A Mixed-Liquid Method for the Determination of the Dielectric Constant of Solids

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The applicability of the mixed-liquid method to the measurement of the dielectric constant of powdered solids was tested with several isotropic crystalline materials: potassium iodide, potassium chloride, sodium chloride and calcium fluoride. By measurements on single crystals and powdered crystals it was found that, within the limits of error (about 2%), neither the amount of powder present nor the physical size of the particles affected the final results. Measurements on the systems were made by a resonance method using substitution techniques to determine capacitance at constant temperature and frequency. The dielectric constants of standard benzene–nitrobenzene solutions of different compositions first were determined in a conventional concentric-cylinder cell. The capacity of each of these solutions then was measured in a rigid parallel-plate cell, and finally redetermined after the addition of the solid material. The intersection of the curves formed on a capacity–dielectric constant plot by the series of solutions containing the given solid determined the dielectric constant of this solid.

In general, several methods are available for the measurement of the dielectric constant (D) of powdered solids. If the solid may be compressed into a cohesive tablet, its dielectric constant may be determined by the classical method applicable to flat-ground crystals. The experimental difficulties involved are not small, and various correction factors usually are necessary to account for the presence of air films between the electrodes and the solid surfaces and for edge effects unless guard rings are utilized.

Powders have been measured by packing in an air or some other fixed-dielectric condenser. It is necessary to know the volume fraction of the powder in the capacitor and, as van Vessem and Bijvoet[1] have shown, the results are affected by grain size and relative size of the measuring capacitor.

The method which holds the greatest promise as to simplicity is a liquid immersion method expounded by deLucas, Campbell and Maas[2] for cellulose nitrate fibers and by Groves and Martin[3] for diamond. The method is a variation of that of Højendahl[4] who placed various solids in chlorobenzene and measured the variation in dielectric constant of the liquid phase as a function of temperature. They obtained increments in dielectric constant of the fluid phase by varying the composition of a binary solution consisting of a polar liquid and a miscible non-polar liquid. Since constant temperature conditions are maintained relatively easily, the latter means promises greater ease in operation.

It was felt that the method should be thoroughly checked since discrepancies beyond those of normal experimental error have been found in the values of the dielectric constant of various common solids. For instance, Højendahl[5] reports the dielectric constant of sodium chloride as being 5.62, Suita[6] reports it as being 5.792 and Kamiyoshi[7] reports it as being 6.03. Other differences are tabulated later. Since it is possible that a particle size effect

might be found here, the values were checked for the salts: sodium chloride, potassium chloride, potassium iodide and calcium fluoride by measuring each of the values obtained for two different size single crystals and a powder and/or small-crystal mixture.

Experimental

The capacity of the dielectric cells was measured by a substitution resonance method. The instrument[8] is highly versatile, capable of a large range in frequencies, although this latter feature was not utilized in these measurements since a fixed frequency of 125 kc. was used. Changes in capacitance were measured with a General Radio Company Type 722-N precision condenser with a precision of about 0.2 $\mu\mu$f. in this range of use, leading to an accuracy of about 1 to 2%. Resonance was determined readily by an electronic voltmeter and extended-range galvanometer. All measurements were made at $30.0 \pm 0.05°$.

Stray capacitance values were eliminated and the portion of capacitance of the cells due to the dielectric material were determined by the use of the known dielectrics air and C.P. benzene which had been redistilled in a closed system.

Large volumes of standard solutions of benzene, the non-polar liquid, and nitrobenzene, the polar liquid, were prepared. Ratios were used such that the dielectric constants of this series of solutions ranged from about 2 to 8. The dielectric constant of each standard solution was determined in a cell with concentric cylindrical electrodes.

The capacity of each of these liquids then was determined in the "solids" cell consisting of two parallel plate electrodes held rigidly 6 mm. apart, area of about 25 sq. cm. When a plot of capacitance as the ordinate versus dielectric constant as the abscissa was made, it, of course, gave a straight line.

The solid, crystal or powder, was placed in the cell and the capacity measured when the cell was filled to the same level as before with each of the standard solutions. These capacities, when plotted as a function of the dielectric constants of the standard liquids, formed a curve which intersected the standard solution line at the point where the capacity contribution per unit volume of the solid and the solution was the same. Thus, the intersection directly determined the dielectric constant of the solid. Measurements on the standard solutions near the intersection point for each salt indicated no discrepancy caused by dissolving solid.

Two single crystals of each salt were obtained from the Harshaw Chemical Company. All were approximately 50 mm. in diameter; one of each was 4 mm. thick and the other was 5 mm. thick. To ensure homogeneity, pieces from the same ingots were obtained and crushed to form the powders.

Results and Discussion

Table IA shows the capacitance values for the standard solutions in the "solids" dielectric cell. A second cell with concentric cylindrical electrodes was used for the powders of sodium chloride and calcium fluoride. The slopes differed because of

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(2) H. A. deLucas, W. B. Campbell and O. Maas, *Can. J. Research*, **16B**, 273 (1938).

(3) L. G. Groves and L. E. Martin, *Trans. Faraday Soc.*, **36**, 575 (1940).

(4) K. Højendahl, *Z. physik. Chem.*, **20B**, 54 (1933).

(5) K. Højendahl, *Kgl. Danske Vidensk. Selskab*, **16**, 2 (1938).

(6) T. Suita, *J. Inst. Elect. Enrrs., Japan*, **61**, 635 (1941).

(7) Kamiyoshi and Kanichi, *Science Reports, Resch. Inst., Tohoku Univ.*, **1A**, 305 (1949).

(8) P. C. Scherer and M. K. Testerman, *J. Polymer Sci.*, **7**, 549 (1951).

the new geometry. These values of capacitance of the standard solutions in the new cell are shown in Table IB. The slopes and positions of these straight lines were calculated using the method of least squares.

TABLE I

CAPACITIES OF STANDARD SOLUTIONS OF DIFFERENT DIELECTRIC CONSTANTS

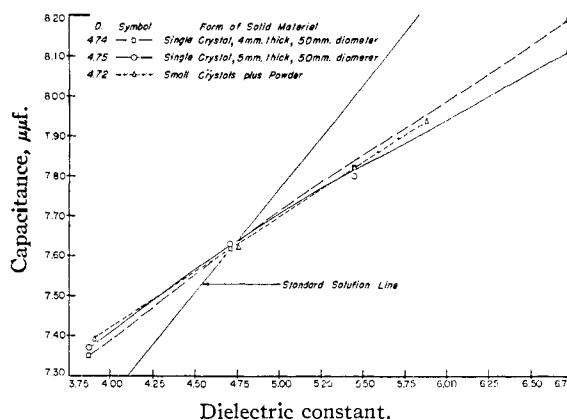| D of std. soln.	Capacity ($\mu\mu$f.)	D of std. soln.	(Capacity ($\mu\mu$f.)
A		**B**	
2.26	63.4	2.26	39.9
3.73	71.0	3.90	58.8
3.87	71.7	4.76	68.3
4.43	74.8	5.45	75.4
4.71	76.3	5.88	81.0
5.09	78.3	6.40	87.1
5.45	79.8	6.78	91.0
5.71	81.4	7.45	97.9
6.32	84.1		
6.36	84.6		
6.73	86.3		
6.80	87.5		
6.88	87.6		
7.50	90.3		
7.57	91.6		

Fig. 1.—Dielectric constant of potassium chloride at 30°.

Even assuming a maximum possible error of 2%, the only result of Kamiyoshi which checks is that for calcium fluoride. In every other case, the results of Højendahl are within the range except for potassium iodide. The results from this method appear to be consistently higher than those results obtained by variation of dielectric constants by a variation in temperature of the supporting dielec-

TABLE II

VALUES OF CAPACITANCE IN $\mu\mu$f., OF SOLID-LIQUID MIXTURES

D of std. soln.	Potassium chloride Single cryst. 4 mm.	5 mm.	Powd.	Sodium chloride Single cryst. 4 mm.	5 mm.	Powd.[a]	Calcium fluoride Single cryst. 4 mm.	5 mm.	Powd.[a]	Potassium iodide Single cryst. 4 mm.	5 mm.	Small cryst.	Powd.
2.26	68.7	70.0		68.9	71.6		68.1	73.4		68.5	70.4	67.5	70.5
3.73										74.2	74.6	73.6	74.0
3.87	73.5	73.7		75.4	77.1								
3.90			73.9										
4.43										76.6	76.8	76.1	76.9
4.71	76.2	76.3		78.1	79.1		79.6	81.4					
4.76		76.2				71.6			76.4				
5.09										78.4	78.4	78.2	78.5
5.45	78.2	78.0	78.2	80.5	80.8	76.6							
5.71										80.3	80.0	80.2	79.7
5.88			79.4			80.4			85.8				
6.32							85.1	85.4					
6.36										82.4	81.3	81.9	81.4
6.40							84.0			88.1			
6.73	81.9	81.1		84.4	81.2		86.3	86.5					
6.78									89.3				
6.88										83.7			
6.90							87.2						
7.45									91.5				
7.50							88.9	88.4					
7.57										85.0			
D as detd. by graphical intersection	4.74	4.75	4.72	5.72	5.68	5.73	6.67	6.65	6.60	5.21	5.17	5.10	5.18
Av. D		4.74			5.71			6.64			5.17		

[a] NaCl and CaF$_2$ powders intersect with standard solution line 2 (see Table IB); all others intersect with standard solution line 1 (see Table IA).

The data obtained for the various salts are shown in Table II, showing the graphical intersection for each type of salt. As an example, Fig. 1 is a reproduction of the plots for potassium chloride.

The average values obtained for the salts are compared with other values, as shown in Table III.

TABLE III

COMPARISON OF DIELECTRIC CONSTANTS OF SOLIDS

Substance	Højendahl[5]	Kamiyoshi[7]	Suita[6]	Above
KI	4.94	6.13		5.17
KCl	4.68	5.13		4.74
NaCl	5.62	6.03	5.792	5.71
CaF$_2$	6.63	6.76		6.64

tric. It is doubtful that the temperature differences of the crystals can account for these increments in the value for the dielectric constant.

The method holds great promise in that the accuracy seems to be limited only by the measuring devices. In addition, it is very simple in application.

tion and difficult experimental controls are kept at a minimum. The method is applicable to the measurement of isotropic crystalline material which cannot be grown to appreciable single-crystal size as well as to single crystals.

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Praseodymium Oxides. I. Phase Study by Dissociation Pressure Measurements

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A phase study of the praseodymium oxide system in the composition range Pr_2O_3 to Pr_6O_{11} has been made by an equilibrium dissociation pressure method involving the construction of isothermal (equilibrium oxygen pressure vs. composition of oxide) curves. The pressure–composition diagram is interpreted as indicating the existence of four separate non-stoichiometric regions in the range Pr_2O_3 to Pr_6O_{11}, and the existence of five stable phases, or regions of stability, in the same range. Conditions for the existence of the various phases are discussed qualitatively in terms of the theory of non-stoichiometric compounds.

Some interesting investigations of the praseodymium oxides beyond Pr_2O_3 have recently been made.[2-6] The results are on some points apparently contradictory and on others quite puzzling, due to difficulties in the interpretation of the data obtained. In particular: (1) there is disagreement as to whether the composition Pr_6O_{11} ($PrO_{1.83}$) represents a point within a non-stoichiometric range of composition or an isolated point in the PrO_x phase diagram; (2) although there is much evidence for the existence of separate non-stoichiometric ranges between $PrO_{1.5}$ and PrO_2, the nature and extent of these regions have not been established. For example, Asprey's dissociation pressure vs. temperature diagram[6] shows eight changes in slope in the composition range $PrO_{1.5}$–$PrO_{1.83}$.

Since it appeared, from the work referred to above, that the PrO_x system might afford a striking example of the existence of non-stoichiometric phases, it was thought that a further study of the range $PrO_{1.5}$–$PrO_{1.83}$ might prove interesting. The $(P,X)_T$ method was selected as one likely to give unambiguous information. This method has the further advantage that the experimental technique can be adopted to cover conveniently a wide composition range.

Experimental Method

Apparatus and Calibration.—An apparatus similar to one which has been used for precise low temperature adsorption studies[7] met the requirements (a) of accurate determination of oxide composition by oxygen absorption measurements on small samples and (b) of measurement at constant volume to simplify calibration and to increase the precision of the data. The apparatus (Fig. 1) consisted mainly of a zero-reference manometer, a water-jacketed gas buret, and a quartz sample tube with small dead space containing the alundum sample crucible. The sample tube was surrounded by a close-fitting furnace which could be regulated to $\pm 0.2°$ at $1000°$.

The various parts of the system were carefully calibrated with mercury in the usual way and by P,T measurements using pure oxygen. The sample tube dead space, without sample, was determined, after the rest of the system had been calibrated, at several furnace temperatures between 400 and $1000°$. The data yielded a smooth curve from which interpolations could be made. A correction was made for the volume occupied by the sample. Since this was only about 0.025 ml., the change in sample volume with oxidation was assumed to be negligible.

With simple precautions, considerable precision was easily obtained with the apparatus. Errors due to adsorption of oxygen on the walls, possible slight reaction with impurities in the alundum crucible, etc., were apparently reproducible and corrections for these effects were implicit in the method of calibration, the conditions for which were the same as for the absorption experiments except that the sample was omitted.

The compositions calculated are probably accurate to ± 0.0007 near $PrO_{1.83}$ and to about ± 0.0002 near $PrO_{1.60}$. Pressures were read (corrected) to ± 0.05 mm.

Materials and Procedure.—The praseodymium oxide used, "greater than 99.9% pure Pr_6O_{11}," was obtained from F. H. Spedding of Iowa State College at Ames. After reduction by hydrogen at $650°$ to Pr_2O_3, a sample was weighed to the nearest 10 μg. (dry atmosphere) into the sample crucible. The weight was redetermined after reduction in vacuo for 15 hours at $1000°$.

The oxygen for both the calibration of the apparatus and for the absorption experiments was prepared by heating outgassed potassium permanganate.

Before each series of equilibrium measurements, the sample was evacuated using an oil diffusion pump at $1000°$ for 8 to 12 hours. Between each series of measurements, the sample was left overnight in vacuo at $1000°$. This procedure ensures that Pr_2O_3 with the same past history is used for each series of measurements, since this annealing process undoubtedly allows recrystallization of the oxide in its equilibrium form.

The equilibrium points were obtained by adding a carefully measured quantity of oxygen to the part of the system containing the sample, allowing time for equilibration, and then determining the final dissociation pressure of the oxide. More oxygen was then added, etc. In this way a series of $(P,X)_T$ points at increasing X was obtained, oxide composition being calculated from the oxygen absorption. Where convenient, the procedure was revised by reducing the oxygen pressure and measuring the oxygen given off by the oxide. The time required for equilibration varied from 5 minutes to 2 hours, and was shorter, generally, at the higher com-

(1) National Bureau of Standards, Washington, D. C. Part of the data reported here were included in a dissertation submitted by R. E. Ferguson to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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