[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

An X-Ray Diffraction and Vapor Pressure Investigation of the Rhenium–Germanium Phase Diagram[1a]

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An X-ray diffraction and vapor pressure investigation of the rhenium–germanium phase diagram reveals that one compound, $ReGe_2$, is formed. $ReGe_2$ decomposes at 1132 ± 15° to solid rhenium and nearly pure liquid germanium. The heat of formation of $ReGe_2$ is -2 ± 10 kcal. Irregular variation in stabilities of carbon family compounds of rhenium is explained. Of common reagents tested only hot concentrated sulfuric acid and fused sodium hydroxide attack $ReGe_2$.

Carbides of transition metals have been the subject of many chemical and metallurgical investigations. Transition metal silicides, however, have been much less extensively investigated, and transition metal germanides have scarcely been studied at all. Because of the unusual hardness and chemical and thermal stabilities exhibited by many of the metal carbides, studies of corresponding silicides and germanides are of both theoretical and practical interest.

Both the carbide[2] and the silicides[3,4] formed by rhenium have been investigated, but the existence or non-existence of rhenium germanides has been unknown. The chemical evidence suggests that rhenium carbide is of very low thermodynamic stability. It is surprising therefore to find that the three silicides of rhenium, $ReSi_2$, ReSi and Re_3Si are of moderately high stability.[4]

The present research was designed to study the rhenium–germanium phase diagram and to determine the stabilities of the compounds formed in order to see how stabilities vary with increasing size of the carbon family elements.

Experimental

Germanium bar was obtained from the Eagle–Picher Company. Rhenium was obtained from the University of Tennessee. The germanium was pulverized, and both it and the rhenium were heated separately to drive out relatively volatile impurities before the elements were mixed for preparative heatings. Weight losses of the germanium during preheating were low, but about 9% of the rhenium samples vaporized. After heating, spectroscopic analysis indicated both the rhenium and the germanium to be highly pure. Graphite crucibles were used for all preparations. X-Ray diffraction investigations of rhenium–graphite and germanium–graphite powder mixtures gave no indication of reaction of either rhenium or germanium with graphite under the conditions of our research. The experimental procedure has been previously described.[4]

Diffraction patterns produced by rhenium–germanium mixtures heated at 950° for 15 hours or less always showed the presence of unreacted rhenium and germanium as well as a product phase. Samples held at 950° for 48 hours yielded only the patterns of the product phase and rhenium or germanium. Such samples with germanium to rhenium mole ratios between 0.0 and 1.7 always yielded the diffraction pattern of rhenium metal as well as the pattern of an intermediate phase. Samples of mole ratios higher than 2.2 yielded the patterns of germanium and of this intermediate phase. The composition of this phase, the only intermediate phase observed, was demonstrated by these results to be $ReGe_{2.0 \pm 0.3}$. Closer composition limits could not be fixed because the strongest lines of the diffraction pattern of $ReGe_2$ corresponded in position with strong lines of the germanium and rhenium patterns. The crystal structure of $ReGe_2$ appears to be too complex to determine from X-ray powder diffraction patterns. It is not the same structure as that found[3] for $ReSi_2$.

Diffraction photographs of samples that had been heated an induction furnace at 1200 to 1500° were also examined. These photographs always yielded patterns of rhenium, $ReGe_2$ and germanium. It seemed probable, therefore, that $ReGe_2$ decomposed at some temperature above 950° to germanium and rhenium. The $ReGe_2$ observed after heating was almost certainly formed by partial reaction of the germanium with rhenium during cooling.

To determine the temperature of decomposition, samples containing excess germanium were heated *in vacuo* to various temperatures and quenched in mineral oil. Table I summarizes data obtained by X-ray diffraction analysis of the products. From the data the decomposition temperature is fixed at 1132 ± 15°.

TABLE I

DECOMPOSITION TEMPERATURE

Temp., °C.	Time of heating, hr.	Phases found
1019	24	$ReGe_2$, Ge
1117	18	$ReGe_2$, Ge
1147	20	Re, Ge
1189	20	Re, Ge
1225	18.5	Re, Ge

Samples quenched from above the transition temperature could be separated mechanically into a black crusty part, which showed a strong rhenium pattern, and into a silver-metallic frozen mass which showed a strong germanium pattern and a very weak rhenium pattern. This evidence suggested strongly that $ReGe_2$ decomposes peritectically at 1132° into rhenium metal and a liquid phase which is nearly pure germanium.

Vapor pressures of mixtures containing rhenium in excess of the composition $ReGe_2$ were measured by the Knudsen effusion method above the decomposition temperature of $ReGe_2$ as a means of estimating the solubility of rhenium in liquid germanium and of confirming the decomposition of $ReGe_2$. The vapor pressure of pure germanium was measured under identical experimental conditions. Results of all determinations are plotted in Fig. 1. It was expected that if $ReGe_2$ decomposes to rhenium and a liquid whose rhenium content is low, the vapor pressure of a rhenium–germanium mixture would be nearly the same as that of pure germanium. Appreciable concentrations of rhenium in the liquid phase should lower the germanium partial pressures. Within the reproducibility of the measurements, the vapor pressures were the same whether or not rhenium was present. The line of the plot is a least squares solution of the data for both the mixture and pure germanium.

The Phase Diagram.—A partial phase diagram for the rhenium–germanium system is shown in Fig. 2. The solid lines of the figure have been established by the experimental work reported in this paper. The dotted lines represent boundaries not directly measured. Since the solubility of rhenium in liquid germanium is very low, the tempera-

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[1] (a) Work supported by the Office of Naval Research. Taken in part from the Ph.D. Thesis of R. A. McNees, Jr. (b) Division of Mineral Technology, University of California, Berkeley.

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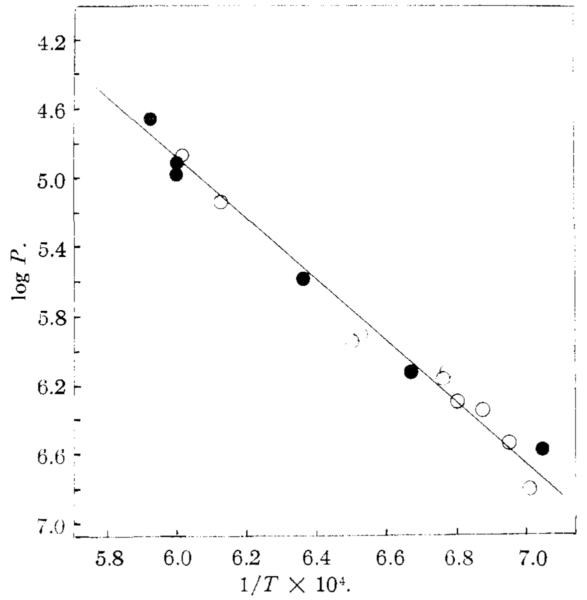

Fig. 1.—Comparison of the vapor pressure of a rhenium-germanium mixture above the dissociation temperature of $ReGe_2$ with the vapor pressure of germanium: ●, germanium vapor pressure; ○, pressures found for the mixture.

ture of eutectic melting between $ReGe_2$ and germanium must be only a few degrees below the melting point of pure germanium. The phase diagram is drawn for a solubility of rhenium in germanium of 3 atomic % and for an eutectic temperature 8° below the melting point of pure germanium. These values are believed to be correct to ± 3 atomic % and ± 8°. The methods employed in this research would not reveal the presence of several mole % of germanium in solid rhenium.

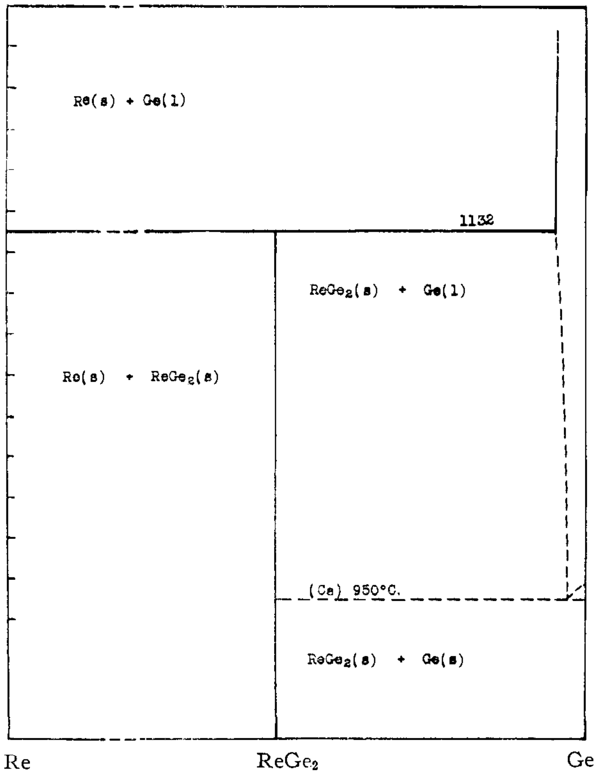

Fig. 2.—Tentative phase diagram for the rhenium-germanium system.

The Heat of Formation of $ReGe_2$.—Heats of formation of the rhenium silicides were determined from measurements of the silicon dissociation pressures of the silicide phases.[4] Because the vapor pressure of $ReGe_2$ is very low at the temperature of its decomposition to solid rhenium and liquid germanium, it was not feasible to determine the partial pressure of germanium over $ReGe_2$ in order to calculate the heat of formation of $ReGe_2$ by the same means. It is possible however to obtain an approximate value of the heat of formation of $ReGe_2$ from our knowledge of the rhenium-germanium phase diagram. For the reaction

$$Re(s) + 2Ge(l) = ReGe_2(s) \qquad (1)$$

$\Delta F^0 = 0$ at the decomposition temperature. From an examination of the entropies of formation of similar compounds, the entropy of the reaction

$$Re(s) + 2Ge(s) = ReGe_2(s) \qquad (2)$$

is estimated to be 0 ± 6 cal. $mole^{-1}$ $deg.^{-1}$. The entropy of reaction 1, therefore, must be essentially twice the entropy of fusion of germanium[5] or −11.6 cal. $mole^{-1}$ deg. The changes in heat capacity for reactions 1 and 2 are estimated by the method of Kelley[6] to be −1.3 ± 2.0 and −0.9 ± 2.0 cal. $mole^{-1}$ $deg.^{-1}$ and can be neglected. For reaction 1 ΔH^0_{298} is then calculated to be −16 ± 10 kcal. and for reaction 2, ΔH^0_{298} is −2 ± 10 kcal. $mole^{-1}$.

Discussion

The rhenium-germanium system resembles the rhenium-silicon system in that the germanide phase corresponds in composition to the most stable rhenium silicide phase, $ReSi_2$, but germanide phases corresponding to Re_3Si and ReSi were not observed even in a sample that was allowed 300 hours to cool from 950° to 100° in order to permit phases stable only at lower temperatures to form. Both $ReGe_2$ and rhenium carbide (whose formula is not known) are much less stable thermodynamically than $ReSi_2$. From its thermal decomposition, the heat of formation of rhenium carbide is estimated to be 0 ± 10 kcal. The heat of formation of $ReSi_2$ is −55 ± 8 kcal.[2]

The surprisingly high stability of $ReSi_2$ compared to $ReGe_2$ and rhenium carbide can be explained by comparing the heats of formation of rhenium carbide, $ReSi_2$ and $ReGe_2$ from solid rhenium and gaseous carbon, silicon and germanium. Using heats of sublimation of carbon,[7] silicon[7] and germanium[8] obtained elsewhere, the following values were obtained for formation of the compounds from one mole of the gaseous carbon family elements

$$1/X\ Re(s) + C(g) \longrightarrow 1/X\ ReC_X(s) \quad \Delta H^0 = -172 \pm 15 \text{ kcal.}$$

$$1/2\ Re(s) + Si(g) \longrightarrow 1/2\ ReSi_2(s) \quad \Delta H^0 = -118 \pm 15 \text{ kcal.}$$

$$1/2\ Re(s) + Ge(g) \longrightarrow 1/2\ ReGe_2(s) \quad \Delta H^0 = -94 \pm 10 \text{ kcal.}$$

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It can thus be seen that the lattice energies of rhenium carbides, silicides and germanides decrease regularly with decreasing electronegativity and increasing size of the group IV elements. The irregular trend in the standard heats of formation is caused by the unusually high stability of the graphite lattice. Other transition metal silicides should also have more negative standard heats of formation than the corresponding carbides even though the silicide lattice energies will always be less than those of the corresponding carbides. The transition metal germanides should in general be somewhat less stable than the corresponding silicides.

Reactivity of $ReGe_2$.—The reactivity of $ReGe_2$ toward common reagents was tested by adding approximately 10-mg. samples of $ReGe_2$ to 2 ml. of each reagent in a test-tube. The mixtures were observed after 15 minutes and again after 24 hours. At the end of this period the mixtures were heated for about 5 minutes at the boiling point and the results observed. Reagents tested were HCl (both concentrated and dilute), HI (concd.), H_2SO_4 (concd. and dil.), HNO_3 (concd and dil.), H_3PO_4 (85%), $HClO_4$ (68%), $KMnO_4$ (0.1 *N*), H_2O_2 (30%, cold only), NaOH (5%), fused NaOH and fused Na_2CO_3. Only hot concentrated H_2SO_4 and fused NaOH attacked the germanide.

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Coefficients of Thermal Expansion of Solids at Low Temperatures. I. The Thermal Expansion of Copper from 15 to 300°K.

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An apparatus for measuring the thermal expansion of solids over the temperature range 15–300°K. by a differential method making use of a Fizeau interferometer is described. Experimental data for copper are presented and are applied to the Grüneisen relations.

Introduction

Two general methods are in use for determining the thermal expansion of solids: (a) direct measurement of elongation of a sample by mechanical or optical means; (b) X-ray determination of thermal changes in crystal lattice constants. The two methods are not always in agreement.[1] Disagreements have been attributed to a difference between the lattice expansion, which measures correctly the over-all expansion in single crystals or in separate crystallites, and the over-all expansion of polycrystalline solids, which may involve reorientation of crystallites or other physical changes that affect the spacings between them. Most investigations of thermal expansion have measured total, or integral, expansions over large temperature intervals rather than differential coefficients for small intervals of temperature.

We have designed an improved apparatus that will determine accurate values of differential coefficients of thermal expansion over small temperature intervals in the range from 15 to 80°K., where the coefficients are changing rapidly. This range of temperature has never been explored before by a differential method.

In the present investigation, the expansions of polycrystalline copper (OFHC) and of single crystal copper were measured from 20 to 300°K., by a technique that employs the Fizeau interferometer.[2,3]

The present interferometer consists of two optical plates, whose plane surfaces are held apart by samples of the material to be measured—in this instance, small copper pillars, machined and polished until their lengths are equal within a half wave length of the light used (sodium D radiation).

When the plates are viewed by a telescope located near the light source, a system of concentric rings appears at the focal plane. Uniformity in ring diameter throughout the field of view indicates that the plates are held parallel by samples of equal length. As the temperature of the interferometer is raised, and the samples are correspondingly lengthened for positive expansion, the rings expand. When the increase in separation of the optical planes corresponds to one half-wave length of the monochromatic radiation, an inner ring will have increased in diameter to the previous value of its encircling neighbor. By making a count of the number of rings that pass a fiducial point, such as a cross hair located on a radius of the system of concentric circles, the distention of the sample is accurately measured.

When these data are correlated with the temperature change of the specimen, the coefficient of thermal expansion is calculated for the mean temperature.

Apparatus and Experimental Technique.—Figure 1 is a diagram of our apparatus, which is constructed somewhat after the manner of the vacuum calorimeters in use in this Laboratory.[4] A brass cryostat vessel, fitted with leveling screws, encloses a 9.5-in. o.d. Pyrex dewar which contains the refrigerant, liquid nitrogen or liquid hydrogen, whose temperatures may be reduced by evacuation of the cryostat. The main body of the apparatus is suspended from the cryostat lid by a 1-in. o.d. nickel tube (F), which also admits the light beam to the optical plates. This tube and the space within the brass container (E) and the lead-filled copper blocks (B) and (D) are highly evacuated through (J) to provide good thermal insulation to the vacuum-tight copper pipet (C) that encloses the interferometer. The purpose of the blocks (A, B and D) is to shield the pipet

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