

TEMPERATURE VARIATION OF THE REFRACTIVE INDEX OF FUSED QUARTZ

BY P. S. NARAYANAN

(Department of Physics, Indian Institute of Science, Bangalore-3)

SUMMARY

Using an interference method the temperature variation of the refractive index of fused quartz of optical quality has been studied from 30° C. to 750° C. The existence of an irregularity close to the α - β transformation temperature of quartz has been confirmed and a secondary maximum close to the transformation temperature of cristobalite has been pointed out.

I. INTRODUCTION

An accurate knowledge of the refractive index of fused quartz and its variation with temperature is of great interest. The earlier measurements of the influence of temperature on the refractive index of fused quartz were made by Martens (1904), by Rinne (1914) who made measurements up to 1000° but at widely separated intervals and by Austin and Pierce (1935) who, using an interference method, studied the variation in the region from 18° to -200° C. Both Martens and Rinne used a prism of the material and the minimum deviation method. However, the three curves reproduced in Rinne's paper showing the variation of refractive index with temperature exhibit a definite and easily observable irregularity in the vicinity of 600° C., and this discontinuity is suggestively near the well-known α - β transformation temperature of quartz. In a recent paper this irregularity has been brought out clearly by S. Chandrasekhar (1951) who plotted the variation with temperature of the shift of the characteristic absorption frequencies calculated from Rinne's refractive index data. It is also known that vitreous silica exhibits an anomaly in its specific heat and thermal expansion at about 600° C. Since such an anomaly, if genuine, would throw light on the nature of the transformation as well as on the constitution of vitreous silica, it was considered desirable to measure accurately the temperature variation of refractive index of fused quartz. Such a study is all the more necessary, as it is possible now to obtain fused quartz specimens of very good optical quality and better than those used by any of the earlier workers.

For the present study, an interference method is better suited than the prism method, as the former yields directly the value of $\frac{dn}{dt}$ and is in addition more accurate.

2. EXPERIMENTAL DETAILS

The fused quartz plates used in the present investigation were presented to Prof. R. S. Krishnan by the Thermal Syndicate Ltd., London, and they were of the best optical quality available. The plates had their faces nearly plane parallel (thickness .052 cm.) and well polished. The experimental method was the same as that employed by T. Radhakrishnan (1950) in the case of lithium fluoride. However, as the temperature up to which the measurements were carried out was considerably higher than that attained in Radhakrishnan's measurements, it was necessary to ensure that the setting of the specimen remained unaltered even at 800° C. Consequently a small specimen was mounted in a groove cut at one end of a fused quartz rod and fixed with dental cement. The chromel-alumel thermo-couple with the aid of which the temperature measurements were carried out passed through two thin-walled fused quartz tubes fused on to the specimen support and was just in contact with the specimen. As the measurements had to be carried out at very high temperatures, a telemicroscope instead of an ordinary microscope had to be used for observing the interference fringes. The telemicroscope was kept at a distance of about 9 cm. from the specimen. A fine scratch on the specimen formed the reference mark across which the fringes shifted when it was heated and the temperature corresponding to the passage of each fringe across the reference mark was determined with an accuracy of $\pm .5^\circ$ C. The rate of heating had to be so small that it took 12 hours to reach a temperature of 750° C. The readings were also taken while cooling and the time for this was also of the same order. The final values taken for calculations were the mean of four such measurements. The measurements were carried out for three different wave-lengths, *viz.*, the λ 4358 and λ 5461 radiations of mercury and the λ 5893 radiation of sodium.

From the observations described above, $\frac{dn}{dt}$ was calculated by means of the relation $\frac{dn}{dt} = \frac{1}{2l} \frac{\lambda}{\Delta t} - na$, where l is the thickness of the specimen, λ the wave-length of light used, a the coefficient of linear expansion at temperature t and Δt the difference in temperature between successive fringe shifts. When $\frac{dn}{dt}$ values calculated in this manner are plotted against the mean temperature t and a smooth curve drawn through them, some of the experimental points diverged a little from the mean and the final curve (Fig. 1) was therefore obtained with values of $\frac{dn}{dt}$ calculated from the

temperature difference as an average over 2 and 3 fringe-shifts. The values read off from these curves are given in Table I.

TABLE I

Mean temperature in ° C.	$dn \times 10^6 / dt$		
	5893	5461	4358
60	10.5	10.8	11.4
80	10.8	11.1	11.8
140	11.8	12.2	12.5
120	12.15	12.7	12.8
220	12.3	13.1	13.15
260	12.25	13.35	13.25
300	12.15	13.5	13.4
340	12.0	13.5	13.4
380	11.9	13.4	13.45
420	12.0	13.15	13.2
460	12.5	12.7	12.9
500	13.3	12.5	12.9
540	14.0	13.0	13.5
580	14.2	14.2	14.9
620	13.55	14.8	14.7
660	12.1	14.6	13.8
700	11.2	13.4	13.1

In these calculations, the value of α , the coefficient of linear expansion was taken from Sosman's book on 'The Properties of Silica' (1929).

3. DISCUSSION

It is seen that the temperature coefficient of refractive index is positive and varies with temperature.

As mentioned earlier the only measurement so far of the variation of n with temperature above room temperature is by Rinne (1914) and the $\frac{dn}{dt}$ values calculated from his refractive index data are shown in Fig. 2. A comparison of Figs. 1 and 2 brings out the following features. While the trend of the curves up to 500° C. is the same in both cases, the author's values are slightly larger. The maximum observed by the author at about 600° C. is absent in Rinne's curves. This is easily understood if one takes into consideration the fact that Rinne measured the refractive index at only three temperatures 475, 590 and 1,000° C. and that the interference method used

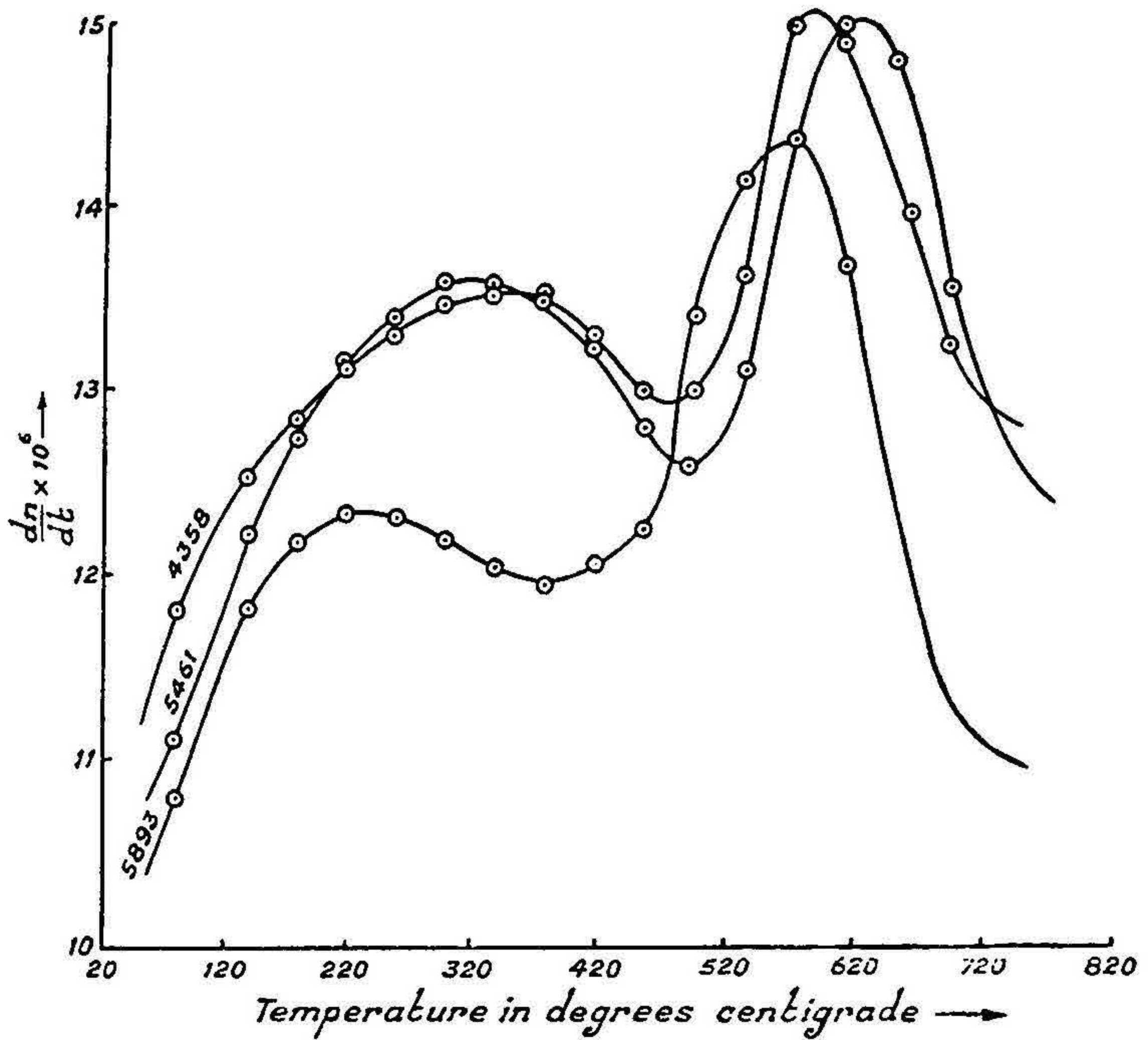


FIG. 1. Variation of $\left(\frac{dn}{dt}\right)$ with temperature.

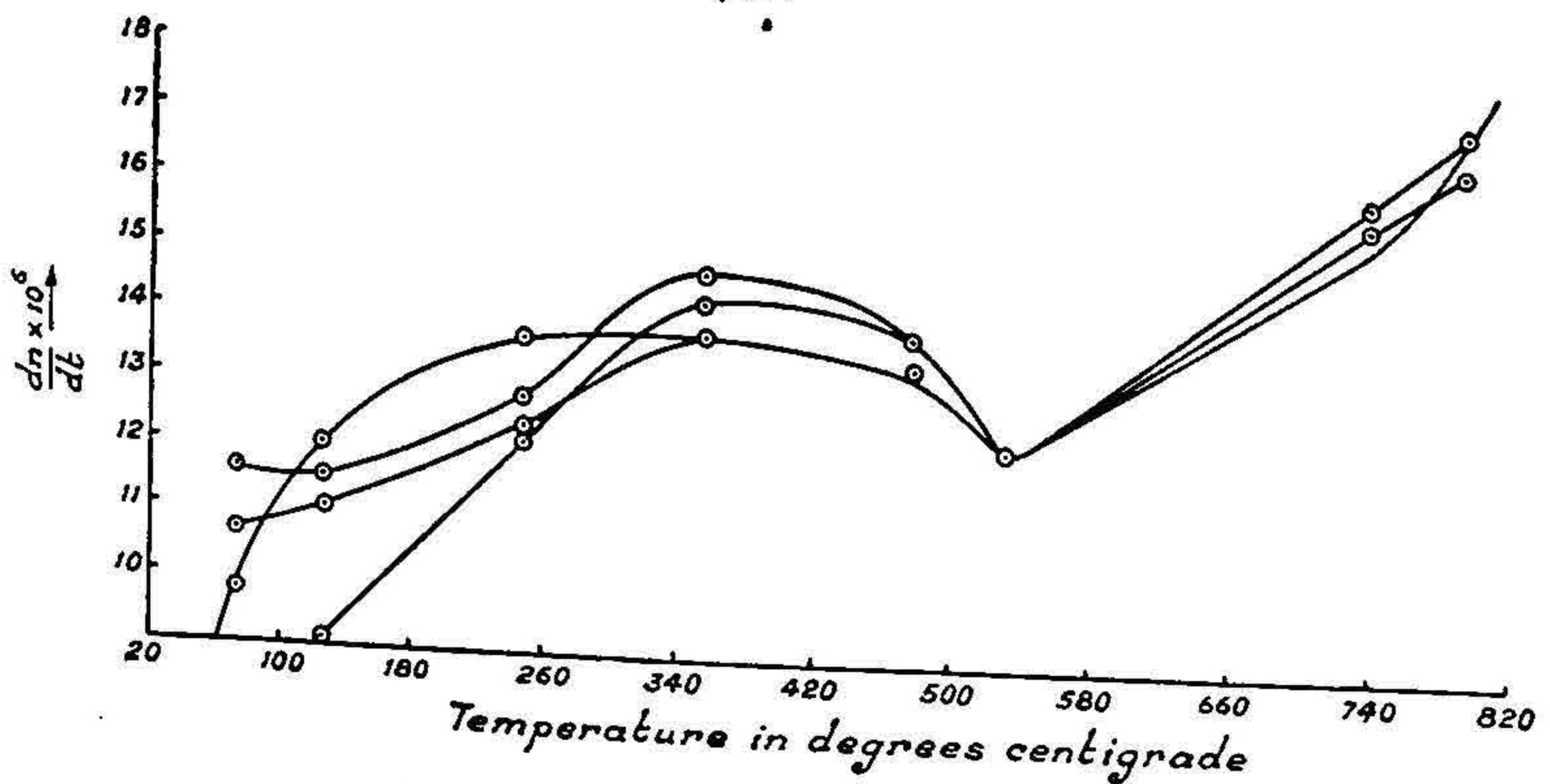


FIG. 2. Variation of $\left(\frac{dn}{dt}\right)$ with temperature.

(Calculated from Rinne's data)

here yields directly an accurate value of $\frac{dn}{dt}$ unlike the prism method. The temperature variation of the coefficient of cubical expansion as reported by Sonder and Hidnert (Sosman, 1929) exhibits two broad maxima roughly in the same temperature regions as the maxima in the $\frac{dn}{dt}$ curves. It might be pointed out that throughout the temperature range investigated, the variation of $\frac{dn}{dt}$ with wavelength is not regular.

The dispersion formula of vitreous silica due to Martens and Micheli (1904) is given by

$$n^2 = 1.36112 + \frac{.74655 \lambda^2}{\lambda^2 - (.107044)^2} - 0.01350 \lambda^2.$$

Differentiating this with respect to t one obtains (Ramachandran, 1947)

$$\frac{dn}{dt} = \frac{-\gamma}{2n} \frac{a_1 \lambda_1^2 \lambda^2}{(\lambda^2 - \lambda_1^2)} + \frac{1}{n} \frac{a_1 \lambda_1^2 \lambda^4}{(\lambda^2 - \lambda_1^2)^2} \chi + \frac{1}{2n} \beta,$$

where $a_1 \lambda_1^2 = .74655$ $\lambda = .107044,$

γ the coefficient of cubical expansion,

$\chi = \frac{1}{\lambda_1} \frac{d\lambda_1}{dt}$ and β arises from a variation of the number of centres and frequency in the contribution to refraction by frequencies in the remote ultraviolet. Using the observed $\frac{dn}{dt}$ values for any two wavelengths we can calculate χ and β and then the values of $\frac{dn}{dt}$ for a series of wavelengths can be calculated. Although the theoretical curve obtained in this way by G. N. Ramachandran (1947) using for χ and β the values 24.77×10^{-6} and -10.8×10^{-6} respectively has been found to fit well the data of Martens (1904) and Tilton and Tool (1929), the calculated values of $\frac{dn}{dt}$ for λ 4358, λ 5461 and λ 5893 are found to be lower than the values obtained by the author (see Table II).

Using the observed $\frac{dn}{dt}$ at 60°C. for λ 4358 and λ 5461 one obtains for χ and β the values 25.95×10^{-6} and -9.38×10^{-6} . A calculation of $\frac{dn}{dt}$ at 60°C. for λ 5893 using these yields a value of 10.6×10^{-6} , which is in good agreement with the observed value of 10.5×10^{-6} . It is possible for us to separate the $\frac{dn}{dt}$ into three parts (Ramachandran, 1947), P, Q

TABLE II

λ	$\frac{dn}{dt} \times 10^6$ at 60° C.	
	Author	From curve
5893	10.5	9.51
5461	10.8	9.65
4358	11.4	10.25

and R, P arising from a change in the number of oscillators per cm.³, Q from a change in polarisability caused by thermal expansion and R due to a pure temperature effect on the polarisability. $P + Q$ can be evaluated from photoelastic data and is equal to $-\frac{2}{n^3} \frac{(p_{11} + 2p_{12})}{3} \gamma$. Utilising the observed $\frac{dn}{dt}$ at room temperature for λ 5893 and the photoelastic constants reported by K. Vedam (1950), one obtains $P = -0.58 \times 10^{-6}$, $P + Q = -0.216 \times 10^{-6}$ (K. Vedam, 1952), $Q = 0.364 \times 10^{-6}$ and $R = 10.3 \times 10^{-6}$.

Thus we find that in the case of fused quartz nearly the whole of the observed $\frac{dn}{dt}$ arises from a pure temperature effect on the polarisability.

A study of the positions of the maxima in the $\frac{dn}{dt}$ vs. temperature curves shows that while the marked irregularity is in the neighbourhood of 600° C., there is a smaller one at about 300° C. It may be pointed out that this secondary maximum is close to the transformation temperature of cristobalite. It has been suggested from X-ray diffraction data that at ordinary temperatures, the radial density distribution in fused quartz over short distances (15 ÅU) has a cristobalite-like distribution based on the usual SiO₄ co-ordination groups (Warren, 1933). In a similar manner, the irregularity close to the α - β transformation temperature of quartz seems to indicate that at high temperatures the distribution of the Si and O atoms in fused quartz over small elements of space is similar to that found in quartz.

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REFERENCES

1. Austin, J. B. and R. H. H. Pierce Jr. *Physics*, 1935, 6, 43.
2. Chandrasekhar, S. .. *Proc. Ind. Acad. Sci.*, 1951, 34 A, 275.
3. Martens and Micheli .. *Zeits. f. Phys*, 1904, 6, 308.
.. *Ibid.*, 1904, 6, 311.
4. Radhakrishnan, T. .. *Proc. Ind. Acad. Sci.*, 1950, 31 A, 224.
5. Ramachandran, G. N. .. *Ibid.*, 1947, 25 A, 266.
.. *Ibid.*, 1947, 25 A, 280.
6. Rinne, F. .. *News. Jahrb. Min.*, 1914, 39, 388.
7. Sosman .. *The Properties of Silica*, 1927.
8. Tilton and Tool .. *J. Res. Bur. Stand.*, 1929, 3, 619.
9. Vedam, K. .. *Phys. Rev.*, 1950, 78, 472.
10. _____ .. *Ph.D. Thesis, Saugor University*, 1925, p. 69
11. Warren .. *Zs. f. Krist.*, 1933, 86, 349.