Hydrogen Chloride Desorption from the Chlorinated Silane Solutions

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Abstract

Rate of hydrogen chloride desorption from the $SiCl_4$ and $SiHCl_3$ solutions was studied in time at gas end pressure $P_{total} = 1.3$ atm in a temperature range of 223–293 K. One may use desorption rate data for choosing better conditions for the HCl recover from chlorinated silanes.

INTRODUCTION

In order to arrange the closed circuit of poly-crystalline silicon production from chlorinated silanes ($SiCl_4$, $SiHCl_3$) it is necessary to regenerate end vapor-gas mixture consisting of hydrogen and hydrogen chloride for their recycling. This approach will definitely reduce production costs, and make the process less harmful to environment.

Regeneration may be organized stage by stage according to the following scheme:

1. Vapour-gas mixture absorption by chlorinated silanes (ChS) accompanied by the hydrogen recycle.

2. Separation of the HCl + ChS mixture *via* its distillation or desorption, and HCl and ChS recycle.

Conventionally it is suggested [1] to separate HCl and ChS *via* distillation at elevated temperatures (≥340 ℃). However, desorption process arranged at the ambient temperature significantly reduces the harmful effect of aggressive media (HCl + ChS) on the process equipment. Therefore, desorption method has several advantages in comparison to distillation.

With this regard we have accumulated physical and chemical data related to the vapor-liquid equilibrium in system HCl + ChS [2]. We believe that these data allow the optimization of the process mixture separation.

For the practical implementation of vapor-gas separation by desorption one should know how desorption rate changes depending on the absorbent-solvent ($SiCl_4$, $SiHCl_3$) system parameters and temperature.

In the present study we check how the rate of HCl desoprtion (dP_{total}/dt) from solutions HCl + $SiCl_4$ and HCl + $SiHCl_3$ changes with time at the given end gas pressure $P_{total} = 1.3$ atm at temperatures 223–293 K. We consider these data as necessary for estimating the efficiency of HCl + ChS separation for their recycling as well as for the correct choice of the process performance conditions.

EXPERIMENTAL

Hydrogen chloride desorption from the chlorinated silane solutions was experimentally studied with one of traditional versions of the boiling point method [3], according to which total gas pressure is varied, temperature being fixed. At a quasi-monovariant state of the system the pressure–time curve reaches a plateau. Points on the plateau correspond to equilibrium, and thus may be used to calculate the compositions of co-existing liquid–gas phases.

Experimental points position before the plateau attainment depends on several factors

such as permanent change of liquid and gas phase compositions, diffusion in gases, pressure release rate, and reactor design.

Therefore, these points may be considered solely for interpreting desorption process performed in some particular equipment.

Nevertheless, basing on these data one may obtain a general idea about the gas phase enrichment with hydrogen chloride, and substantiate the absorbent choice and process temperature, which is important for reactor design.

In paper [2] one may find the description of set-up we used to determine the rate of gas desorption, allowing the simultaneous investigation of desorption rate time dependence at various temperatures and of liquid-vapor equilibrium in system HCl + ChS. Investigation involves the following stages:

1. Chlorinated silane is saturated with vapor-gas mixture (HCl + H$_2$) in a dynamic regime at temperature T_1, equal to 213 and 203 K for SiCl$_4$ and SiHCl$_3$, respectively, total pressure being P_{total} = 6 atm, hydrogen chloride pressure being P_{HCl}= 1.3 atm. Initial vapour-gas mixture composition (H$_2$, HCl, ChS) is close to the real final composition at polycrystalline silicon production.

2. Then reactor is cooled to 143 K for the gas mixture condensation and gaseous hydrogen removal under vacuuming. Saturated vapor pressure over solid HCl, SiHCl$_3$ and SiCl$_4$ at P_{total}= 6 atm and T = 143 K is 19.4, 1.6 10^{-3}
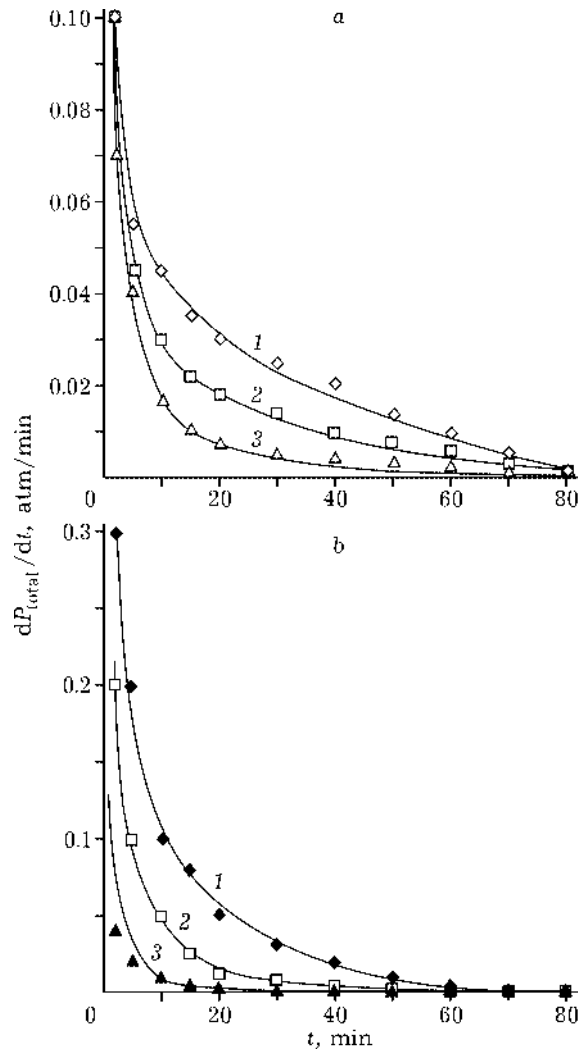
Fig. 1. Desorption rate dP_{total}/dt *vs.* time in the case of solutions HCl + SiCl$_4$ (*a*) and HCl + SiHCl$_3$ (*b*) depending on the process temperature (K): *a* − 233 (*1*), 253 (*2*), 293 (*3*); *b* − 223 (*1*), 253 (*2*), 293 (*3*).

TABLE 1

Time dependencies of desorption rate (dP_{total}/dt), pressure (P_{total}, P_{HCl}, P_{SiCl_4}), concentration (x_{HCl}) and desorption coefficient (η) at the HCl desorption in the SiCl$_4$ solution at various temperatures

t, min	T = 233 K				T = 253 K				T = 293 K					
	dP_{total}/dt, atm/min	P_{total} = P_{HCl}, atm	x_{HCl}	η	dP_{total}/dt, atm/min	P_{total} = P_{HCl}, atm	x_{HCl}	η	dP_{total}/dt, atm/min	P_{total}, atm	P_{HCl}, atm	P_{SiCl_4}, atm	x_{HCl}	η
2	0.100	3.10	0.36	−	0.100	3.00	0.28	−	0.07	2.30	1.86	0.44	0.111	−
5	0.055	2.80	0.32	0.19	0.045	2.80	0.26	0.12	0.04	1.75	1.42	0.33	0.085	0.54
10	0.045	2.53	0.29	0.33	0.030	2.12	0.20	0.50	0.016	1.63	1.32	0.31	0.079	0.67
15	0.035	2.30	0.27	0.43	0.022	1.90	0.18	0.62	0.010	1.55	1.26	0.29	0.075	0.75
20	0.030	2.08	0.24	0.57	0.018	1.82	0.17	0.69	0.007	1.48	1.20	0.28	0.072	0.81
30	0.025	1.78	0.21	0.71	0.014	1.64	0.15	0.81	0.005	1.41	1.14	0.27	0.068	0.89
40	0.020	1.53	0.18	0.85	0.010	1.51	0.14	0.87	0.004	1.37	1.11	0.26	0.066	0.94
50	0.014	1.33	0.15	1.00	0.008	1.41	0.13	0.94	0.003	1.34	1.09	0.25	0.065	0.96
60	0.010	1.32	0.15	1.00	0.006	1.35	0.12	1.00	0.002	1.32	1.07	0.25	0.064	0.98
70	0.005	1.31	0.15	1.00	0.003	1.31	0.12	1.00	0.001	1.31	1.06	0.25	0.063	1.00
80	0.001	1.30	0.15	1.00	0.001	1.30	0.12	1.00	0.000	1.30	1.05	0.25	0.063	1.00

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and $3 \cdot 10^{-5}$ torr, respectively. Therefore, vapour-gas mixture freezing out at this temperature provides total hydrogen recover.

3. Temperature of remaining HCl + ChS solution is raised to T_2 equal to 233 and 223 K for $SiCl_4$ and $SiHCl_3$, respectively.

4. After temperature T_2 is set, gas pressure in reactor is gradually released through a valve (see Fig. 1 in paper [1]) to $P_{total} = 1.3$ atm, pressure change versus time dP_{total}/dt being fixed on time t. Pressure release to 1.3 atm is repeated until $dP_{total}/dt = 0$. This means that liquid-vapour equilibrium is attained at $P_{total} = 1.3$ atm.

5. Then reactor temperature is risen to $T_3 = 253$ K, and pressure release procedure is repeated to $P_{total} = 1.3$ atm, and so on.

We have chosen final value $P_{total} = 1.3$ atm, since it corresponds to the almost complete gaseous HCl removal from the ChS solutions with a simple enough hardware. In the general case ($P_{total} = P_{HCl} + P_{ChS}$) at elevated solution temperatures (293 K for $SiCl_4$, 293 and 253 K for $SiHCl_3$) we introduced corrections for the presence of ChS vapours in the desorbed gas according to the data of [1] (Tables 1, 2).

RESULTS AND DISCUSSION

Figure 1 and Tables 1, 2 show dP_{total}/dt measured at time moment t, as well as functions $P_{total} = f(t)$ and $P_{HCl} = f_1(t)$ calculated basing on these measurements. Using Henry constant [2] we have calculated the corresponding time dependence of HCl concentration ($x_{HCl} = f_2(t)$) in the liquid phase to determine relative desorption efficiency according to desorption coefficient η:

$$\eta = (x_s - x_t)/(x_s - x_\infty) = F(t)$$

where x_s, x_∞ and x_t are the starting, final concentrations of HCl and its concentration at time t, respectively.

In Fig. 2 one may see values $\eta = F(t)$, calculated according to above written equation and characterizing the change in the portion of adsorbed gas in solution at time t for various temperatures T.

For desorption efficiency estimation one often uses value $\eta = 0.5$, i.e. when half of dissolved gas is absorbed, and the corresponding

TABLE 2

Time dependencies of desorption rate (dP_{total}/dt), pressure (P_{total}, P_{HCl}, P_{SiHCl_3}), concentration (x_{HCl}) and desorption coefficient (η) at HCl desorption in the $SiHCl_3$ solution at various temperatures

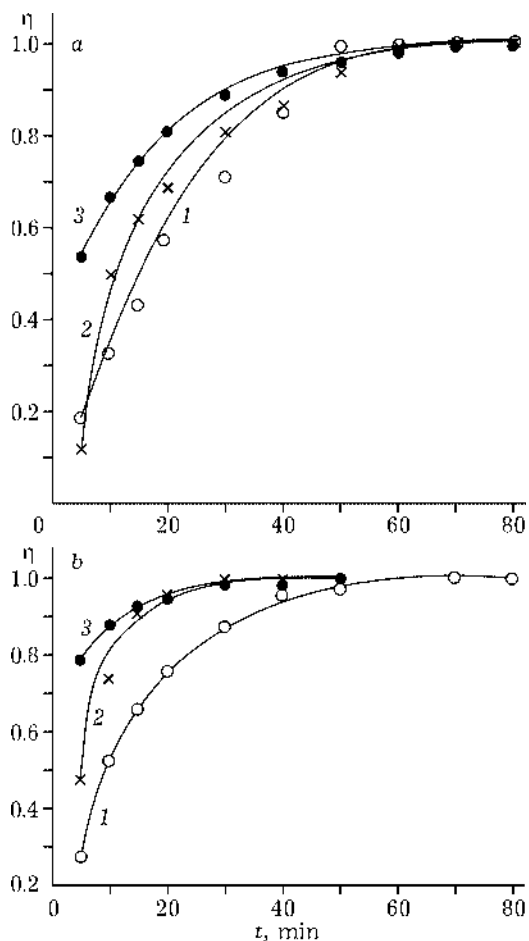| t, min	$T = 233$ K				$T = 253$ K						$T = 293$ K					
	dP_{total}/dt, atm/min	$P_{total} = P_{HCl}$, atm	x_{HCl}	η	dP_{total}/dt, atm/min	P_{total}, atm	P_{HCl}, atm	P_{SiHCl_3}, atm	x_{HCl}	η	dP_{total}/dt, atm/min	P_{total}, atm	P_{HCl}, atm	P_{SiHCl_3}, atm	x_{HCl}	η
2	0.300	5.50	0.84	–	0.200	3.31	3.07	0.24	0.38	–	0.040	2.55	1.308	0.97	0.087	–
5	0.200	4.33	0.66	0.28	0.100	2.33	2.14	0.19	0.27	0.48	0.020	1.55	0.795	0.76	0.053	0.79
10	0.100	3.33	0.50	0.53	0.050	1.84	1.69	0.15	0.21	0.74	0.010	1.44	0.738	0.70	0.049	0.88
15	0.080	2.80	0.42	0.66	0.025	1.51	1.39	0.12	0.17	0.91	0.004	1.39	0.713	0.68	0.047	0.93
20	0.050	2.33	0.35	0.76	0.012	1.44	1.32	0.12	0.16	0.96	0.001	1.34	0.687	0.65	0.046	0.95
30	0.030	1.83	0.28	0.88	0.008	1.32	1.23	0.09	0.15	1.00	0.000	1.32	0.677	0.64	0.045	0.98
40	0.020	1.53	0.23	0.96	0.004	1.32	1.21	0.11	0.15	1.00	0.000	1.31	0.672	0.64	0.045	0.98
50	0.010	1.43	0.22	0.97	0.001	1.31	1.20	0.11	0.15	1.00	0.000	1.30	0.667	0.63	0.044	1.00
60	0.005	1.33	0.20	1.00	0.000	1.30	1.20	0.10	–	–	–	–	–	–	–	–
70	0.001	1.30	0.20	1.00	0.000	1.30	1.20	0.10	–	–	–	–	–	–	–	–
80	0.000	1.30	0.20	1.00	0.000	1.30	1.20	0.10	–	–	–	–	–	–	–	–

Fig. 2. Desorption coefficient η_{HCl} in the case of solvent SiCl$_4$ (*a*) and SiHCl$_3$ (*b*) *vs.* time depending on the process temperature (K): *a* − 233 (*1*), 253 (*2*), 293 (*3*); *b* − 223 (*1*), 253 (*2*), 293 (*3*).

time moment ($t_{0.5}$) is determined. According to Fig. 2 in the case of solvent SiCl$_4$ $t_{0.5}$ is 5, 10 and 15 min for *T* equal to 293, 253 and 233 K, respectively, while in the case of SiHCl$_3$ desorption is so active that at *T* = 293 K η exceeds 0.5 and attains ~0.79 at *t* = 2 min. Unfortunately we failed to estimate desorption activation ener-

gy by the temperature dependence of $\eta_{0.5}$ due to uncertainty of η determining at 293 K.

Experimental dependencies $dP_{total}/dt = f(t)$ (see Fig. 1) refer to the non equilibrium state of the system, and depend on reactor design. Nevertheless, correspondingly calculated P_{HCl} and concentration x_{HCl} in solution for final $dP_{total}/dt = 0$ at $P_{total} = 1.3$ atm well agree with the values of HCl concentration in the solution determined with the mass spectrometry method for the system thermodynamic equilibrium as reported in [1] (see Tables 1 and 2).

Therefore, our choice of the method and results obtained with this method seem to be quite reliable and give evidence of the good efficiency of vapour-gas mixture (HCl + ChS) separation by desoprtion in temperature range 223−293 K for solvents SiCl$_4$ and SiHCl$_3$. Most efficientl desorption is realized at *T* = 293 K (HCl molar fraction in this case is 0.063 and 0.0044 in SiCl$_4$ and SiHCl$_3$, respectively).

CONCLUSION

Our investigation shows that vapour-gas mixture (HCl + ChS) separation using desorption, performed at *P* = 1.3 atm and at temperatures *T* = 223−293 K, is rather efficient with respect to the rate of process performance and to the desorbing component recover.

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