n-propyltriisocyanatosilane or *n*-butyltriisocyanatosilane, both of which gave approximately 20% yields of partially-chlorinated compounds; tetrabromosilane and *n*-dodecyltrichlorosilane, which furnished a 10% yield of tribromochlorosilane.

Reactions which included decomposition resulted when sulfur monochloride was warmed with dimethyldianilinosilane or with *n*-dodecyltriiodosilane; the former yielded a dark mess, while the organosilicon iodide reacted to liberate much iodine, showing the non-existence or very low stability of a sulfur iodide.

No reaction or an extremely slow reaction occurred in the twenty-three following instances: $Ge(NCO)_4$ and $HgCl_2$ or $AsCl_3$ or *n*-$C_{12}H_{25}SiCl_3$ or S_2Cl_2; $Si(NCO)_4$ and $TiCl_4$; $EtSi(NCO)_3$ and $HgCl_2$; $C_7H_7Si(NCO)_3$ and diphenylsilane; $(MeO)_2Si(NCO)_2$ and S_2Cl_2; $EtOSi(NCO)_3$ and $PhPCl_2$ or PhCOCl or $AlCl_3$ or *n*-$C_{12}H_{25}SiCl_3$; $MeSi(NCS)_3$ and $AsCl_3$ or $GeBr_4$; $Me_3Si(NCS)$ and $AsCl_3$ or $GeBr_4$; $Et_3Si(NCS)$ and NH_4Cl or $PhBCl_2$ or diphenylsilane; *n*-$PrSi(NCS)_3$ and $PhCH_2Cl$ or $PbCl_2$; *i*-$PrSi(NCS)_3$ and $PhBCl_2$; $GeBr_4$ and *n*-$C_{12}H_{25}SiCl_3$. Mr. Robert C. West, Jr., of Harvard University kindly furnished the sample of diphenylsilane, a liquid of b.p. about 270°. Table I includes the abbreviations Ph for phenyl, Dod for dodecyl and Bz for benzyl, also those for methyl, ethyl, propyl and butyl.

Experimental Method.—The same small distillation units, of five theoretical plates, used previously with reactions of anilinosilanes[2] were used; 0.5–4.0 ml. of liquid could be used in equipment which may be described elsewhere at a later date. A solid such as mercuric chloride was weighed and then transferred into the distilling unit before addition of the liquid halide or ester. An uncalibrated microchemical transfer pipet and a calibrated syringe served adequately for the transfer of all liquid samples. After the transfer, the two starting compounds in each reaction in the table were brought to a gentle reflux such as would allow escape of the relatively-pure most volatile component at the top of the distilling unit—using a microburner. In both the collection and quantitative estimation of the newly-formed most volatile member a calibrated one-ml. test-tube was adequate. True boiling points often could be obtained only by transferring the distillate to an uncalibrated test-tube and then remeasuring. Most heating periods were 5–10 minutes. Weights of products depended on volumes and available densities. Starting materials consisted of pure isocyanates and isothiocyanates, in sealed tubes, from previous researches; of commercially available compounds such as benzoyl chloride; of *p*henylphosphorus dichloride, kindly furnished by Victor Chemical Works, Chicago 4, Ill. Reaction residues were not investigated further.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Silicides of Rhenium[1-3]

BY ALAN W. SEARCY AND ROBERT A. MCNEES, JR.[4]

RECEIVED AUGUST 6, 1952

Two new rhenium silicides, Re_3Si and ReSi, have been prepared and identified. The vapor pressures of these phases and of $ReSi_2$ have been measured by the Knudsen effusion method. From the vapor pressures, heats and free energies of formation have been calculated for these phases.

The chemistry of transition metal carbides has been studied extensively and is discussed in most textbooks of inorganic chemistry. Little is known, however, of the chemistry of transition metal silicides. Not even the formulas of the compounds formed by silicon with many of the transition metals are yet known, and apparently no vapor pressures or stability data have been reported. In this research the formulas of the rhenium silicides have been determined and their heats and free energies of formation have been determined from vaporization data.

Phase Study

The existence of $ReSi_2$ and the determination of its crystal structure have been reported by Wallbaum[5]; no other compounds of rhenium with silicon have been reported. Experience with other transition metal systems suggested that other rhenium silicide phases might exist. The X-ray diffraction patterns obtained from mixtures of rhenium and silicon which had been heated to high temperatures were examined for evidence of the existence of other phases. Detailed examples of the use of the method have been given previously.[6]

Experimental

All samples were prepared by direct synthesis. Rhenium metal powder was obtained from the University of Tennessee. It contained 8.2% of impurities which could be driven off by heating at 1000° under vacuum and a small amount of silver which did not interfere with the phase studies, but which was driven off at 1500° before vapor pressures were determined. The silicon powder was obtained from the Union Carbide and Carbon Company. Spectroscopic and X-ray diffraction analyses revealed only a trace of iron in the silicon.

Samples were heated in graphite crucibles. X-Ray diffraction photographs of mixtures of rhenium and graphite powders heated to 1600° showed only the diffraction patterns of the elements. Silicon carbide lines were found in the diffraction patterns of rhenium–silicon samples after heating only if they contained silicon in excess of the atomic ratio 2Si:1Re. This is believed to be the ratio in the most silicon-rich compound formed by rhenium. Reaction with the graphite crucibles, therefore, did not interfere with our studies.

The rhenium-silicon samples did not reach equilibrium even when heated for several days at 1000°, but high silicon samples reached equilibrium when heated for 45 minutes

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[1] Abstracted from a thesis presented by Robert A. McNees, Jr., in partial fulfillment of the requirments for the Ph.D. degree.

[2] This research was supported by the Office of Naval Research.

[3] For tables of data order Document 3710 from American Documentation Institute, ℅ Library of Congress, Washington 25, D. C., remitting $1.00 for microfilm (image 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[4] Purdue Research Foundation Fellow 1950–1952.

[5] H. J. Wallbaum, *Z. Metallkunde*, **33**, 378 (1941).

[6] L. Brewer, A. W. Searcy, D. H. Templeton and C. H. Dauben, *J. Am. Ceram. Soc.*, **33**, 291 (1950).

at 1550° and low silicon samples when heated for 60 to 90 minutes above 1600°.

Weight losses in the preparations could be kept to less than 1% if the samples were held at 1450° for 15 minutes before annealing at higher temperatures. The final compositions of the samples were obtained by assuming that the small weight losses which occurred were due to vaporization of silicon.

An induction furnace was used for most preparations. The heating tube of 75 mm. Pyrex was connected to the vacuum line by a 71/60 standard taper joint. A water cooling jacket and an induction coil of $^1/_4$ in. copper tubing were set concentrically about the heating tube. The crucible and sample were supported on a tungsten wire holder. Temperatures were read with an optical pyrometer through a window set above the tube. A magnetically operated shutter protected the window. Power was supplied to the work coil by a 15 KW General Electric electronic converter. Constant current was maintained in the work coil by means of a regulator.[7] A 260-liter capacity oil diffusion pump maintained the pressure in the system near 10^{-5} mm. during a heating.

After being heated the samples were found to be lightly sintered powders. The powders were crushed and ground in an agate mortar. X-Ray diffraction photographs were then taken of the powders in a 114.59 mm. diameter Phillips powder camera. Four to five hour exposures with filtered Cu Kα radiation gave clear photographs.

Diffraction photographs of four samples with silicon to rhenium atomic ratios between 0.0 and 0.3 showed the pattern characteristic of rhenium as well as that of a rhenium silicide phase (designated α) after heating. Six samples with silicon to rhenium atomic ratios between 0.4 and 0.9 gave the diffraction pattern of the α-phase plus the pattern of a second (β) phase. The α-phase therefore has the composition $ReSi_{0.35 \pm 0.05}$ or Re_3Si.

Photographs of five samples with silicon to rhenium atomic ratios between 1.1 and 1.9 showed the pattern of the β-phase and the pattern of a third (γ) phase. The β-phase composition was fixed, therefore, at $ReSi_{1.0 \pm 0.1}$ or ReSi. The formula of the phase was corroborated by the determination of its crystal structure, which will be reported elsewhere. The phase is cubic and isostructural with FeSi, CoSi, NiSi and MnSi.

At a silicon to rhenium atomic ratio of 2.0 only the γ-phase pattern was obtained. At higher silicon compositions molten silicon attacked the crucibles and silicon carbide patterns were observed in equilibrium with the γ-phase. The γ-phase pattern was found to be identical with that of the $ReSi_2$ phase whose structure was determined by Wallbaum.[5]

None of the above samples melted when heated to 1700°. Long heating at lower temperatures (1000°) did not produce any change in the diffraction patterns of the samples. Comparison of films showing the same phases but of different silicon to rhenium ratios showed no evidence for a shift in lattice constants. Therefore, the extent of solid solution range of the various phases is believed to be small.

Vapor Pressure Determinations

Because silicon is much more volatile than rhenium, it was expected that a rhenium silicide when heated would lose silicon by vaporization and be converted to the phase of next higher rhenium content

$$ReSi_2\,(s) = ReSi\,(s) + Si\,(g) \qquad (1)$$
$$^3/_2ReSi\,(s) = {}^1/_2Re_3Si\,(s) + Si\,(g) \qquad (2)$$
$$Re_3Si\,(s) = 3Re\,(s) + Si\,(g) \qquad (3)$$

Each of these reactions should give an equilibrium silicon partial pressure which depends only on the temperature as long as both solid phases are present, and the equilibrium constant for each reaction can be determined from the silicon partial pressure above the two solids.

The disproportionation of ReSi to Re_3Si (s) and Si (g) by reaction (2) was demonstrated by spectroscopic analysis of the sublimate obtained from heating a mixture of Re_3Si and ReSi. The sublimate contains silicon, but no rhenium.

The X-ray diffraction studies indicate that ReSi is thermodynamically stable at high temperature; it can only be thermodynamically stable if the silicon partial pressure for reaction 1 is higher than that for reaction 2. Since the measured vapor pressure over a mixture of $ReSi_2$ and ReSi is less than a factor of two greater than that over a mixture of ReSi and Re_3Si, $ReSi_2$ must vaporize primarily by disproportionation through reaction (1). It is assumed that Re_3Si also vaporizes by disproportionation.

Experimental.—Vapor pressure determinations were made by the Knudsen effusion method already described.[8] The residual pressure in the system was held between 1×10^{-5} and 5×10^{-6} mm. No dependence of results on the residual pressure was observed. Pyrometer and window corrections were made.

The Knudsen cell consisted of two concentric graphite crucibles and lids surrounded by a turn of 1 mil thick tantalum sheet for radiation shielding. The inner graphite crucible was seated snugly within the outer crucible. A lid for the inner crucible was in close contact with the top of the inner crucible and with the lid of the outer crucible. The inner lid was drilled with an effusion hole. The outer lid was drilled with a larger, tapered hole. A balance accurate to 0.01 mg. was used to weigh the inner crucible and lid before and after heating. Vapor pressure runs were usually about two hours long and the weight losses varied from 0.04 to 10 mg.

Since silicon reacts with graphite at the temperatures at which the vapor pressure determinations were made, the importance of reaction between graphite and the silicon vapor was investigated. During the first few hours of heating the inner crucible and lid gained a few milligrams weight and a thin film became visible on the under side of the inner lid. After this initial period, however, the weight of the inner lid was found to remain constant. Apparently a thin layer of silicon carbide formed which protected the graphite from further attack by the silicon vapor.

The Knudsen equation[8] as ordinarily used assumes the effusion hole to be in a wall of infinitesimal thickness. For uniform heating in an induction furnace, it is necessary that the effusion holes be pierced through lids of appreciable thickness. Clausing[9] has derived an equation for the probability of passage of gaseous particles through tubes of finite length, but the derivation of the Clausing equation assumes that specular reflection from the walls of the tube can be neglected. Data accumulated in this Laboratory[10] suggest that this assumption may not always be valid. We, therefore, used a cylindrical hole and three different tapered holes in the course of our measurements. The dimensions of these holes are listed in Table I.

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(7) W. J. Chalmers, Master's Thesis in Electrical Engineering, Purdue University, 1952.

(8) M. Knudsen, *Ann. Physik*, [4] **28**, 999 (1909).

(9) P. Clausing, *ibid.*, [5] **12**, 961 (1932).

(10) A. W. Searcy and R. J. Peavler, unpublished work.

The results of our vapor pressure determinations are listed in Tables II, III and IV.[3] The logarithms of the silicon partial pressures for Re_3Si, ReSi and $ReSi_2$ are plotted as functions of $1/T$, °K. in Figs. 1, 2 and 3. The probability of escape of an atom through the cylindrical hole was assumed to be 0.546 in making these plots, as predicted by the Clausing equation, and the probability of escape through the tapered holes was assumed to be unity. The data obtained using the three different tapered holes were in excellent agreement, though this agreement probably arises from a fortuitous cancelling of errors in the case of the largest hole size. Vapor pressures for ReSi obtained with the tapered holes are about 80% as great as those obtained with the cylindrical hole. It appears that the probability of escape of atoms through the tapered holes of the dimensions used here is about 0.80. This value seems very reasonable. Accordingly when equations for log P *vs.* $1/T$ were derived from data of this paper, all pressures obtained with the tapered holes were first divided by 0.80 to correct for the probability of escape through the holes.

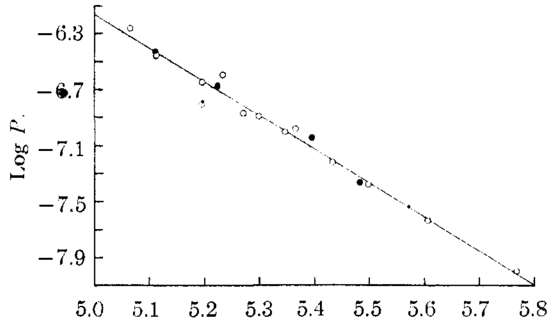

Fig. 1.—Vapor pressure of Re_3Si: O, 0.472 cm. dia. knife-edged hole; ●, 0.188 cm. dia. knife-edged hole.

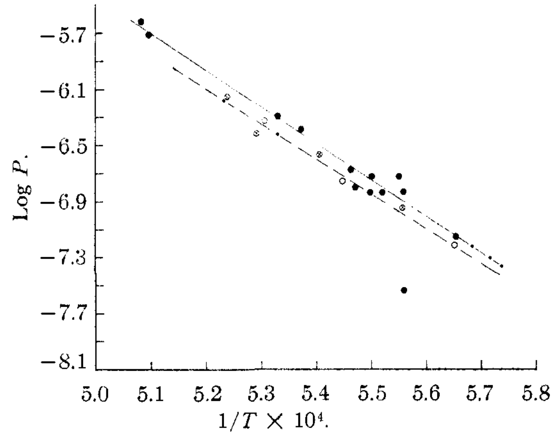

Fig. 2.—Vapor pressure of ReSi: --O--, 0.472 cm. knife-edged hole; --⊗--, 0.188 cm. knife-edged hole; -●-, 0.425 cm. dia., 0.371 cm. long cylindrical hole.

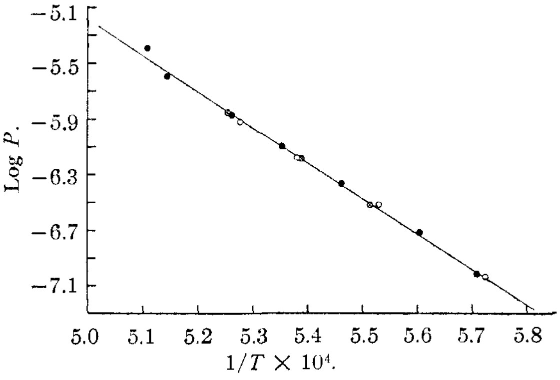

Fig. 3.—Vapor pressure of $ReSi_2$: O, 0.472 cm. dia. knife-edged hole; ●, 0.327 cm. dia. knife-edged hole; ⊗, 0.188 cm. dia. knife-edged hole.

TABLE I

DIMENSIONS OF EFFUSION HOLES

Depth of holes (mm.)	Diameter at bottom (mm.)	Diameter at top (mm.)
3.71	4.25	4.25
1.85	1.88	6.78
1.10	3.27	5.71
2.00	4.72	9.18

The corrected least squares equations relating pressure and temperature are

$$Re_3Si(s) = 3Re(s) + Si(g) \quad \log P = 5.953 - 24{,}040/T$$

$$\frac{3}{2}ReSi(s) = \frac{1}{2}Re_3Si(s) + Si(g) \quad \log P = 7.444 - 25{,}800/T$$

$$ReSi_2(s) = ReSi(s) + Si(g) \quad \log P = 7.518 - 25{,}610/T$$

Combining the equations for the free energies of sublimation of Re_3Si, ReSi and $ReSi_2$ obtained from the above vapor pressure equations with the heat of sublimation of silicon at its melting point,[11] one obtains the following equations for the free energies of formation from the solid elements at 1500°K.

$$Re_3Si \quad \Delta F^\circ = -21{,}250 - 5.49T$$

$$ReSi \quad \Delta F^\circ = -26{,}580 - 0.94T$$

$$ReSi_2 \quad \Delta F^\circ = -55{,}030 + 0.74T$$

These free energies of formation predict that both Re_3Si and ReSi are unstable at room temperature with respect to disproportionation to $ReSi_2$ and rhenium.

Acknowledgment.—The authors wish to thank Professors Yearian and Geibe of the Physics Department and Professor Whistler of the Agricultural Chemistry Department of Purdue University for the use of their X-ray diffraction equipment.

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[11] L. Brewer, National Nuclear Energy Series, Vol. 19B, paper 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1950.