THE TEMPERATURE VARIATION OF THE ROTATORY POWER OF QUARTZ FROM 30° TO 410° C.

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IT has long been known that the rotatory power of quartz increases when the temperature of the crystal is raised (Soleil, 1845; Dubrunfaut, 1846). Numerous investigations dealing with this effect are on record, and these have been reviewed in detail by Sosman in his treatise on the properties of silica (*A.C.S.*, 1927, pp. 688–97). Measurements are available over a wide range of temperatures, from − 180° to 900° C., but no attempt appears to have been made to give a theoretical explanation of the phenomenon.

In an earlier paper (1952) the present author had shown that the rotatory dispersion of quartz is accurately represented from the visible to the extreme ultraviolet by a simple formula involving only two constants, *viz.*,

$$\rho = k\lambda^2/(\lambda^2 - \lambda_0^2)^2 \tag{1}$$

where $k = 7 \cdot 186$ and $\lambda_0 = 0 \cdot 0926283\,\mu$. The above formula is also expressible in the form

$$\rho = a\nu^2/(\nu_0^2 - \nu^2)^2 \tag{2}$$

where $\nu = 1/\lambda$ and $a = k/\lambda_0^4$. Taking 'a' to be constant but ν_0 to vary with the temperature, we get on differentiating (2)

$$\frac{d\rho}{dt} = \frac{4a\nu^2\nu_0^2}{(\nu_0^2 - \nu^2)^3}\chi_0 = \frac{4k\lambda^4}{(\lambda^2 - \lambda_0^2)^3}\chi_0 \tag{3}$$

where

$$\chi_0 = -\frac{1}{\nu_0}\frac{d\nu_0}{dt} = \frac{1}{\lambda_0}\frac{d\lambda_0}{dt}.$$

Hence, the temperature coefficient

$$\frac{1}{\rho}\frac{d\rho}{dt} = \frac{4\lambda^2}{(\lambda^2 - \lambda_0^2)}\chi_0 \tag{4}$$

It was shown earlier (*loc. cit.*) that the temperature variation of the rotatory power was calculable on the basis of (3), the rate of shift of the characteristic frequency with temperature being found to be roughly the same as that estimated from the thermal variation of the refractive indices of quartz. However, the available data are inadequate for a complete verification of the theory. From (4), it will be seen that one of the consequences of the theory is that the temperature coefficient should exhibit an increase with decrease of wavelength. Soret and Sarasin (1878) have reported a slight increase in the temperature coefficient in the ultraviolet, a fact which appears to be supported by Molby's observations (1910). But a series of measurements extending over a wider range of wavelengths is necessary before we can arrive at any definite conclusion regarding this matter.

In the present work, the thermal variation of the rotatory power of quartz has been measured from 30° to 410° C. for a range of wavelengths extending from about 6000 Å to 2500 Å. It is shown that the theoretical calculations agree very well with the observational data. The temperature coefficient is found to increase with decrease of wavelength, a fact which is also to be expected from the theory.

2. Experimental Details

Two rods of quartz, cut perpendicular to the optic axis and of fairly good optical quality were used for these experiments. By measuring their rotatory powers at room temperature for a few wavelengths they were tested to be homogeneous and untwinned. The length of the rods were 90·02 mm. and 41·05 mm. respectively.

The quartz crystal selected for the measurement was first wrapped up completely by a thin copper foil (except for two small apertures at the two ends to allow for the passage of light), so as to eliminate any possible variations of temperature along its length. A layer of asbestos was wrapped around the copper foil and the crystal was pushed into a thin-walled porcelain tube whose length was about two or three times the length of the quartz. Nichrome wire of suitable gauge was wound on the outer wall of the tube. By passing a current through this coil, the crystal could be heated to any desired degree. A calibrated thermocouple inserted between the copper foil and the asbestos served to measure the temperature of the crystal. The spectropolarimetric arrangement and the method of procedure were the same as described in Section 2 (*c*) of an earlier paper on the redetermination of the rotatory dispersion of sodium chlorate (1953). The positions of extinctions of the different spectral lines were measured first for the room temperature and then for the higher temperatures. The differences in the rotations could be read off directly for several wavelengths from 5800 Å to 2536 Å. In order to have large increases of rotation, so that the accuracy of experiment may not be too low, measurements were not made at very small intervals of temperature. With the larger specimen, it was possible to go only upto 200° C. as it unfortunately developed cracks at higher temperatures. But with the smaller specimen, the readings were extended upto about 410° C. The values of $d\rho/dt$ obtained with the two specimens for the different temperature ranges are tabulated below. The data obtained with the bigger specimen are more accurate on account of the larger increases in rotation. As is the convention generally adopted (Sosman, *loc. cit.*), the values of the rotatory power at all temperatures are expressed in terms of the thickness at room temperature. Throughout ρ is expressed in degrees per mm. and λ in microns.

TABLE I

λ	Specimen I Thickness 90·02 mm.		Specimen II Thickness 41·05 mm.			
	31° to 185° C.		28° to 199° C.		199° to 410° C.	
	Increase in Rotation measured in degrees	$\frac{d\rho}{dt}\times 10^3$	Increase in Rotation measured in degrees	$\frac{d\rho}{dt}\times 10^3$	Increase in Rotation measured in degrees	$\frac{d\rho}{dt}\times 10^3$
·2536	380	27·4	200	28·5	300	34·6
·2652	340	24·5	180	25·6	270	31·2
·2753	..	..	..	..	239	27·6
·2804	295	21·3	150	21·4	230	26·6
·2894	260	18·8	137	19·5	210	24·2
·2967	247	17·8	125	17·8	200	23·1
·3022	235	17·0	121	17·2	188	21·7
·3126	210	15·1	110	15·7	170	19·6
·3340	180	13·0	96·5	13·7	141	16·3
·3650	143	10·3	76	10·8	112·5	13·0
·4046	111·5	8·0	60	8·5	86·5 (199–406° C.)	10·2
·4358	97·5	7·0	50	7·1	75 (199–406° C.)	8·8
·5461	55·5	4·0	31·5	4·5	42·5 (199–406° C.)	5·0
·5790	50	3·6	27·5	3·9	37·5 (199–406° C.)	4·4

The temperature coefficient τ may be defined as $\frac{1}{\rho_0}\,\frac{\Delta\rho}{\Delta t}$ where ρ_0 is the rotatory power at room temperature. For the range 31° to 185° C. we get

for λ 5790, $\tau = 160 \times 10^{-6}$
for λ 2536, $\tau = 184 \times 10^{-6}$

The present value for λ 5790 compares favourably with Gumlich's value of 154×10^{-6} for the range 15° to 174° C. and Le Chatelier's value of 163×10^{-6} for the range 20° to 280° C. (Sosman, *loc. cit.*). Also it will be seen that *the temperature coefficient exhibits an increase with decrease of wavelength.* As has already been pointed out, this is to be expected from (4).

3. Theoretical Calculation

Substituting for k and λ_0 and giving a suitable value for χ_0 in equation (3), the values of $\frac{d\rho}{dt}$ have been calculated for the different wavelengths and for different temperatures. These are given together with the experimental values in Table II. The agreement can be seen to be very satisfactory.

Table II

λ	$d\rho/dt \times 10^3$					
	31° to 185° C.		28° to 199° C.		199° to 410° C.	
	Expt.	Theor. $\chi_1=4\cdot0 \times 10^{-5}$	Expt.	Theor. $\chi_0=4\cdot13 \times 10^{-5}$	Expt.	Theor. $\chi_0=5\cdot05 \times 10^{-5}$
·2536	27·4	27·5	28·5	28·4	34·6	34·7
·2652	24·5	24·2	25·6	24·9	31·2	30·5
·2753	..	..	..	..	27·6	27·5
·2804	21·3	20·7	21·4	21·4	26·6	26·1
·2894	18·8	19·0	19·5	19·6	24·2	24·0
·2967	17·8	17·8	17·8	18·3	23·1	22·4
·3022	17·0	16·9	17·2	17·5	21·7	21·4
·3126	15·1	15·5	15·7	16·0	19·6	19·6
·3340	13·0	13·1	13·7	13·5	16·3	16·5
·3650	10·3	10·5	10·8	10·9	13·0	13·3
·4046	8·0	8·3	8·5	8·5	10·2	10·4
·4358	7·0	7·0	7·1	7·2	8·8	8·8
·5461	4·0	4·2	4·5	4·3	5·0	5·3
·5790	3·6	3·7	3·9	3·8	4·4	4·7

Molby (*loc. cit.*) has measured the rotatory power both at liquid air temperature and at room temperature over the entire visible spectrum. The temperature coefficient for this range has been calculated earlier (*loc. cit.*)