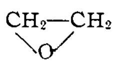
ties of the dialkyl ethers, starting with diethyl ether, with those of their isomeric normal alcohols, it is observed that the water solubilities are quite similar.

| Ether | Water solubility[a] near room temp. | Isomeric *n*-alcohol | Water solubility[a] near room temp. |
|---|---|---|---|
| Diethyl | 7.5% | *n*-Butyl | 9% |
| Ethyl *n*-propyl | Slightly soluble | *n*-Pentyl | 2.7 |
| Di-*n*-propyl | Slightly soluble | *n*-Hexyl | 0.6 |
| Diisopropyl | 0.2 | *n*-Hexyl | 0.6 |
| *n*-Propyl isopropyl | 0.5 | *n*-Hexyl | 0.6 |
| Di-*n*-butyl | 0.05 | *n*-Octyl | Slightly sol. |

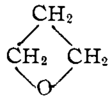
[a] "Lange's Handbook of Chemistry," 6th edition, Handbook Publishers, Inc., Sandusky, Ohio.

Only the first three alcohols, methyl, ethyl and propyl, are water soluble, which can be attributed to co-association with water through hydrogen bonds. The desolubilizing effect of the larger alkyl groups of the higher homologs outweighs the solubilizing effect of hydrogen bonding. It appears that the low solubility of the first few dialkyl ethers is due to a steric effect. If one attributes the infrared frequency shift of the H–Cl bond, upon solution in various solvents, to hydrogen bonding with the solvent molecules, the frequency-shift will be affected by the basicity of the solvent and steric factors. The steric factor should be negligible with HCl, so that it is not unreasonable to correlate the basicity of the ethers with observed frequency shifts,[1] which is in the order diisopropyl ether > diethyl ether = dibutyl ether > dioxane. This is about what one would expect considering electrical effects alone.[2] Toward a larger acid, the steric effect should upset this order. This is indeed the case, for the reported[3] relative basicities of ethers toward $BF_3$ decreases in the order tetrahydrofuran, dimethyl ether, diethyl ether, diisopropyl ether. In the absence of steric effects, one would expect the opposite order, with tetrahydrofuran being about the same as diethyl ether.

Considering water solubility again, tetrahydrofuran and dioxane are completely soluble, as also are ethylene oxide and 1,3-propylene oxide.

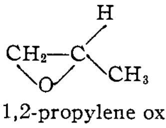


ethylene oxide

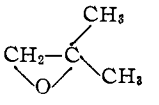


1,3-propylene oxide

This is not due to their having cyclic structures because the water solubility of 1,2-propylene oxide is only 33% and for 1,1-dimethylethylene oxide it is only 5.8%.



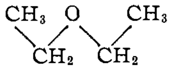
1,2-propylene oxide



1,1-dimethylethylene oxide

Apparently liquid water can offer an appreciable steric hindrance to association with its molecules. This is not hard to believe when one regards liquid water as large polymeric aggregates of $H_2O$ molecules. Sterically unhindered ethers can associate with the polymers to make them water soluble, just as can small alcohol molecules. Therefore, when attributing the low water solubility of small dialkyl ethers, in comparison to their isomeric alcohols, to a lack of association or hydrogen bonding, attention should be focused upon the steric factor. In its absence, the ethers would be water soluble, similarly as are tetrahydrofuran, dioxane, ethylene oxide and 1,3-propylene oxide.

The steric effect in dimethyl ether is surprising but not so in diethyl ether. Based on its dipole moment and other factors,[4] the most stable form of diethyl ether is



in which the methyl groups partially shield the oxygen atom. Fisher–Hirschfelder models of dimethyl ether do not reveal much interference from the methyl groups but evidently it is sufficient to prevent its solubilization by water. The same spatial interference from the methyl groups is found in 1,1-dimethylethylene oxide, which has a low water solubility. In tetrahydrofuran and in dioxane, the alkyl chains are held back away from the oxygen atoms to permit association with water and complete water solubility.

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(1) W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939).

(2) The steric effect begins to show up when methyl alcohol is the acid. The frequency shift of the O–D band of $CH_3OD$ in different ethers is in the order, diethyl ether > diisopropyl ether > ethyl *n*-butyl ether > di-*n*-butyl ether > dioxane (W. Gordy and S. C. Stanford, *ibid.*, **8**, 170 (1940)).

(3) H. C. Brown and R. M. Adams, THIS JOURNAL, **64**, 2557 (1942).

(4) H. A. Stuart, "Molekülstruktur," J. Springer, Berlin, 1934, p. 101.

CHEMISTRY DEPARTMENT
HOWARD UNIVERSITY
WASHINGTON 1, D. C.

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## The Density of Pentaborane

BY PAUL S. GAKLE AND STANLEY TANNENBAUM

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The present literature contains two values for the density of pentaborane at 0°: 0.61 g./ml. reported by Stock,[1] and Smith and Miller's[2] value of 0.643 g./ml. In this research a range of densities *vs.* temperatures was measured from −8 to 25°, and the value at 0° was found to be 0.637 ± 0.002 g./ml. The equation for the density–temperature curve is: $d = -0.000733t + 0.637$, where $t$ is in degrees centigrade. The maximum deviation of any measured point from the curve was ±0.05% over a 30° range in temperature.

### Experimental

The density of pentaborane was measured in a straight tube pycnometer similar to that described in ref. 3. The unit was calibrated with distilled water in a 0° ice-bath. The calibration was checked with toluene (J. T. Baker Analyzed Reagent Grade) and agreed within 0.2% with the values from Timmerman.[4]

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(1) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(2) S. H. Smith, Jr., and R. R. Miller, THIS JOURNAL, **72**, 1452 (1950).

(3) S. Tannenbaum, S. Kaye and G. Lewenz, *ibid.*, **75**, 3753 (1953).

(4) J. Timmerman, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950.

A sample of pentaborane obtained from the Mathieson Chemical Co. was fractionated in a high vacuum line and then distilled directly into the densitometer. The vapor pressure of 65–66 mm. at 0° agrees well with the literature value[5] of 66 mm. The infrared spectrum showed only the bands expected for pentaborane. The densitometer was sealed off, the weight of the liquid obtained, and the entire tube submerged in a well stirred low temperature bath. A calibrated copper–constantan thermocouple was placed directly against the bulb of the densitometer. The e.m.f. of the thermocouple was measured with a Leeds and Northrup Model 8662 potentiometer. The bath was warmed up slowly and a series of temperature *vs.* height-of-liquid readings were made between −8 and +25°. The volume of the pentaborane was calculated to the nearest 0.001 ml.

## Results and Discussion

The scale on the densitometer was read to the nearest 0.25 mm. which corresponds to an uncertainty in the density of ±0.05%. The measurement of temperature was accurate to ±0.3° which corresponds to an uncertainty in density of ±0.05%. The maximum weighing error was less than 0.1%. The net variability, therefore, should be no larger than 0.3%. This leads to a value of 0.637 ± 0.002 g./ml. for the density of pentaborane at 0°.

This value is essentially in agreement with that of Smith and Miller[2] and indicates that the value of Stock[1] is in error.

(5) Ohio State University Research Foundation, Technical Report No. 6 (Project RF-309), "The Heat Capacity of Pentaborane from 13° to 296°K.," 1949.

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# The Crystal Structure of Rhenium Monosilicide

BY ROBERT A. MCNEES, JR.,[1] AND ALAN W. SEARCY[2]

RECEIVED MAY 19, 1955

Recently we investigated the phases formed by reaction of silicon with rhenium.[3] The crystal structure of one of the phases, whose composition was shown by a comparison of X-ray diffraction powder patterns with compositions to be $ReSi_{1.0\pm0.1}$, has been determined from X-ray powder data.

### Experimental

Preparative procedures have been described previously.[3] Diffraction data were obtained for the structure determination from five hour exposures with copper $K\alpha$ radiation. Density of the ReSi phase was measured by water displacement of a powder sample.

## Results and Discussion

All lines of diffraction patterns from heated equimolar mixtures could either be fitted to a cubic unit cell with $a = 4.775 \pm 0.002$ Å. (Cu $K\alpha_1 = 1.54050$ Å. and Cu $K\alpha_2 = 1.54434$ Å.) or could be identified as lines of another rhenium–silicon phase. The unit cell has a calculated density of 13.1 g. cm.$^{-3}$ if it is assumed to contain four molecules of ReSi. The experimental density is 13.4 ± 0.6 g. cm.$^{-3}$.

Previous workers have shown that FeSi,[4,5] CoSi,[4] MnSi[4] and RhSi[6] all belong to space group $T_4$-$P2_13$ with metal and silicon atoms in two sets of fourfold (a) positions: $x,x,x$; $^1/_2 + x$, $^1/_2 - x$, $-x$; $^1/_2 - x$, $-x$, $^1/_2 + x$; $-x$, $^1/_2 + x$, $^1/_2 - x$. In all those silicides the values of $x$ were about 0.84 for the silicon atoms and 0.14 for the metal atoms.

The planes found for ReSi were those to be expected if it is isostructural with FeSi. Intensities of diffraction lines accordingly were calculated on the assumption that ReSi has the FeSi structure with $x = 0.84$ for the silicon atoms and $x = 0.14$ for the rhenium atoms. The equation $I = 10^{-5} \cdot F^2P(1 + \cos^2 2\theta)/\sin^2\theta \cos\theta$, in which all terms have their usual meaning, was used for intensity calculations. Plane assignments, observed and calculated planar spacings, and observed and calculated intensities are presented in Table I.

TABLE I

DIFFRACTION DATA FOR ReSi

| Plane | Spacing (Å.) Obsd. | Spacing (Å.) Calcd. | Intensity Obsd.[a] | Intensity Calcd. |
|---|---|---|---|---|
| 110 | 3.375 | 3.376 | M+ | 52 |
| 111 | 2.749 | 2.757 | M | 24 |
| 200 | 2.391 | 2.388 | VW | 3.7 |
| 210 | 2.132 | 2.135 | VS | 90 |
| 211 | 1.949 | 1.949 | S | 38 |
| 220 | 1.686 | 1.688 | VVW | 0.2 |
| 221 | 1.593 | 1.592 | VVW | 3.0 |
| 310 | 1.509 | 1.510 | M | 14.7 |
| 311 | 1.438 | 1.440 | M | 11.5 |
| 222 | 1.376 | 1.378 | M | 9.8 |
| 320 | 1.322 | 1.324 | M | 13.5 |
| 321 | 1.275 | 1.276 | M+ | 15.4 |
| 400 | 1.192 | 1.194 | M | 6.8 |
| 322, 410 | 1.158 | 1.158 | VVW | 2.7 |
| 330, 411 | 1.125 | 1.125 | W | 6.8 |
| 331 | 1.095 | 1.095 | W | 7.4 |
| 421 | 1.041 | 1.042 | M+ | 16.7 |
| 332 | 1.018 | 1.018 | W | 3.5 |
| 422[b] | 0.9728 | 0.9747 | VVW | 1.2 |
| 431, 510 | .9361 | .9365 | M | 12.3 |
| 333, 511 | .9187 | .9189 | M | 8.3 |
| 432, 520 | .8867 | .8867 | S | 26 |
| 521 | .8718 | .8718 | M | 9.9 |
| 440 | .8442 | .8441 | M | 9.8 |
| 433, 530 | .8190 | .8190 | M | 12.2 |
| 531 | .8071 | .8071 | M | 8.8 |
| 610 | .7850 | .7850 | M+ | 18.3 |
| 611, 532 | .7745 | .7746 | VS | 105 |

[a] S = strong, M = moderate, W = weak, V = very.
[b] The last ten spacings are for Cu $K\alpha_1$ reflections.

Agreement between observed and calculated planar spacings and agreement between observed and calculated intensities are good. The precision of the visually estimated intensity data does not warrant attempts to fix the values of $x$ for rhenium and silicon more closely, however.

It can be concluded that ReSi belongs to space group $T_4$-$P2_13$ with $x \sim 0.84$ for silicon atoms and $x \sim 0.14$ for rhenium atoms. No indication of variability in composition of the phase was found.

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(1) Purdue Research Foundation Fellow, 1950–1952.

(2) Division of Mineral Technology, University of California, Berkeley.

(3) A. W. Searcy and R. A. McNees, Jr., THIS JOURNAL, **75**, 1578 (1953).

(4) B. Boren, *Ark. Kemi Min. Geol.*, **11A**, 1 (1933).

(5) L. Pauling and A. M. Soldate, *Acta Cryst.*, **1**, 212 (1948).

(6) S. Geller and E. A. Wood, *ibid.*, **7**, 441 (1954).