

## DIELECTRIC CONSTANT OF SILICA

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**ABSTRACT.** The dielectric constant of crystal quartz and fused silica plates are 4.54 and 3.2 respectively as determined by the plate method. The mixture method gives the dielectric constant of powdered quartz as 4.55.

The dipole moment of silica calculated by the new equation  $(\epsilon - n^2)M/d = 4\pi N\mu^2/k(T - \theta)$  where  $\theta$ , the critical temperature is  $575^\circ\text{C}$ . ( $\alpha\beta$  quartz inversion temperature) is 1.0 D. Considering  $\text{SiO}_2$  moment as a vector of two mutually tetrahedrally inclined Si-O bonds the moment (observed) of Si-O bond is 0.86 D. The true moment of a free Si-O bond is  $0.86 \times 2$  (co-ordination number) = 1.72 D agreeing with the calculated value,  $n \times d \times \frac{Z_{\text{Si}}}{Z_{\text{Si}} + Z_0} \times n$  where  $Z$ 's are atomic numbers and  $n = 1/3$ . At low temperatures ( $\theta = 0$ ) the observed Si-O moment is 0.43 D so that the true moment of the free Si-O bond is again 1.72 D ( $0.43 \times 4$ , the co-ordination number).

## INTRODUCTION

Considerable amount of work has been done on the dielectric constant of quartz. Still the data are not quite satisfactory. Various observers have reported values which differ considerably from one another. The results of the previous investigators are summarised as follows in Table I.

TABLE I

Method	$\epsilon$		Authors
	Field $\parallel$ (optically active)	Field $\perp$ (piezo-electric)	
Plate condenser ...	4.49	4.55	Curie (1889)
	4.60	...	Richardson (1915)
	...	4.65	Rubens (1915)
	...	4.58	Jaeger (1917)
Liquid replacement ...	4.46	4.38	Ferry (1897)
	4.73	4.73	Starke (1897)
Measurement of forces on a fragment.	4.34	4.60	Schmidt (1904)
	5.06	4.70	Fellinger (1902)
	4.55	4.60	Thornton (1909)

TABLE I (contd.)

## VITREOUS SILICA

Method	$\epsilon$	Author
Plate condenser ... ..	3.72	Jaeger (1917)
Liquid replacement ... ..	3.20	Schulze (1904)
Measurement of forces on a fragment ...	3.78	Thornton (1909)

The present work has been undertaken not only with a view to confirming the rather old and inconsistent data on the dielectric constant of quartz but also with the idea of investigating the dipole moment of the Si-O bond in silica. Three types of plates (1) optically active (2) piezo-electric and (3) vitreous silica were used. Obviously the applied field was parallel and perpendicular to the optical axis for (1) and (2) respectively.

The fact that the dielectric constants of ionic solids like silica are higher than the squares of their refractive indices implies that in addition to an electronic polarisation, an orientative effect also comes into play. The new

relationship between dielectric constant and dipole moment :  $(\epsilon - n^2) \frac{M}{d} = \frac{4\pi N \mu^2}{kT}$

(Jatkár *et al* (1946) which has been successfully applied to the case of a large number of liquids (normal and associated) and plastics can be used to interpret quantitatively the dielectric constants of solids in terms of the dipole moment of the constituent molecules. The equation is based on the concept of hindered orientation (along and opposite field direction) in quasi-crystalline liquids and solids. In the latter case the mechanism of orientation may involve either a complete turn over of the molecule as in the case of molecules of spherical contour (*e.g.*, hydrogen halides) or a mere "rattling of ions" in the crystalline structure (*cf.* symposium on "Dielectrics" Trans. Farad. Soc. 1946). Both cases conform to idea of orientations being confined to the direction of the field and opposite. In the case of ionic solids this may happen by a tunnel effect.

In the case of the ferro-electric class of solids, which show an electric Curie point, the new equation becomes  $(\epsilon - n^2) \frac{M}{d} = \frac{4\pi N \mu^2}{k(T - \theta)}$ . It has been found that  $\theta = m.p.$  for associated liquids and transition point ( $\lambda$ ) for crystalline solids. It will be shown elsewhere that this equation has successfully accounted for the high dielectric constants and the temperature coefficient of  $TiO_2$ , titanates, rochelle salt, etc., in terms of the dipole moments of the molecules indicating thereby that there exists some form of dipole orientation in solids. The co-ordination number diminishes the moment below transition point. In the present paper the dielectric constant of silica has been interpreted on the above basis.

## EXPERIMENTAL

*Dielectric Constant of Silica by the Plate Condenser method*

The apparatus used and the experimental technique is similar to that described by Jatkar and Nagamani, (1942). Measurements were conducted on a number of quartz plates, piezo electric, optically active as well as vitreous silica. Some of the specimens used were silvered on the surface so as to ensure good contact with the applied electrodes while even in the rest of the cases good contact was ensured in as much as the quartz surface as well as the surface of the electrode were optically plane. Special care was taken to see in the later case that the entire area of the electrode rested on the surface of the quartz. In all the measurements a correction was applied to account for the stray capacity of the leads connecting the electrode to the circuit and also for the capacity of the switch establishing the connection with the H. T. It was possible to obtain a value for these corrections by the following method. After measuring the capacity of the silica condenser, the specimen as well as the electrode were removed. Then two readings of capacity were taken, one with the switch on and also with a wire similar and equivalent in dimensions to the lead wire connected on to the switch and the second reading with the switch off. The difference between the readings gives the correction for the switch plus the leads.

If  $c$  is the observed capacity of the specimen condenser in  $\mu\mu\text{f}$  then the dielectric constant is given by  $\epsilon = \frac{4\pi d(C-a)}{A \times 1.1}$  where  $a$  is the stray capacity,  $d$  = thickness of plate, and  $A$  = its area.

The thickness of the plates was accurately measured by a sensitive spherometer while a screw guage was employed for measuring the other larger dimensions.

The results are tabulated in Table II.

The mean value for optically active quartz plate (field  $\parallel$ ) is 4.58 while that for piezo electric quartz plate (field  $\perp$ ) is 4.50. This compares very well with the most probable values of 4.6 and 4.5 for the respective specimens as given by Sosman (1927) in a survey of dielectric properties of silica.

The dielectric constants of the two specimens of vitreous silica studied are found to be 3.21 and 3.32 respectively. This is in accordance with the value of 3.2 given by Schulze while Thornton (1909) and Jaeger (1927) give higher values of 3.78 and 3.72.

## RESULTS

TABLE II

<i>Piezo-electric quartz</i>							
(Field $\perp$ )							
$f^{\text{nat.}}$	25	45 200	50	125 560	300	500	800
$\epsilon$	4.44	(4.27)	4.50	4.52	4.53	4.61	4.42 $\epsilon_{\text{lit}} : 4.5$

  

<i>Optically active quartz</i>				
(Field $\parallel$ )				
Specimen No.	1	2	3	4
$\epsilon$	4.70	4.45	4.53	4.62 $\epsilon_{\text{lit}} : 4.6$

  

<i>Fused quartz.</i>			
Specimen No.	1	2	
$\epsilon$	3.24	3.31	$\epsilon_{\text{lit}} : 3.2, 3.8$

\* natural frequency of vibration

 $\epsilon_{\text{lit}}$  (Sostman (1927))DIELECTRIC CONSTANT OF POWDERED SILICA  
USING THE MIXTURE METHOD

The method consists in finding by graphical methods the dielectric constant of that liquid mixture whose dielectric constant remains unchanged when powdered silica is introduced into it.

The powdered silica used in these experiments was purified by repeated washings with warm dilute hydrochloric acid, followed by washing with water and dried in an oven and finally stored dry before being used in experiments. Thoroughly purified nitrobenzene and xylene were used as the components for the liquid mixture in the experiments.

After preliminary trials a series of mixtures was prepared of such compositions as to possess dielectric constants whose range was in the neighbourhood of the approximately known value of the dielectric constant of silica.

The dielectric constant of each of these mixtures was at first determined as such and then again after the addition of the powdered silica.

Special care was taken to see that the condenser was filled up to a particular level each time and further it was seen that the excess of liquid above this mark which would come up when the powdered solid was put in was removed and the level adjusted to the original mark.

The results are given in Table III.

TABLE III

Composition of liquid mixture.	Dielectric constant of liquid mixture	Dielectric constant of liquid mixture with powdered silica.
8.3% nitrobenzene 91.7% xylene	3.50	4.16
10.1% nitrobenzene 89.9% xylene	3.75	4.25
12.3% nitrobenzene 87.7% xylene	4.05	4.36
16.6% nitrobenzene 83.4% xylene	4.65	4.59
20.5% nitrobenzene 79.5% xylene	5.18	4.79

The differences between the dielectric constant with and without the powdered silica were plotted against dielectric constant of liquid mixtures. The value corresponding to zero difference gives the dielectric constant of the suspended silica. This was found to be 4.55.

#### DIELECTRIC CONSTANT OF SILICA AT A HIGHER TEMPERATURE

A mixture of xylene and nitrobenzene of a slightly higher dielectric constant than that of silica was prepared. The temperature coefficient of the dielectric constant of this liquid mixture with and without the solid was determined and the two corresponding curves were plotted. The curves meet at 65°C corresponding to a value of 4.60 for the dielectric constant of the mixture. Hence 4.60 is the value of the dielectric constant of the powdered quartz at 65°C.

Liquid mixture used 18.74% nitrobenzene; 81.26% xylene.

TABLE IV

Temperature °C	€ of liquid mixture.	€ of liquid mixture with powdered quartz.
20	5.18	4.79
30	5.04	4.74
40	4.90	4.69
60	4.62	4.59
70	4.48	4.48 (80°)

Results of the mixture method :—

TABLE V

t°C	€
20	4.55
65	4.57

Thus the dielectric constant is practically the same over a range of 45°. It is interesting in this connection to recall the experiments of Gagnebin on the effect of temperature on the dielectric constant of optically active as well as piezo-electric quartz pieces. He reports a nearly constant value for the former from 0 to 200° and for the latter from 0 to 500°.

#### ELECTRIC MOMENT OF SILICA AT ORDINARY TEMPERATURES

Using the values of dielectric constants 4.55 and 3.25 for crystal quartz and vitreous quartz plates respectively the electric moments were determined by using a new relationship

$$(\epsilon - 1)\frac{M}{d} - (n^2 - 1)\frac{M}{d} = 4\pi N\mu^2/kT \text{ [Jatkar, Iyengar and Sathe (1946)]},$$

with the usual notations. The moments for vitreous silica and crystal quartz so calculated come out as 0.48D and 0.58 D respectively.

#### ELECTRIC MOMENT OF SILICA AT HIGHER TEMPERATURES

It is well known that quartz has an inversion point at 573°C when the  $\alpha$  to  $\beta$  transition occurs. The inversion point is marked by abrupt changes in the temperature dependence of the various physical properties of quartz, e.g., heat capacity, specific volume, axial ratio, Young's modulus, refractive

index, rotatory power, etc. In interpreting the dielectric constant of quartz this transition temperature has to be taken into account. Accordingly moments have been calculated by the modified new equation

$$(\epsilon - n^2) \frac{M}{d} = \frac{4\pi N \mu^2}{k(T - \theta)} \tag{1}$$

where  $\theta$  = transition temperature = 575°C ( $\alpha \rightarrow \beta$  quartz inversion temperature). The results are tabulated (Table VI).

TABLE VI

Piezo-electric quartz (Field $\perp$ )				$P_F = 32.2$ $\theta = 575^\circ\text{C}.$	Optically active quartz (Field $\parallel$ )			
$t^\circ\text{C}$	$\epsilon^*$	$P_0$	$\mu$	$t^\circ\text{C}$	$\epsilon^*$	$P_0$	$\mu$	
623	8.50	145.6	0.35	591	12.00	228.8	0.26	
676	9.65	172.6	0.56	639	12.11	231.2	0.52	
804	11.75	222.2	0.96	748	12.15	231.8	0.85	

\* Gagnebin (1924)

The moments which initially increase with temperature show a definite trend towards attaining a constant value at a higher temperature. The initially lower values are due to the fact that at lower temperatures the dielectric constant has not yet reached the static value but is still in the dispersion region. At higher temperatures the dielectric constants at the measured frequencies approach the static values. It can be seen by extrapolation that at higher temperature the moment tends to attain the constant value of 1.00D. In the low temperature region (25°C) the moment is 0.48 (calculated by equation (1) putting  $\theta = 0$ ).

The three main forms of silica, namely, quartz, tridimite and cristobolite are all built up of  $\text{SiO}_4$  tetrahedra (*i.e.*,  $\text{O} \setminus \text{Si} / \text{O}$  angle =  $109^\circ 28'$ ). The Si-O distance in some silicates has been observed as 1.60Å [Wells (1945)] The ionic character of the Si-O bond has been given as 50 per cent by Pauling (1944) and 37 per cent by Hannay and Smyth (1946). Recently Jatkar and

TABLE VII

—	C.N	$n$	$i = \frac{Z_A}{(Z_A + Z_B)} n$	$\mu_{(\text{Si-O}) \text{ Calc}}$ $\left( = \frac{e \times d \times i}{C N} \right)$	$\mu_{(\text{Si-O}) \text{ obs}}$ $\left( = \frac{\mu_{\text{SiO}_2}}{1.16} \right)$
$T > \theta (= 573^\circ\text{C}) \dots$	2	1/3	0.21	0.81	0.86
$T = 25^\circ\text{C} (\theta = 0^\circ\text{K}) \dots$	4	1/3	0.21	0.41	0.43

Gopaldaswamy (1948) have found that the ionic character "i" of a bond is related to the atomic numbers  $Z_A$  and  $Z_B$  of the constituents of the bond by the relation  $i = \frac{Z_A}{Z_A + Z_B} n$  where  $n$  is a fraction or an integer. Table VII gives the calculated and observed moments of Si—O bond.

The first column gives the co-ordination number. It appears that above the transition ( $T > \theta$ ) the co-ordination number is only two while below ( $T < \theta$ ) it is four. Thus the  $\alpha \rightarrow \beta$  inversion has the effect of apparently halving the co-ordination. In fact it has been found that the structure of the  $\alpha$  and  $\beta$  form of silica differ from each other only in detail and might involve a mere relative rotation of  $\text{SiO}_4$  tetrahedra (Wells (1945)). The latter fact could be the cause of a change in the co-ordination number of the Si—O bond at the  $\alpha \rightarrow \beta$  inversion. The last column in the tables gives the moment of Si—O bond which is  $\frac{\mu_{\text{SiO}_2}(\text{obs})}{1.16}$  since  $\mu_{\text{SiO}_2}(\text{obs})$ , the vector of two Si—O bond moments mutually inclined at a tetrahedral angle is 1.16 times the moment of each Si—O bond. In the absence of co-ordination it is seen that the true moment of the Si—O bond =  $0.4 \times 4 = 1.6\text{D}$ . It can be predicted that the observed Si—O moment will reach this value at higher temperatures where a Curie point of dielectric constant ought to be realized.

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