PHYSICAL CHEMISTRY

LIQUID–VAPOR EQUILIBRIUM IN HIGHLY DILUTE SOLUTIONS
FORMED BY SILANE WITH CERTAIN CARBON-CONTAINING
SUBSTANCES AND VOLATILE INORGANIC HYDRIDES

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Silane, produced according to the disproportionation of triethoxysilane, contains impurities of organic
substances and inorganic volatile hydrides [1]. The literature contains no data on the distribution coeffi-
cients for the silane–impurity systems in the region of microconcentrations. In view of this, the present
work was devoted to an investigation of the liquid–vapor equilibrium in solutions formed by silane with
impurities, which possess boiling points close to silane or have the most harmful effect on the properties
of semiconductor silicon.

In highly dilute solutions, when the concentration of dissolved substance $x \ll 1$, the coefficient of
separation is related to the coefficient of thermodynamic activity of the dissolved substance $\gamma_2$ and the ideal
distribution coefficient $a_0$ in the following way

$$ a = \frac{a_0}{\gamma_2} $$

(1)

where

$$ a_0 = \frac{P_1^0}{P_2^0} $$

(2)

$P_1^0$ and $P_2^0$ are the vapor pressures of the pure first and second components. The dependence of the activity
coefficient on the concentration can be expressed by an equation of the type [2]

$$ \ln \gamma_2 = a_1 + a_2 x^{n-1} + a_3 x^n + ... $$

(3)

where $n > 1$; $a_1$, $a_2$, and $a_3$ are constants.

From formula (2) it follows that there is some value of the concentration $x_0$, a further decrease in
which produces a change in the activity coefficient, which does not exceed the accuracy of the experimental
methods of investigation. Therefore, in the case when $x \ll x_0$, the dependence of $\gamma_2$ on $x$ can be neglected.
The experimental material accumulated thus far permits us to assume that for solutions of nonelectrolytes
with limited solubility of the components, the distribution coefficient is already independent of the concen-
tration in the region of $x \lesssim 10^{-2}$–$10^{-1}$ [3]. To confirm this hypothesis we conducted experiments on the
determination of $a$ in the concentration interval $10^{-5}$–$10^{-1}$ mole fraction. The measurement of the distribu-
tion coefficient is of great importance for evaluating the possibility of profound purification of silicon hy-
dride by the method of fractional distillation. Together with the experimental determinations, calculations
were made with the aid of the statistical theory.

EXPERIMENTAL METHOD

The distribution coefficient was determined by the method of Rayleigh distillation and a static method
on the apparatus, the scheme of which is presented in Fig. 1. A glass cell 3 with the investigated mixture
was placed in the copper block of the cryostat 1. The cell contained a mixer 4, prepared in the form of a

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steel wire spring. The mixer was moved vertically by the electromagnetic coil 5, supplied with alternating current. The vibration frequency of the mixer was set with the aid of a time relay. The system of temperature regulation consisted of a gas thermometer 2, a contact mercury manometer 12, an electromagnetic relay 27, and a Nichrome coil for electrical heating of the inner block of the cryostat. The gas thermometer was filled with pure silane. The temperature in the cryostat was estimated according to the vapor pressure of silane. To establish thermodynamic equilibrium under static conditions, the solution was kept for a definite time at the set temperature, after which a sample for chromatographic analysis was collected from the vapor phase. The composition of the liquid phase was assumed equal to the composition of the initial mixture.

To determine \( \alpha \) by the method of Rayleigh distillation, the liquid in cell 3 was slowly evaporated. The vapors were condensed in the trap 14, cooled with liquid nitrogen. After definite periods of time, samples of the vapor phase were collected and subjected to chromatographic analysis. At the same time the amount of liquid remaining in the cell was determined. The distribution coefficient was calculated according to these data. The distribution coefficient was determined by a static method in the systems formed by silane with ethylene, diborane, phosphine, and benzene, and by the method of Rayleigh distillation in the silane-arsine system. The results are presented in Table 1.

**DISCUSSION OF RESULTS**

From Table 1 it is evident that the distribution coefficient remains constant within the investigated concentration interval. This result agrees with the conclusion of independence of the relative volatility from the concentration in highly dilute solutions of nonelectrolytes [3]. All the systems considered show a positive deviation from Raoult's law.

It seems interesting to explain the experimental data from the standpoint of the statistical theory of solutions. The possibilities of the free volume theory, modified by the introduction of holes, i.e., unfilled points of the crystal lattice of the liquid, into the model of the liquid [2, 5, 6], are of special interest. The configurational integral in this case takes the following form:

\[
\Omega (T) = \frac{1}{N!} \left[ \psi \exp \left( -\frac{E}{RT} \right) \right]^N
\]

where \( N \) is Avogadro's number; \( R \) is the gas constant; \( E \) is the potential energy of the molecules in the equilibrium position. The free volume (the volume accessible for molecular motion) is determined by the function

\[
\psi = -V \frac{RT}{E}
\]

Here \( V \) is the molar volume.

For a binary solution with a number of molecules of the first and second components equal to \( N_1 \) and \( N_2 \), the configurational integral (4) will take the following form

\[
\Omega_x (T) = \frac{1}{N_1! N_2!} \left[ \psi_{1s} \exp \left( -\frac{E_{1s}}{RT} \right) \right]^{N_1} \left[ \psi_{2s} \exp \left( -\frac{E_{2s}}{RT} \right) \right]^{N_2}
\]

The free volume of a molecule of the \( i \)-th type in solution is determined by the formula

\[
\psi_{is} = -V_{is} \frac{RT}{E_{is}}
\]

and the potential energy of molecules of this type