Solubility of Methylsilane in Methyltrichlorosilane

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In conjunction with a study of the redistribution of hydrogen and chlorine atoms in alkylchlorosilanes (*2*), the solubility of methylsilane in methyltrichlorosilane was measured over the temperature range of -20° to 50° C. and at liquid compositions varying from 12 to 80 mole % methylsilane. The measurements were made using the total pressure method because it is simple and particularly well suited to methylsilane-methyltrichlorosilane systems, in which one component has a low vapor pressure relative to the other. For these systems the equilibrium liquid composition and the partial pressure of the solute may be reliably calculated directly from the total pressure-temperature data, if the charge composition, vapor volume, and the vapor pressures of the pure components are known.

EXPERIMENTAL

Materials. The methyltrichlorosilane was redistilled reagent grade material which was shown by mass spectrographic analysis to contain less than 0.5% of other chlorosilanes. The methylsilane was prepared by reducing the redistilled methyltrichlorosilane with lithium aluminum hydride followed by distillation.

Procedure and Data. Measured quantities of methylsilane and methyltrichlorosilane were charged to six small stainless steel cylinders, each fitted with a calibrated Bourdon gage (Table I). The cylinders were attached to rocker arms in a controlled-temperature bath, and equilibrium pressures were read at several temperatures. The temperature levels were selected in random order rather than proceeding in successive steps from one limit to the other, in order to check for cumulative effects such as cylinder leaks or irreversible chemical reactions which would cause large deviations from a smooth curve when pressures are plotted against temperature. Because there is little scatter in the data, Figure 1, it is concluded that there were no permanent changes in the system.

Table I. Test Solutions

Cylinder No.	1	2	3	4	5	6
Cylinder vol., cc.	97.0	96.0	93.0	95.0	95.0	101.0
CH_3SiH_3, mole	0.0287	0.0464	0.0708	0.1146	0.1367	0.1969
CH_3SiCl_3, mole	0.1759	0.1706	0.1462	0.1194	0.0906	0.0421

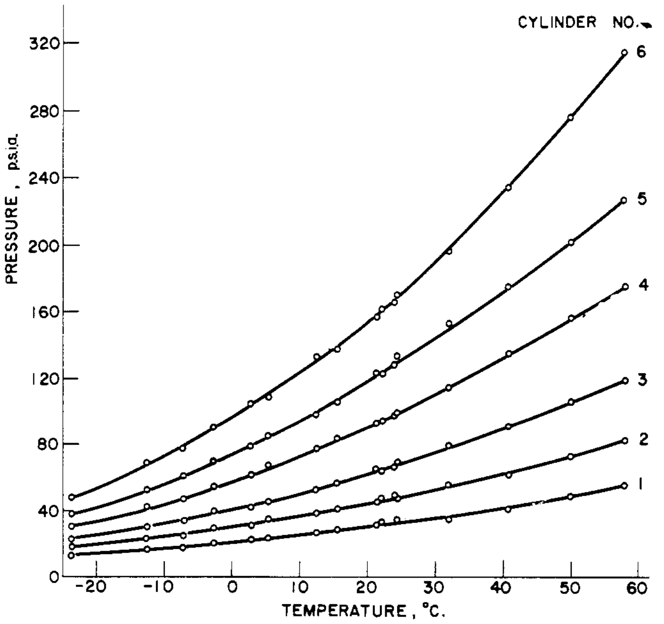

Figure 1. Total pressure of methylsilane–methyltrichlorosilane solutions

CALCULATIONS

The solubility, expressed as the partial pressure of methylsilane in equilibrium with a liquid phase of known composition, was computed as follows: Total pressures were read from the smooth curves of Figure 1 at temperature intervals of 10° over the range of -20° to +50° C. For each temperature and pressure, the volume of vapor in the cylinder was estimated by subtracting the calculated liquid volume from the total cylinder volume. The partial pressure of methyltrichlorosilane was calculated from Raoult's law and subtracted from the total pressure to yield the partial pressure of methylsilane. With the temperature, volume, and partial pressures known, the moles of each of the components in the vapor was calculated from the perfect gas law. The moles of each in the liquid phase was found from the difference between the moles charged and the moles in the vapor.

The solubility computations required several assumptions. To find the liquid volumes it was assumed that the volume of the solution was equal to the sum of the volumes of the pure components, and that their specific volumes were constant at

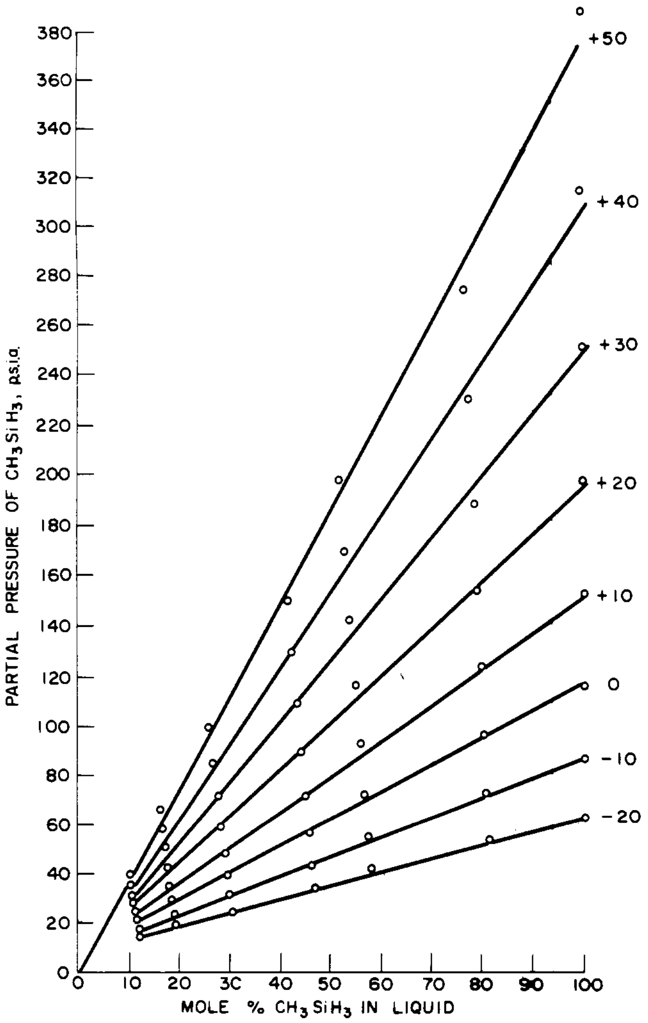

Figure 2. Partial pressure of methylsilane in methyltrichlorosilane solutions

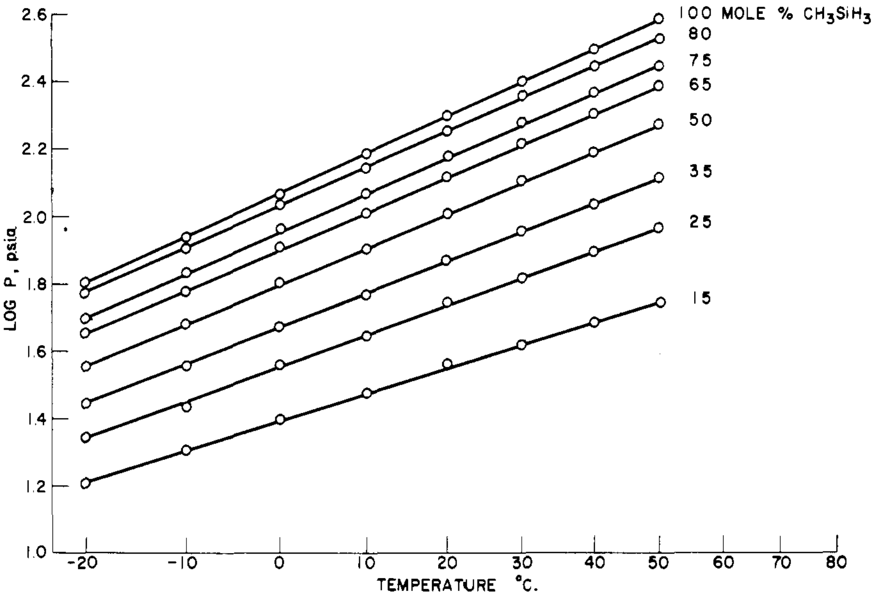

Figure 3. Partial pressure of methylsilane in methyltrichlorosilane solutions

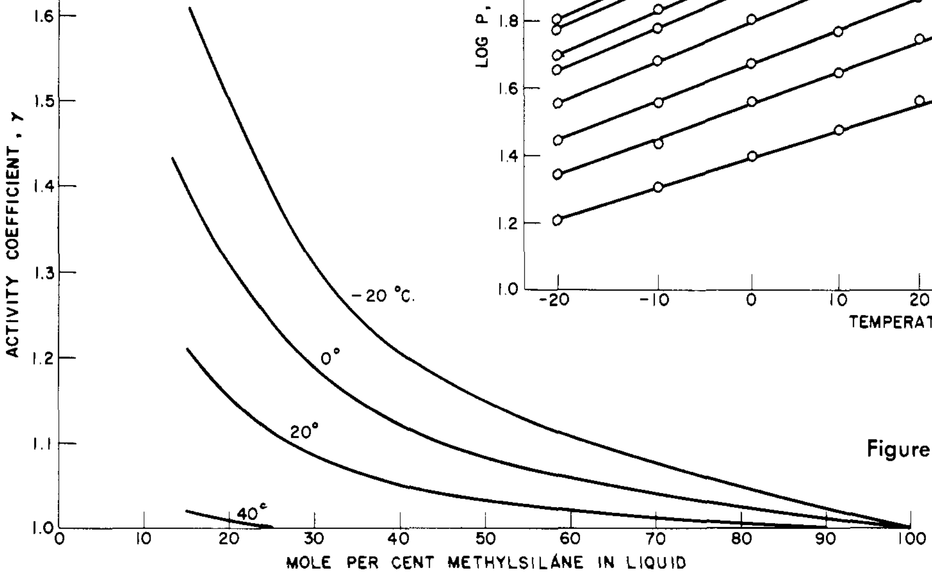

Figure 4. Activity coefficient of methylsilane in methyltrichlorosilane solutions

0.786 cc. per gram for methyltrichlorosilane (*1*) and 1.612 for methylsilane (*4*). This assumption is justified by the fact that a 50% error in the liquid volume would change the calculated mole per cent of methylsilane in the liquid by a maximum of 1.5% and usually by less than 1%. Such a change in the liquid composition causes negligible changes in the vapor composition and the methylsilane partial pressure.

Deviations from Raoult's law behavior for methyltrichlorosilane influence the calculated solubility by changing the partial pressure of this component in the vapor and in turn changing the calculated liquid composition (*6*). However, both effects are small. Since under all conditions employed the methyltrichlorosilane partial pressure was only a few per cent of the total pressure, even large deviations would be reflected as a small correction in the methylsilane partial pressure. In addition, the region where the methyltrichlorosilane exerts its greatest partial pressure is also the one where Raoult's law would be expected to be most nearly obeyed—for solutions rich in methyltrichlorosilane. As for the change in the liquid composition, at no time was more than 1% of the charged methyltrichlorosilane in the vapor phase; so the calculated amount of this component remaining in the liquid phase is not significantly affected by deviations from Raoult's law.

Perhaps the largest inaccuracy in the calculation is introduced by assuming that the perfect gas equation is applicable to the methylsilane vapor. The departure from perfect gas behavior is not known, but from calculated critical properties for methylsilane, T_c = 365° K, P_c = 807 p.s.i.a. (*3,5*), it is estimated that the compressibility factor varies between 0.8 and 1.00—i.e., 0 to 25% deviation. For the low temperature region only 5 to 13% of the charged methylsilane is in the vapor and so any deviations have a small effect on the final results. However, with a rise in temperature this proportion is increased and deviations would cause a more serious error. In the highest temperature computation, 50° C., the vapor contains 25 to 30% of the methylsilane charged. The errors that might be expected at this temperature and for a 25% deviation from perfect gas behavior are shown by the following two examples. For cylinder 1 the calculated mole per cent methylsilane in the liquid is 10.8 when the perfect gas relationship is obeyed, and 9.8 when there is a 25% deviation. At the other composition extreme, represented by cylinder 6, a deviation of this magnitude changes the mole per cent of methylsilane in the liquid from 76.6 to 74.5. It is believed that these values are representative of the maximum errors incurred from this source.

RESULTS

The partial pressure of methylsilane in equilibrium with methylsilane—methyltrichlorosilane solutions as a function of temperature and liquid composition is presented in Figure 2. Values from these curves are plotted as the logarithm of the partial pressure versus the reciprocal of the absolute temperature in Figure 3. The pressures corresponding to 100% methylsilane were calculated from the vapor pressure equation(*5*)

$$\log P_{\text{mm.}} = 7.1454 - \frac{919.05}{T}$$

The methylsilane partial pressure is usually more than 95% of the total pressure.

The methylsilane partial pressure curves Figure 2 show positive deviations from Raoult's law which decrease with increasing temperature until at 50° C. no deviation is apparent. The magnitude of the deviations is indicated by Figure 4 in which activity coefficients, calculated from the equation

$$\gamma = \frac{\text{methylsilane partial pressure}}{\text{mole fraction methylsilane} \times \text{methylsilane vapor pressure}}$$

are plotted versus the mole per cent of methylsilane.

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RECEIVED for review August 14, 1958. Accepted October 6, 1958.