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Summary

A condition under which the explosive gaseous reaction may run its course at constant pressure, thereby eliminating a variable factor affecting the concentrations of the explosive gases the flame is entering, may be closely realized in practice by holding temporarily the gases within a soap film container and firing the bubble from the center. This device functions as a bomb of constant pressure and thus provides the complement to the bomb of constant volume in the relation $pv = nRT$. Being transparent, it permits an accurate photographic time-volume record of the reaction to be secured. This record gives the initial volume v^0 of the active components of known concentrations, and, at the instant the action is completed, it gives the volume v^s of the equilibrium products which is the volume corresponding to the reaction constant

$$K = \frac{[A]^{n_1} [B]^{n_2} [C]^{n_3}}{[A']^{n'_1} [B']^{n'_2} [C']^{n'_3}}$$

Because the concentrations of the explosive gases that the flame is entering remain constant under the condition of constant pressure, it is found that the flame velocity under these conditions also remains constant during the reaction and that its value, s , is proportional to the product of the initial concentration of the gases,

$$s = k_1[A]^{n_1} [B]^{n_2} [C]^{n_3}$$

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THE CRYSTAL STRUCTURE OF MAGNESIUM PLUMBIDE

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Magnesium is known to form intermetallic compounds with at least three elements in the fourth group of the periodic table, silicon,¹ tin² and lead.^{3,2a} The crystal structures of magnesium stannide, Mg_2Sn and of magnesium silicide, Mg_2Si , have been completely determined by Pauling⁴ and by Owens and Preston⁵ and that of magnesium plumbide, Mg_2Pb , has been

¹ Vogel, *Z. anorg. Chem.*, **61**, 46 (1909). Lebeau and Bossuet, *Rev. métal.*, **6**, 273 (1909).

² (a) Kurnakow and Stepanow, *Z. anorg. Chem.*, **46**, 177 (1905). (b) Grube, *ibid.*, **46**, 76 (1905).

³ Grube, *ibid.*, **44**, 117 (1905).

⁴ Pauling, *THIS JOURNAL*, **45**, 2777 (1923).

⁵ Owens and Preston, *Proc. Phys. Soc. London*, **36**, 341 (1924).

partially determined by Sacklowski⁶ who states that magnesium stannide and plumbide have face-centered cubic structures but does not specify the atomic arrangement in more detail. This paper confirms Sacklowski's results on the size and shape of the unit cell of magnesium plumbide and completes the determination of its structure by giving the way in which the atoms are arranged in the unit cell.

Magnesium plumbide was prepared by melting together the calculated amounts of magnesium and lead under a molten mixture of sodium and potassium chlorides to prevent oxidation. Since the compound is readily attacked by air, it was ground to a powder under kerosene, transferred to a piece of paper and covered with a thin coat of paraffin which effectually protected it from the action of the air. The flat sample was mounted on an X-ray spectrograph where it was rotated during the exposure and the powder diffraction pattern was photographed on a plate. Unfiltered radiation from a molybdenum target was used.

The observed values for the interplanar distances for all the planes producing reflections on the plate are shown in the second column of Table I and have the ratios required by a cubic crystal, the indices of the planes being those given in the first column. The third column of the table shows the values for a_0 , the side of the unit cube, computed from the interplanar distances and the indices of the planes, and the last two columns show the

TABLE I

Plane	Interplanar distance	a	Intensity	
			Obs.	Calcd.
111 β	3.926	6.800	5.5	6.5
111 α	3.915	6.781	16.0	19.5
200 α	3.390	6.779	5.4	5.2
220 β	2.400	6.788	5.4	5.1
220 α	2.400	6.788	13.5	15.3
113 β	2.038	6.760	4.5	4.2
113 α	2.043	6.772	12.0	12.5
222 α	1.956	6.776	2.0	1.9
400 β	1.692	6.770	1.4	1.1
331 β	1.551	6.760	3.0	2.2
400 α	1.698	6.791	3.9	3.4
331 α	1.555	6.780	7.0	6.6
240 α	1.518	6.789	3.5	3.1
333, 511 β	1.300	6.756	2.9	2.0
224 α	1.384	6.782	5.8	8.4
333, 511 α	1.307	6.792	4.0	5.9
440 α	1.203	6.808	2.1	3.0
351 α	1.149	6.796	2.9	6.4
600 α	1.130	6.777	Faint	0.4
620 α	1.073	6.789	1.8	4.6
Mean 6.78				

⁶ Sacklowski, *Ann. Physik*, 77, 241 (1925).

observed and computed intensities. The observed intensities are visual estimates made by comparison with a plate which had been given a series of known exposures. The mean value for a_0 is 6.78 Å. which is in good agreement with the value, 6.76 Å., given by Sacklowski.⁶ With $a_0 = 6.78$ Å. and the density 5.5416,³ the computed number of molecules in the unit cell is 4.09, or 4 within the limits of error.

The presence of only such reflections as have all indices odd, or all even, definitely eliminates the body-centered space-groups and strongly suggests that the only space groups which need to be considered are those based on a face-centered lattice. Reference to a tabulation of the results of the theory of space groups⁷ shows that with this restriction there are three ways of arranging four lead and eight magnesium atoms in the unit cell, irrespective of any assumptions as to the equivalence of chemically like atoms. The intensities of the different lines were computed on the basis of each of these arrangements by the use of the customary intensity proportionality⁸ $I\alpha(A^2 + B^2) \times j \times \left(\frac{d}{n}\right)^{2.35}$ where A and B have their usual significance as sine and cosine summations and j is the number of planes contributing to a single powder line. For two of the arrangements the computed intensity is greater for 200 than for 113 and as this conflicts with the data, these two arrangements are excluded. In the other arrangement the atoms have the following positions.

Pb at 0,0,0; $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; $0, \frac{1}{2}, \frac{1}{2}$

Mg at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $\frac{1}{4}, \frac{3}{4}, \frac{3}{4}$; $\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$; $\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$; $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$; $\frac{3}{4}, \frac{1}{4}, \frac{1}{4}$; $\frac{1}{4}, \frac{3}{4}, \frac{1}{4}$; $\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$.

The intensities computed for this structure on the assumption of direct proportionality between scattering power and atomic number are shown in the last column of Table I and are in satisfactory agreement with the observed intensities. This is the simplest atomic arrangement that will account for the observed intensity relations in the powder diffraction pattern from magnesium plumbide and is known as the calcium fluoride arrangement. More complicated structures containing one or more variable parameters may be obtained from space groups based on a simple cubic lattice, but since these space groups should give odd order reflections from planes other than those with all indices odd except for values of the parameters which give them approximately the face-centered form, and since the calcium fluoride structure is in agreement with the data, there seems to be no necessity for resorting to these more general structures.

The positions of magnesium, silicon, tin and lead in the periodic table together with the fact that magnesium silicide, stannide and plumbide have

⁷ Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," Carnegie Inst., Washington, 1922.

⁸ Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, 1924, p. 201.

the same kind of crystal structure as a typical polar compound, calcium fluoride, suggests that these three intermetallic compounds of magnesium are polar compounds.

Summary

The crystal structure of the intermetallic compound, magnesium plumbide, has been determined from X-ray diffraction data. The unit cell is cubic with an edge equal to 6.78 Å. and contains four molecules. The positions of the atoms are given by the calcium fluoride arrangement.

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THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS.¹ V. A CONSTANT CURRENT APPARATUS

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In the determination of a transference number T from the motion of a single boundary the results are computed from the formula

$$T = VF/\phi it$$

V being the volume through which the boundary has swept, ϕ the volume containing a gram equivalent, F is the faraday, and i and t are, respectively, the current and time. It has not, in this work, been found convenient to obtain the product it with a coulometer, since the number of coulombs is too small to measure with accuracy. It has, therefore, been necessary, until our most recent work, to keep the current i constant by hand regulation. Since the solution whose transference numbers are to be measured is gradually replaced by indicator solutions which have lower conductances, the applied potential must be gradually increased if the current is to remain constant. This increase is accomplished by shifting the sliding contact of a rheostat shunting a portion of the storage cells used to supply the voltage. Hand regulation was found to be very tedious, and, especially, as readings of the position of the boundary must be made from time to time, not always accurate. We therefore decided to devise an apparatus for the automatic adjustment of the current. This apparatus has proved to be so satisfactory in operation that it should undoubtedly be useful in other connections.

The device finally adopted is shown in Fig. 1. Current is furnished to

¹ The papers that have already appeared in this series are: I. MacInnes and Smith, *THIS JOURNAL*, **45**, 2246 (1923); II. Smith and MacInnes, *ibid.*, **46**, 1398 (1924); III. MacInnes and Brighton, *ibid.*, **47**, 994 (1925); IV. Smith and MacInnes, *ibid.*, **47**, 1009 (1925).