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The Equilibrium Behavior of the Silicon-Hydrogen-Chlorine System*

Abstract: The composition of the gas phase is calculated for various temperatures, pressures, and chlorine-to-hydrogen ratios for the two-phase system consisting of solid silicon in equilibrium with the gas phase. It is shown that in the range of variables most frequently used for vapor growth of silicon, the principal species under equilibrium conditions are H_2, HCl, $SiHCl_3$, and $SiCl_2$.

Introduction

Reactions involving the hydrogen reduction of $SiCl_4$ or $SiHCl_3$ are industrially important for both the manufacture of very pure silicon and the deposition of epitaxial layers.[1-3] While numerous workers have attempted to relate the observed behavior of the silicon-hydrogen-chlorine system to kinetic factors,[4] thermodynamic analyses have never considered the simultaneous presence of more than two silicon bearing species,[5,6] largely because thermodynamic data for the silicon halides was not available for some time after the system became important. Recently, however, with the work of Wolf[7] on the heats of formation of $SiCl_4$ and $SiHCl_3$ and Mikawa[8] on the entropies of $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl and SiH_4, it has become possible to develop fairly complete calculations for the system.

The calculations presented in this paper have been made with the vapor growth of silicon firmly in mind. Such calculations cannot, as a general rule, predict exactly what will happen in a vapor growth experiment, since kinetic factors are frequently of great importance. Nevertheless, the equilibrium information they afford provides a firm foundation for a basic understanding of the system and, specifically, enables one to calculate the maximum yield of the system for various operating conditions.

Choice of variables

To make equilibrium calculations on a vapor growth system, one must first decide what quantities should be calculated, and in terms of which independent variables. It can be assumed that only two phases are present, solid silicon[9] and the gas phase, in the regions where dissolution or precipitation of silicon is taking place. Since the system has three components (silicon, hydrogen, and chlorine) the phase rule indicates that three degrees of freedom exist. In most practical cases, two of these will be temperature and total pressure. For a typical "open tube" system, where the silicon-bearing gas mixture flows past the heated substrate, it is easily seen that the third experimentally independent variable is the *chlorine-to-hydrogen ratio* in the gas phase. This is demonstrated as follows: consider a gas stream containing hydrogen, hydrogen chloride, and various chlorides and hydrochlorides of silicon. As indicated above, the only solid phase interacting with the gas phase is silicon; condensed silicon halides are specifically excluded from the active region. It is thus clear that the total fluxes of chlorine, J_{Cl}, and hydrogen, J_H, through the system are constant.[10] At any given point in the system (except very close to the solid silicon, where diffusion is important) we have

$$J_{Cl} = n_{Cl} Av, \tag{1}$$

$$J_H = n_H Av, \tag{2}$$

where J represents the flux in moles sec^{-1}, n the density in moles cm^{-3}, A the cross-section of the system in cm^2, and v the stream velocity in cm sec^{-1}.

In a practical flow system, where the total pressure decreases from input to output and where the cross section

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may vary widely, the quantities n_{Cl}, n_{H}, A, and v are not constants throughout the system at any given time. However, dividing Eq. (1) by Eq. (2), we have

$$J_{\mathrm{Cl}}/J_{\mathrm{H}} = n_{\mathrm{Cl}}/n_{\mathrm{H}} = \phi.$$

This quantity ϕ, the Cl/H ratio, is a constant throughout the system which is determined by adjustment of the input conditions. For example, if hydrogen is bubbled through $SiCl_4$ at a total pressure of one atmosphere, and a partial pressure of 60 torr of $SiCl_4$ is established in the gas stream, then $\phi = 2 \times 60/(760 - 60) = 0.171$.

For open-tube growth systems, the dependent variable of primary interest is J_{Si},[10] the flux of silicon in the system. If equilibrium calculations show that J_{Si} should decrease, then the system will tend to deposit silicon, or if J_{Si} should increase, there will be a tendency for dissolution. As above, we have

$$J_{\mathrm{Si}} = n_{\mathrm{Si}} A v. \tag{3}$$

It would be desirable to obtain an intensive quantity η with which to characterize the gas stream such that a decrease in η would require deposition of silicon while an increase in η would require a dissolution of silicon into the gas stream. Such a quantity is readily obtained if one remembers that J_{Cl} is constant. Hence, dividing Eq. (3) by Eq. (1), one may write

$$J_{\mathrm{Si}}/J_{\mathrm{Cl}} = n_{\mathrm{Si}}/n_{\mathrm{Cl}} = \eta.$$

Since J_{Cl} is constant, a change in η necessitates a change in J_{Si}. It should be noted that n_{Si}, the density of silicon in gas phase solution, while undoubtedly an intensive quantity, does not have the desired properties. For example, in a region of uniform cross section with negligible pressure gradient, dissolution of silicon into a gas stream consisting initially of pure $SiCl_4$, by the reaction $Si + SiCl_4 = 2\,SiCl_2$, does not result in any change in n_{Si}. At a given temperature, n_{Si} is given simply by the total pressure, inasmuch as each gas molecule contains one silicon atom. However, the gas streaming velocity increases since, for each silicon atom dissolved, one $SiCl_4$ molecule in the gas phase is replaced by two $SiCl_2$ molecules. There will, of course, be a corresponding decrease in n_{Cl} so that η would increase as expected.

One may also consider a closed isothermal system of variable volume. It is clear that the total chlorine and hydrogen contents of the gas phase cannot change since the only other phase present consists of pure solid silicon. Thus, the ratio of chlorine to hydrogen densities, $n_{\mathrm{Cl}}/n_{\mathrm{H}}$, must also be invariant. Dissolution or growth of the solid silicon, however, clearly requires a change in the total silicon content of the gas phase and hence a change in the ratio $n_{\mathrm{Si}}/n_{\mathrm{Cl}}$, even though the quantity n_{Si} need not change. For vapor growth in "closed tube" systems, under conditions where transport is diffusion limited, it has already been shown that η and ϕ are the appropriate variables.[11] In all cases, there is some freedom in choosing both η and ϕ. For example, it would be quite legitimate to define them as $\eta = n_{\mathrm{Si}}/(n_{\mathrm{Cl}} + n_{\mathrm{H}})$ and $\phi = 2(n_{\mathrm{Cl}} + n_{\mathrm{H}})/n_{\mathrm{H}}$.

In this paper, $n_{\mathrm{Si}}/n_{\mathrm{Cl}}$, the Si/Cl ratio, will be calculated in terms of $n_{\mathrm{Cl}}/n_{\mathrm{H}}$, the Cl/H ratio, as a function of temperature, T°K, and pressure, P atmospheres. In addition, the mole fractions of the various species will also be displayed under various conditions of T, P, and $n_{\mathrm{Si}}/n_{\mathrm{Cl}}$. Similar calculations may be readily made for other systems, e.g., the Si-H-Cl-He system. The latter system, for example, would depend on T, P, $n_{\mathrm{Cl}}/n_{\mathrm{H}}$, and $n_{\mathrm{H}}/n_{\mathrm{He}}$. The results of diluting the gas stream with helium would be somewhat similar to those of reducing P, although different in detail.

Thermodynamic data

The calculations in this paper include the species H_2, HCl, SiCl, $SiCl_2$, $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, and SiH_4.[12] For a rigorous solution the enthalpies of formation and entropies of all species would be required as a function of temperature. In this paper, the enthalpies of formation and entropies at 1500°K have been used as a basis for calculations over the range 800° to 1750°K. The temperature 1500°K was chosen since it is in the middle of the range in which Schaefer and Nickl[13] have measured the reaction $Si + SiCl_4 = 2\,SiCl_2$, and thus the need is avoided to estimate the specific heat of $SiCl_2$. The thermodynamic constants of the other species were adjusted from 298°K to 1500°K using the data of Mikawa[8] and Kelley.[14]

- *Enthalpies of formation*

The sources of the enthalpy data for the various compounds were Wolf[7] ($SiCl_4$ and $SiHCl_3$), Brimm and Humphreys[45] (SiH_4), Schaefer[16] (SiCl), and Kubaschewski and Evans[17] (HCl). The enthalpies of formation of SiH_2Cl_2 and SiH_3Cl are not known. They were estimated by simple linear interpolation between $SiHCl_3$ and SiH_4 in the final equations (a justification for this is that the heats of formation of the corresponding carbon compounds do not deviate too widely from an arithmetic progression). This estimation assumes that in the compounds SiH_4, SiH_3Cl, SiH_2Cl_2, $SiHCl_3$, and $SiCl_4$ the bond energies are additive. That this is not strictly true is borne out by the fact that the equation for $SiCl_4$ does not fit exactly into the pattern. Since SiH_3Cl and SiH_2Cl_2 are only minor constituents under most conditions of operation, the inevitable inaccuracy in their partial pressures as calculated here should not detract greatly from the value of these calculations. Admittedly, however, if the enthalpies of formation of either of these two species were very much more negative than is here assumed, these species could dominate and the model presented in this paper would be incorrect.

- *Entropies*

The entropies of $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, and SiH_4 were taken from Mikawa.[8] The entropies of H_2, HCl, and SiCl are taken from Kelley[18]. The thermodynamic constants for $SiCl_2$ were derived from those of $SiCl_4$ using the data of Schaefer and Nickl[13] for the reaction of Si + $SiCl_4$ = $2SiCl_2$.

- *Description of the system*

Since elemental chlorine is not present in appreciable quantities, it is convenient to write the formation reaction for each species using silicon, hydrogen chloride, and hydrogen as the only other permitted species. This procedure uniquely defines the reactions listed below, where the equilibrium constant K for each reaction is denoted by the same suffix as the species for which the reaction is written:

$$Si + 4HCl = SiCl_4 + 2H_2,$$
$$K_{SiCl_4} = P_{SiCl_4} P_{H_2}^{2} P_{HCl}^{-4}.$$
$$Si + 3HCl = SiHCl_3 + H_2,$$
$$K_{SiHCl_3} = P_{SiHCl_3} P_{H_2} P_{HCl}^{-3}.$$
$$Si + 2HCl = SiH_2Cl_2,$$
$$K_{SiH_2Cl_2} = P_{SiH_2Cl_2} P_{HCl}^{-2}.$$
$$Si + HCl + H_2 = SiH_3Cl,$$
$$K_{SiH_3Cl} = P_{SiH_3Cl} P_{H_2}^{-1} P_{HCl}^{-1}.$$
$$Si + 2H_2 = SiH_4,$$
$$K_{SiH_4} = P_{SiH_4} P_{H_2}^{-2}.$$
$$Si + 2HCl = SiCl_2 + H_2,$$
$$K_{SiCl_2} = P_{SiCl_2} P_{H_2} P_{HCl}^{-2}.$$
$$Si + HCl = SiCl + H_2/2,$$
$$K_{SiCl} = P_{SiCl} P_{H_2}^{\frac{1}{2}} P_{HCl}^{-1}.$$

Table 1 **Values of $\triangle S_{1500}$ and $\triangle H_{1500}$ for various species, for the formation reactions given in the text.** *Values marked with an asterisk are interpolated to form an arithmetic progression with adjacent values.*

Species	ΔS_{1500}	ΔH_{1500}
$SiCl_4$	−35.9	−59.8
$SiHCl_3$	−29.9	−49.3
SiH_2Cl_2	−26.0	−31.1*
SiH_3Cl	−23.7	−12.9*
SiH_4	−23.6	+5.2
$SiCl_2$	+5.1	+7.7
SiCl	+21.5	+61.4

In the listing above, the values of the K's were determined from the relation $4.574 \log_{10} K = \Delta S_{1500} - \Delta H_{1500}/T$, which is exact only at 1500°K but is certainly sufficiently accurate for the purposes of these calculations over the temperature range here employed, 800° to 1750°K. In Table 1, values of ΔS and ΔH are displayed for the various species.

Method of calculation

It is convenient to work with partial pressures rather than molar densities. It will be assumed that the partial pressure of species i is related to its molar density by the ideal gas law, $P = nRT$. The following sums are defined

$$P_{Si} = P_{SiCl_4} + P_{SiHCl_3} + P_{SiH_2Cl_2} + P_{SiH_3Cl} + P_{SiH_4} + P_{SiCl_2} + P_{SiCl},$$

$$P_{Cl} = 4P_{SiCl_4} + 3P_{SiHCl_3} + 2P_{SiH_2Cl_2} + P_{SiH_3Cl} + P_{HCl} + 2P_{SiCl_2} + P_{SiCl},$$

$$P_{H} = P_{HCl} + P_{SiHCl_3} + 2P_{SiH_2Cl_2} + 3P_{SiH_3Cl} + 4P_{SiH_4} + 2P_{H_2}.$$

As was explained in the Introduction, P_{Si}/P_{Cl} is required as a function of P_{Cl}/P_{H}, temperature, and total pressure. Since an explicit solution of the system in these terms would be clumsy and tedious, a parametric approach was adopted.[19] It is convenient to pick as a parameter the ratio P_{HCl}/P_{H_2}, which will be called X. The system may then be solved in terms of T, P, and X by writing the total pressure as the sum of the partial pressures and substituting for the partial pressures in terms of the appropriate K, X, and P_{HCl}.

Hence,

$$P = P_{HCl}^{2}(K_{SiCl_4}X^{2} + K_{SiHCl_3}X + K_{SiH_2Cl_2} + K_{SiH_3Cl}/X + K_{SiH_4}/X^{2}) + P_{HCl}(K_{SiCl_2}X + 1 + 1/X) + P_{HCl}^{1/2}K_{SiCl}X^{1/2}.$$

Solutions to this equation may be generated by taking X as a parameter and solving for P_{HCl}. However, the solutions are more readily obtained if P_{SiCl} is considered negligible in comparison with the other pressures. The last term then disappears and the above equation becomes a simple quadratic. The calculation of P_{SiCl} is still made, and the total pressure is considered to be $(P + P_{SiCl})$ atmospheres instead of P atmospheres. Since $P_{SiCl} \ll P$, this is unimportant in practice. After solving the quadratic for P_{HCl}, it is then a simple matter to evaluate all the other partial pressures and hence P_{Si}, P_{Cl}, P_{H}, and the desired ratios P_{Si}/P_{Cl} and P_{Cl}/P_{H}.

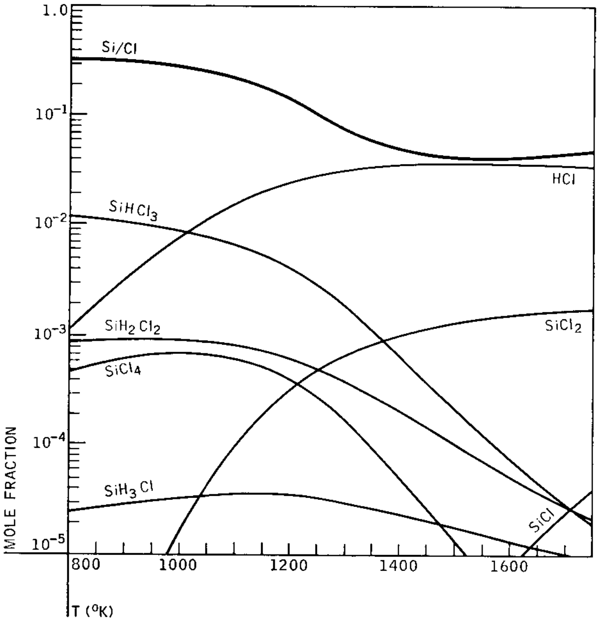
For graphical display of the results, it is convenient to evaluate P_{Cl}/P_{H} in terms of fixed values of P_{Si}/P_{Cl}.

Also, since P_{Cl}/P_H is experimentally fixed in a given system, it is convenient to obtain P_{Si}/P_{Cl} and the various mole fractions P_i/P for a given value of P_{Cl}/P_H. This was done by using a computer to generate a number of solutions to the system for various X and then arriving at the values of X corresponding to the desired values of P_{Si}/P_{Cl} or P_{Cl}/P_H by inverse interpolation. Most of the calculations were undertaken for $P =$ one atmosphere. Calculations on the effects of varying P were made for only a few values of P_{Cl}/P_H. In this latter instance, the solutions corresponding to an exact value of P_{Cl}/P_H (e.g., $P_{Cl}/P_H = 0.02$) were obtained by writing $X = 10^Q$ and performing a simple binary search over the range $-6 < Q < +2$. Sixteen iterations were performed, starting with an initial value of $Q = -2$ (i.e., $X = 0.01$).

Results

The behavior of the Si-H-Cl system is illustrated in Figs. 1–5. Since there are three degrees of freedom (temperature, total pressure, and the Cl/H ratio) the complete behavior cannot be displayed in a single plot. In Fig. 1, the mole fractions of the various species together with the Si/Cl ratio are displayed as a function of temperature for a Cl/H ratio of 0.02, a value commonly used in practical systems. It is seen that the major constituents are $SiHCl_3$ and HCl, in addition to H_2 which is at a pressure of approximately 1 atmosphere. The effect of raising the temperature is to cause the hydrogen reduction of $SiHCl_3$ to HCl and Si. Below 1050°K, the Si/Cl ratio is greater than 0.25. This means that if the starting vapor were $SiCl_4$, the gas stream would be capable of etching silicon below 1050°K since the actual gas stream Si/Cl ratio would be less than the equilibrium value.

Figure 1 **Composition of the gas phase versus temperature at a total pressure of 1 atmosphere and a chlorine/hydrogen ratio of 0.02.**



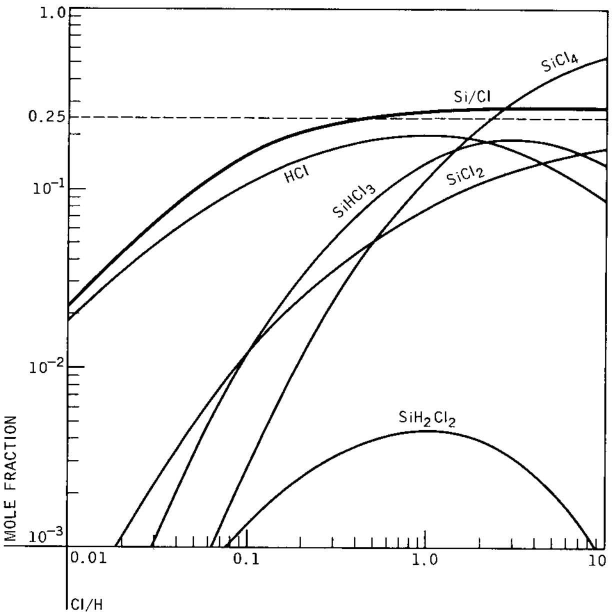


Figure 2 **Composition of the gas phase versus chlorine/hydrogen ratio at 1450°K for a total pressure of 1 atmosphere.**

In Fig. 2, the mole fractions together with the Si/Cl ratio are plotted as a function of Cl/H ratio at a temperature of 1450°K, a commonly used deposition temperature. As would be expected, the effect of increasing the Cl/H ratio is to increase the fractions of the silicon chlorides at the expense of hydrogen-containing compounds. Above a Cl/H ratio of 0.4, the Si/Cl ratio is greater than 0.25, indicating as before that a gas mixture obtained by bubbling H_2 through $SiCl_4$ will dissolve silicon at high concentrations of $SiCl_4$. Figure 3 indicates the effect of pressure on the equilibria at 1200°K and Cl/H = 0.02. It is seen that increasing pressure favors molecules containing four rather than two solvent atoms. It may also be of interest to note that the decreasing mole fraction of HCl with increasing pressure implies a decreasing HCl/H_2 ratio, since most of the molecules present are those of hydrogen. Hence, examination of reactions such as $SiHCl_3 + H_2 = SiH_2Cl_2 + HCl$ shows that the ratios $SiCl_4/SiHCl_3$, $SiHCl_3/SiH_2Cl_2$, and SiH_2Cl_2/SiH_3Cl will also decrease.

Figure 4 shows the effect of pressure on the Si/Cl ratio over the complete range of temperatures. In general, the solubility of silicon in the gas phase per gram atom of chlorine increases with pressure and decreases with temperature. This trend is reversed at high temperatures and

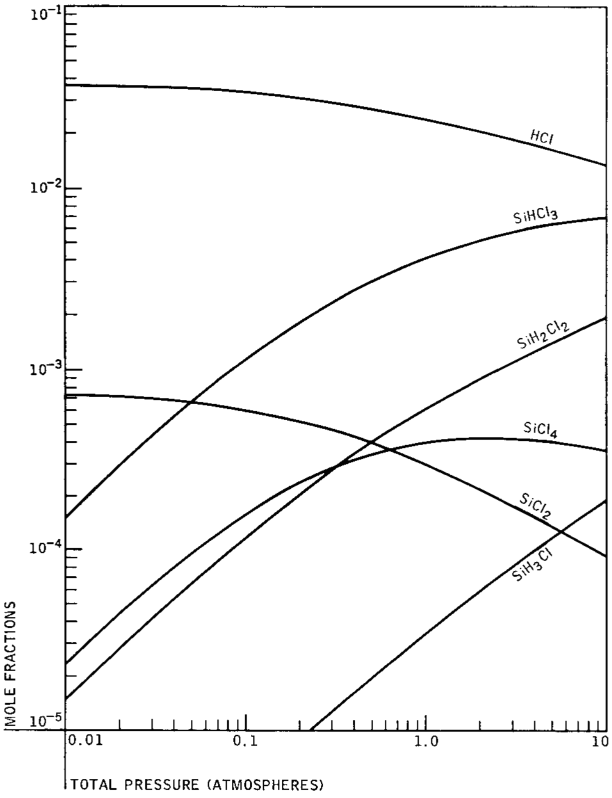


Figure 3 **Composition versus total pressure at 1200°K for a chlorine/hydrogen ratio of 0.02.**

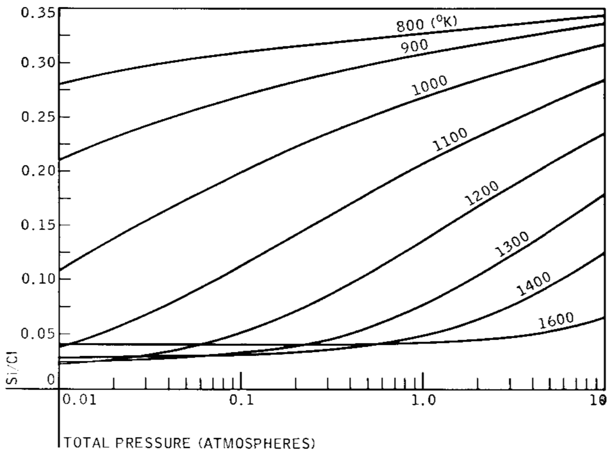


Figure 4 **The effect of total pressure on the equilibrium silicon/chlorine ratio of the gas phase.** *Various temperatures are shown for a chlorine/hydrogen ratio of 0.02.*

low pressures because of the increasing importance of $SiCl_2$, the presence of which is favored by high temperatures and low pressures.

It can be assumed for most practical purposes that the total pressure of operation is very close to one atmosphere, and temperature and Cl/H ratio are the only independent variables. Consequently, one may plot lines of constant Si/Cl ratio on a plot of Cl/H versus temperature, as in Fig. 5. In this figure, the large "valley" to the lower right, indicating a low Si/Cl ratio, is due to the predominance of HCl, while the broad ridge on the left is dominated by $SiHCl_3$. The strongly rising tendency at the upper right is due to increasing quantities of $SiCl_2$, while the effect of very high Cl/H ratios at temperatures below 1200°K is to increase $SiCl_4$ at the expense of $SiHCl_3$. It is worth noting that for the pure gases, the Si/Cl ratios are as follows: $SiCl_4$, 0.25; $SiHCl_3$, 0.33; $SiCl_2$, 0.5; and HCl, 0.0, but that other species are not present in concentrations sufficient to dominate. If one uses $SiCl_4$ as the source of Si and Cl, then the Si/Cl ratio is necessarily 0.25. In this case, operating points above the shaded line will result in etching, not growth. It may be noted that if $SiHCl_3$ is used as starting material, etching could occur only at very high Cl/H ratios and temperatures above 1500°K. It may be further noted that for Cl/H ratios in the range 10^{-2} to 10^{-1}, little is gained in reaction efficiency by going above 1400°K since, as is illustrated in Fig. 1, the decreasing quantities of silicon present in the gas phase as $SiHCl_3$ are balanced by increasing quantities of $SiCl_2$.

Conclusion

Examination of the results presented above shows that in the range of variables most frequently used for vapor growth, the principal equilibrium species are H_2, HCl, $SiHCl_3$, and $SiCl_2$. Except for $SiCl_4$ at high pressures or high Cl/H ratios, no other species ever dominates the system. An examination of published values of reaction efficiencies in the light of these considerations has been undertaken by Sedgwick and submitted for publication[4].

Acknowledgments

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References and footnotes

1. H. C. Theuerer, *J. Electrochem. Soc.* 108, 649 (1961).
2. J. M. Charig and B. A. Joyce, *J. Electrochem. Soc.* **109**, 957 (1962).
3. E. G. Bylander, *J. Electrochem. Soc.* **109**, 1171 (1962).
4. T. O. Sedgwick, to be published in J. Electrochem. Soc.
5. E. Wolf and R. Teichmann, *Z. Chem.* **2**, 343 (1962).
6. W. Steinmaier, *Philips Res. Reports* **18**, 75 (1963).
7. E. Wolf, *Z. Anorg. Allg. Chemie* **313**, 228 (1961).
8. Y. Mikawa, *Nippon Kagaku Zasshi* **81**, 1512 (1960).
9. The minute amounts of Cl and H which may be dissolved in the solid silicon are quite negligible for the purposes of this treatment.
10. The fluxes J_{Cl}, J_H, and J_{Si} refer to the total fluxes of the chlorine, hydrogen, and silicon components irrespective of their state of chemical combination. In fact, none of the

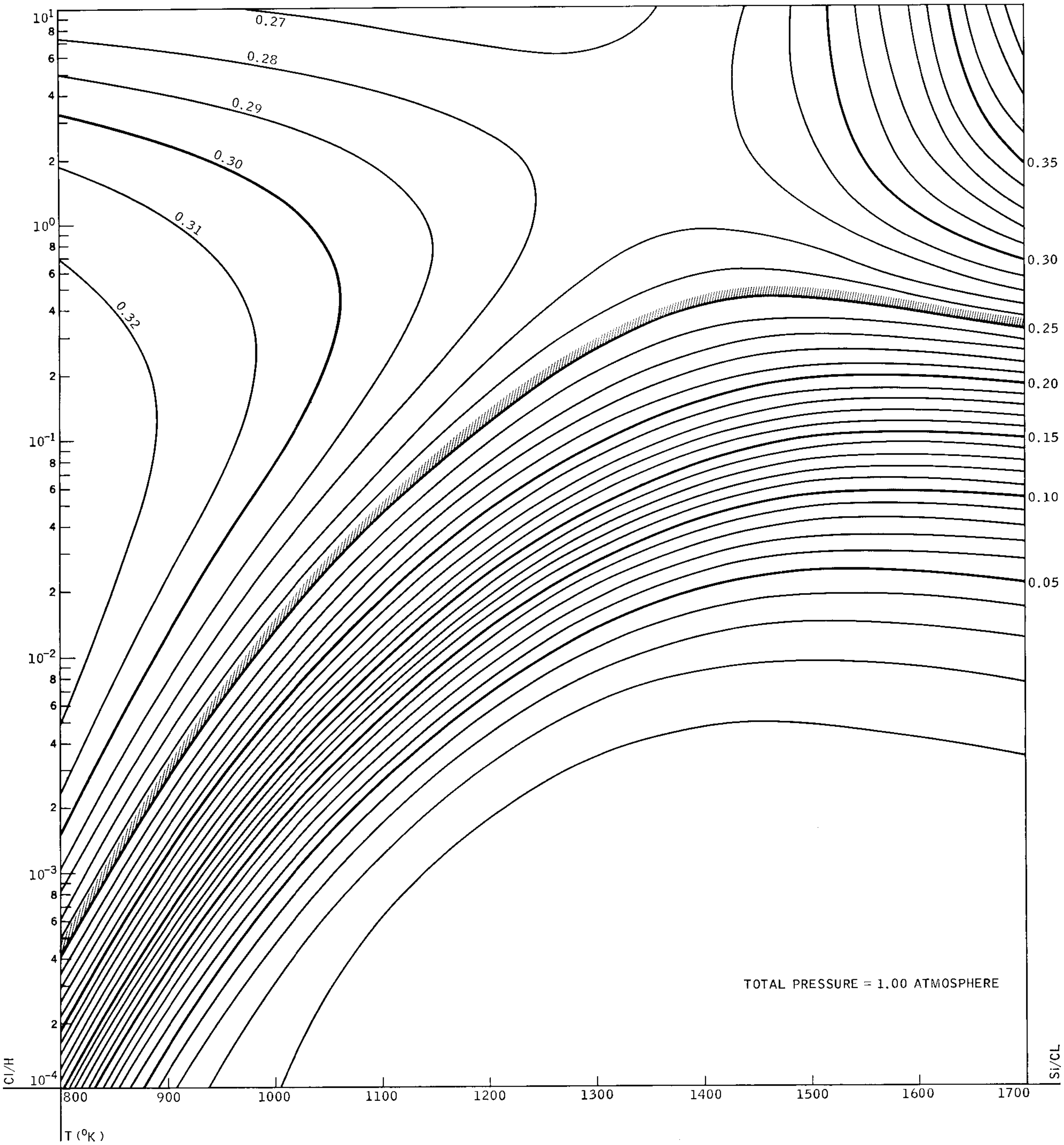

Figure 5 **A plot of chlorine/hydrogen ratio versus temperature for various fixed values of the silicon/chlorine ratio.** *The total pressure is one atmosphere.*

components occur in the vapor phase as isolated atoms in appreciable quantities.

11. R. F. Lever, *J. Chem. Phys.* **37**, 1078 (1962).
12. It is readily shown from simple thermodynamic considerations that free chlorine cannot occur in appreciable concentration in the presence of solid silicon.
13. H. Schaefer and J. Nickl, *Z. Anorg. Allg. Chemie* **274**, 250 (1953).
14. K. K. Kelley, *Bureau of Mines Bulletin* **584**, U. S. Gov't. Printing Office, Washington, 1961.
15. E. O. Brimm and H. M. Humphreys, *J. Phys. Chem.* **61**, 829 (1957).
16. H. Schaefer, "Silicium, Schwefel, Phosphate," *Colloq. Sek Anorg. Chem. Intern. Union Reine u. Angew. Chem. Münster* 1954 (Pub. 1955). p. 24.
17. O. Kubaschewski and E. L. Evans, *Metallurgical Thermochemistry*, Pergamon Press, New York, 1958.
18. K. K. Kelley, *Bureau of Mines Bulletin* 592, U. S. Gov't. Printing Office, Washington, 1961.
19. L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, New York, 1953, p. 218.

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