

The results obtained indirectly for the dissociation of  $\text{Ge}_3\text{N}_4$  are not analogous to those found for the dissociation of  $\text{Si}_3\text{N}_4$ .<sup>9</sup> The pressure of nitrogen in equilibrium with silicon and silicon nitride is only a few mm. at  $1600^\circ\text{K}$ ., and this pressure is found to increase with increasing temperature up to  $1800^\circ\text{K}$ . Likewise, the sign of the heat effect accompanying the dissociation of  $\text{Si}_3\text{N}_4$  is positive in contrast to the negative value found for the  $\text{Ge}_3\text{N}_4$  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  $937^\circ\text{K}$ .

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.

<sup>9</sup> Hincke and Brantley, *THIS JOURNAL*, **52**, 48 (1930).

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM VANDERBILT UNIVERSITY]

## SOME REACTIONS OF VANADIUM CARBIDE

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

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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  $750^\circ$  or higher in a current of dry hydrogen chloride, vanadium carbide reacted to form methane and hydrogen as gaseous products and vanadium dichlo-

ride, trichloride and carbon as solids. This is contrary to statements by Moissan<sup>1</sup> and Friend<sup>2</sup> that the carbide does not react with hydrogen chloride at red heat. The dichloride, especially at lower temperatures, is the chief solid product formed. An average of analyses on the dichloride was: V, 41.97%; Cl, 58.90%. No carbon dioxide was found in the gases given off by the reaction. After being freed from hydrogen chloride, the evolved gases were exploded over mercury and extracted for carbon dioxide in an Orsat apparatus. Averages of analyses on gases collected at the indicated temperatures were

|                  |      |      |      |      |      |
|------------------|------|------|------|------|------|
| Temp., °C.....   | 815  | 880  | 950  | 985  | 1025 |
| Methane, %.....  | 24.2 | 21.9 | 26.4 | 27.1 | 27.5 |
| Hydrogen, %..... | 45.5 | 41.4 | 40.6 | 38.1 | 38.2 |

From the contraction on explosion and the amount of carbon dioxide found, the gases were assumed to be methane and hydrogen. These gases were collected from one to one and one-half hours after the first signs of reaction. Analyses on gases caught after five hours gave a methane content of 19.3% and a hydrogen content of 53.5%. Small quantities of  $VCl_3$  were produced in all runs, but considerable amounts were produced when the reaction was allowed to go on for five hours. A decided increase in the hydrogen content of the evolved gases was also noticed. This was probably due to a secondary reaction of  $VCl_2$  with  $HCl$ .

The vanadium dichloride is a green solid which when thrown upon water does not sink at once, but floats on the surface of the liquid. It dissolves slowly to give a lavender solution which precipitates silver from a solution of silver nitrate and decolorizes indigo, litmus and potassium permanganate solutions. The dichloride is stable in moist air for some length of time, contrary to the statement of Friend<sup>2</sup> that it is an exceedingly hygroscopic compound. It dissolves readily in nitric acid with the liberation of chlorine or hydrogen chloride. Analysis for chlorine was made by first dissolving in potassium hydroxide solution to retain the chlorine and then acidifying with nitric acid. On treatment with potassium hydroxide, it seemed to dissolve and immediately reprecipitate as a black solid, probably  $V(OH)_2$ .

The fact that part of the carbon goes to form methane while the remainder is changed to elementary carbon indicates that some of the carbon atoms in vanadium carbide bear a different relation to the vanadium than others, and that the molecular formula is  $(VC)_n$ .

### Summary

Vanadium carbide reacts with hydrogen chloride at elevated temperatures forming methane, hydrogen, vanadium dichloride and some vana-

<sup>1</sup> Moissan, *Compt. rend.*, **122**, 1297 (1896).

<sup>2</sup> Friend, "Text-Book of Inorganic Chemistry," Vol. VI, iii, p. 104.

dium trichloride. It is insoluble in aqueous hydrochloric acid, but is soluble in hot oxidizing acids forming hydrated pentoxides.

NASHVILLE, TENNESSEE

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## REACTIONS OF COMPOUNDS WITH EVEN NUMBERS OF ELECTRONS. NITROGEN TRICHLORIDE AND NITROGEN TETROXIDE

By WILLIAM ALBERT NOYES

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Some years ago it was suggested<sup>1</sup> that if we assume that the pair of electrons forming a covalence remain with one of the atoms which separates during a chemical reaction, a reconciliation between the positive-negative theory of the reactions of non-electrolytes and Lewis's theory of shared electrons could be effected. A further, very important, reconciliation between the older valence theories and Lewis's theory, has been furnished by the sharp distinction between doubled covalences and semipolar unions given us by Sugden's parachor,<sup>2</sup> and by the optically active sulfoxides of Phillips and his co-workers.<sup>3</sup>

In the first paper referred to it was pointed out that compounds having a covalence may, in reactions, separate either into electrically neutral parts, each with an odd electron, or into positive and negative ions by the method suggested above. Coleman and Howells<sup>4</sup> have shown that nitrogen trichloride reacts with butylene in the latter manner, the positive chlorine going to the end carbon atom.

In an extensive study of the reaction between nitric oxide, which has an odd electron, and nitrogen trichloride, it has been shown<sup>5</sup> that the nitric oxide takes an electrically neutral chlorine atom, with an odd electron, from the trichloride, leaving the ephemeral compound, nitrogen dichloride, also with an odd electron.

Nitrogen tetroxide is a compound containing only paired electrons, although it begins to dissociate to two molecules of nitrogen dioxide, each with an odd electron, at temperatures below zero. It has seemed of interest, therefore, to study the reaction of this compound with nitrogen trichloride.

It was expected that the reaction would prove to be a typical covalence reaction, the positive chlorine ion going to the negative oxygen, the nega-

<sup>1</sup> W. A. Noyes, *THIS JOURNAL*, **45**, 2959 (1923).

<sup>2</sup> Sugden, *J. Chem. Soc.*, **127**, 1525 (1925).

<sup>3</sup> Phillips, *ibid.*, **127**, 2552 (1925); Harrison, Kenyon and Phillips, *ibid.*, 2079 (1926).

<sup>4</sup> G. H. Coleman and H. P. Howells, *THIS JOURNAL*, **45**, 3084 (1923).

<sup>5</sup> *Ibid.*, **50**, 2902 (1928); **52**, 428 (1930); **53**, 2137 (1931).