Pressure (atm)	W (g Si)	Silicon conversion (%)	Production of silanes (g/hr)	r_0 $\left(\frac{\text{g CH}_3\text{Cl}}{\text{g Si·hr}}\right)$	Composition of the products[b] (wt %)					
						D	T	M	DH	Q	TH
B14–1	25.9	59.0	13.8	9.00	0.120	78.2	12.5	2.8	4.2	1.4	0.6
2	22.8	56.8	17.0	8.80	0.121	75.2	11.4	3.1	7.9	1.6	0.4
3	19.8	53.9	21.7	8.24	0.120	75.2	10.5	2.4	8.1	3.0	0.8
4	16.6	51.2	24.0	6.57	0.099	76.0	9.7	2.6	7.8	3.0	0.8
5	13.5	50.9	25.8	5.48	0.084	75.4	8.5	2.5	8.7	3.5	1.4
6	13.5	50.3	26.6	5.04	0.079	77.8	9.0	2.2	7.4	2.5	1.1
7	10.4	49.5	27.6	4.02	0.064	79.6	8.3	2.3	6.3	2.5	1.2
8	10.4	49.2	28.0	4.29	0.068	80.5	8.6	2.4	5.4	3.4	0.8
9	7.0	48.8	28.7	2.96	0.048	80.5	8.5	1.9	3.5	3.1	2.5
10	4.2	48.4	29.2	2.18	0.035	81.6	7.8	1.8	3.6	3.2	2.1
11	4.2	48.2	29.5	1.76	0.029	83.4	8.1	1.5	3.7	2.0	2.3

[a] Initial weight of the silicon 68.2 g. The particle sizes ranged from 420 to 500 μm. Prior to the measurements the silicon was converted for about 12%. Methyl chloride feed rate about 200 g/hr. Methyl chloride conversion less than 3% Temp, 295°C.

[b] See Footnote *a*, Table 3.

pressure of the products in the reactor.* An integral reactor is far more suitable for this type of measurements.

4. Discussion

The contact masses used in the experiments described in this paper, differed in the way they were prepared. Consequently the structural characteristics of the alloys, and namely the sizes of the silicon crystallites, varied.

As the contact masses were used under variable conditions, it is not possible to compare their activities in the synthesis of methylchlorosilanes directly. To allow such a comparison the reaction rates at arbitrarily chosen standard conditions of temperature and pressure are calculated approximately. The conditions chosen are 320°C and 12 atm. In the calculation the temperature dependence of the reaction rate, being characterized by the activation energy of 25.8 kcal/mole, is used. The influence of the pressure is accounted for by the use of the relation visualized in Fig. 9.

In Table 2 the reaction rates of the various contact masses are given, relative to the activity of the first type of alloy. Obviously, alloys prepared by rapidly cooling a copper-silicon melt show the highest activity. These alloys show small silicon crystallites (60–150 μm). Two methods to effect this rapid cooling are solidification in small diameter steel molds, or pelleting the melt while pouring it out into a cooling oil. By the latter method a residue of oil and coke sticks to the contact-mass particles. This has to be withdrawn to prevent a nearly twentyfold reduction of the activity (compare alloys of Types 1 and 2).

The influence of the temperature on the course of the reaction of methyl chloride and copper-silicon alloys, in the fixed-bed reactor employed, is evidently very small in the temperature range studied. The same fact resulted from work in fluid-bed and stirred-bed reactors (*1*, *14*). Most fixed-bed experiments recorded earlier showed a remarkable influence of the temperature on the composition of the products (*16*, *17*). The diverging experiences may be explained by the differing heat transfer velocities of the various reactor types.

Reactors with small heat transfer coefficients (e.g., normal fixed-bed reactors) will easily give rise to hot spots, the composition of the products consequently being highly dependent on the temperature. Reactors with high heat transfer coefficients (e.g., stirred-bed and fluid-bed reactors and very small diameter fixed beds with high gas velocities) do not contain hot spots and yield products with an approximately temperature-independent composition.

The insensitivity of the product composition to variations of the temperature, the pressure, and the preparation method of the contact mass, which is shown in the present paper, leads to the supposition that the high selectivity and the constant composition of the products are intrinsic properties of the contact mass, dependent on the composition of the contact mass only. In this respect it is interesting to note that the main active compound in all mentioned copper-silicon masses is the η phase ($\sim Cu_3Si$) of the binary copper-silicon system. It is also noteworthy, that copper-silicon contact masses consisting entirely of the more copper-rich ϵ phase ($\sim Cu_{15}Si_4$) yielded silane products with about the same composition as the η phase (*2*).

However, the detection of any significant difference in the composition of the products from the two types of alloys is hindered because the ϵ phase is not stable in the presence of free silicon. The latter fact implies that it is not possible, as in the case

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* It was attempted to analyze the effluent from the reactor by labeling the methyl chloride feed, rectifying the effluent to separate methyl chloride from the silanes, and measuring the amount of radioactive chlorosilanes in the mixture of silanes collected in the still. Tritium or C^{14} could be used to label methyl chloride, but their radiation is so weak that it has to be measured by liquid scintillation counting methods. However, most known scintillation compounds reacted with dimethyldichlorosilane. For this reason, Cl^{36} was used to label the methyl chloride. However, chlorine exchange between dimethyldichlorosilane and methyl chloride happened in the reactor, according to the following equation: $CH_3Cl^* + (CH_3)_2SiCl_2 \rightarrow CH_3Cl + (CH_3)_2ClCl^*$. This prevents the outlined measuring method from succeeding.

of the η phase, to contact methyl chloride with an ε-phase–silicon mixture. Hence, silicon reacting from the ε phase cannot be resupplied and the ε phase decomposes rapidly during reaction with methyl chloride.

The probability that the constant composition of the silane products is an intrinsic property of the η phase (which is shown in the range of 280° to 350°C) is important in the elucidation of the mechanism of the synthesis of methylchlorosilanes, as will be shown later (*18*).

The relation of the initial reaction velocity and the methyl chloride pressure, shown in Fig. 9, which is measured in the differential reactor, indicates that the interpretation by Czechoslovakian authors (*12*, *14*) of the kinetic data resulting from work in a batch reactor and in an integral reactor device is substantiated by the present results. The relations, presented by the above-cited authors, and those shown in Fig. 9, indicate that the reaction of methyl chloride and silicon-copper may be regarded as a heterogeneous catalytic reaction in which the reactants (and according to the cited authors also the products) are adsorbed on the surface, using two active centers. The surface reaction is the rate-limiting step. Other imaginable kinetic mechanisms (*9*) do not agree with the experimental data.

5. CONCLUSIONS

From the results and discussions presented above the following may be concluded:

(a) The reaction velocity of the reaction of methyl chloride and silicon-copper alloys is substantially influenced by the method of preparation of the alloy. Rapid cooling of the melt, by the resulting small silicon particles, tends to produce highly active contact masses. The composition of the products is not related to the reactivity in a series of alloys with the same chemical composition.

(b) Pressure and temperature do not influence the composition of the silane products in the ranges of 1 to 26 atm and 280° to 360°C. This indicates that the high selectivity of the reaction is an intrinsic property of the silicon-copper alloys.

(c) The relation of the reaction velocity and the methyl chloride pressure is in accordance with the view of Joklík *et al.* that the synthesis of methylchlorosilanes may be regarded as a heterogeneous catalytic reaction, the reaction rate being limited by the velocity of the chemical process in the chemisorbed layer. Methyl chloride is adsorbed on two active centers of the surface.

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