

The exponent 2 in a/v^2 indicates that the liquids are like gases, from a kinetic standpoint, for if the molecules were uniformly spaced, the inverse sixth power of intermolecular potential, deduced by London for van der Waals forces, would lead to a/V^3 .

The magnitude of a is approximately but not exactly a function of the interhalogen distance for the tetrachlorides.

The following values of compressibility at 25° were calculated: CCl₄, 1105; SiCl₄, 1652; TiCl₄, 898; SnCl₄, 1080; SiBr₄, 866; each in reciprocal atmospheres $\times 10^7$.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

NITROGEN COMPOUNDS OF GERMANIUM. II. EQUILIBRIUM IN THE SYSTEM Ge-NH₃-Ge₃N₄-H₂. THE DISSOCIATION OF GERMANIC NITRIDE¹

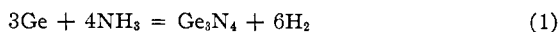
BY GLEN H. MOREY AND WARREN C. JOHNSON

RECEIVED MAY 28, 1932

PUBLISHED SEPTEMBER 5, 1932

Introduction

Finely-divided germanium has been shown to react with ammonia gas at temperatures ranging from 600–750° to produce germanic nitride according to the equation²



This reaction was found to be readily reversible in the same temperature interval. Since germanium and germanic nitride exist as solid phases at these temperatures, the equilibrium constant for the reaction may be expressed as³

$$K_1 = (f_{\text{H}_2})^6 / (f_{\text{NH}_3})^4 \quad (2)$$

From the ammonia equilibrium



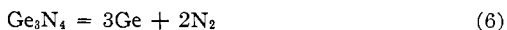
an expression for the constant may be written as

$$K_2 = (f_{\text{NH}_3})^4 / (f_{\text{N}_2})^2 (f_{\text{H}_2})^6 \quad (4)$$

It then follows that

$$K_1 \times K_2 = K_3 = 1 / (f_{\text{N}_2})^2 \quad (5)$$

Germanic nitride is known to dissociate at high temperatures to yield nitrogen and metallic germanium^{2,4,5}



¹ Presented at the meeting of the American Chemical Society in Indianapolis, Indiana, April, 1931.

² Johnson, *THIS JOURNAL*, **52**, 5160 (1930).

³ The fugacity is used in this paper in place of the pressure since the magnitude of the latter assumes relatively high values. At low pressures the two terms are identical.

⁴ Schwarz and Schenk, *Ber.*, **63**, 296 (1930).

⁵ Hart. Master of Science Thesis, University of Chicago, August, 1930.

For this equilibrium (6) we may write

$$K_4 = 1/K_3 = (f_{N_2})^2 \quad (7)$$

Since K_2 has been determined experimentally over a considerable temperature range, it is evident that when K_1 is known, K_4 and the pressure of nitrogen in equilibrium with germanic nitride and metallic germanium may be readily calculated for reaction (6). It was found necessary to resort to this indirect method for a determination of K_4 since the dissociation of germanic nitride, as will be shown later, cannot be determined directly.

The present paper describes the determination of K_1 at the temperatures 610, 614, 638, 654 and 664°. It was not found practical to employ a static method for the determination of this equilibrium since, at these temperatures, ammonia is readily dissociated. Accordingly, a dynamic method was used which consisted in passing different mixtures of ammonia and hydrogen over finely-divided germanium at a definite temperature. The formation of germanic nitride was easily observed by the color and the increase in weight of the germanium.

The values obtained indirectly, as described above, for K_4 show why germanic nitride is not produced when metallic germanium is heated with nitrogen at ordinary pressures. The only explanation of the apparent stability of germanic nitride, even at temperatures as high as 500°, is that the rate of dissociation to germanium and nitrogen must be exceedingly low.

Experimental

Materials.—Small amounts of purified germanic oxide were reduced with hydrogen at 600° to the gray germanium powder. For a further purification, the metal was heated in chlorine at 250° to form GeCl_4 , the chloride was hydrolyzed to the oxide, and finally the oxide was again reduced with hydrogen to germanium. Small samples of the oxide were used in this reduction process in order to ensure complete reaction.

Anhydrous ammonia of commerce was siphoned from its container into a steel cylinder containing several small pieces of sodium which served to remove the water completely. In the course of an experiment the ammonia was allowed to escape from this cylinder as a gas.

Tank hydrogen of the best grade was used without further purification. The presence of a small amount of water or oxygen in the hydrogen was not objectionable in the experiments.

Apparatus and Procedure.—The apparatus used in the investigation is shown in Fig. 1. Approximately 1 g. of the gray germanium powder was placed in a boat and inserted into a Vitreosil tube P which in turn was heated by an electric furnace J. The temperature of the furnace was measured by a platinum-platinum-rhodium thermocouple K calibrated by the usual Bureau of Standards metals. The e. m. f. developed by the thermocouple was measured with a White potentiometer. The temperature of the furnace was readily controlled with outside rheostats with a variation of not more than $\pm 1^\circ$ during the course of an experiment.

Ammonia and hydrogen were allowed to enter at A_1 and A_2 , respectively, at a rate dependent upon the composition of the mixture desired for a given experiment. The composition of the gas mixture was controlled by the calibrated flowmeters C_1 and C_2 , the capillaries of which were obtained from broken thermometer stems. Some of these

capillaries were sufficiently small to allow a gas flow of less than 20 cc. per minute with a pressure difference of 10 cm. in the two arms of the flowmeter. Flowmeters with larger capillaries were used when rates as high as 300–350 cc. per minute were found necessary for certain compositions. In order to maintain a constant pressure in the flowmeters, the mercury levels in the blow-off tubes B_1 and B_2 were adjusted accordingly. Thus a constant flow of ammonia and hydrogen could be readily maintained with any excess amount of either gas passing through the tubes B_1 and B_2 continuously. The inlet of each of these tubes contained a small capillary inner-sealed in the side wall so as to produce small bubbles of the exit gases and thus avoid any appreciable disturbances in the height of the mercury columns in the flowmeters.

D_1 and D_2 were employed as traps to catch any mercury that might be removed from the meters due to the introduction of too much gas in the initial stages of a run. These traps were found to be advantageous in that the mercury could be easily returned to the meters without the necessity of dismantling the apparatus.

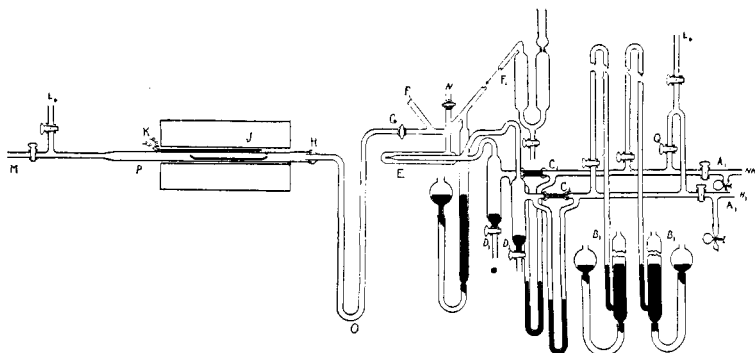


Fig. 1.

When the gases had passed through the meters at a definite rate of flow, they were allowed to enter chamber E through a small opening as shown in the figure. This chamber served to mix the hydrogen and ammonia before entering the furnace and coming in contact with the germanium. A de Khotinsky seal was made at H between the Pyrex and Viteosil tubes. The U-tube O was employed merely to obtain some flexibility in making the seal at H.

F_1 represents a gas absorption pipet which was filled with glass tubes in order to obtain as high a surface area as possible. (F_2 leads to a second pipet of the same type not shown in the figure.) These pipets contained 50 cc. of approximately 0.1 *N* hydrochloric acid protected from gases of the atmosphere such as ammonia and moisture by a calcium chloride tube. In a given experiment the flowmeters were set to give only approximate values of the composition of the gas mixture, while accurate values were obtained through the absorption of the mixture by the hydrochloric acid in the pipets. The excess hydrochloric acid was titrated with approximately 0.1 *N* sodium hydroxide with methyl orange as the indicator. The percentage of ammonia in the different gas mixtures was thus obtained from the titration values. In order to be certain of a constant gas composition throughout an experiment, four hours for the usual case, a sample of the gas mixture was collected in F_1 during the first hour and a second sample collected in F_2 during the fourth hour. In general, a variation between the two samples was found not to exceed 0.5% ammonia.

During the course of a determination, the exit gases were allowed to pass through the tube at M into the atmosphere. Stopcock G was opened when the furnace had

reached a definite and constant temperature to permit the gases to come in contact with the germanium. It was closed when samples of the gas mixture were collected in the absorption pipets. (Between the main tubes and F_1 and F_2 were inserted stopcocks to control flow of the gases into the pipets. These stopcocks are not shown in the figure.) G was also closed at the beginning of a determination during the process of establishing a satisfactory gas flow. In this procedure the exit gases were allowed to pass into the atmosphere through N . L_1 and L_2 represent stopcocks leading to a mercury vapor pump supported by a Hyvac oil pump. According to the position of these stopcocks, it was possible to evacuate the entire apparatus on both sides of the flowmeters at the same time. This was found to be essential in the evacuation of the system since the capillaries of the flowmeters were of such a diameter as to be comparable with the mean free path of the gas molecules at low pressures.

The above description of the apparatus indicates the procedure followed to determine the equilibrium relations for equation (1) at a given temperature. When the gases had passed through the apparatus for a period of about four hours, the furnace was rapidly cooled to a temperature below that required for any appreciable reaction between ammonia and germanium. The composition of the gas mixture was maintained throughout the cooling. Then the seal at H was removed and finally the boat was taken from the tube in the furnace. Any increase in weight of the boat and contents was due to the presence of Ge_3N_4 . In order to establish the presence of Ge_3N_4 , in several instances the contents of the boat were reduced with hydrogen at 700° , the ammonia produced was collected in standard acid solution and determined as nitrogen. The nitrogen determination was found to check with the original increase in weight of the germanium. In the initial experiments at a given temperature, a composition of the gas mixture was used which would produce a considerable quantity of Ge_3N_4 during a four-hour heating. In the subsequent experiments, the ammonia content of the mixture was reduced until no reaction resulted with the germanium. These experiments were repeated several times at each temperature. By this procedure it was found possible to obtain equilibrium values quite accurately to approximately $\pm 0.5\%$ of ammonia.

Results

Table I gives a set of typical data at five temperatures. Column 1 of the table gives the temperature; column 2 the percentage of ammonia in the gas mixture, the first value representing an analysis of the mixture taken during the first hour of the experiment while the second value is obtained from a sample taken during the last hour; column 3, the weight of Ge_3N_4 calculated from the increase in weight due to nitrogen; column 4, the rate of flow of the gases through the meters; and column 5, the time of flow at the temperature in question. All of these data were checked several times by additional experiments.

Table II shows the equilibrium data recorded and calculated from the results given in Table I. The values given in column 3 for the percentage of ammonia in the equilibrium mixture are derived from a large amount of data, a typical set of which is recorded in Table I. In calculating K_1 , partial pressures were taken to be identical with the fugacities at the temperatures and pressures employed in our experiments. It is surprising that these equilibrium values can be easily obtained and duplicated with a considerable degree of accuracy. The method employed allows for some

TABLE I
RESULTS OBTAINED IN PASSING MIXTURES OF AMMONIA AND HYDROGEN OVER
GERMANIUM POWDER AT DIFFERENT TEMPERATURES

Temp., °K.	Composition of gas mixture, % NH ₃	Ge ₃ N ₄ formed, g.	Rate of flow, cc./minute		Time, hrs.
			H ₂	NH ₃	
883	95.3-95.7	0.328	29	...	4
	91.2-91.6	.103	44	...	4
	90.4-90.5	.024	47	...	4
	89.9-89.9	No reaction	44	...	4
	89.6-89.8	No reaction	44	...	4
887	92.6-93.0	0.078	37	...	3.5
	89.4-90.1	.029	47	...	4
	89.0-88.5	No reaction	48	324	4
911	92.2- ..	0.141	35	...	4
	91.6-91.3	.093	35	325	4
	89.2-88.8	.078	35	295	4
	88.2-88.3	.049	35	275	4
	88.2-88.1	.049	35	270	4
	84.5-84.8	.029	35	206	4
	84.4-84.6	.019	35	214	4
	82.3-82.1	No reaction	23	123	3
	79.7-79.3	No reaction	23	105	4
927	85.7-85.9	0.054	52	289	3
	82.0-82.2	.029	74	319	4
	80.8-80.9	No reaction	79	319	3
937	84.3-83.8	0.268	52	304	3
	81.0-81.5	.195	80	316	3
	79.2- ..	.054	79	290	3.5
	77.7-78.0	No reaction	92	288	2.5
	74.2-75.3	No reaction	74	267	3

errors such as those due to changes in the rate of flow of the gases and changes in temperature of the reactants. However, these errors must be small in magnitude since the results of the experiments are readily reproducible. On the other hand, the values given for K_1 cannot be highly accurate since a small deviation in the percentage of ammonia at equilibrium becomes greatly magnified in the calculation of K_1 .

TABLE II
EQUILIBRIUM DATA FOR THE REACTION $3\text{Ge} + 4\text{NH}_3 = \text{Ge}_3\text{N}_4 + 6\text{H}_2$

Temp., °K.	$10^3/T$	NH ₃ at equilibrium, %	$K_1 = (f_{\text{H}_2})^6 / (f_{\text{NH}_3})^4$	Free energy, ΔF (cal.)
883	1.133	90.0 ± 0.2	1.52×10^{-6}	23,500
887	1.128	89.0 ± .3	2.82×10^{-6}	22,500
911	1.097	84.0 ± .4	3.37×10^{-6}	18,600
927	1.079	81.3 ± .4	9.97×10^{-6}	17,000
937	1.067	78.5 ± .4	2.60×10^{-4}	15,400

In Fig. 2 are plotted the values of $\log K_1$ against $1/T$. A straight line is drawn through the five points in this plot. The maximum deviation of

any one point from this line is well within the limits of the deviations expressed in column 3 of Table II.

Thermodynamic Calculations.—The free energy increase (ΔF) accompanying reaction (1) is noted in the last column of Table II. It is derived from the equilibrium constant K_1 by means of the equation $\Delta F = -RT \ln K_1$, where K_1 is defined as above, T is the absolute temperature and R has a value of 1.987 cal./mole degree.

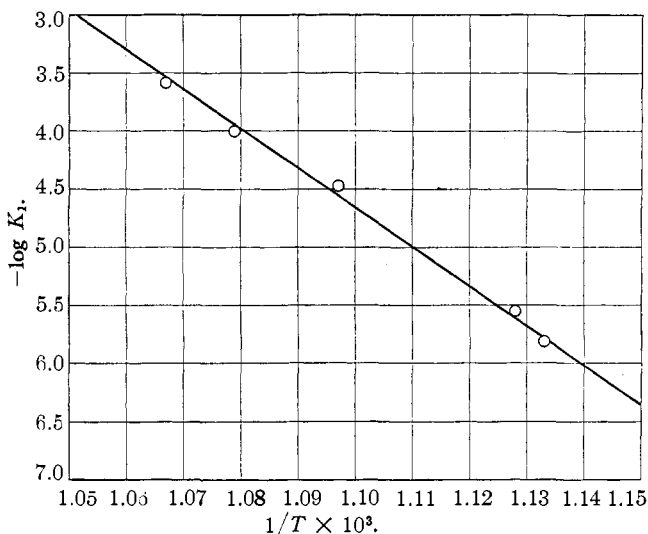


Fig. 2.

Since no data are available for the specific heat of germanic nitride, it is not possible to obtain an accurate value for ΔH of reaction (1). However, the slope of the curve in Fig. 2 gives an average value of ΔH over the temperature range between 883 and 937°K. According to this calculation, ΔH is 155,600 calories.

The dissociation pressure of germanic nitride may be calculated, as previously shown, by combining the equilibrium constant determined for reaction (1) with the known values⁶ of K_2 for the ammonia equilibrium. The product of these two constants gives K_3 , which is equal to the reciprocal of the square of the fugacity of the nitrogen. Since germanic nitride and germanium exist as solid phases, $K_4 = 1/K_3 = (f_{N_2})^2$ the equilibrium expression for the dissociation of germanic nitride. The free energy change accompanying the dissociation may be calculated as described above. The data are given in Table III.

⁶ The equilibrium constant for the reaction, $1/2N_2 + 3/2H_2 = NH_3$, was calculated from the general free energy equation given by Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 557. This constant was then raised to the fourth power in order to satisfy equation (3).

TABLE III
DATA FOR THE DISSOCIATION OF GERMANIC NITRIDE

Temp., °K.	$K_2 \times 10^{12}$	$K_4 \times 10^{-14}$	$f_{N_2} \times 10^{-3}$ (atm.)	Free energy ΔF , in cal.
883	3.351	19.63	4.43	-69,900
887	2.930	12.10	3.48	-69,300
911	1.334	2.224	1.49	-68,150
927	0.8027	1.250	1.12	-68,300
937	0.5916	0.6501	0.806	-67,800

An average value of the heat effect, between the temperatures 883 and 937°K., accompanying reaction (6) may be obtained from the plot of $\log K_4$ against $1/T$. This procedure gives a value of $\Delta H = -102,000$ calories. By adding the ΔH values for equations (1) and (3), one obtains $\Delta H = -103,000$ calories for reaction (6).

Discussion

The results of this investigation are in accord with the failure to prepare germanic nitride directly from germanium and nitrogen at atmospheric pressure.⁷ They also show the impossibility of preparing this nitride from its elements at any pressure experimentally attainable. The equilibrium fugacities calculated for the dissociation of germanic nitride are not to be taken as being highly precise, inasmuch as any small error in the determination of K_1 becomes considerably magnified in the calculation of K_4 .

The procedure followed in the work under discussion is similar to that employed by Emmett, Hendricks and Brunauer⁸ in the determination of the dissociation pressure of Fe_4N . Their calculations give a dissociation pressure of 5600 atmospheres for Fe_4N at 525°. They identified the Fe_4N phase in a determination of the equilibrium, $2Fe_4N + 3H_2 = 2NH_3 + 8Fe$, by means of x-ray powder photographs. We were not compelled to use this method of identification since it has been shown that Ge_3N_4 is the only new phase that appears when germanium reacts with ammonia gas and that only germanium and ammonia are produced when Ge_3N_4 is reduced with hydrogen.² In the case of the action of dry ammonia on iron, several nitrides of the element have been shown to be present.

Since germanic nitride is known to be thermally stable at a temperature as high as 500° and since the calculated nitrogen fugacity in equilibrium with germanium and the nitride at 650° is of the order of magnitude of 1×10^8 atmospheres, it must be concluded that the rate of dissociation at low temperatures is exceedingly low. The data given in Table III show the nitride to be less stable thermally at the lower than at the higher temperatures; on the other hand, it does not appear to dissociate to any measurable extent at ordinary temperatures.

⁷ Experiments carried out in this Laboratory. The results of this work will be discussed in a later paper in connection with the properties of germanous nitride.

⁸ Emmett, Hendricks and Brunauer, *THIS JOURNAL*, **52**, 1456 (1930).

The results obtained indirectly for the dissociation of Ge_3N_4 are not analogous to those found for the dissociation of Si_3N_4 .⁹ The pressure of nitrogen in equilibrium with silicon and silicon nitride is only a few mm. at 1600°K ., and this pressure is found to increase with increasing temperature up to 1800°K . Likewise, the sign of the heat effect accompanying the dissociation of Si_3N_4 is positive in contrast to the negative value found for the Ge_3N_4 dissociation.

In conclusion, we would like to thank Professor T. R. Hogness for the helpful suggestions and criticisms offered in the preparation of this article.

Summary

The equilibrium in the system $\text{Ge-NH}_3\text{-Ge}_3\text{N}_4\text{-H}_2$ has been determined by a dynamic method at temperatures ranging from 883 to 937°K .

Known data for the ammonia equilibrium are used to calculate the dissociation pressure of germanic nitride. The results demonstrate the failure to produce germanic nitride by heating metallic germanium with nitrogen.

The free energy and heat content changes are calculated from the $\log K$ values and the $\log K-1/T$ plots, respectively, according to the usual procedures.

⁹ Hincke and Brantley, *THIS JOURNAL*, 52, 48 (1930).

CHICAGO, ILLINOIS

[CONTRIBUTION FROM VANDERBILT UNIVERSITY]

SOME REACTIONS OF VANADIUM CARBIDE

BY S. E. OLDHAM AND W. P. FISHEL

RECEIVED MAY 28, 1932

PUBLISHED SEPTEMBER 5, 1932

Chemically pure vanadium carbide, obtained from The Vanadium Corporation of America, was used in these experiments. Analysis corresponded to the simple formula, VC.

Vanadium carbide was found not to react with aqueous hydrochloric acid at ordinary or elevated temperatures. With nitric acid at room temperature, there was only a slight reaction, but on heating it dissolved rapidly. Prolonged heating produced an orange precipitate of hydrated vanadium pentoxide, or vanadic acid. Perchloric acid did not react with the carbide at room temperature, but boiling produced a vigorous reaction and eventually an orange precipitate as in the case of nitric acid. Large amounts of chlorine were liberated along with carbon monoxide, carbon dioxide, oxygen and some hydrocarbons. Sulfuric acid had no effect until raised to the temperature at which it became a strong oxidizing agent.

When placed in a combustion tube and heated to a temperature of 750° or higher in a current of dry hydrogen chloride, vanadium carbide reacted to form methane and hydrogen as gaseous products and vanadium dichlo-