TABLE I

ANALYSES OF RARE EARTH CARBONATES

Carbonate	% R_2O_3	% CO_2	% H_2O	$\frac{CO_2}{R_2O_3}$	$\frac{H_2O}{R_2O_3}$	Suggested formula
Lanthanum	58.55	23.60	17.85	2.98	5.51	$La_2(CO_3)_3 \cdot 5.5H_2O$
Neodymium	65.80	25.35	8.85	2.95	2.51	$Nd_2(CO_3)_3 \cdot 2.5H_2O$
Samarium	65.88	23.43	10.69	2.82	3.14	$Sm_2(CO_3)_3 \cdot 3H_2O$

Conclusions.—It was concluded that the carbonates are normal carbonates of the formula $R_2(CO_3)_3 \cdot xH_2O$. This conclusion is based upon a comparison of the experimental and calculated values for the mole ratio CO_2/R_2O_3. This ratio is 3 for normal carbonates, 2 for $R(OH)CO_3$, and 6 for $R(HCO_3)_3$. It is observed from Table I that the mole ratios are approximately 3 in all cases, with the value for the samarium being the lowest; this could indicate a slight tendency toward basic salt formation which would be expected since samarium is the least basic of the elements studied.

The preparation of anhydrous neodymium carbonate was attempted. Samples of neodymium carbonate were dried under different conditions and analyzed for neodymium oxide and carbon dioxide. The mole ratios CO_2/Nd_2O_3 and H_2O/Nd_2O_3 are listed in Table II.

TABLE II

EFFECT OF HEAT ON HYDRATED NEODYMIUM CARBONATE

Sample	Drying conditions	% Nd_2O_3	% CO_2	% H_2O	$\frac{CO_2}{Nd_2O_3}$	$\frac{H_2O}{Nd_2O_3}$
A	Air dried[a]	65.8	25.4	8.8	2.96	2.50
B	1 hr. at 110°	68.2	26.7	5.1	3.00	1.40
C	12 hr. at 110°	70.8	27.9	1.3	3.02	0.34
D	3 days at 120°	71.4	27.8	0.8	2.98	0.21
$Nd_2(CO_3)_3$ (theoretical)		71.8	28.2	0.0	3.00	0.00

[a] Washed first with alcohol and ether.

The mole ratio CO_2/Nd_2O_3 remained approximately 3 for the above drying conditions; the mole ratio H_2O/Nd_2O_3 decreased continually, indicating dehydration. For an extended drying period an essentially anhydrous neodymium carbonate (Sample D) was obtained.

The preparation of rare earth normal carbonates by the decomposition of the trichloroacetates from hot water solution is very satisfactory since no interfering ions, such as the alkali ions, are introduced into the reaction mixture.

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Magnesium in Fourfold Coördination in Glass

BY RUSTUM ROY

Incident to other investigations[1] on the use of molar refraction data to indicate the coördination of ions, some interesting data regarding the coördination of Mg^{2+} in glass were encountered.

Fajans and Kreidl[2] have shown that the coördination number of Zn^{2+} is related to the molar volume. Previous work of Fajans and co-workers[3a,b,c,d] has demonstrated a relationship between molar refraction and molar volume. They have also shown a relationship in cesium and ammonium halides, between molar refraction and coördination number. Safford and Silverman[4] have presented evidence to show that a change of coördination of an ion alters the molar refraction contribution of the ion or more correctly of the group immediately surrounding the ion. These authors have shown that the Al^{3+} in fourfold coördination in glass or in certain crystals has a molar refraction contribution of 12.3 (calculated for Al_2O_3), whereas in sixfold coördination it is 10.5. Kreidl[5] first indicated that MgO may assume both "basic" and "acidic" properties in glass. Huggins[6] later pointed out that the magnesium ion may be surrounded "by but four oxygen neighbours" in some glasses containing magnesium, and Dietzel[7] has recently mentioned the possibility that Mg^{2+} may go partly into fourfold coördination in glass.

The data referred to at the outset substantiating the above claims regarding the fourfold coördination of Mg^{2+} are shown in Table I. The refractive indices and densities are reasonably well established and may be found either in Larsen and Berman[8] or in the "Data on Chemicals for Ceramic Use."[9] It will be seen that the difference in molar refraction between the crystalline and glassy states is about 0.65. It is known that Mg^{2+} is in sixfold coördination in enstatite and diopside. This difference in molar refractivity of crystals and glasses, when compared with that for Al^{3+}

TABLE I

MOLAR REFRACTION DATA

Substance		d	$\bar{n}$	R[a]	Δ
$MgSiO_3$	Enstatite	3.175	1.646	11.48	0.63
$MgSiO_3$	Glass	2.757	1.5801	12.11	
$^1/_2(CaMg(SiO_3)_2)$	Diopside	3.275	1.676	12.44	.67
$^1/_2(CaMg(SiO_3)_2)$	Glass	2.854	1.607	13.11	
MgO	Periclase	3.5761	1.738	4.538	.64
$MgAl_2O_4$	Spinel	3.578	1.719	5.18[b]	
$Ca_2MgSi_2O_7$	Akermanite	2.944	1.635	33.19	.09
$Ca_2MgSi_2O_7$	Glass	2.955	1.641	33.28	

[a] The values of molar refraction are obtained by the Lorentz–Lorenz equation $R = (n^2 - 1)\ M/(n^2 + 2\ )d$, see references (2) and (4). [b] This is obtained by subtracting 10.50 as the contribution of Al_2O_3 with Al^{3+} in sixfold coördination,[4] from the total value of 15.68.

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(1) R. Roy and E. F. Osborn, THIS JOURNAL, **71**, 2086 (1949).

(2) K. Fajans and N. J. Kreidl, *J. Am. Ceram. Soc.*, **31**, 105 (1948).

(3) (a) K. Fajans and G. Joos, *Z. Physik*, **23**, 1 (1923); (b) K. Fajans, *Z. physik. Chem.*, **130**, 724 (1927); (c) P. Wulff and H. K. Cameron, *ibid.*, **B10**, 347 (1930); (d) K. Fajans, "Radioelements and Isotopes," McGraw-Hill Book Co., Inc., New York, N. Y., 1931, p. 81.

(4) H. W. Safford and A. Silverman, *J. Am. Ceram. Soc.*, **30**, 203 (1947).

(5) N. J. Kreidl, *Glastechn. Ber.*, **7**, 313 (1929).

(6) M. L. Huggins, *J. Optical Soc. Amer.*, **30**, 420–430 (1940).

(7) A. Dietzel, *Naturwiss.*, **36–37**, 538 (1941).

(8) E. S. Larsen and H. Berman, U. S. Geol. Sur. Bulletin 848, 1934.

(9) "Data on Chemicals for Ceramic Use," Bulletin of Natl. Res. Council, No. 107, 1943.

(see above), is of the right order of magnitude and in the right direction to be caused by a change of Mg^{2+} to fourfold coördination in the glass. This does not indicate, however, whether *all* or part of the Mg^{2+} is in fourfold coördination, although the constant value obtained would seem to favor the former situation. Further evidence is found in the difference between the values for periclase (Mg^{2+} in sixfold coördination) and the MgO in spinel (Mg^{2+} probably in fourfold coördination).[10] The value of 0.64 for this difference can be attributed to the difference in coördination of the Mg^{2+} in the two compounds and also supports the view that *all* the Mg^{2+} is in fourfold coördination in glasses of diopside and enstatite compositions. Finally, it is to be expected that since Mg^{2+} is already in fourfold coördination in crystalline akermanite,[11] no change in molar refraction would occur in the glassy state. The data for akermanite bear this out and give values which show a distinctly smaller difference in the $R_{\text{glass}}-R_{\text{crystal}}$ value.

[10] E. J. W. Verway and E. L. Heilmann, *J. Chem. Phys.*, **15**, 174–180 (1947), have presented indirect evidence that the Mg^{2+} is in fourfold coördination, forming a "normal" spinel structure.

[11] B. E. Warren, *Z. Krist.*, **74**, 131–138 (1930).

"KISMET," HAZARIBAGH, INDIA RECEIVED MAY 28, 1949

Isophthalic and Terephthalic Acids[1]

BY PAUL G. SCHEURER[2] AND GENE M. LE FAVE[3]

Recently McBee and Frederick proved the structures of some chlorine substituted bis-(perfluoroalkyl)-benzenes by hydrolysis with 60–80% sulfuric acid,[4] following a procedure employed by Wertyporoch.[5] We felt that extending this method to a mixture of *m*- and *p*-bis-(trifluoromethyl)-benzenes made available through the work of McBee[6] would provide an excellent procedure for the preparation of iso- and terephthalic acids, particularly since bis-(trifluoromethyl)-benzenes are now commercially available as a mixture consisting of approximately 60% meta and 40% para isomers.[7]

Refluxing bis-(trifluoromethyl)-benzene with an excess of 80% sulfuric acid for several hours causes charring and does not give acceptable yields. Quantitative yields of the corresponding phthalic acids were obtained by reaction with 100% sulfuric acid and subsequent hydrolysis of the reaction product,[8] but long initiation periods were required and often large-scale reactions were controlled only with difficulty. However, a method was devised which proved entirely satisfactory. It has the very suitable advantage that only small amounts of hydrogen fluoride are evolved during the course of the reaction and may be conducted in an all-glass apparatus. Equimolar quantities of concentrated sulfuric acid and chlorosulfonic acid in slight excess were used; the reaction starts immediately upon heating and an even evolution of hydrogen chloride takes place throughout the reaction.

There appear to be two possibilities for the course of the reaction. The chlorosulfonic acid may react with the trifluoromethyl groups to give the partially substituted chloro compound with subsequent accelerated hydrolysis by the sulfuric acid,[9,10] or the sulfuric acid may act directly on the trifluoromethyl groups giving hydrogen fluoride and fluorosulfonic acid. The former will very probably be in equilibrium with the sulfuric acid[11]

$$HF + H_2SO_4 \longleftrightarrow FSO_3H + H_2O$$

However, under this equilibrium condition the chlorosulfonic acid will not be stable since it will react with the water formed giving hydrogen chloride and sulfuric acid, thereby shifting the equilibrium to the right and accounting for the evolution of hydrogen chloride and not hydrogen fluoride. Both mechanisms probably operate.

The acids formed upon pouring the reaction mixture into water were separated advantageously by virtue of their barium salts, the barium isophthalate being readily soluble in water while the terephthalate salt is quite insoluble in the same solvent. Of interest is that qualitative analysis of the acids showed that no chlorine was present indicating the superiority of hydrolyzing the fluorine compounds in lieu of the chlorine analog, which usually contains nuclear chlorine.

Experimental

A mixture of 60 g. of chlorosulfonic acid, 50 g. of concentrated sulfuric acid, and 53.5 g. (0.25 mole) of bis-(trifluoromethyl)-benzene was heated in a flask fitted with a reflux condenser and the usual hydrogen chloride trap until the reaction commenced and only intermittently thereafter. After the evolution of hydrogen chloride had ceased, the reaction mixture was cautiously poured with stirring into ice-water, the resultant precipitate filtered, washed thoroughly with cold water, and finally dissolved in 500 ml. of warm water containing 27 g. of sodium carbonate and 3 g. of Norit. This solution was then filtered, 130 g. of barium chloride dihydrate added, and refiltered. The filtrate was neutralized, the precipitate collected, washed, and recrystallized from methanol. The isophthalic acid thus obtained weighed 30 g. (55.5%) based on the weight of the starting material. It melted at 347–349°.

Anal. Calcd. for $C_8H_6O_4$: C, 57.83; H, 3.63. Found: C, 57.99; H, 3.71.

The insoluble barium salt of terephthalic acid was washed and neutralized, the precipitated terephthalic acid collected and washed thoroughly with cold water by suspension, stirring and refiltration, finally drying in the oven at 100°. It weighed 21 g. (39%) and sublimed

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[1] Paper III of the Series entitled, "Some Reactions of the Trifluoromethyl Group in the Benzotrifluoride Series."

[2] The Graduate School, The Ohio State University, Columbus, Ohio.

[3] J. I. Holcomb Research Fellow, 1948–1950.

[4] McBee and Frederick, THIS JOURNAL, **71**, 1490 (1949).

[5] Wertyporoch, *Ann.*, **493**, 1536 (1932).

[6] See Murray, Beanblossom and Wojcik, *Ind. Eng. Chem.*, **39** 302 (1947).

[7] Hooker Electrochemical Company, Niagara Falls, N. Y.

[8] Le Fave, THIS JOURNAL, **71**, 4148 (1949).

[9] Kracker and Herrlein, U. S. Patent 2,119,882 (June 7, 1938).

[10] E. Spreckels, *Ber.*, **52B**, 317 (1919).

[11] Traube, *ibid.*, **46**, 2525 (1913).