

CHLORO-SILANE DISPROPORTIONATION MODELING A MONO-CHAMBER REACTOR

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Abstract

Content

This document presents an estimation of the chemical concentrations in a disproportionation reactor chamber, based on Gibbs free energy minimization. The modeling assumes thermodynamic equilibrium and mono-chamber reactor.

Context

This is documented as a R&D support to silane production activities. It follows a previous report on the techno-evolution of TCS disproportionation.

Summary

The Gibbs free energy is estimated in a mono-chamber reactor with given temperature, stoichiometry and pressure, and considering both liquid and vapour phases at a fixed ratio. This function is minimized to estimate the concentrations of the chemicals at equilibrium.

As expected from Denal data (available for a liquid phase only), the disproportionation of HSiCl_3 gives ~10% of H_2SiCl_2 in the liquid phase, and 17.7% in the vapour phase. The disproportionation of H_2SiCl_2 is also compatible with Denal data (18.6% H_3SiCl in the liquid phase, 31.6% H_3SiCl in the vapour phase), but we note some divergence for the other chemicals (to be reconsidered).

After the changing various parameters of the model we conclude that:

- Adding a liquid catalyst that is little volatile is a way to reduce the pressure, and in return pressure regulates the concentration of the catalyst.
- Disproportionation of HSiCl_3 at lower temperature gives a significantly lower amount of H_2SiCl_2 in output.
- From a thermodynamic perspective, HCl reacts with the chlorosilanes to suppress the H-Si bounds, and evolve H_2 .
- An hypothetical decomposition of HSiCl_3 to SiCl_4 , Si , HCl and H_2 is found thermodynamically viable (although it may not be observed).

Anticipated steps:

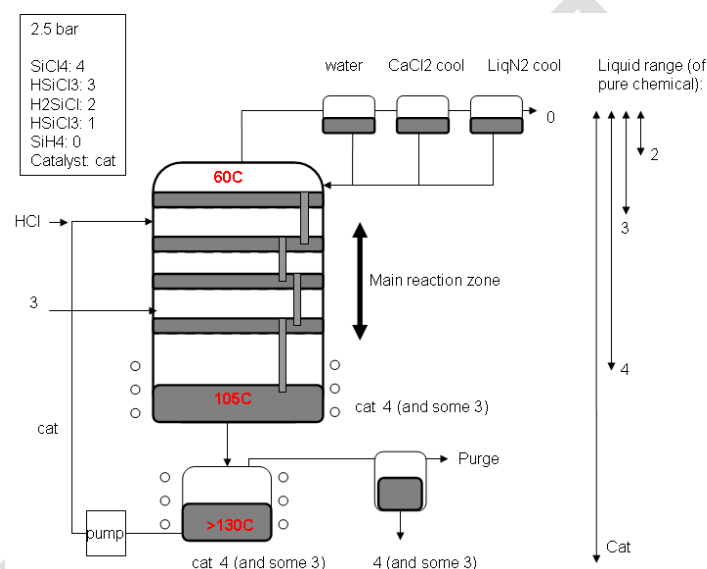
The present mono-chamber model will be used to estimate concentrations in a multi-plateau disproportionation reactor, using an iterative approach. Also, this document will be followed by a study on chlorosilane disproportionation kinetics.

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1. INTRODUCTION

In the Denal plant, HSiCl_3 (trichlorosilane or TCS) or H_2SiCl_2 (dichlorosilane or DCS) is transformed into SiH_4 (silane) and SiCl_4 (tetrachlorosilane). This is obtained by several reaction and distillation steps which progressively separate hydrogen-containing (volatile) species and chloride containing (non-volatile) species. The disproportionation reactions are led directly within a plateau-type distillation column. A non-volatile liquid catalyst is flown (and cycled) from top to bottom of the distillation column, so that disproportionation reactions occur in the liquid phase, on each plateau (3.5 bar).



Denal disproportionation apparatus

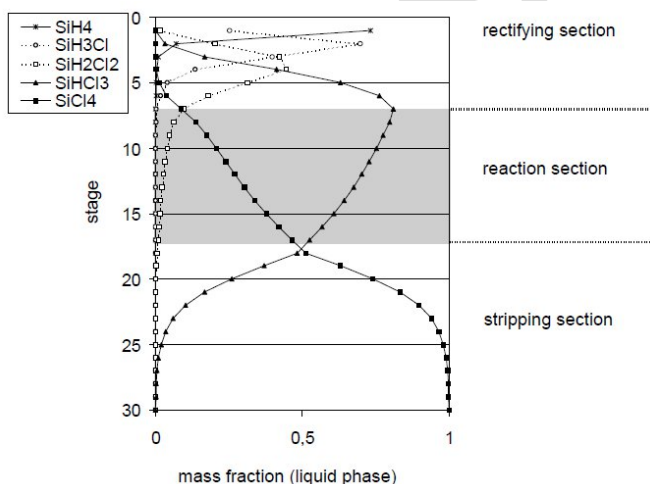
In a UC solid catalyst disproportionation apparatus, disproportionation reactions and separations are led in separate chambers, each reactor being at a given temperature and containing a solid bed of catalyst.

In the following, we use a model for a reactive chamber that is mono-temperature. This can be understood both as a single plateau in the Denal type reactive distillator, or as a single reactor in a UC apparatus. The present model depends only on temperature, stiochiometry, pressure, and liq to vapour molar ratio.

Some experimental and model data for such chemical concentrations are available from Denal, UC and Bayer, however, this data is not complete (mono-phase in particular) and not always usable because of lack of details on the conditions. For instance a report from Denal (ref. 1) mentions the values below that we interpret as concentration in the liquid phase for a mono-chamber reactor.

vol% at equil (at 80C)					
Start chemical	SiCl ₄	SiHCl ₃	SiH ₂ Cl ₂	SiH ₃ Cl	SiH ₄
SiHCl ₃	11.8	77.1	10.6	0.52	0.04
SiH ₂ Cl ₂	0.65	34.7	38.8	15.6	10.2

Similar data is also available in UC report for the Nasa (ref 11). There is also an article from Bayer AG (ref. 2), that describe concentrations at different heights of a reactive distillator packed with solid catalyst (technological mix between Denal and UC apparatus), but there is no indication on temperatures.



Data from D. Muller et al., Bayer AG (ref. 2)

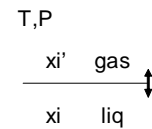
2. HOW TO FIND THE CHEMICAL CONCENTRATIONS?

We can modelize the mono-chamber reactor as a closed (atoms in = atoms out) liquid-vapour equilibrium system where HSiCl₃ (or H₂SiCl₂) is allowed to disproportionate and reach a chemical equilibrium. Disproportionation reactions are expected to follow thermodynamic equilibrium thanks to the active catalyst (to be demonstrated in the kinetic study). On the other hand, we assume that decomposition is slow enough for the formation

of pure silicon to be neglected (further discussed in paragraph 10). Hence, by default, we only consider the following chemicals: SiCl₄, SiHCl₃, SiH₂Cl₂, SiH₃Cl, SiH₄, HCl, and H₂.

Notations:

- P pressure (bar),
- T temperature (K)
- N total molar amount of molecules in liquid phase
- N' total molar amount of molecules in vapour phase
- R gas constant



For a chemical i:

- x_i concentration in liquid phase
- x_i' concentration in vapour phase
- n_i molar amount in liquid phase
- n_i' molar amount in vapour phase
- G Gibbs free energy of liquid phase (kJ)
- G' Gibbs free energy of vapour phase (kJ)
- VP_i vapour pressure at T (bar)
- μ_i⁰ the molar Gibbs free energy of the pure liquid chemical i (kJ/mol)
- μ_i⁰' the molar Gibbs free energy of the pure vapour chemical i (kJ/mol)
- V_i molar volume of liquid chemical i, (unit must be chosen so that V_iP in kJ/mol)

Free energy minimization is not a simple problem as we have to consider both a liquid-vapour equilibrium and a reactive equilibrium (with a fairly large number of chemicals). At liquid-vapour equilibrium, the relation between the concentrations in the liquid phase and in the vapour phase is very simple and deduced from Raoult law (this assumes an ideal gas, and an ideal liquid mixture, see ref. 8):

$$\frac{x_i'}{x_i} = \frac{VP_i}{P} \quad [1]$$

On the other hand, the reactive equilibrium must be found by a numerical minimization (we use the “solver” routine of the excel software, see ref. 3) of the Gibbs free energy, which must be summed in the two phases. If we assume that chemical activities are equal to molar concentrations we have similar relation for the two phases (see ref. 4):

$$G = N \sum_i x_i [\mu_i^0(T, P) + RT \ln x_i] \quad [2]$$

$$G' = N' \sum_i x_i' [\mu_i^{0'}(T, P) + RT \ln x_i'] \quad [3]$$

2.1. What is fixed, and what is not?

Such atomically closed system can be described by the following parameters,

- T, P
- N/N' (liquid-vapour ratio of molecules)
- Total (vapour + liquid) amount of each Si, Cl and H atoms

In the usual case, those parameters should be determined (~fixed) before the minimization (which is used to determine each chemical concentrations). However, as will be seen below, the pressure P often can not be fixed and must be determined during/by the minimization.

Neither N or N' are fixed (the number of molecules may change). For this reason, we have to minimize not on the x_i (or x_i') but on the molar amount n_i (or n_i'). Hence, we replace variables in equation [2] and [3] following:

$$x_i' = \frac{n_i'}{N'} \quad \text{and} \quad x_i = \frac{n_i}{N} \quad [4]$$

In order to get rid of half of the variables for the minimization, we assume that the system is at liquid-solid equilibrium during the minimization and hence we use relation [1], which translates into:

$$n_i' = \frac{N'}{NP} n_i VP_i \quad [5]$$

We must choose initial values such that the system is already at liquid-vapour equilibrium before minimization. For instance, we may start with 100% HSiCl_3 and $P =$ vapour pressure of HSiCl_3 .

2.2. Case with only chlorosilane chemicals

If we consider only SiCl_4 , HSiCl_3 , H_2SiCl_2 , H_3SiCl , H_4Si as chemicals, we have 10 variables (each n_i and n_i') to determine, and the above would give 10 equations as constraints:

- [5] => 5 equations
- Fixed amount of Si, Cl and H atoms => 3 equations
- Fixed pressure: $P = \frac{\sum n_i VP_i}{\sum n_i} \Rightarrow 1$ equation

- Fixed N/N' : $\frac{N}{N'} = \frac{\sum n_i}{\sum n'_i} \Rightarrow 1$ equation

The number of equations being equal to the number of variables, no (further) minimization is actually possible unless we free a variable. So, for this case we can either:

- free the values of P and use the minimization to set it (the system is free to set its own equilibrium pressure).
- fix P , but introduce the catalyst as an additional chemical of null vapor pressure and no reactivity. The concentration of the catalyst simply “regulates” the pressure of the system to the initial pressure value.

3. MINIMIZATION IN VAPOUR PHASE ONLY

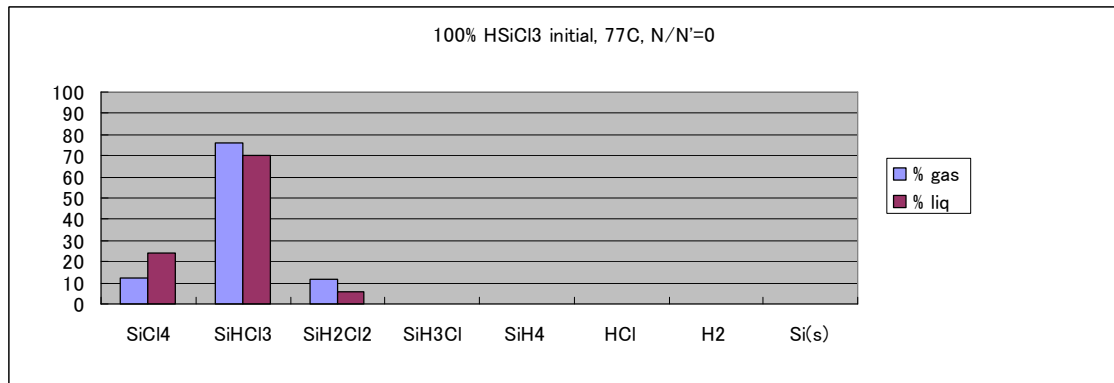
Firstly, we may consider the case where the vapour phase is dominant $N' \gg N$ (close to dew point) and hence minimize only G' . This approximation is valid for a solid type catalyst reactor (UC-REC type), where only a small amount of liquid is in contact with the catalyst.

Considering that data for molar Gibbs free energies is only available in vapour phase at 1 bar (actual pressure is several bars) in NIST or JANAF databases, we have to replace as follows in [3] (valid for ideal gas, see ref. 5):

$$\mu_i^{0'}(T, P) = \mu_i^{0'}(T, 1bar) + RT \ln P \quad [6]$$

with [4], this gives: $G' = \sum_i n'_i [\mu_i^{0'}(T, 1bar) + RT \ln(P \frac{n'_i}{N'})]$

The numerical minimization of G' to find the n'_i values is straightforward. Then, x_i and x'_i values are simply deduced following [4].



	SiCl ₄	SiHCl ₃	SiH ₂ Cl ₂	SiH ₃ Cl	SiH ₄	HCl	H ₂	Si(s)
% gas	12.09258604	76.08394616	11.5589	0.260017195	0.004550526	1E-97	1E-97	1E-97
% liq	23.92378124	70.42208399	5.59848	0.055560733	9.48624E-05	4.8E-99	1.9721E-100	3.63E-57
Pressure	3.63257694 bars							

4. MINIMIZATION IN LIQUID PHASE ONLY

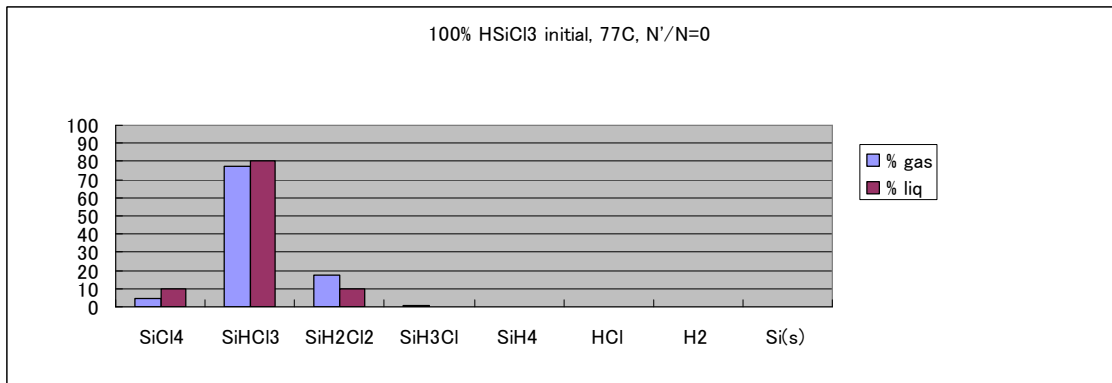
Secondly we may consider the case where the liquid phase is dominant $N \gg N'$ (close to boiling point) and hence minimize only G. This approximation is valid for a Denal type reactor if a large amount of liquid remains on the plateau.

Again, considering that the data for molar Gibbs free energies is only available in vapour phase at 1 bar in NIST or JANAF databases, we have to replace in [2] as follows:

- $\mu_i^0(T, P) = \mu_i^0(T, VP_i) + v_i(P - VP_i)$ [7] (valid for incompressible liquid, see ref. 5)
- $\mu_i^0(T, VP_i) = \mu_i^{0'}(T, VP_i)$ [8] (liq-vapour equilibrium of the pure chemical i)
- $\mu_i^{0'}(T, VP_i) = \mu_i^{0'}(T, P) + RT \ln(VP_i / P)$ [9] (valid for ideal gas, see ref. 5)
- and then use relation [6]

with [4], this gives:
$$G = \sum_i n_i [\mu_i^{0'}(T, 1bar) + RT \ln(VP_i \frac{n_i}{N})] + n_i v_i(P - VP_i)$$

The numerical minimization of G to find the n_i values is straightforward. Then, x_i and x_i' values are simply deduced following [4].



	SiCl4	SiHCl3	SiH2Cl2	SiH3Cl	SiH4	HCl	H2	Si(s)
% gas	4.434540054	77.3839791	17.6626	0.509800158	0.009033825	1.87E-96	4.51614E-95	2.5E-138
% liq	9.850636325	80.42146278	9.60538	0.122312526	0.000211451	1E-97	1E-97	1E-97
Pressure	4.078682401 bars							

As can be seen from the above, the amount of volatile species in vapour phase (silane in particular) is higher than in the case of paragraph 3. This indicates that it is favorable to have a liquid phase within the reactor.

5. MINIMIZATION IN BOTH LIQUID AND VAPOUR PHASES

In the real case, the amount of liquid versus vapour (N/N' ratio) is not well known and it may vary with operation conditions. It is therefore of interest to consider the intermediate situation of an arbitrary N/N' ratio.

In this case, the Gibbs free energy must be minimized on both phase simultaneously by summing G+G'. We can use the expressions of G and G' as estimated in 3. and 4. In order to keep only half of the variables, we replace the ni variables by ni' variable in G using relations [5] (we keep only the vapour variables, although we could keep only the liquid variables as well). This leads to:

$$G + G' = \sum_i n_i' [\mu_i^{0'}(T, 1bar) + RT \ln(P \frac{n_i'}{N'})] [1 + \frac{N}{N'} \cdot \frac{P}{VP_i}] + n_i' \frac{N}{N'} v_i P (\frac{P}{VP_i} - 1)$$

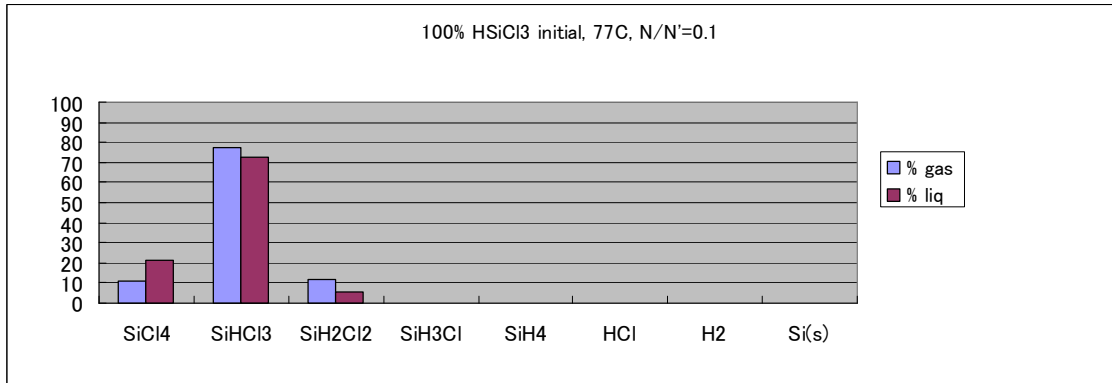
A

B

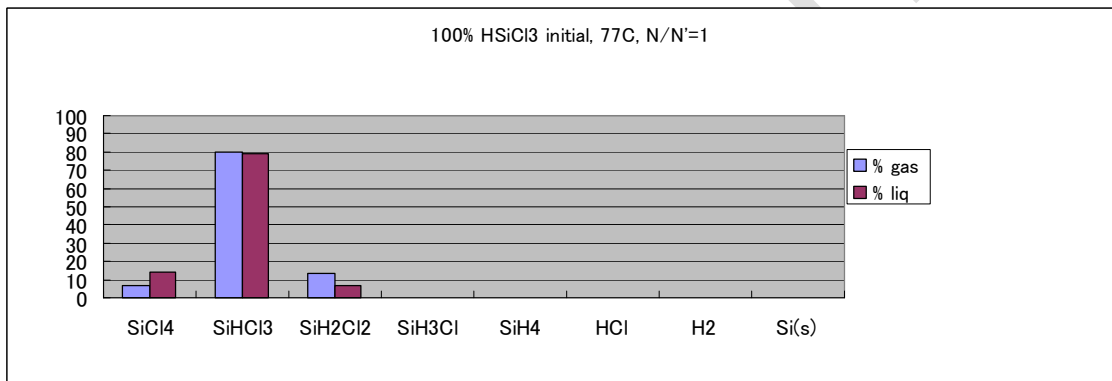
C

The A term corresponds to the vapour phase only (same as case 2.1). The B term gives the correction for the non-zero N/N'. The C term is a small correction for the liquid volume (may be neglected).

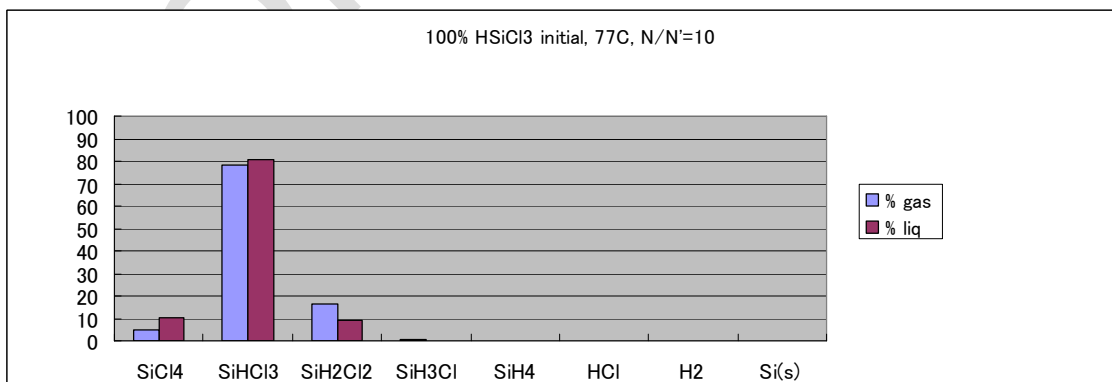
The numerical minimization of $G+G'$ to find the n_i' values is straightforward. Then, x_i and x_i' values are simply deduced following [4].



	SiCl ₄	SiHCl ₃	SiH ₂ Cl ₂	SiH ₃ Cl	SiH ₄	HCl	H ₂	Si(s)
% gas	10.71256249	77.28298984	11.7371	0.262891311	0.004417848	1E-97	1E-97	1E-97
% liq	21.52362079	72.64589622	5.77334	0.057049713	9.35308E-05	4.8E-99	2.0028E-100	3.69E-57
Pressure	3.6891486 bars							



	SiCl ₄	SiHCl ₃	SiH ₂ Cl ₂	SiH ₃ Cl	SiH ₄	HCl	H ₂	Si(s)
% gas	6.6100368	79.99796926	13.1132544	0.27385671	0.004882812	1E-97	1E-97	1E-97
% liq	13.98152079	79.16527144	6.79053426	0.06256467	0.000108828	5.0947E-99	2.1085E-100	3.88378E-57
Pressure	3.883780894 bars							

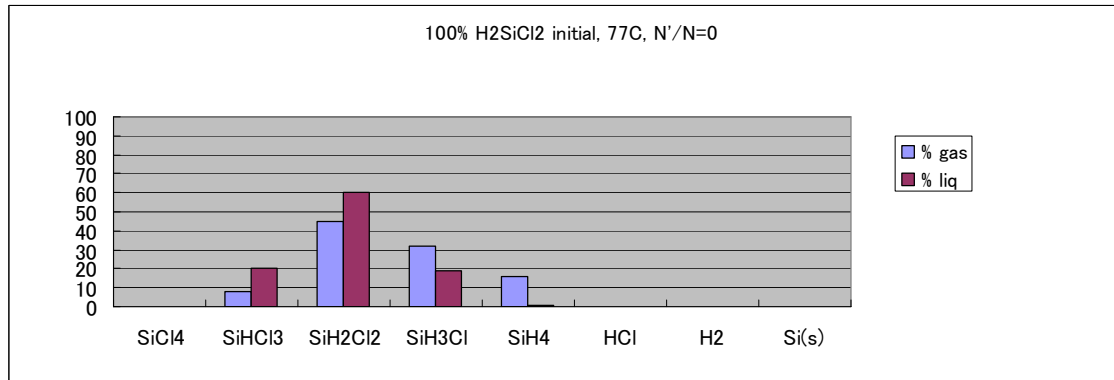


	SiCl ₄	SiHCl ₃	SiH ₂ Cl ₂	SiH ₃ Cl	SiH ₄	HCl	H ₂	Si(s)
% gas	4.793696916	77.96453786	16.4986245	0.70948789	0.033652851	1E-97	1E-97	1E-97
% liq	10.56219409	80.36850458	8.89967672	0.1688433	0.000781317	5.307E-99	2.1963E-100	4.04564E-57
Pressure	4.045644865 bars							

Note that the minimization is less precise as N/N' increases.

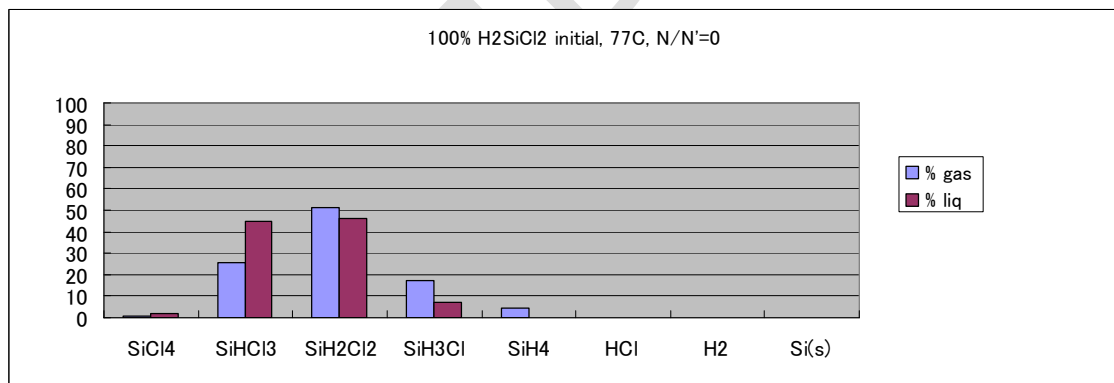
6. MINIMIZATION WITH 100% H₂SICL₂ INITIAL

Considering pure liquid phase ($N' = 0$):



	SiCl4	SiHCl3	SiH2Cl2	SiH3Cl	SiH4	HCl	H2	Si(s)
% gas	0.018316685	7.917941501	44.8432	31.58610746	15.6344009	7.59E-97	1.83357E-95	1E-138
% liq	0.100214815	20.26761074	60.0655	18.66536262	0.901338878	1E-97	1E-97	1E-97
Pressure	10.0459091 bars							

Considering pure vapour phase ($N = 0$):

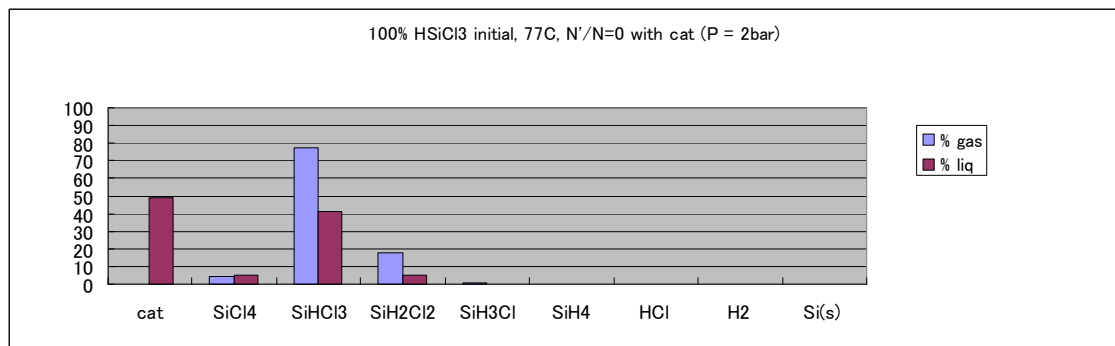


	SiCl4	SiHCl3	SiH2Cl2	SiH3Cl	SiH4	HCl	H2	Si(s)
% gas	0.533863947	25.907628	51.3708	17.40007601	4.787639945	1E-97	1E-97	1E-97
% liq	1.965554611	44.62594041	46.3035	6.919280406	0.185736734	8.9E-99	3.67E-100	6.76E-57
Pressure	6.760186959 bars							

7. MINIMIZATION WITH THE CATALYST

From now, we consider only the pure liquid phase case ($N'=0$).

As mentioned earlier, it is possible to run the minimization with a determined pressure if we use the catalyst as a “pressure regulator”. Here we have fixed pressure to 2 bars:

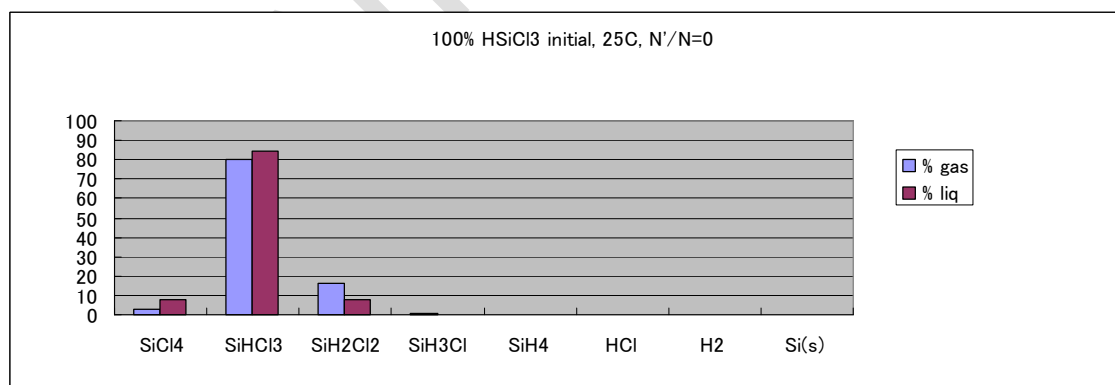


	cat	SiCl4	SiHCl3	SiH2Cl2	SiH3Cl	SiH4	HCl	H2	Si(s)
% gas	0	4.4497282	77.29817202	17.717	0.517184661	0.017888795	1.87E-96	4.51507E-95	2.5E-138
% liq	48.97959	5.044253002	40.99565293	4.91697	0.063323407	0.000213681	5.1E-98	5.10204E-98	5.1E-98
Pressure	2.081458 bars								

Note that the results in the vapour phase are not much different from the result without catalyst (around 4 bar).

8. MINIMIZATION WITH LOWER TEMPERATURE

Running the minimization at lower temperature gives lower concentration of disproportionated compounds. From 77C to 25C, H₂SiCl₂ concentration in liquid phase falls from 9.6% to 7.6%.

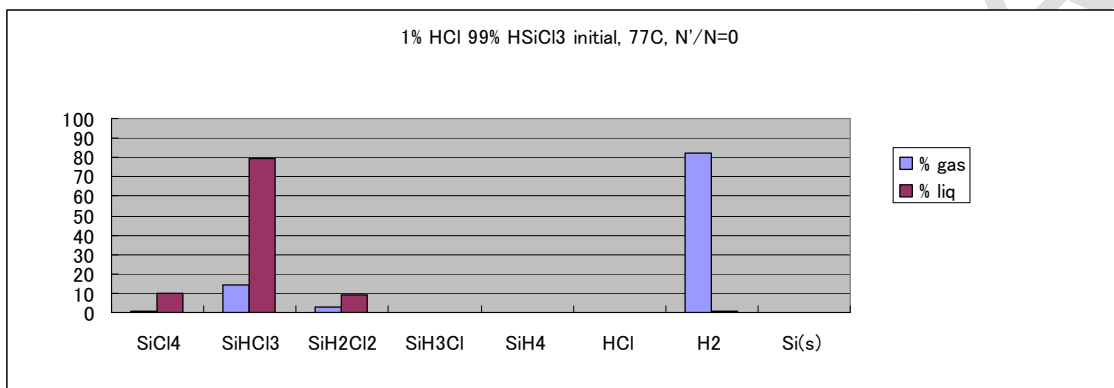


	SiCl4	SiHCl3	SiH2Cl2	SiH3Cl	SiH4	HCl	H2	Si(s)
% gas	2.943286237	80.31982345	16.3598	0.369168495	0.007895102	4.1E-96	1.97117E-94	1.2E-137
% liq	7.755080434	84.55729162	7.62026	0.067286865	8.28109E-05	1E-97	1E-97	1E-97
Pressure	0.838423605 bars							

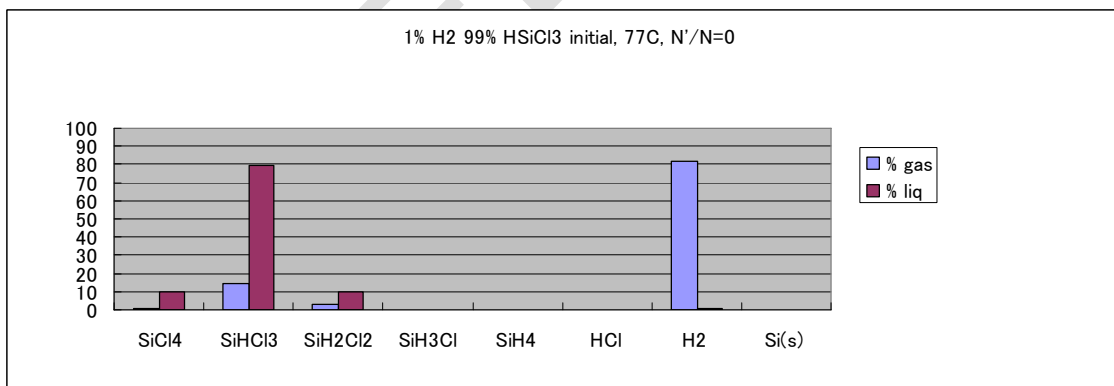
9. MINIMIZATION WITH SOME HCL OR H2

Starting with 99% HSiCl₃ and 1% HCl, we find a convergence toward H₂. Hence, HCl reacts with chlorosilanes to reduce their H content. If we start with H₂ 1% instead of HCl, we end up with similar values. This corresponds to the experimental case: H₂ is found in the output of the disproportionation reactor when adding HCl.

Note that the final amount of chlorosilanes in vapour phase is reduced due to gas volume occupation by H₂.



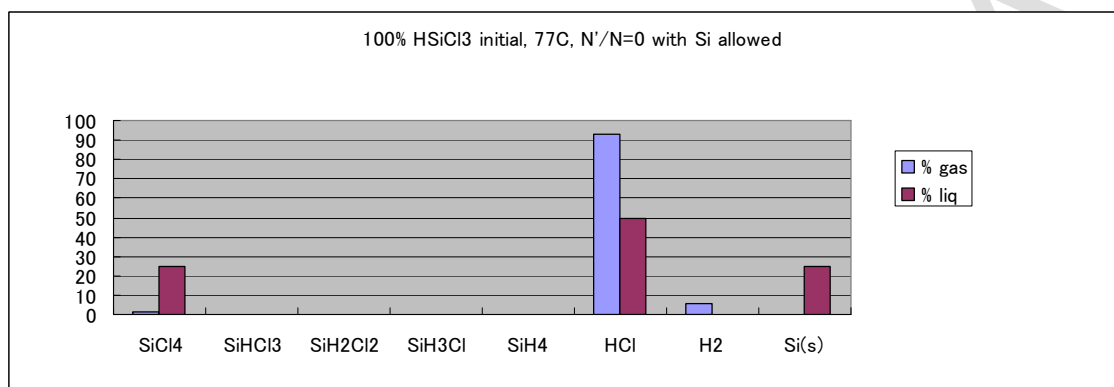
	SiCl ₄	SiHCl ₃	SiH ₂ Cl ₂	SiH ₃ Cl	SiH ₄	HCl	H ₂	Si(s)
% gas	0.846484546	14.04118644	3.04915	0.084444632	0.001290249	3.39E-97	81.97744574	4.5E-139
% liq	10.25672792	79.59738758	9.04506	0.110513953	0.000164735	9.9E-98	0.990149316	9.9E-98
Pressure	22.24815423 bars							



	SiCl ₄	SiHCl ₃	SiH ₂ Cl ₂	SiH ₃ Cl	SiH ₄	HCl	H ₂	Si(s)
% gas	0.804612671	14.02534983	3.20614	0.090950455	0.001455039	3.39E-97	81.87149227	4.4E-139
% liq	9.761493727	79.60646175	9.52258	0.119176206	0.000186005	9.9E-98	0.99009901	9.9E-98
Pressure	22.27581473 bars							

10. MINIMIZATION WITH DECOMPOSED CHEMICALS

The minimization above have been led with the following chemicals: SiCl₄, SiHCl₃, SiH₂Cl₂, SiH₃Cl, SiH₄, HCl, H₂. We have excluded other possible chemicals from the minimization, and in particular we have excluded decomposition toward Si. If we allow Si as a chemical, we find a convergence toward Si, H₂, HCl and SiCl₄. This indicates that from the thermodynamical perspective, the hydrosilanes are not stable. Practically, they are metastable.



	SiCl ₄	SiHCl ₃	SiH ₂ Cl ₂	SiH ₃ Cl	SiH ₄	HCl	H ₂	Si(s)
% gas	1.128300767	4.8108E-99	9E-99	2.08383E-98	2.13598E-97	92.95491	5.916792392	6.11E-41
% liq	25.09839776	5.00656E-98	5E-98	5.00656E-98	5.00656E-98	49.8032	0.131197015	24.9672
Pressure	40.84372088 bars							

11. CONCLUSIONS

We have presented a model to estimate equilibrium concentrations of chloro-silanes, at given temperature, and stoichiometry. From the cases considered we conclude that:

- Disproportionation of HSiCl_3 roughly gives 10% of H_2SiCl_2 . However if liquid HSiCl_3 is maintained in sufficient amount in reactor, we obtain 17.7% H_2SiCl_2 in the gas output
- Disproportionation of H_2SiCl_2 with liquid H_2SiCl_2 maintained in sufficient amount in reactor, gives 31.6% H_3SiCl and 15.6% silane in the gas output.
- It is possible to reduce the pressure by increasing the amount of catalyst, little changing the equilibrium concentrations.
- Disproportionation of HSiCl_3 at lower temperature gives a significantly lower amount of H_2SiCl_2 in output.
- HCl reacts with chlorosilanes to reduce the H content, and produces H_2 .
- Decomposition to Si is found thermodynamically viable (although it may not be observed). Decomposition of HSiCl_3 gives SiCl_4 , Si, HCl and H_2 .

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