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Thermodynamic Simulation of Separation Processes of Gaseous Hydrogen–Hydrogen Chloride Mixtures by the Method of Absorption with Chlorosilanes

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Abstract

The problem of gaseous hydrogen–hydrogen chloride mixture separation with the use of chlorosilanes as sorbents is considered. The possibility of hydrogen purification from HCl up to 0.1 mol. % and its reentry into the process cycle at the stage of trichlorosilane reduction with hydrogen is demonstrated. The hydrogen chloride purified from admixed chlorosilanes can be used as a reactant for the trichlorosilane production from metallurgical silicon.

INTRODUCTION

Ultra-pure hydrogen and hydrogen chloride are the most important reactants for the trichlorosilane technology of semiconductive polycrystalline silicon preparation. Hydrogen chloride with a dew point not higher than −70 °C is used at the stage of trichlorosilane preparation. Hydrogen of the same purity is used to reduce trichlorosilane to silicon. The vapour–gas mixtures generated by this reaction contain hydrogen, hydrogen chloride and chlorosilanes. Upon condensation of chlorosilanes, it is necessary to solve the problem of hydrogen–hydrogen chloride mixture separation with the aim of recycling the reactants to the process cycle.

Judging from the physicochemical characteristics of hydrogen chloride, its freezing out is not improbable, however this procedure is energy consuming. The use of the traditional adsorbents in this case is also undesirable for reasons of possible pollution of gases by uncontrolled impurities. The mixtures $HCl–H_2$ contain traces of chlorosilanes, that is why the water-free chlorosilanes would be appropriate for use as absorbents. In this case hydrogen as well as hydrogen chloride can be recycled as reactants to the corresponding stages of the process.

According to [1, 2], the deviation of the liquid solution $SiCl_4–SiHCl_3$ from an ideal is no more than 10 %; that is, the heat of mixing is less than 200 kJ/mol of mixture. Solutions $SiCl_4–SiH_2Cl_2$ and $SiHCl_3–SiH_2Cl_2$ have similar properties. The data [2] appear as highly reliable, since the heat of mixing for a related system $CCl_4–CHCl_3–CH_2Cl_2$ also is no more than ~200 kJ/mol of mixture [3]. A different situation arises with the liquid solutions $SiCl_4–HCl$ and $SiHCl_3–HCl$. As an example, the measurements [4] show that the heat of mixing HCl with $SiCl_4$ at 203–293 K comprises 10.6 kJ/mol, whereas the enthalpy of mixing $SiHCl_3$ and HCl under these conditions is equal to 9.7 kJ/mol.

From these results it may be deduced that Raoult's law is valid for silicon-containing components of solution, whereas for HCl there is a need to introduce the corresponding corrections for Henry's constant.

The temperature dependence of Henry's constants in the range 203–293 K was found in [4]: $\ln K_{SiCl_4}$ (atm.) = 5.13 − 687/T (enthalpy of desorption intogas $\Delta_d H_{SiCl_4}$ = 5.69 kJ/mol); $\ln K_{SiHCl_3}$ (atm.) = 5.37 − 800/T ($\Delta_d H_{SiHCl_3}$ = 6.67 kJ/mol). Analysis of [4] shows that these equations are workable on condition that the molar fraction of HCl in the liquid (x_{HCl}) is no more than 0.3. Although $SiHCl_3$ does better as a sorbent, sometimes technologically it is convenient to use the mixtures of chlorosilanes. Effective Henry's constant in this situation can be estimated on the principle of additivity:

$$\ln K_{eff}\ (\text{atm.}) = x_{SiHCl_3}\ln K_{SiHCl_3} + (1 - x_{SiHCl_3})\ln K_{SiCl_4}$$

Molar volume of the vapour-gas mixture (VGM) can be expressed as $V = RT/P_{total}$. The inlet and outlet volumes of gas are identical. Then, according to the conservation laws, the following number of moles passes into solution at a given temperature:

$$n_{SiHCl_3}/1\ \text{mol of VGM} = (P_{SiHCl_3}(\text{in}) - P_{SiHCl_3}(\text{out}))/P_{total} \quad (1)$$

$$n_{SiCl_4}/1\ \text{mol of VGM} = (P_{SiCl_4}(\text{in}) - P_{SiCl_4}(\text{out}))/P_{total} \quad (2)$$

$$n_{SiH_2Cl_2}/1\ \text{mol of VGM} = (P_{SiH_2Cl_2}(\text{in}) - P_{SiH_2Cl_3}(\text{out}))/P_{total} \quad (3)$$

$$n_{HCl}/1\ \text{mol of VGM} = (P_{HCl}\ (\text{in}) - P_{HCl}\ (\text{out}))/P_{total} \quad (4)$$

This is a system of four equations with four unknowns which correspond to the quantities of compounds passing into the condensed phase.

The condensation of chlorosilanes is carried out at −5...−60 °C. Depending on the pressure in the reactor of hydrogen reduction, the molar fraction of HCl in gas makes up 0.6–1.6 % (for starting relation between trichlorosilane and hydrogen flows that is equal to 1 : 3.5) and 0.8–2.5 % (for the relation that is equal to 1 : 6). For definiteness, we shall assume that P_{total} for the condensation unit is equal to 4 atm.

To reduce HCl content in hydrogen to 0.1 mol. %, for example, at HCl concentration in gas (y_{HCl}) equal to 0.006, it is necessary that 0.005 mol of hydrogen chloride of every mole of gas mixture should be transferred to solution. The residual partial pressure of HCl may not exceed $0.001P_{total}$. According to Henry's law, this pressure is calculated as the product of Henry's constant at given temperature and of the molar fraction of HCl in solution:

$$0.001P_{total} = Kx_{HCl} = Kn_{HCl}/(n_{HCl} + n_{sorb})$$

where n_{HCl} is the number of hydrogen chloride moles of one mole of gas; n_{sorb} is the required amount of sorbent.

In our case $0.001P_{total} = K0.005/(0.005 + n_{sorb})$. Hence it is easy to evaluate that 6.3 mol of $SiHCl_3$ absorb 0.005 mol of HCl from 1 mol of gas phase at −60 °C; 5.2 mol of $SiHCl_3$ are required at −70 °C and 4.25 and 2.63 mol at −80 and −100 °C. In a similar manner, the required quantity of one or other sorbent may be calculated for gas mixture of a different composition.

Thus hydrogen incorporating no more than 0.1 mol. % HCl and only a tolerable content of water can be recycled to the reactor of trichlorosilane reduction with hydrogen.

To make an estimate of HCl content in the liquid mixture, let us call attention to the following facts. It is known that HCl concentrations in gas mixture (y_{HCl}), prior to the onset of condensation and absorption, vary from 0.006 to 0.025. As a result of performing these processes, essentially all chlorosilanes (molar fraction $y_{ch/s}$) and hydrogen chloride are transferred to liquid phase, and the calculated number of sorbent moles (n_{sorb}) is added to solution in the process.

By this means one mole of gas phase ($n_{HCl} + n_{ch/s} + n_{H_2} = 1$) gives rise to liquid phase ($N = n_{HCl} + n_{ch/s} + n_{sorb}$) leaving practically pure hydrogen in the gas phase. We emphasize that the values for concentrations y_i in the case of one mole of gas agree with the corresponding quantities n_i. Prior to the onset of condensation and absorption the quantity y_{H_2} is known, that is why $N = 1 + n_{sorb} - n_{H_2}$. Consequently, the molar fraction of HCl in the liquid is defined as $x_{HCl} = n_{HCl}/N = y_{HCl}/N$.

The desorption of hydrogen chloride is to be carried out at higher temperatures, in so doing standard distillation may be used with one or more dephlegmators [5, 6]. Let us build a model of such a set-up at different temperatures of the evaporation (distillation) still and one dephlegmator. For simplicity, we shall consider a solution involving only two components

– HCl and $SiHCl_3$. In this case we have for a still: $P_{total} = K(T)x_{HCl} + P^0(1 - x_{HCl})$, and $x_{HCl} = (P_{total} - P^0(T))/(K(T) - P^0(T))$, where K is Henry's constant at the distillation temperature; x_{HCl} is the molar fraction of HCl in solution; P^0 is the pressure of pure $SiHCl_3$. Equations (1)–(4) demonstrate that a change to situations with different starting conditions is readily available.

The characteristics of gas phase are presented in Table 1 as functions of solution composition, still and dephlegmator temperatures. The liquid composition and the distillation temperature determine pressures of HCl and $SiHCl_3$ in the still, the total pressure is the sum of partial ones, and the mole fraction of HCl in the gas (y_{HCl}) is the ratio of partial pressure to total one. The dephlegmator temperature T_1 is below the still temperature T. Consequently, the partial pressure as well as the total one are reduced before condensation: $P_{deph} = T_1P_{still}/T = P_{inlet}$. The concentrations of $SiHCl_3$ and dissolved HCl from 1 mol of gas mixture can be found from a set of equations:

$$P_{inlet}(HCl) - K(T_1)n_{HCl}/(n_{HCl} + n_{SiHCl_3}) = P_{inlet}(total)n_{HCl}$$

$$P_{inlet}(SiHCl_3) - P^0(T_1)n_{SiHCl_3}/(n_{HCl} + n_{SiHCl_3}) = P_{inlet}(total)n_{SiHCl_3}$$

Using the obtained data for the solution as the basis, one may easily calculate the purity of gas as it leaves the dephlegmator.

It is evident from Table 1 that 1 mol of gas transfers from solution y_{HCl} mol.% HCl dissolved in (y_{HCl}/x_{HCl}) moles of liquid. This is a heat-absorbing process that for $SiHCl_3$ is accompanied by energy consumption $E = y_{HCl}\Delta_dH_{SiHCl_3}$. Figure 1 illustrates a character of the change of this consumption as a function of the degree of solution purification as well as the change of the derivative of the energy consumed for desorption. From this figure we notice that the derivative shows a rise as the HCl content of the liquid is reduced. By this means the process is progressively retarded as hydrogen chloride is removed.

The content of hydrogen chloride in the gas phase is plotted in Fig. 2 as a function of the

TABLE 1

Composition of liquid and gas phases in the process of hydrogen chloride desorption

Still				Dephlegmators								
	T = 40 °C			−40 °C			−70 °C			−100 °C		
x_{HCl} (liq), mol. %	P_{HCl}, Torr	P_{total}, Torr	y_{HCl}(g), mol. %	P_{HCl}, Torr	P_{total}, Torr	y_{HCl}(g), mol. %	P_{HCl}, Torr	P_{total}, Torr	y_{HCl}(g), mol. %	P_{HCl}, Torr	P_{total}, Torr	y_{HCl}(g), mol. %
0.05	6.3	437.6	1.45	4.5	11.1	40.21	3.8	4.4	86.45	3.05	3.08	99.253
0.10	12.7	443.8	2.86	8.9	15.5	57.38	7.6	8.2	92.74	6.10	6.13	99.626
0.15	19.0	449.9	4.23	13.4	20.0	66.90	11.3	11.9	95.05	9.15	9.18	99.751
0.20	25.4	456.0	5.56	17.8	24.4	72.95	15.1	15.7	96.24	12.20	12.23	99.813
0.25	31.7	462.1	6.86	22.3	28.9	77.14	18.9	19.5	96.97	15.25	15.28	99.8501
0.50	63.4	492.8	12.87	44.5	51.1	87.14	37.8	38.4	98.47	30.48	30.50	99.926
0.75	95.1	523.4	18.17	66.8	73.4	91.08	56.7	57.3	98.98	45.67	45.69	99.951
1.00	126.8	554.0	22.89	89.1	95.6	93.18	75.5	76.1	99.24	60.84	60.86	99.964
1.50	190.2	615.3	30.92	133.6	140.0	95.39	113.3	113.8	99.50	91.08	91.10	99.976
2.00	253.6	676.5	37.49	178.1	184.5	96.53	150.9	151.5	99.63	121.20	121.22	99.982
2.50	317.0	737.8	42.97	222.5	228.9	97.23	188.5	189.1	99.70	151.18	151.20	99.986
3.00	380.4	799.0	47.61	267.0	273.3	97.70	226.1	226.6	99.76	181.02	181.04	99.989
4.00	507.3	921.5	55.05	355.8	362.0	98.29	301.1	301.6	99.82	240.28	240.30	99.992
5.00	634.1	1044.0	60.73	444.6	450.7	98.65	375.8	376.3	99.86	298.89	298.91	99.994
6.00	760.9	1166.5	65.23	533.3	539.2	98.89	450.3	450.8	99.89	356.82	356.84	99.995
7.00	887.7	1289.0	68.87	621.8	627.7	99.07	524.6	525.1	99.91	413.98	414.00	99.996

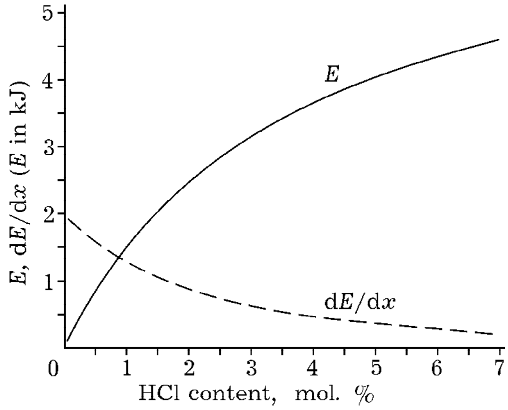

Fig. 1. Dependence of energy consumption in HCl removal from liquid by 1 mol of gas phase on the hydrogen chloride concentration in this liquid.

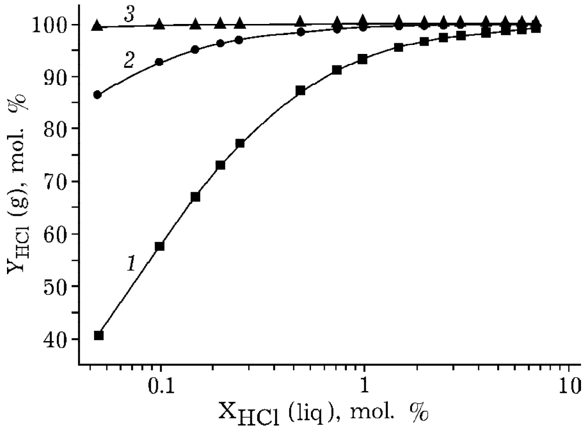

Fig. 2. Content of hydrogen chloride at inlet and outlet of desorption unit.

liquid composition in the still and the dephlegmator temperature. It is evident that practically complete removal of chlorosilane impurities is possible only at −100 °C. But for practical purposes the product purity of such a level is not needed because the presence of chlorosilane impurities in minor amounts in hydrogen chloride recycled to the process at the stage of trichlorosilane preparation is not of crucial importance.

Workers of SverdNIIKhimMash JSC have designed and realized the set-up for the absorption separation of hydrogen chloride and hydrogen. The foundation of this development is the design presented in this paper. Characteristic property of this set-up is a combination of two inverse processes: sorption and desorption. This combination allows a more effective redistribution of heat and material flows between the units corresponding to processes of sorption and desorption. The blocks of hydrogen purification are designed to be operated at low temperatures and elevated pressures. The pressure in the still is nearly equal to atmospheric one, and the top temperature is 48 °C.

REFERENCES

1 N. N. Lapidus, N. A. Niselson, Tetrakhlor i khlorsilan, Khimiya, Moscow, 1970.
2 V. M. Vorotyntsev, V. V. Balabanov, D. A. Shamrakov, A. G. Petrik, *Zh. Prikl. Khim.*, 59, (1986) 2369.
3 V. P. Belousov, A. G. Morachevskiy, Teploty smesheniya zhidkostey (Handbook), Khimiya, Leningrad, 1970.
4 L. A. Borisova, M. F. Reznichenko, P. P. Semyannikov *et al., Khim. Ust. Razv.*, 9, 4 (2001) 523.
5 G. Looks, Experimentalnye metody v neorganicheskoy khimii, Mir, Moscow, 1965.
6 Charles D. Holland, Mnogokomponentnaya rektifikatsiya, Khimiya, Moscow, 1969.