Due to the small quantities of metals used, these small deviations may be regarded as within the limits of experimental error. Such determinations show that osmium may be removed quantitatively from a mixture containing one of its salts with that of ruthenium by means of strychnine sulfate.

Summary

A new quantitative method for the determination of osmium is given. The metal is removed from a solution of sodium chlorosmate by means of a saturated aqueous solution of strychnine sulfate. The composition of the compound formed was found to be $(C_{21}H_{22}O_2N_2)_3Os$, a coördinated salt in which osmium exhibits a coördination number of six. By use of the gravimetric factor, 0.1758, the percentage content of the osmium may be obtained from a direct weighing of the canary-yellow precipitate.

Strychnine sulfate reacts with the formation of precipitates with all of the platinum metals, but the precipitate formed with ruthenium is soluble in boiling ethyl alcohol, from which it does not easily separate on cooling even after a period of several days. This method may be used in effecting a separation of osmium from ruthenium since the former compound reprecipitates completely on cooling the alcoholic solution.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 224]

THE HIGH-TEMPERATURE EQUILIBRIUM BETWEEN SILICON NITRIDE, SILICON AND NITROGEN

BY W. B. HINCKE AND L. R. BRANTLEY

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Plan of the Investigation

This investigation is a continuation of the researches in progress in this Laboratory on high-temperature equilibria.[1] The method devised by Prescott and used by Prescott and Hincke[1d] in studying the equilibrium of the system aluminum carbide, nitrogen, aluminum nitride and carbon was employed. This method consists in heating by an electric current to various temperatures (measured by an optical pyrometer) the solid reaction mixture (in this case the silicon nitride and silicon) within a graphite tube a few millimeters in diameter and a few centimeters long placed within a pyrex bulb, and in measuring the pressures produced. In this article are described measurements made of the dissociation pressures of silicon nitride from 0.27 to 5.49 mm. through a temperature range from 1606 to 1802°K.

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[1] (a) Prescott, THIS JOURNAL, **48**, 2534 (1926); (b) Prescott and Hincke, *ibid.*, **49**, 2744 (1927); (c) Prescott and Hincke, *ibid.*, **49**, 2753 (1927); (d) Prescott and Hincke *ibid.*, **50**, 3228 (1928); (e) Prescott, *ibid.*, **50**, 3237 (1928); (f) Prescott and Hincke, *Phys. Rev.*, **31**, 130 (1928).

It has been shown by Weiss and Engelhardt[2] and by Funk[3] that the compound produced, when silicon is heated in nitrogen at 1300 to 1450° as long as the gas continues to be absorbed, is the normal nitride, Si_3N_4. The nitride produced in the experiments here described presumably had this composition, since the conditions of heating were substantially the same.

The authors wish to express their thanks to Dr. C. H. Prescott, Jr., whose suggestions and criticisms have been of great assistance.

Apparatus and Procedure

The temperature measurements in this investigation were made by means of an optical pyrometer with a disappearing filament; the details, corrections and limitations of these measurements have already been described.[1b,f] The furnace, the devices for introducing nitrogen and the McLeod gages have also been described.[1d]

The silicon used was a c. p. Eimer and Amend preparation which had been ground to pass a 200-mesh sieve. The preparation upon treatment with hydrofluoric and nitric acids, evaporation with nitric acid and ignition of the residue yielded 2% of oxides, corresponding to about 1% of metallic impurity.

In the procedure adopted there was placed loosely in the middle zone of the graphite tube a charge of 0.1 g. of finely powdered silicon. After complete evacuation, the apparatus was filled at one atmosphere with (tank) nitrogen that had been passed through a purifying train, and the furnace was heated to 1675°K. for thirty minutes. This converted about 75% of the charge to silicon nitride.[4] The apparatus was then evacuated, after which it was ready for the equilibrium measurements.

In all of the determinations the temperature of the furnace was held constant, and the equilibrium pressure was found by taking the mean of the final pressures of a forward and a reverse reaction wherein the pressure in the glass bulb containing the graphite furnace increased and decreased, respectively. To hold the furnace at a constant temperature it sufficed to keep the current through it constant, which was done by means of a standard resistance and a potentiometer. A shower of tap water was caused to play continuously over the glass bulb containing the graphite tube while equilibrium measurements were being made. This prevented excessive outgassing of the glass walls and contamination of the nitrogen. A gas micro-analysis apparatus[1d] was used to determine the partial pressure of nitrogen at the end of each experiment. In all the satisfactory runs the nitrogen formed more than 92% of the gases in the bulb.

For the preliminary formation of silicon nitride the current was drawn from a 1-kilowatt transformer. During the measurements it was taken from storage batteries. To maintain the furnace at 1802°K. about 80 amperes at 10 volts was required.

The Equilibrium Measurements

The first equilibrium determination was made at 1675°K. The pressure of the nitrogen in the bulb built up from a vacuum to 0.47 mm. in the course of one hour, the gas then containing 92% of nitrogen. The apparatus was then again evacuated and filled to 0.90 mm. of nitrogen, as measured when the furnace had become hot; in this case the pressure of the gas decreased

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[2] Weiss and Engelhardt, *Z. anorg. Chem.*, **65**, 78 (1910).

[3] Funk, *ibid.*, **133**, 67 (1924).

[4] No silicon carbide was formed at this nitrogen pressure by the reaction of silicon with the graphite furnace; moreover, it was found that silicon carbide is inert to nitrogen under the conditions of these experiments.

in one hour to 0.762 mm., and the gas contained 95% of nitrogen. Two one-hour runs were then made, one at 0.57 mm. and the other at 0.675 mm. of nitrogen, but these showed no measurable change in pressure. Finally a run of two hours with increasing pressure was made, starting from an initial pressure of 0.336 mm. and stopping at 0.553 mm. of nitrogen. The gas analysis showed 100% of nitrogen in this run, which was to be expected because of the pumping off of the outgassed impurities in the previous runs. It was observed that a pellet reacted more slowly after some hours of heating, probably owing to loss of some of the silicon from the charge by volatilization and to sintering of the silicon nitride into a more compact mass.

The pellets removed from the furnaces after each equilibrium determination always gave the characteristic ammonia test on heating with concentrated alkali, and under a low powered microscope showed a white sintered mass speckled with darker particles of silicon.

In each determination the true equilibrium pressure of the nitrogen corresponding to any temperature was assumed to be the average of the two pressures which had been attained in a forward and a reverse run. Each of the two pressures always approached a limiting value that seemed to be as far as the reaction would go within a reasonable time. These pressures, however, did not differ very greatly from one another. At temperatures above 1800 °K. sublimation of the silicon and sintering of the silicon nitride were so rapid that a pellet became only slowly reactive after a few runs. This permitted, nevertheless, a range of about 200° over which the equilibrium could be studied.

Table I gives the final pressures (in millimeters) observed at each temperature. There are shown in each case the highest pressures (marked "increasing") which were attained by the forward reaction (decomposition of the nitride) and the lowest pressures (marked "decreasing") which were attained by the reverse reaction. These pressures are always the partial pressure of the nitrogen in the gas (found by multiplying the total pressure by the fraction of nitrogen present). The mean values of these two pressures for each pair are taken as the equilibrium pressures. The correspond-

TABLE I

EQUILIBRIUM PRESSURES OF THE REACTION AT VARIOUS TEMPERATURES AND THE CORRESPONDING FREE ENERGIES

Absolute temp., T	$10^4/T$	Final pressure in mm.			Pressure $\times 10^4$ in atm.	Free energy, ΔF
		Increasing	Decreasing	Mean		
1606	6.225	0.179	0.361	0.27	3.5	50,800
1638	6.110	.382	.537	.46	6.0	48,300
1675	5.971	.553	.762	.66	8.7	46,900
1709	5.850	1.110	1.335	1.22	16.1	43,700
1739	5.750	2.215	2.675	2.44	32.0	39,700
1779	5.625	3.560	4.65	4.11	54.0	36,900
1802	5.550	5.05	5.93	5.49	72.0	35,300

ing values expressed in atmospheres are given in an adjoining column. In the last column of the table are given also the values (derived as described below) in calories of the free-energy increase (ΔF) attending the reaction $Si_3N_4(s) = 3Si(s) \text{ or } (l) + 2N_2(g)$.

In Fig. 1 are plotted as full circles the mean values of $\log_{10} p$ (in mm.) against $10^4/T$. The straight line was drawn so as to fit best the full circles. The corresponding observed "increasing" and "decreasing" values are shown by half-circles.

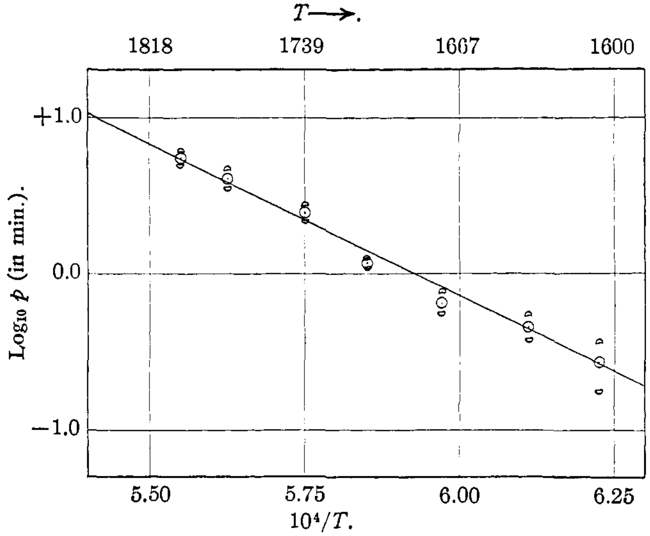

Fig. 1.

The final relation between the equilibrium pressures in atmospheres and the absolute temperature is given by the equation

$$2.3 \log_{10} p \text{ (in atm.)} = 19.75 - \frac{44{,}500}{T}$$

Since the melting point of silicon is approximately 1687°K., there should be a slight change in slope of the line at this temperature due to the heat of fusion of the silicon, but the data are not accurate enough to show this change in slope.

Thermodynamic Calculations

The chemical reaction is $Si_3N_4 = 3Si + 2N_2$. The free-energy increase (ΔF) attending it when the nitrogen pressure is one atmosphere may then be derived from the equilibrium pressure p in atmospheres by the familiar equation $\Delta F = -RT \ln K$, where $K = p^2$ and $R = 1.987$. From the determinations of the equilibrium pressure p are thus obtained the values of ΔF given in the last column of Table I.

From these values of the free-energy increase one obtains the function

$\Delta F = 176{,}300 - 78.35T$ for absolute temperatures between 1600 and 1800°. From this it follows that the heat-content increase ΔH is 176,300 calories in this temperature range. The function shows also that at an absolute temperature of 2250° (assuming it to hold up to this temperature) the free-energy increase becomes zero and therefore that the dissociation pressure becomes one atmosphere at this temperature.

Summary

The pressure of nitrogen at which equilibrium prevails between silicon nitride, Si_3N_4, and its elements at absolute temperatures ranging from 1606 to 1802°K. has been determined by an experimental method previously described. This pressure is 0.27 mm. at 1606°K. and 5.5 mm. at 1802°K. Within this temperature interval the free-energy increase ΔF at one atmosphere attending the reaction $Si_3N_4 = 3Si + 2N_2$ was found to be expressed by the function $\Delta F = 176{,}300 - 78.35\ T$ calories. From this it follows that the heat-content increase ΔH at 1700°K. is 176,300 cal.; also that the dissociation pressure of the nitride becomes one atmosphere at about 2250°K.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
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THE RATE OF REACTION IN A CHANGING ENVIRONMENT

BY GEORGE SCATCHARD

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In the study of the reaction rates described in the following paper[1] there were developed methods which are of general applicability to the treatment of rates in non-ideal solutions in which the deviations change during the course of the reaction. Graphical methods applicable to this problem were presented in an earlier paper;[2] the present method is analytical and therefore much easier to apply. Although approximate, it is in most cases as accurate as the rate measurements.

The treatment is based upon the theory of Brönsted[3] that the mechanism of the reaction is the formation and decomposition of a "critical complex," so that for the simple bimolecular reaction

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{X}(=\mathrm{AB}) \longrightarrow \mathrm{D} + \mathrm{E}$$

the rate is given by

$$-\frac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}t} = KC_\mathrm{A}C_\mathrm{B}\frac{f_\mathrm{A}f_\mathrm{B}}{f_\mathrm{X}} \tag{1}$$

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[1] Ashdown, THIS JOURNAL, **52**, 268 (1930).

[2] Scatchard, *ibid.*, **48**, 2259 (1926).

[3] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922), and many later papers. The method is more general than this theory, however. For example, it may be applied to the simple activity theory merely by replacing f_X by 1.