is less than the visible volume. A correction for this free space was made by adding a *known* volume of nitrogen *gas* (determined by difference) at 77.35°K. and gradually increasing the pressure to its liquefaction point, until a thin layer of liquid nitrogen appeared over the solid ozone. It was found that this layer remained stable and unchanged for 3 hr. at 77.35°K. The solubility of ozone in nitrogen at this temperature, in equilibrium with liquid ozone, has been determined[13] and found to equal 4.41 ± 0.14 mole % ozone. In view of this small solubility, the correction for the amount of ozone dissolved in the liquid nitrogen may be discarded. The results of our measurements are given in Table I.

In experiment 3, the height of liquid ozone was determined also at 77.35°K. and found to equal 11.81 cm., while the ozone remained *liquid*. The ratio of the two heights = 1.0246 and thus the density of liquid ozone at 77.35°K. = 1.6140, *i.e.*, in excellent agreement with the Jenkins and DiPaolo value, within experimental error (±0.0004).

TABLE I

Pyrex tube, i.d. = 1.815 mm., area = 2.585 mm.^{2}

Exp. no.	Height of liquid O_3 at 90.19°K., cm.	Height of solid O_3 at 77.35°K., cm.	Mm.^{3} of liquid N_2 in pores at 77.35°K.	Mass of solid ozone used, g.	Cor. vol. of solid O_3 at 77.35°K., cm.^{3}	Density of solid ozone at 77.35°K.
1	11.52	10.55	2.42	0.4684	0.2703	1.7327
2	11.48	10.55	2.42	.4667	.2703	1.7267
3	12.12	11.23	4.44	.4927	.2859	1.7237

Discussion and Conclusions

The lengths of the solid ozone cylinders, and therefore the density, are easily measured and readily reproducible. The correction for pore volume in solid ozone is a comparatively small one, being in the range of 1–2% of the ozone's bulk volume. The density of solid ozone, averaged from the experimental data of Table I, at the normal boiling point of nitrogen, or 77.4°K. = 1.728 ± 0.002 g./cm.^{3}. The molar volumes of solid and liquid ozone, at the same temperature, are 27.8 and 29.75 cm.^{3}, respectively. The volume expansion of ozone on melting or

$$\Delta V/V\ \text{solid} = +7.1\%$$

It is appropriate to compare here the volume requirements of solid ozone with solid oxygen. The γ or cubic modification of solid oxygen is stable from its melting point or 54.5°K., to the transition point of the γ to the β form, or 43.6°K. It crystallizes in the T_h^6 space group with a lattice constant of 6.83 A.(8 molecules per unit cell) and has a density of 1.328. Thus the molar volume of solid oxygen, close to its melting point, = 24.2 cm.^{3}. The volume per oxygen atom in the two solid modifications of the element oxygen is substantially smaller in the case of O_3 (*i.e.*, 9.3 cm.^{3}) than for O_2 (12.1 cm.^{3}).

PHILADELPHIA, PENNA.

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(13) A. Streng and A. V. Grosse, *J. Inorg. & Nucl. Chem.* (in press).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Fluorination of Carbides

BY WALTER C. SCHUMB AND JAMES R. ARONSON

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A group of eight carbides—carbides of silicon, boron, iron, chromium, tungsten, titanium, aluminum and calcium—representing the various structural types, has been fluorinated. The fluorinating agents were elementary fluorine gas and cobalt trifluoride, respectively. The volatile products included low molecular weight, fully saturated fluorocarbons in every case. These products were identified by means of infrared spectroscopy and gas chromatography. No structural correlations between the product fluorocarbons and the original carbides were observed. It is felt that the conditions of fluorination were too drastic for such effects to be seen.

Moissan[1] observed the reactions of the carbides of lithium, strontium, barium, cerium, lanthanum, aluminum, beryllium, uranium and zirconium with elementary fluorine. However, he did not characterize the volatile products, except to say in some cases that carbon tetrafluoride was produced. Musgrave and Smith[2] in a more recent work stated that some of the lower fluorocarbons, together with polymeric fluorocarbons, may be produced by the fluorination of metallic carbides, such as calcium carbide, uranium carbide and thorium carbide. Priest[3] reported the preparation of high purity carbon tetrafluoride by the action of elementary fluorine on carborundum.

It was felt that a comparative study of the volatile products resulting from the fluorination of carbides might conceivably show correlations with the structures of the various original carbides. These structures are known to be widely diverse, both as to the type of bonding involved (ionic, covalent or interstitial) and as to the carbon groupings in the structure (discrete, acetylenic, chain-like, etc.).

With this purpose in mind, calcium carbide (CaC_2), aluminum carbide (Al_4C_3), titanium carbide (TiC), tungsten carbide (WC), iron carbide (Fe_3C), chromium carbide (Cr_3C_2), silicon carbide (SiC) and boron carbide (B_4C) were fluorinated using elementary fluorine and cobalt trifluoride when a milder agent was suggested.

Experimental

The apparatus for use with elementary fluorine was similar to that described by Priest.[4] Fluorine gas was passed through copper tubing (mostly $^1/_4$ in.) with flared pressure fittings, past a sulfuric acid atmospheric seal to a junction with a prepurified dry nitrogen tank. The system then continued into a 19 in. monel reactor tube of $^7/_8$ in. inside diameter, fitted with a Teflon gasket and a thermocouple well. The reactor was enclosed by an electric tube furnace. Nickel boats containing the carbides were introduced into this reactor in the various runs. Three monel tubes containing freshly dried soda lime granules were placed directly

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(1) H. Moissan, "Le Fluor et ses Composés," Steinheil, Paris, 1900, p. 234.

(2) W. K. Musgrave and F. Smith, *J. Chem. Soc.*, 3021 (1949).

(3) H. Priest, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 178.

(4) Ref. 3, p. 171.

following the reactor tube. The purpose of the soda lime was to remove any fluorine which may have passed through the reactor. Furthermore, these traps served to aid the control of the rate of supply of fluorine gas, since development of heat within them was taken as an indication of the presence of free fluorine, the progress of which through the system could thus be followed, and hence controlled by regulation of the needle valve on the fluorine cylinder. The reactor for use with cobalt trifluoride was simply a monel tube which was placed in a furnace set for the desired temperature. An exit line led to the soda lime traps. In either system the line continued through a Housekeeper seal to a liquid nitrogen trap, with sulfuric acid and sodium hydroxide bubblers at various points to remove unwanted by-products.

Most of the runs with elementary fluorine were initiated at room temperature by means of a fuse of elementary silicon (about 0.1 g.). From 5 to 10 g. of the carbide was placed with the fuse in the reactor and reaction induced by passing fluorine into the system. Nitrogen was used as a diluting gas and to aid in the control of the reaction. Runs generally lasted approximately 90 minutes. For the runs with cobalt trifluoride, a few grams of the carbide were rapidly mixed with cobalt trifluoride and placed in the reactor, which then was heated to 440° to start the reaction. Runs lasted approximately 9 hr.

The products were identified by means of infrared spectroscopy, as reference spectra were available.[5] The mixtures were analyzed using the Beer–Lambert law in a standard manner and separated when necessary by gas chromatography, using an activated alumina column 6 feet in length, at room temperature and 184°, with helium as the eluting gas. It was found that room temperature was quite satisfactory for the separation of the first two members of the fluorocarbon series, and 184° proved to be an optimum temperature for the separation of the higher members (C_3F_8 and *i*- and *n*-C_4F_{10}).

Results

All of the carbides gave quite similar fluorination products. CF_4, C_2F_6, C_3F_8, *n*-C_4F_{10} and probably some *i*-C_4F_{10} were present in comparable mixtures in every case. SF_6, SO_2F_2 and OF_2 were found in some cases as the result of impurities in the carbides. Typical results of runs, using elementary fluorine as the fluorinating agent, are as tabulated.

Carbide	Mole % of product fluorocarbons				
	CF_4	C_2F_6	C_3F_8	*n*-C_4F_{10}	*i*-C_4F_{10}
SiC	68	16	14	2.2	Trace
B_4C	88	9.2	2.4	0.5	Trace
TiC	86	11	2.9	.4	Trace
WC	67	26	7.0	.6	Trace
Fe_3C	86	9.5	3.5	.7	Trace
Cr_3C_2	91	6.4	2.4	.5	Trace
Al_4C_3	88	9.2	2.9	..	Trace
CaC_2	75	19	5.5	0.6	Trace

The results of the different runs were all qualitatively quite similar and the variations that were present were felt to be due to slight differences in flow rates or in the reaction temperatures prevailing at the site. It was observed that in general higher temperatures gave greater percentages of CF_4. The cobalt trifluoride runs gave similar mixtures of products also.

The findings indicate that the use of elementary fluorine and cobalt trifluoride result in experimental conditions too drastic for any structural correlations to be observed between composition of the carbide and nature of the product fluorocarbons. Some type of polymerization mechanism must be postulated to explain the mixtures of products that were obtained. Some sort of abstraction of the carbon atoms or ions from the carbides as fluorinated fragments appears necessary, but whether the combination of these fragments occurs on the surface of the carbide or in the gas phase is not known. Further, the possibility of the formation of an intermediate such as $(CF)_x$ should be pointed out. It is known that this substance decomposes on heating to give fluorocarbons.[6]

A similar study of the fluorination of various types of nitrides has been completed recently and will be reported in a future issue.

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CAMBRIDGE, MASS.

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[5] D. G. Weiblen, "Fluorine Chemistry," J. H. Simons, Editor, Vol. II, Academic Press, Inc., New York, N. Y., 1954, pp. 469–503.

[6] L. A. Bigelow, ref. 5, Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 379.

[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES CORPORATION]

Heterogeneous Equilibria in the System K_2CO_3–Na_2CO_3

BY ARNOLD REISMAN

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The heterogeneous equilibria in the system K_2CO_3–Na_2CO_3 have been investigated in the range room temperature to their melting points, using differential thermal analysis and X-ray techniques. Data obtained for the melting and freezing curves are in good agreement with previously reported values and indicate the formation of a minimum melting composition at 710 ± 2° somewhere between 55 and 58 mole % Na_2CO_3. In the subsolidus range the results were found to be in marked disagreement with the literature concerning the number of homogeneous and heterogeneous regions and their temperature and compositional intervals of stability. X-Ray examination of the room temperature diagram indicated the formation of an intermediate solid solution in the range 30–45 mole % Na_2CO_3.

Introduction

In 1894, Le Chatelier[1] described the solidus curve for the system Na_2CO_3–K_2CO_3. The carbonates were found to be completely miscible, exhibiting a melting point minimum at approximately 58 mole % Na_2CO_3 and 690°. Makarov and Shulgina[2] reexamined the fusion characteristics of the system and reported that the minimum occurred "at about 40 mole % K_2CO_3 and 706°." In addition, these

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[1] H. Le Chatelier, *Compt. rend.*, **118**, 350 (1894).

[2] S. Makarov and M. P. Shulgina, *Bull. Acad. Sci. U.R.S.S.*, **6**, 691 (1940).