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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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 185]

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

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RECEIVED MAY 10, 1926 PUBLISHED JULY 6, 1926

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

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[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).

the moving-boundary apparatus M (which in all our later work has been of the type devised by MacInnes and Brighton) by the storage batteries A and B, the first yielding about 150 volts and the latter 100 volts. Battery B is shunted across the adjustable rheostat R of 1680 ohms. The potential across the terminals of the moving-boundary apparatus M can therefore be varied by shifting the contact point C. The current passing through the cell M is measured by determining the potential drop in the resistance R′, of 200 ohms, by means of the potentiometer P. The adjustment of this potentiometer is determined with the aid of the galvanometer G, the moving coil of which carries a pointer arm on which has been placed a light vane V of aluminum foil, the purpose of which will be made clear below.

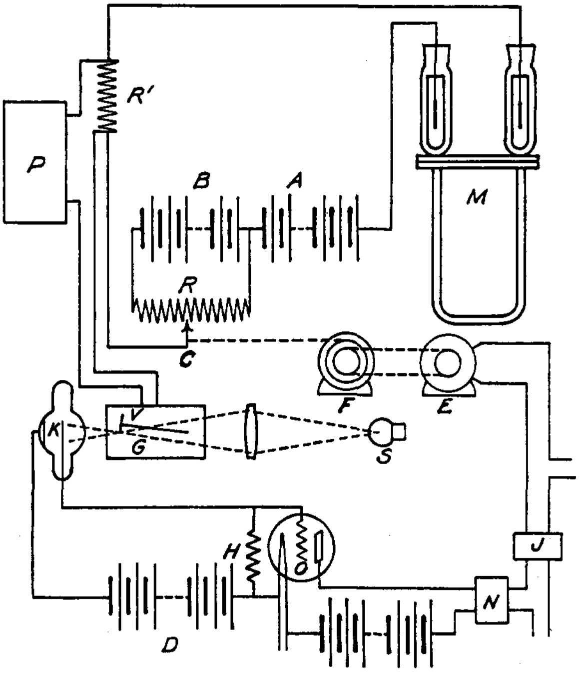

Fig. 1.

The contact point C of the rheostat R is moved mechanically by means of the electric motor E, which operates the reducing gears F. The motor is started and stopped by means of the following relay system. The line current (110 volts) passes through the ordinary relay J which is operated by the sensitive relay[2] N which in turn is actuated by the current, about one milliampere, that passes from the filament to the plate in the radio tube O. This current can be interrupted by placing a stopping potential on

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[2] Western Electric B 108 telephone relay.

the grid of the radio tube. This is accomplished by placing the photo-electric cell[3] K in series between the grid and the filament and the source of potential (about 100 volts) D. When the photo-electric cell is illuminated, sufficient current passes to keep the grid at a high enough potential to stop the current between the filament and the plate. An essential portion of the apparatus is the grid leak, H. Since it and the photo-electric cell K are in series with the potential D, the potential on the grid will depend on the relative resistances of the grid leak and the illuminated cell. A grid leak having a very large resistance (30 megohms) was thus found advisable. The illumination of the photo-electric cell is regulated by the motion of the vane V on the galvanometer G. An image of the filament of the light source S (a 21 c. p. headlight lamp) is focused sharply on the vane V by means of a lens, and a small motion (about 0.3 mm.) of the vane is sufficient to illuminate the cell or to darken it.[4] Thus a slight movement of the needle of the galvanometer is sufficient to stop and start the motor E. With our apparatus a difference of potential (between the drop in the resistance R′ and that furnished by the potentiometer) of 0.0003 volt is sufficient to actuate the relay system. Since the total potential drop in R′ is from 1.0 to 1.5 volts the regulation is from 0.03 to 0.02%. Accuracy of regulation is, however, limited by the lack of continuity of the adjustable resistance R which is of the usual sliding contact type with fine wires wrapped around a tube. Inaccuracies from this source are harder to estimate but they seem to be of the same order of magnitude as those just given.

TABLE I

TRANSFERENCE NUMBERS OF 0.1 *N* POTASSIUM NITRATE AT 25°

Indicator solutions: 0.068 *N* $LiNO_3$ and 0.072 *N* $KC_2H_3O_2$

Reading, cm.	Potassium ion			Nitrate ion		
	Volume, cc.	Seconds	Trans. no.	Volume, cc.	Seconds	Trans. no.
7	1.1247	3025	0.5123	0.9994	2825	0.4875
8	1.2831	3453	.5121	1.1416	3230	.4870
9	1.4423	3880	.5122	1.2821	3629	.4868
10	1.6016	4309	.5122	1.4207	4015	.4876

Probably the most effective method of showing the successful operation of this apparatus is to give the values from a typical determination of a transference number. The data obtained in such a determination are given in Table I. From these data the transference numbers of both ions of potassium nitrate have been computed from measurements made when the boundaries had moved through 7 to 10 cm. of the graduated tubes. By comparing the times in seconds (Cols. 3 and 6), with the corresponding

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[3] We have used the Kunz potassium photo-electric cell and one of the General Electric potassium hydride type and have found them equally satisfactory for this purpose.

[4] A galvanometer with a moving mirror was first used but a far more powerful light source was then found necessary.

transference numbers, it is evident that the movement of the boundary past a graduation mark must have been read, at least in the case of the positive ion, to the nearest second and, also, that the current must have been constant in this interval, within the range of error of the measurements, which was about 0.02%. The sum of the average values of the two transference numbers is $0.5122 + 0.4872 = 0.9994$, or within 0.06% of unity. The only previously recorded value for a transference number of potassium nitrate (0.501 for the positive ion) is given by Denison and Steele;[5] this is evidently in error. A series of measurements on transference numbers of a series of nitrates, which present peculiarities which are interesting in the light of the modern theories of electrolytic dissociation, is now in progress.

The authors are indebted to the Warren Fund of the American Academy of Arts and Sciences for an appropriation which was of great assistance in this work.

Summary

An apparatus involving a photo-electric relay system is described. This device maintains a constant current, within 0.02–0.03%, through a moving-boundary apparatus, the resistance of which steadily increases during a determination. Data are given on the moving-boundary measurements on potassium nitrate solutions which indicate that regulation to that precision has been attained in practice.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TUFTS COLLEGE]

THE VISCOSITIES OF SEVERAL AQUEOUS SOLUTIONS OF ORGANIC SUBSTANCES AND THE POLYMERIZATION OF WATER

BY HARRIS MARSHALL CHADWELL

RECEIVED MAY 18, 1926 PUBLISHED JULY 6, 1926

This investigation is a continuation of the study of aqueous solutions of non-polar materials from the point of view of the polymerization of water. In a recent paper[1] in collaboration with T. W. Richards it was shown that the changes in volume and in compressibility on solution of various organic materials could be explained adequately by consideration of (1) the cohesive affinities concerned, (2) the effect of polymerization of one or both liquids (and the possible formation of complex solvated molecules), and (3) the effect of the several compressibilities of the cohering substances. The present paper reports the determination of another property of the solutions and an attempt to explain the data by the same considerations.

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[5] Denison and Steele, *Trans. Roy. Soc. London.*, **205A**, 449 (1906).

[1] Richards and Chadwell, THIS JOURNAL, **47**, 2283 (1925).