[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

The Density of Solid Ozone[1]

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The density of solid ozone was determined at 77.4°K., and found to = 1.728 (±0.002) g./cm.^{3}. The liquid density, at the same temperature = 1.6137 g./cm.^{3}, so that expansion on melting or $\Delta V/V_{sol}$ = 7.1%.

Recent surveys[2,3] show that the density of solid ozone has not been determined. This is due to the extreme sensitivity of pure solid ozone and its ability to detonate at the slightest provocation. It detonates with a bright, white flash, shattering glassware containing it to a fine powder.

Now that the specific heat of liquid ozone has been accurately determined at the Armour Research Foundation[4] it is possible to calculate the heat of explosion of liquid ozone and estimate that of solid ozone. The heat of formation of gaseous ozone from gaseous oxygen at 1.00 atm. and at 291°K. = + 33.920 (± 0.180) kcal./mole.[2] The corresponding value for *liquid* ozone at 90.19°K. (*i.e.*, normal boiling point of oxygen) from gaseous oxygen at the same temperature of $\Delta H_{90.19}$°K., = + 29.83 (±0.20) kcal./mole. The heat of fusion of solid ozone has not yet been determined but may be estimated to be about 0.5 kcal./mole. Thus, the heat of formation of solid ozone, from gaseous oxygen, at its melting point, or 80.7°K., should be about 29.3 kcal./mole.

Our successful experience in handling pure gaseous[5–7] and liquid[8] ozone prompted us to determine the density of the solid.

Experimental

Safety Measures.—In view of the ease with which solid ozone detonates all standard safety precautions should be taken. Safety plate glass or plastic shield face masks and gloves were used.

Preparation of Pure Ozone.—Pure ozone was prepared in a Welsbach Ozonator from so-called pure "medicinal" oxygen, containing 99.9+% oxygen and eliminating all organic impurities above about 20 p.p.m. according to the manner described in the Clark Thorp patent.[9] The excess oxygen was pumped off from the ozone until it contained less than 0.1% oxygen and the pure ozone redistilled for final purification.

Freezing of Pure Ozone.—The melting point of pure ozone is 80.7 ± 0.5°K. It is known that pure ozone can be supercooled and can be kept for long periods of time in boiling liquid nitrogen, *i.e.*, at 77.35°K. It was found that pure ozone invariably freezes if at least part of it is cooled in melting solid nitrogen (m.p. 63.14°K.). Solid nitrogen can now be prepared easily in quantities of the order of a few hundred cm.^{3} by evaporating liquid nitrogen in standard Dewar flasks by means of a high-speed oil pump, such as the W. M. Welch Scientific Company's Duo-Seal Model No 1402. We have frozen ozone in quantities of about 0.5 gram by using either cylindrical (1–3 mm. i.d.) or flat Pyrex tubes (1.2 cm. broad, about 10 cm. high and an inside width of 0.2 to 1.0 mm.).

If liquid ozone in such tubes is suddenly immersed to the full length of the ozone layer into solid nitrogen, detonation usually occurs. This probably is due to the fact that ozone crystals appear over the entire height of the tube and by friction of one set of crystals against another enough heat is developed to initiate ozone detonation. On the other hand, if only the bottom of the ozone tube is inserted into solid nitrogen, the crystallization of solid ozone proceeds slowly from the bottom toward the top and no detonation takes place. After the ozone has been solidified, it can be inserted into boiling liquid nitrogen (*i.e.*, at 77.35°K.) and will remain solid for an indefinite period of time at that temperature.

It was found that if tungsten wires are inserted into the glass tubes previous to the condensation of ozone in order to initiate its crystallization on cooling, detonation of the ozone usually occurs.

Properties of Solid Ozone.—The solidification of ozone can be observed very nicely in the flat tubes. On tilting the tubes at an angle, the liquid ozone will immediately change its level, whereas if it has once solidified, it will retain its shape.

In the flat tubes, the ozone will solidify in homogeneous layers which are transparent if the thickness is in the range of 0.2 to 0.5 mm. It is almost opaque in a layer of 1.0 mm. thickness at 77°K. At the same temperature, liquid ozone is transparent in layers of 1.0 to 1.8 mm. At 90°K., the liquid ozone becomes transparent in a 1.8 mm. thick layer. Thus, with some experience, it is possible to determine the solidification of ozone from its relative transparency.

Temperature Determinations.—Pure liquid oxygen and nitrogen were used, with a normal boiling point of 90.19 and 77.35°K., respectively. By preparing mixtures of those two liquids, any desired intermediate temperature could be obtained. The data for the liquid oxygen–nitrogen system were taken from the measurements of Baly,[10] corrected to the recent more accurate values of the N.B.P.'s of O_2 and N_2. The usual correction for variations in atmospheric pressure was made; standard precautions for uniformity of temperature also were taken. The most important point is to know the exact composition of the initial liquids; they were checked by standard gas analytical methods.

Determination of Density.—Our density determinations of solid ozone are based on the *known densities* of *liquid* ozone, as determined by Jenkins and DiPaolo[11] (and corrected to the N.B.P.'s of O_2 and N_2), namely, at 90.19°K. = 1.5727 g./cm.^{3} and at 77.35°K. = 1.6137 g./cm.^{3} with an accuracy of ±0.0004. These values are in good agreement with the less precise values of Brown and Franson.[12] About 0.5 g. of liquid ozone was distilled into uniform bore cylindrical glass tubes of i.d. = 1.815 mm. The height of the column of the liquid or solid ozone was determined by means of a cathetometer, with an accuracy of ±0.01 cm. The weight of liquid O_3 was calculated from its volume and density at the respective temperatures.

The solid ozone crystallizing in these tubes produces some cracks, fissures or pores so that the actual volume occupied

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[1] This work sponsored by the Army Ballistic Missile Agency, Redstone Arsenal, Alabama.

[2] Clark E. Thorp, "Bibliography of Ozone Technology," Vol. II, "Physical and Pharmacological Properties," Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill., 1955.

[3] A. V. Grosse and A. G. Streng, "Pure Ozone Flames, Alone and with Various Fuel Gases," Technical Note No. 4, Contract No. AF-18(600)-1475, Project No. 7-7968, AFOSR-TN-511, AD 136497, The Research Institute of Temple University, August 1, 1957.

[4] R. I. Brabets and T. E. Waterman, *J. Chem. Phys.*, **28**, 1212 (1958).

[5] A. G. Streng and A. V. Grosse, THIS JOURNAL, **79**, 1517 (1957).

[6] A. G. Streng and A. V. Grosse, "The Ozone to Oxygen Flame," Proc. VIth International Combustion Symposium, Reinhold Publ. Corp., New York, N. Y., 1957, pp. 264–273.

[7] A. G. Streng and A. V. Grosse, THIS JOURNAL, **79**, 3296, 5583 (1957).

[8] See R. Sandri, *Can. J. Chem.* (in press).

[9] Clark E. Thorp, U. S. Patent 2,700,648.

[10] See Baly, "International Critical Tables," Vol. VIII, McGraw-Hill Book Co., New York, N. Y., p. 309.

[11] A. C. Jenkins and F. S. DiPaolo, *J. Chem. Phys.*, **25**, 296 (1956).

[12] Callaway Brown and K. D. Franson, *ibid.*, **21**, 5, 917 (1953).

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}).

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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

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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.