# THEORETICAL AND EXPERIMENTAL STUDY OF CHEMICAL EQUILIBRIUM IN THE SYSTEMS Si–Cl AND Si–Cl–H. CALCULATION OF CHEMICAL EQUILIBRIUM IN THE SYSTEMS Si–Cl AND Si–Cl–H

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*Dedicated to late Academician Eduard Hála.*

From the calculations of heterogeneous chemical equilibria in the systems Si–Cl and Si–Cl–H the equilibrium composition of the gas phase and the amount of deposited or reacted solid silicon have been determined. For these calculations, the method based on the minimization of the Gibbs energy of the system and critically judged and selected values of input thermodynamic data have been used. The calculations have been performed for the temperature range 1 000—1 600 K, for the pressure 101·325 kPa and 10·133 kPa and for various input compositions of the gaseous phase. In the case of the system Si–Cl, the reaction of solid leading to the formation of silicon subchlorides takes place at all conditions investigated. At atmospheric pressure and at temperatures in the neighbourhood of 1 300 K, the dominant components of the gas phase are the following substances: $SiCl_4$, $SiCl_3$ and $SiCl_2$. The dependence of the amount of deposited solid silicon on temperature and on the initial composition of the gas phase in the system Si–Cl–H shows — in the investigated range of variables — a maximum, the position of which depends on the total pressure of the system. At atmospheric pressure, at temperatures around 1 300 K and at the initial molar ratio $Cl/H = 0·01$, the dominant components of the gas phase are the following substances: $SiCl_4$, $SiCl_3$, $SiCl_2$, $SiHCl_3$, $SiH_2Cl_2$ and HCl. The substance SiHCl which has been included into the equilibrium calculations for the first time, is present in a significant amount at higher temperatures and especially at lowered pressure.

Silicon belongs to the most important materials processed in the electrotechnical industry where it is used both as single crystal and in the form of thin surface layers which are either monocrystalline, polycrystalline or amorphous. The production of a very pure polycrystalline silicon which serves for single-crystal pulling as well as the preparation of silicon layers starts from various chlorosilanes (most frequently from $SiHCl_3$ or $SiCl_4$) which at temperatures above 1 200 K are reduced by hydrogen to elementary silicon. For the determination of the optimum techno-

logical conditions of these processes, it is necessary to know a lot of informations, the data on equilibrium composition of the respective system being among them.

A great attention has been paid to the calculation of chemical equilibrium especially in the system Si–Cl–H and the results of these calculations were published by several authors[1–9]. The various papers differ among themselves by different initial conditions for which the calculations have been performed, by the number of gaseous substances taken into account, and, first of all, by the values of the input thermodynamic quantities used. This paper is devoted to the calculation of the equilibrium composition of the Si–Cl–H system for such conditions which are for the most part used for the deposition of silicon, and further of the Si–Cl system; this system has been studied in order to get some information on the influence of the change of the input thermodynamic quantities on the calculated equilibrium composition and to get the possibility of comparing the calculated results with those obtained experimentally. For these calculations, a set of critically selected and internally consistent values of the input thermodynamic functions has been used and in the case of the Si–Cl–H system, some of the gaseous substances which were omitted in the previous studies have been taken into account.

CALCULATIONS

For the calculation of chemical equilibrium, the modified White–Johnson–Dantzig method[10,11] based on the Gibbs-energy-minimization of the system has been used. It has been assumed that in equilibrium the system contains solid silicon and the gaseous phase is formed by eight components in the case of the Si–Cl system ($SiCl_4$, $SiCl_3$, $SiCl_2$, $SiCl$, $Si_2Cl_6$, $Cl_2$, $Cl$ and $Si$) and by 19 components in the case of the Si–Cl–H system ($SiCl_4$, $SiCl_3$, $SiCl_2$, $SiCl$, $Si_2Cl_6$, $SiH_4$, $SiH_3$, $SiH_2$, $SiH$, $SiH_3Cl$, $SiH_2Cl_2$, $SiHCl_3$, $SiHCl$, $H_2$, $H$, $Cl_2$, $Cl$, $HCl$ and $Si$). The gaseous phase was taken as an ideal mixture of ideal gases in all these calculations and this is a very good approximation to the actual state under conditions given (temperature 1 000 to 1 600 K and atmospheric pressure or lower).

We used standard heats of formation $\Delta H_f^\circ(298\ K)$ and the $G$-functions, i.e. $[G^\circ(T) - H^\circ(298\ K)]/T$ as input thermodynamic properties. In Table I, the values of the heats of formation of gaseous silicon-containing substances, taken from different sources in the literature and used in our equilibrium calculations, are given. From this survey it is obvious that for some substances the values recommended differ significantly among themselves; the use of a set of such data can — in some instances — lead to an equilibrium composition of the system under investigation which is quite different from that obtained starting with another set. Therefore, the choice of a consistent set of values of $\Delta H_f^\circ(298\ K)$ has been made with great care[12]; the values critically judged and selected and used in our calculations are summarized in Table II. The values of the $G$-functions given by different authors do not differ

TABLE I

Values of $\Delta H_f^o$(g, 298 K) of selected gaseous substances in the system Si–Cl–H taken from various sources (kJ mol$^{-1}$)

| Substance | Hunt and Sirtl[1] (1972) | Farber and Sri-vastava[13,14] (1977, 1979) | Wolf and Teich-mann[15] (1980) | Rusin et al.[16–18a] (1979) |
|---|---|---|---|---|
| $SiCl_4$ | −655·63 | (−662·75 ± 1·26)$^b$ | −659·82 ± 6·69 | (−657·34)$^b$ |
| $SiCl_3$ | −326·35 | −390·37 ± 2·09 | | −390·38 + 15·06 |
| $SiCl_2$ | −159·83 | −169·87 ± 2·51 | −162·31 | −162·21 ± 14·23 |
| SiCl | 191·21 | 197·07 ± 2·51 | | 80·74 ± 7·53 |
| $Si_2Cl_6$ | −987·42 | | | |
| $SiH_4$ | 30·54 | | | |
| $SiH_3$ | | | | |
| $SiH_2$ | | | | |
| SiH | | | | |
| $SiH_3Cl$ | −142·26 | −135·6 ± 10·5 | | |
| $SiH_2Cl_2$ | −313·80 | −315·1 ± 8·4 | | |
| $SiHCl_3$ | −489·11 | −499·2 ± 6·3 | −497·06 ± 5·86 | |
| SiHCl | | | | |

| Substance | Walsh[19] (1983) | JANAF[20] (1974—1982) | Barin et al.[21,22] (1973, 1977) | Glushko[23] (1979) |
|---|---|---|---|---|
| $SiCl_4$ | −662·74 ± 5·44 | −662·75 ± 1·26 | −657·3$^c$ | −662·20 ± 0·80 |
| $SiCl_3$ | −334·72 ± 8·34 | −390·37 ± 16·74 | −401·5 | −396·3 ± 10·0 |
| $SiCl_2$ | −168·62 ± 3·35 | −168·62 ± 3·35 | −157·5 | −163·1 ± 4·2 |
| SiCl | 154·81 ± 41·84 | 198·32 ± 6·69 | 191·1 | 142·4 ± 41·8 |
| $Si_2Cl_6$ | | | | |
| $SiH_4$ | | 34·31 ± 2·09 | 30·5 | 34·7 ± 1·5 |
| $SiH_3$ | | | | 209·4 ± 15·0 |
| $SiH_2$ | | | | 245·4 ± 15·0 |
| SiH | | 376·56 ± 8·37 | 348·4 | 368·6 ± 8·0 |
| $SiH_3Cl$ | −133·56 ± 10·46 | −141·84 ± 8·4 | | |
| $SiH_2Cl_2$ | −315·06 ± 8·34 | −320·49 ± 12·55 | | |
| $SiHCl_3$ | −499·15 ± 6·69 | −496·22 ± 4·18 | | |
| SiHCl | | | | 40·9 ± 17·0 |

$^a$ In the cited paper, the value of $\Delta H_f^o$ is given for the temperature 0 K. For the calculation of $\Delta H_f^o$ (298 K), the values of $H_{298}^o - H_0^o$ of the respective substances taken from the tables[22] have been used. $^b$ The value given in parentheses has been used for the calculation of all other data given. $^c$ In the cited monograph, the value $\Delta H_f^o$ ($SiCl_4$, l, 298 K) is given. To recalculate it to the gaseous state, the value $\Delta H_{vap}$ ($SiCl_4$, 298 K) = 30·33 kJ mol$^{-1}$ taken from the tables[20] has been used.

significantly among themselves; the values chosen for our equilibrium calculations are given in Table III.

## RESULTS AND DISCUSSION

### The System Si–Cl

The equilibrium calculations in the system Si–Cl have been made for the temperature range 1 000 – 1 600 K, for the pressures 101·325 kPa and 10·133 kPa and for various input compositions of the gaseous phase. For the sake of comparison of calculated and experimental results, the inert gas has been included in some of these calculations. In order to get to know the influence of the variation of input thermodynamic data on calculated equilibrium composition, some of these calculations have been carried out for different values of the heats of formation of selected substances. The respective sets of the values of $\Delta H_f^0(298\ K)$ are given in Table IV. The calculated results are summarized in Table V and shown graphically in Fig. 1.

TABLE II

Values of $\Delta H_f^0$ (g, 298 K) (kJ mol$^{-1}$) of the substances in the system Si–Cl–H selected for the calculations of chemical equilibrium

| Substance | $\Delta H_f^0$ (g, 298 K) kJ mol$^{-1}$ | Ref. |
|---|---|---|
| SiCl$_4$ | −662·75 | 20 |
| SiCl$_3$ | −390·37 | 13, 20 |
| SiCl$_2$ | −168·62 | 20 |
| SiCl | 198·32 | 13, 20 |
| Si$_2$Cl$_6$ | −987·4 | 1 |
| SiH$_4$ | 34·31 | 20, 23 |
| SiH$_3$ | 209·36 | 23 |
| SiH$_2$ | 245·33 | 23 |
| SiH | 376·56 | 20 |
| SiHCl$_3$ | −499·2 | 14, 19 |
| SiH$_2$Cl$_2$ | −315·1 | 14, 19 |
| SiH$_3$Cl | −135·6 | 14, 19 |
| SiHCl | 40·95 | 23 |
| Si | 450·62 | 20 |
| H | 218·00 | 20 |
| Cl | 121·29 | 20 |
| HCl | −92·13 | 20 |

TABLE III

Values of $G$-functions, $-[G°(T) - H°(298 \text{ K})]/T$ (J mol$^{-1}$ K$^{-1}$) of substances in the system Si–Cl–H for the temperature range 1 000 to 1 600 K

| Substance | Ref. | Temperature, K | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 000 | 1 100 | 1 200 | 1 300 | 1 400 | 1 500 | 1 600 |
| Si(s) | 20 | 30·388 | 32·045 | 33·627 | 35·141 | 36·593 | 37·982 | 39·137 |
| Si(g) | 20 | 178·799 | 180·247 | 181·611 | 182·904 | 184·125 | 185·284 | 186·389 |
| SiCl$_4$(g) | 20 | 380·828 | 387·639 | 394·396 | 400·672 | 406·639 | 412·321 | 417·739 |
| SiCl$_3$(g) | 20 | 356·941 | 362·330 | 367·443 | 372·297 | 376·911 | 381·300 | 385·489 |
| SiCl$_2$(g) | 20 | 308·921 | 312·733 | 316·348 | 319·779 | 323·034 | 326·134 | 329·084 |
| SiCl(g) | 20 | 256·341 | 258·868 | 261·262 | 263·529 | 265·680 | 267·726 | 269·671 |
| Si$_2$Cl$_6$(g) | 1 | 503·482 | 514·937 | 525·836 | 536·201 | 546·080 | 555·501 | 564·497 |
| SiH$_4$(g) | 20 | 233·501 | 238·157 | 242·701 | 247·124 | 251·421 | 255·592 | 259·642 |
| SiH$_3$(g) | 23 | 241·011 | 244·881 | 248·656 | 252·266 | 255·776 | 259·170 | 262·458 |
| SiH$_2$(g) | 23 | 229·266 | 232·614 | 235·835 | 238·932 | 241·902 | 244·756 | 247·492 |
| SiH(g) | 20 | 213·505 | 215·677 | 217·748 | 219·723 | 221·652 | 223·421 | 225·154 |
| SiHCl$_3$(g) | 20 | 357·540 | 363·857 | 369·887 | 375·648 | 381·150 | 386·409 | 391·447 |
| SiH$_2$Cl$_2$(g) | 20 | 324·938 | 330·653 | 336·143 | 341·414 | 346·481 | 351·347 | 356·029 |
| SiH$_3$Cl(g) | 20 | 283·922 | 289·073 | 294·064 | 298·888 | 303·549 | 308·047 | 312·394 |
| SiHCl(g) | 23 | 274·403 | 277·734 | 280·914 | 283·951 | 286·859 | 289·642 | 292·303 |
| HCl(g) | 20 | 201·752 | 203·807 | 205·671 | 207·627 | 209·405 | 211·108 | 212·744 |
| H$_2$(g) | 20 | 145·427 | 147·440 | 149·348 | 151·164 | 152·892 | 154·549 | 156·122 |
| H(g) | 20 | 125·173 | 126·591 | 127·930 | 129·194 | 130·394 | 131·532 | 132·616 |
| Cl$_2$(g) | 20 | 241·095 | 243·584 | 245·944 | 248·187 | 250·312 | 252·337 | 254·266 |
| Cl(g) | 20 | 176·502 | 178·038 | 179·485 | 180·849 | 182·142 | 183·364 | 184·523 |

The results of these calculations of chemical equilibrium in the system Si–Cl lead to the following conclusions:

*1.* The change of the input values of $\Delta H_f^o(298\ K)$ exerts a great influence upon the calculated equilibrium composition, especially upon the equilibrium concentrations of the substances whose heat of formation has been changed. The lowering of the value of $\Delta H_f^o(298\ K)$ corresponds to an increase of the thermodynamic stability of the respective substance and, therefore, leads to the increase of its content in the equilibrium gaseous mixture.

*2.* In the absence of an inert in the gas phase and at a pressure of 101·325 kPa, the chemical reaction between $SiCl_4$ and solid silicon does not start before reaching

TABLE IV

Various sets of the values of $\Delta H_f^o$ (g, 298 K) (kJ mol$^{-1}$) used for the calculation of chemical equilibrium in the system Si–Cl

| | Variant no. | | | |
| --- | --- | --- | --- | --- |
| Substance | 1 Our choice | 2 Glushko[23] | 3 Rusin[18] | 4 Walsh[19] |
| $SiCl_4$ | − 662·75 | − 662·20 | − 659·43 | − 662·75 |
| $SiCl_3$ | − 390·37 | − 396·27 | − 387·03 | − 334·72 |
| $SiCl_2$ | − 168·62 | − 163·07 | − 162·21 | − 168·62 |
| SiCl | 198·32 | 142·37 | 80·74 | 154·81 |

TABLE V

Temperature dependence of the amount of reacted silicon in the system Si–Cl for various values of $\Delta H_f^o$ (298 K) used in the calculations (see Table IV); $p = 101·325$ kPa, $n_{SiCl_4}^o = 1$ mol, solid silicon in excess

| | Variant no. | | | |
| --- | --- | --- | --- | --- |
| $T$, K | 1 | 2 | 3 | 4 |
| 1 000 | 0·0030 | 0·0052 | 0·0026 | 0·0006 |
| 1 200 | 0·0251 | 0·0307 | 0·0203 | 0·0105 |
| 1 400 | 0·1298 | 0·1178 | 0·1087 | 0·0834 |
| 1 600 | 0·4109 | 0·3188 | 0·4365 | 0·3631 |
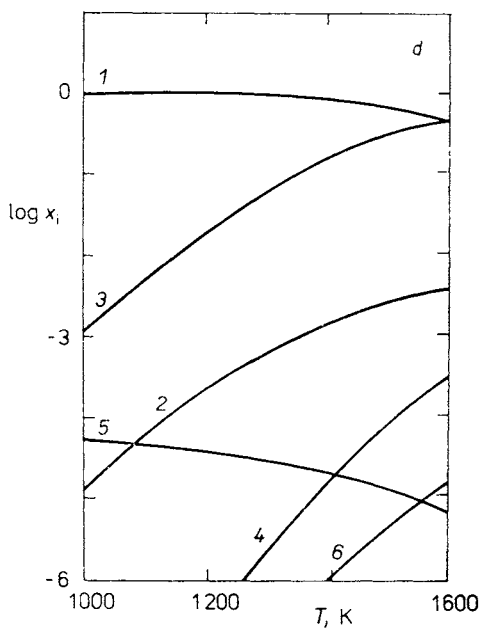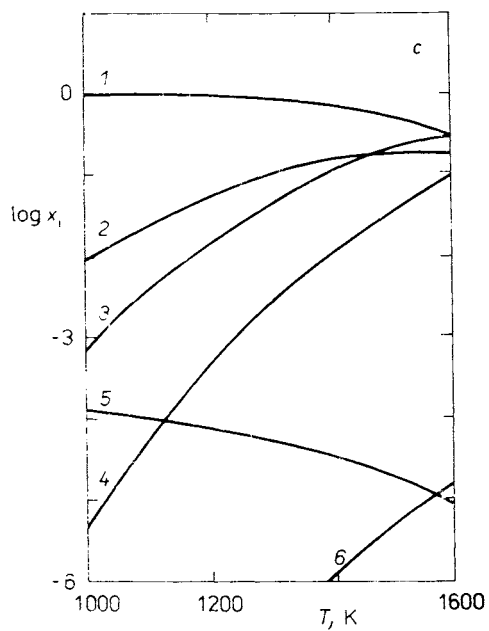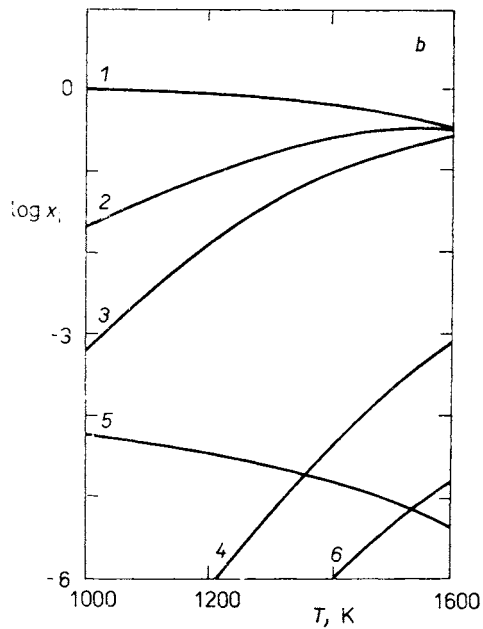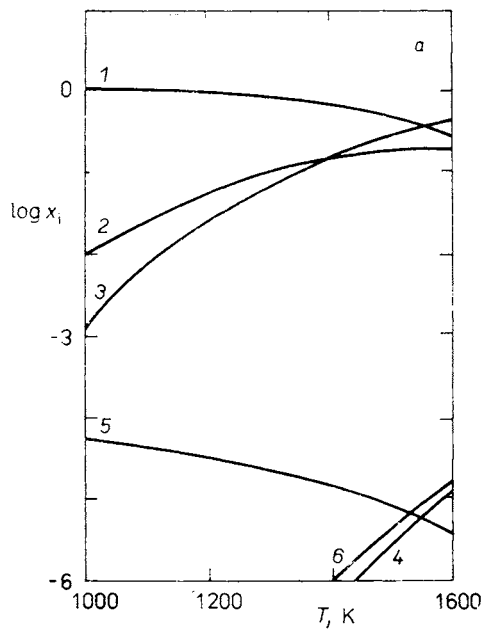
a temperature higher than 1 200 K. The addition of an inert substance or a lowering of the total pressure brings forth the lowering of this temperature threshold.

*3.* At all experimental conditions, the gas phase etches solid silicon and the loss of the solid increases with the rise of temperature, with the decrease of pressure and with the growing amount of the inert added.

*4.* The concentrations of $Si_2Cl_6$, Cl and Si in the equilibrium gaseous phase can be neglected at all investigated conditions. The dominant components at equilibrium are $SiCl_4$, $SiCl_3$ and $SiCl_2$, and their relative amounts vary with temperature, pressure and with the amount of inert added.

For the comparison of these calculations with experiments, the data given by Ban[24] (see Table VI) and by Farber and Srivastava[13] (see Table VII) are available; in both cases, these data were evaluated from mass-spectroscopic measurements.

The equilibrium concentrations of $SiCl_4$ and of $SiCl_2$ found by Ban[24] are in a good agreement with the values calculated on the basis of our choice of the set of $\Delta H_f^o(298\ K)$ values. However, the presence of $SiCl_3$ was not experimentally proved in the cited paper[24], although our calculations lead to an equilibrium concentration of $SiCl_3$ comparable to that of $SiCl_4$ and of $SiCl_2$. Taking for granted that the values of the input thermodynamic properties of $SiCl_3$ – especially of $\Delta H_f^o(SiCl_3,\ g,\ 298\ K)$ – used in the equilibrium calculations are correct, the disagreement can be explained by further chemical reactions taking place during the time interval between the sampling of the gaseous phase in the reactor and the analysis of the sample in the mass spectrometer: the drop in pressure and temperature causes the change of $SiCl_3$ to more stable substances $SiCl_4$ and $SiCl_2$.

The agreement of the experimental results of Farber and Srivastava[13] with our calculations is very good; this is, of course, caused mainly by the selection of input thermodynamic properties: the values of $\Delta H_f^o(298\ K)$ of the dominant substances have namely been derived from the experimental results of the paper cited.

## The System Si–Cl–H

The equilibrium calculations of the system Si–Cl–H have been made for the temperature range 1 000 – 1 600 K, for the pressures 101·325 kPa and 10·133 kPa and various input compositions of the gaseous phase. For the sake of comparison of calculated and experimental results (se the 2nd part of this communication), the inert gas was

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FIG. 1

Temperature dependence of the equilibrium composition of the gaseous phase in the Si–Cl system for various values of $\Delta H_f^o$ (298 K) used in the calculations; $p = 101\cdot325$ kPa, $n_{SiCl_4}^0 =$ = 1 mol, solid Si in excess; *1* $SiCl_4$, *2* $SiCl_3$, *3* $SiCl_2$, *4* SiCl, *5* $Si_2Cl_6$, *6* Cl; *a* $\Delta H_f^o$ — variant no. 1 (Table IV), *b* $\Delta H_f^o$ — variant no. 2, *c* $\Delta H_f^o$ — variant no. 3, *d* $\Delta H_f^o$ — variant no. 4

included in some of these calculations. The calculated results are shown graphically in Figs 2 – 4.

The results of these calculations of chemical equilibrium in the system Si–Cl–H lead to the following conclusions:

*1.* The temperature dependence of the amount of silicon deposited or reacted shows a maximum in the temperature range 1 000 to 1 600 K, its position depending on pressure and on the initial composition of the system.

TABLE VI

Comparison of calculated and experimentally determined composition of the gaseous phase in the system Si–Cl–inert; $T = 1\ 300$ K, $p = 101\cdot352$ kPa, $n^o_{SiCl_4} = 1$ mol, $n^o_{inert} = 20$ mol, solid silicon in excess

| Substance | $x_{calc}$ | $x_{exp}$ (Ban[24]) |
|-----------|------------|---------------------|
| $SiCl_4$ | $3\cdot40 \cdot 10^{-2}$ | $4\cdot1 \cdot 10^{-2}$ |
| $SiCl_3$ | $8\cdot71 \cdot 10^{-3}$ | $—^a$ |
| $SiCl_2$ | $1\cdot33 \cdot 10^{-2}$ | $1\cdot2 \cdot 10^{-2}$ |
| $SiCl$ | $1\cdot67 \cdot 10^{-8}$ | $—^a$ |
| $Si_2Cl_6$ | $1\cdot99 \cdot 10^{-7}$ | $—^a$ |
| $Si$ | $3\cdot95 \cdot 10^{-11}$ | $—^a$ |

$^a$ Presence of these substances has not been proved experimentally.

TABLE VII

Comparison of calculated and experimentally determined composition of the gaseous phase in the system Si–Cl; $T = 1\ 593$ K, $p = 0\cdot01$ kPa, $n^o_{SiCl_4} = 1$ mol, solid silicon in excess

| Substance | $x_{calc}$ | $x_{exp}$ (Farber and Srivastava[13]) |
|-----------|------------|---------------------------------------|
| $SiCl_4$ | $1\cdot51 \cdot 10^{-4}$ | $9\cdot63 \cdot 10^{-5}$ |
| $SiCl_3$ | $7\cdot72 \cdot 10^{-3}$ | $6\cdot45 \cdot 10^{-3}$ |
| $SiCl_2$ | $0\cdot987$ | $0\cdot991$ |
| $SiCl$ | $1\cdot67 \cdot 10^{-3}$ | $1\cdot73 \cdot 10^{-3}$ |
| $Si_2Cl_6$ | $6\cdot27 \cdot 10^{-13}$ | $—^a$ |
| $Si$ | $7\cdot62 \cdot 10^{-4}$ | $8\cdot61 \cdot 10^{-4}$ |

$^a$ Presence of this substance has not been proved experimentally.

*2.* The dependence of the amount of silicon deposited or reacted on the initial composition of the gaseous phase shows a maximum in the range of mole fractions $x^0(SiCl_4)$ from 0·005 to 0·1, its position being temperature and pressure-dependent

*3.* The lowering of the total pressure exerts the same inflence as the dilution of the reacting mixture with an inert, i.e. it leads to an increase of the amount of silicon deposited.

*4.* The gaseous mixture in equilibrium with solid silicon contains a large number of substances and their relative abundancies are determined by the initial computing conditions. At lower temperatures, the dominant components are $SiCl_4$, $SiHCl_3$, $SiH_2Cl_2$ and HCl, at higher temperatures $SiCl_2$, $SiHCl$, $SiCl_3$ and HCl. The lowering of the initial concentration of $SiCl_4$ in the mixture with hydrogen causes an increase of the equilibrium concentrations of substances containing more hydrogen atoms in the molecule ($SiH_4$, $SiH_3$, $SiH_3Cl$), to the detriment of substances having in the molecule more chlorine atoms ($SiCl_4$, $SiCl_3$, $SiHCl_3$). The lowering of total pressure of the system, as well as the addition of an inert gas, brings forth the shift of equilibrium in favour of substances having a smaller number of atoms in the molecule
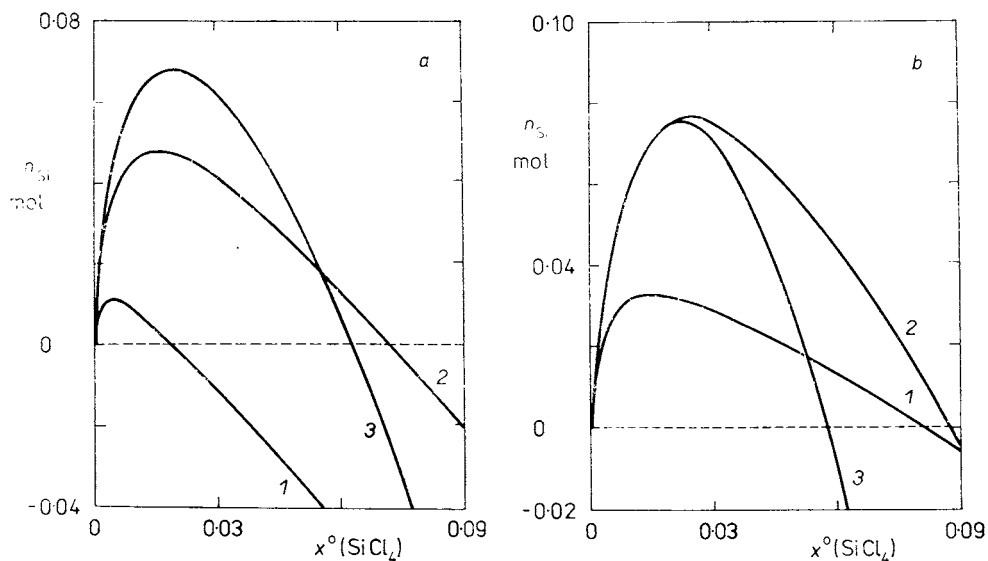


FIG. 2

Amount of deposited or reacted Si in the system Si–Cl–H as a function of the initial concentration of $SiCl_4$; $n^0_{SiCl_4} + n^0_{H_2} = 10$ mol, solid Si in excess, *1* $T = 1\,100$ K, *2* $T = 1\,300$ K, *3* $T = 1\,500$ K; *a* $p = 101\cdot325$ kPa, *b* $p = 10\cdot133$ kPa

$(SiCl_2, SiCl, SiH_2, SiH, SiHCl)$, at the expense of substances having a greater molecule $(Si_2Cl_6, SiCl_4, SiHCl_3, SiH_2Cl_2, SiH_3Cl, SiH_4)$.

5. The only gaseous substance which has not been included in equilibrium calculations by previous authors and which is present in significant amounts is SiHCl: at higher temperatures and especially at lower pressures this substance represents one of the dominant components of the gaseous phase.

When comparing the results of this study with the calculated data published previously[1-9], one finds the main differences between the compositions of the gaseous phase; on the other hand, the dependencies of the amount of silicon deposited or reacted on temperature, pressure and on the initial composition of the gas do not differ significantly among themselves.

The calculated equilibrium concentrations of the gaseous substances in the system Si–Cl–H are compared with the experimental values obtained from mass spectrometry[24] in Table VIII. From this comparison it follows that in some instances the calculated values differ from experimental ones almost by an order of magnitude. Similarly as in the case of the system Si–Cl, there is no experimental evidence for the presence of $SiCl_3$, the calculated equilibrium concentration of which is comparable
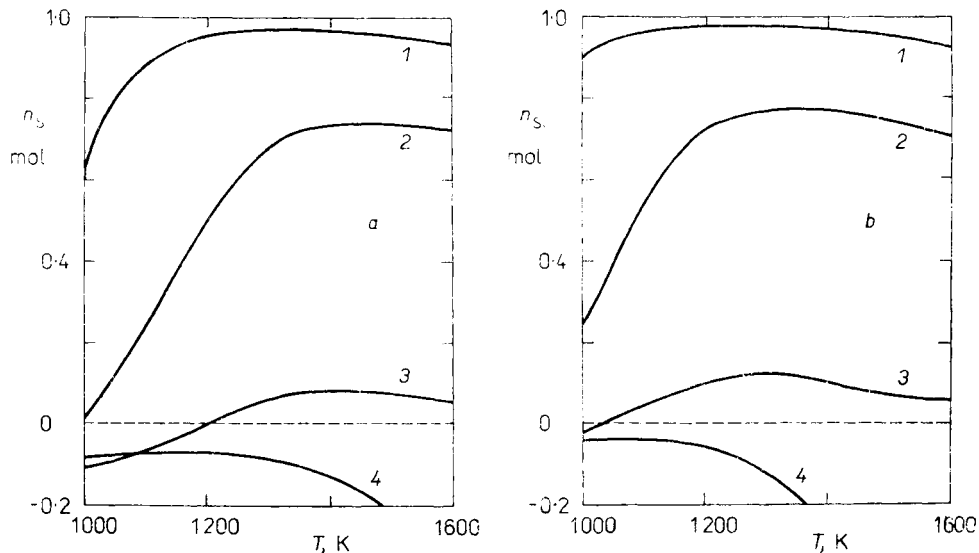


FIG. 3

Temperature dependence of the amount of Si deposited or reacted in the Si–Cl–H system; $n^0_{SiCl_4} = 1$ mol, *1* Cl/H = 0·001, *2* Cl/H = 0·01, *3* Cl/H = 0·1, *4* Cl/H = 1; *a* $p = 101·325$ kPa, *b* $p = 10·133$ kPa

with the concentrations of substances that have been detected. This disagreement can be explained using the previous argument.

CONCLUSION

The calculated results yield a number of valuable informations for the choice of proper technological conditions for the preparations of very pure polycrystalline silicon and of silicon layers for the applications in electronics. The calculated amount of deposited silicon represents the theoretical efficiency (i.e. the maximum possible yield) of the given process and can serve even for the estimation of the maximum possible rate of formation (deposition) of solid silicon. The deposition of silicon layers takes place at relatively high temperature and, therefore, the resulting kinetic characteristics of the process is determined mainly by the velocity of diffusion of the reactants to the solid surface where the proper chemical reaction takes place and it is possible to assume the establishment of local chemical equilibrium between the
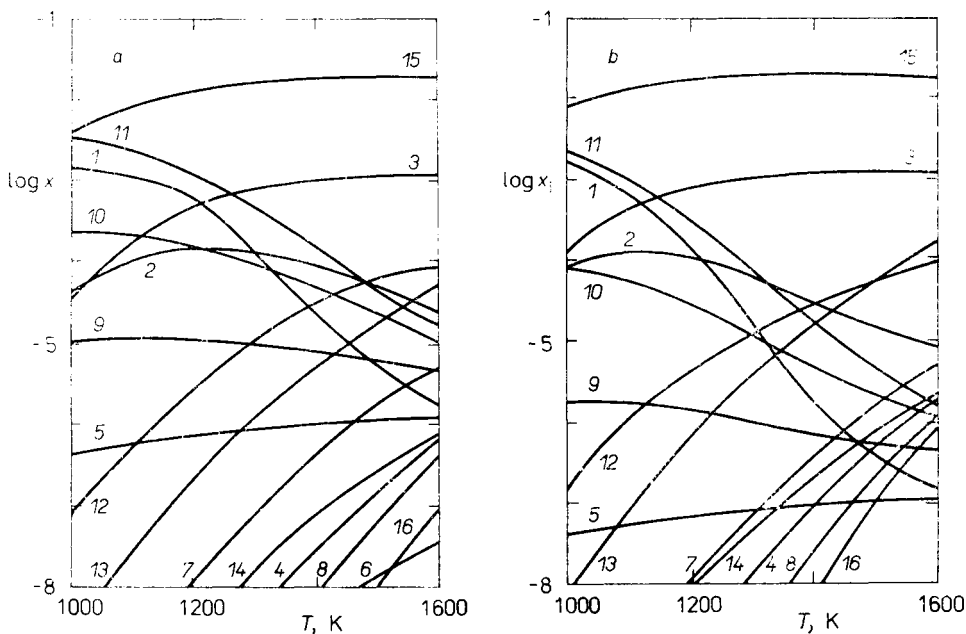


FIG. 4

Temperature dependence of the equilibrium composition of the gaseous phase in the Si–Cl–H system; $n^0_{SiCl_4} = 1$ mol, $n^0_{H_2} = 200$ mol; 1 $SiCl_4$, 2 $SiCl_3$, 3 $SiCl_2$, 4 $SiCl$, 5 $SiH_4$, 6 $SiH_3$, 7 $SiH_2$, 8 $SiH$, 9 $SiH_3Cl$, 10 $SiH_2Cl_2$, 11 $SiHCl_3$, 12 $SiHCl$, 13 H, 14 Cl, 15 HCl, 16 Si; a $p = 101·325$ kPa, b $p = 10·133$ kPa

depositing solid substance (i.e. silicon) and the gaseous phase in its closest neighbourhood. The driving force of diffusion is in this case the difference between the concentrations of the reactants in the bulk phase of the gas and in the layer adhering to the solid surface; thus, from the known equilibrium composition of the gas it is possible to calculate the rate of diffusion (the diffusion flux) of silicon-containing substances toward the gas–solid interface and from this even the velocity of growth of silicon layers.

The comparison of calculated and experimental data on the equilibrium composition of the gaseous phase in the system Si–Cl–H reveals, however, certain differences which might be caused by incorrect values of input thermodynamic data used in the calculations and/or by the limitations of experimental methods used till now for the detection of highly reactive radicals and substances which are stable at high temperatures only. To elucidate these problems, it is necessary to investigate further both the thermodynamic properties of "critical" components of the gaseous phase in the system Si–Cl–H and directly the composition of the gaseous phase in equilibrium with solid silicon. The results of our experimental investigations of the

TABLE VIII

Comparison of calculated and experimentally determined composition of the gaseous phase in the system Si–Cl–H; $T = 1\ 300$ K, $p = 101.325$ kPa, $n^0_{SiCl_4} = 1$ mol, $n^0_{H_2} = 20$ mol, solid silicon in excess

| Substance | $x_{calc}$ | $x_{exp}$ (Ban[24]) |
|---|---|---|
| $SiCl_4$ | $1.48 \cdot 10^{-2}$ | $1.7 \cdot 10^{-2}$ |
| $SiCl_3$ | $4.29 \cdot 10^{-3}$ | $-^a$ |
| $SiCl_2$ | $8.27 \cdot 10^{-3}$ | $1.7 \cdot 10^{-2}$ |
| $SiCl$ | $1.32 \cdot 10^{-8}$ | $-^a$ |
| $Si_2Cl_6$ | $4.81 \cdot 10^{-8}$ | $-^a$ |
| $SiH_4$ | $6.56 \cdot 10^{-7}$ | $-^a$ |
| $SiH_3$ | $1.05 \cdot 10^{-9}$ | $-^a$ |
| $SiH_2$ | $7.04 \cdot 10^{-8}$ | $-^a$ |
| $SiH$ | $7.17 \cdot 10^{-10}$ | $-^a$ |
| $SiHCl_3$ | $1.62 \cdot 10^{-2}$ | $3.9 \cdot 10^{-3}$ |
| $SiH_2Cl_2$ | $8.79 \cdot 10^{-4}$ | $5.3 \cdot 10^{-3}$ |
| $SiH_3Cl$ | $2.67 \cdot 10^{-5}$ | $-^a$ |
| $SiHCl$ | $3.11 \cdot 10^{-5}$ | $-^a$ |
| $Si$ | $3.96 \cdot 10^{-11}$ | $-^a$ |
| $HCl$ | $4.89 \cdot 10^{-2}$ | $6.4 \cdot 10^{-2}$ |
| $H_2$ | $0.9066$ | $0.8721$ |

$^a$ Presence of these substances has not been proved experimentally.

equilibrium composition of the gaseous phase in the systems Si–Cl and Si–Cl–H are presented in the second part of this communication.

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