

THE EFFECT OF TEMPERATURE UPON THE INFRA-RED
ABSORPTION OF CERTAIN GLASSES.

BY G. E. GRANTHAM.

SYNOPSIS.

Change of the infra-red transmission of glass with rise of temperature.—Dr. K. S. Gibson has studied the effect of temperature rise upon the absorption spectra of certain glasses in the visible region. He found a shift toward the longer wave-lengths and a decrease in transmission. The infra-red transmission ($0.6\ \mu$ to $4.0\ \mu$) of the same specimens has been studied at 80°C ., 307°C . and 440°C . Rise of temperature increases the transmission in the region of an absorption band. There is a shift of the transmission bands toward the longer wave-lengths. The same results are obtained whether one observes a series of ascending or a series of descending temperatures.

THE effect of temperature upon infra-red absorption spectra has been investigated by L. C. Martin¹ for black biotite. It was found that in general the absorption was greatly increased by a rise of temperature and that this effect was reversible. He also found that a rise of temperature had a tendency to obliterate an absorption band which existed at a lower temperature. With rise of temperature the maximum of transmission moved toward the less refrangible part of the spectrum. The suggested explanation of these effects is that a temporary chemical change within the crystal is caused by a rise of temperature.

K. S. Gibson² has investigated the effect of temperature upon the absorption spectra of several glasses of known composition in the visible region ($0.5\ \mu$ – $0.7\ \mu$). He found that there was an increase of absorption with rise of temperature and that this was accompanied by a shift of the less refrangible edge of an absorption band toward the red end of the spectrum. On account of these changes the edge of the band became less steep and there was therefore a change in color of the specimen. The object of this investigation was to study the effect of temperature upon the infra-red absorption spectra of the same specimens used by Gibson, and to see whether the shift of the edge of an absorption band, as found by him, was coincident with a shift of a transmission band lying largely in the infra-red or resulted in a narrowing of such a transmission band.

¹ Proc. of the Royal Soc., Series A, Vol. 96, 1919.

² The PHYSICAL REVIEW, N.S., Vol. VII., 1916.

The glasses used were:

No.	Color.	Coloring Material.	Glass.	Thickness.
1	Red	Cadmium-selenium	Zinc	1 mm.
2	Orange	Cadmium-selenium	Non lead	2 mm.
3	Light amber	Cadmium-selenium	Borosilicate	2 mm.
4	Lemon yellow	Cadmium-sulphide	Zinc	2 mm.

These glasses have transmission curves which are very similar and investigation of these specimens indicated the advisability of trying a specimen with well defined transmission and absorption bands. A specimen of Corning G.585 blue glass of 1.98 mm. thickness was chosen.

These specimens were placed in a furnace and the absorption spectra studied between 0.6μ and 4.0μ for these temperatures; 80°C. , 307°C. and 440°C.

APPARATUS.

The Furnace.—The construction of the furnace is shown in Fig. 1. A cylindrical piece of iron, *I*, 12 cm. long and 8 cm. in diameter was

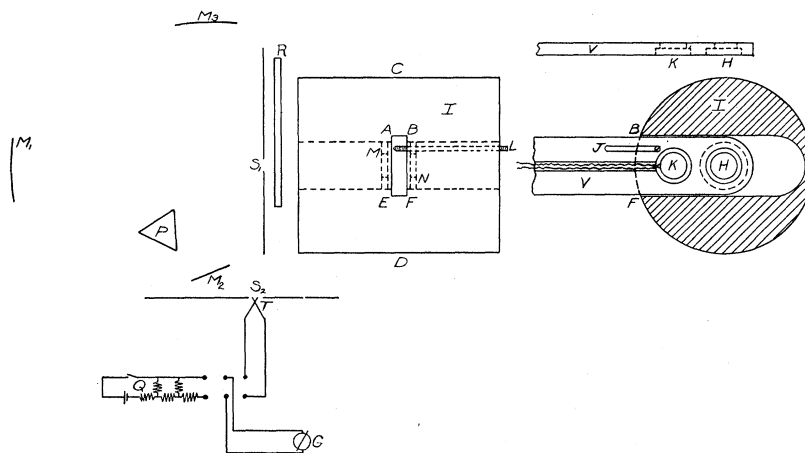


Fig. 1.

chosen as the core of the furnace. A hole 2.5 cm. in diameter was bored lengthwise through its center. The cylinder was then cut in halves at *CD* and a rectangular slot *ABEF* was milled into the end of each half and the halves fitted together and fastened by screws. An iron slide *V* was made which would fit the slot in *I* snugly. Two holes *K* and *H* 2.2 cm. diameter were bored half way through the slide, and, then using the same center, a hole 1.7 cm. diameter was bored the remaining distance through the slide. This afforded a shoulder against which the specimen

could be fastened by means of cement. A slot *J* cut through the slide served by means of the stop *L* to keep the holes *H* and *K* concentric with the cylindrical hole in the block *I*. Two iron washers *M* and *N* of internal diameter 1.5 cm. served the double purpose of diminishing the effect of reflection in the furnace and to correct for any error due to the hole *H* not being in the same position relative to the furnace as *K*, when the slide was at the limits of its path as determined by the slot *J*. The cylinder was heated by means of an electric current passing through a coil of iron wire, which was wound around the cylinder between layers of asbestos paper soaked in water-glass. At first the ends of the cylinder were covered with thin sheets of mica. This gave a large percentage of reflection and trial showed that if the bulb of the lamp giving the source of radiation was placed against the end of the furnace, there was no difficulty in keeping the sample at a constant temperature. The specimen was placed in the hole *K* and the junction of a copper-constantin thermocouple, was placed in contact with the specimen. The leads were buried in fire clay in the groove cut in the slide. The thermocouple was placed in conjunction with a Wolff potentiometer and was calibrated at 99.2° C., 232° C., 419° C. and 630° C. corresponding to the boiling point of water, and the melting points of tin, zinc and antimony respectively. The maximum temperature variation from the values given was probably not greater than five to eight degrees.

The Spectrometer.—A Hilger infra-red constant deviation spectrometer equipped with a Coblentz bismuth-silver thermopile was used. Rays on entering the collimating slit *S*₁, were rendered parallel by the concave nickel steel mirror *M*₁ of 27 cm. focal length, and 2.7 cm. aperture, and passed through the rock salt prism *P* to the Wadsworth¹ mirror system. The polished faces of the prism were 3.2 cm. high and 4.2 cm. long. After reflection by the plane mirror *M*₂ and the concave mirror *M*₃, identical with *M*₁ an image of the spectrum was formed on the slit *S*₂. The prism and plane mirror were mounted on a table which was rotated by a screw to which was attached a drum, calibrated to read wave-lengths between 0.5 μ and 10.0 μ . When the instrument was properly adjusted each ray which entered the slit *S*₁ passed through the prism at minimum deviation. The faces of the rock salt prism and the concave mirrors were repolished at the beginning of this investigation, and the most careful adjustment of the prism for minimum deviation for the D lines, gave the following values for three absorption bands of water and the carbon dioxide emission band respectively 1.48 μ , 1.98 μ , 3.0 μ and 4.36 μ . These bands as observed by Coblentz² occur at 1.5 μ , 2.0 μ , 3.0 μ and

¹ Phil. Mag., S. 5, Vol. 38, 1894.

² Bulletin of the Bureau of Standards, Vol. 7, No. 4.

4.4 μ respectively. These points were checked from time to time throughout this investigation, and it was found that the calibration did not change as long as no attempt was made to remove the prism from the spectrometer table. The spectrometer was covered completely by a glass case, which was in turn covered by a sheet iron case. The inside walls of the glass case were covered with black cloth to prevent reflection. A 2.5-watt electric lamp was kept burning continuously under the spectrometer so that the temperature of the instrument was above that of the surroundings. The drum was turned by means of a belt, which passed around the drum, and a pulley located under the table upon which the instrument was mounted. Within the glass case were kept several beakers containing P_2O_5 to prevent moisture from attacking the faces of the prism. During these investigations the two slits S_1 and S_2 were 0.25 mm. wide. The range of spectrum embraced by this slit width at the thermopile end is indicated for four regions in the spectrum at the bottom of each curve.

The Galvanometer.—A Coblentz¹ astatic galvanometer was used. The astatic system consisted of two groups of four magnets each. The magnets were about two millimeters long. This system was suspended by a very delicate quartz fiber so that each magnet group hung at the center of a pair of coils embedded in Swedish iron. The galvanometer was mounted on a concrete pier, the top of which was covered by 2.5 cm. of sheet transformer iron. Immediately surrounding the galvanometer was a cylinder of transformer iron, the wall of which was 1 cm. thick. Surrounding this were five cylinders of increasing diameter. These cylinders were cut from wrought iron gas pipe and the walls of each were approximately one centimeter thick. Covering the galvanometer and cylinders was a two centimeter layer of sheet iron. The sensibility of the galvanometer was adjusted by means of control magnets placed under the galvanometer and cylinders. Throughout this investigation the sensibility did not vary much from 3.3×10^{-11} amperes per mm. at three meters distance. This sensibility was measured by means of the testing box Q , which was furnished with the galvanometer. The leads between the galvanometer and thermopile were in iron conduit which was grounded. Even with these precautions, changes in current throughout the building caused induction effects, which were troublesome in the day time, and most of the data reported on here were obtained at night. No scale deflection greater than 35 cm. at three meters

¹ Bulletin of the Bureau of Standards, 4, 1908.

Bulletin of the Bureau of Standards, 9, 1912.

Scientific Papers of the Bureau of Standards, No. 282.

distance was used. The resistance of the galvanometer and thermopile were 8.9 ohms and 9.6 ohms respectively.

The Source of Radiation.—The source of radiation was a 400-watt nitrogen-filled tungsten lamp, which was connected across the terminals of a 120-volt storage battery.

METHOD OF TAKING OBSERVATIONS.

The trials at the lower temperature were made with the specimen in the furnace, when no current was flowing in the heating coils. An equilibrium temperature of about 80° C. was attained due to radiation from the source. For these trials the order of observations were as follows: The drum of the spectrometer was set for a given wave-length.

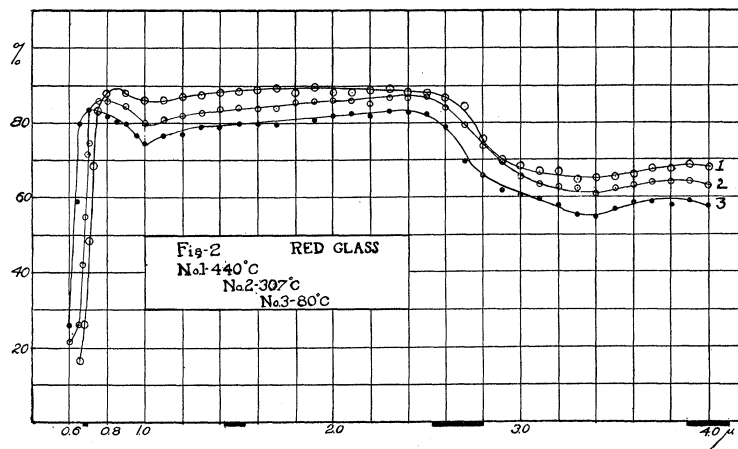


Fig. 2.

With the shutter R covering the slit S_1 , the zero of the galvanometer was determined. Then with the radiation from the source passing through the specimen the shutter was opened and galvanometer deflection d_1 recorded. The slide V was now quickly pulled out, allowing the radiation to fall directly on the slit and the galvanometer deflection d_2 taken. The shutter R was again closed and the zero determined. This process was repeated until consistent results were obtained. For portions of the spectrum, where the energy emitted by the source was small, the mean of twenty such trials was used to locate the point on the curve. The average number of trials for each point was six. The ratio of d_1 to d_2 when multiplied by 100 is called the percentage transmission for that wave-length. This value was corrected for reflection and the value of transmittance obtained in the following manner: assuming the index of

refraction to be 1.5 and the Fresnel formula for the per cent. of reflection at normal incidence $[(n - 1)/(n + 1)]^2$ the per cent. reflected at each surface of the glass became 4 per cent. Assuming this reflection to remain constant throughout the range 0.6μ to 4.0μ the transmittance was obtained from the expression:

$$\text{Transmittance} = T = \frac{d_1}{.96^2 d_2} \times 100.$$

Although the percentage of reflection decreased with increase of wavelength this assumption introduced a maximum error of less than 2 per cent. Rubens¹ has measured the dispersion of flint glass and found the value $\mu = 1.7510$ for $\lambda = 0.5893 \mu$ and $\mu = 1.6688$ for $\lambda = 4.12 \mu$. If these specimens, with an index of refraction approximately equal to 1.5,

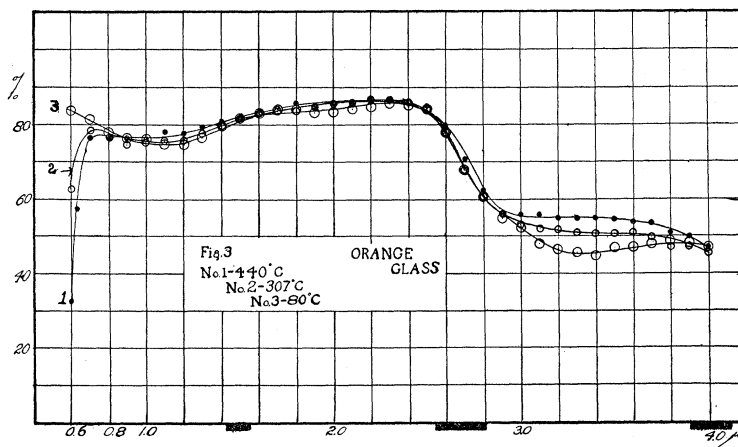


Fig. 3.

should change proportionately to the flint glass, the value for the index of refraction at $\lambda = 4.12 \mu$ would be $\mu = 1.43$, which would cause 3.13 per cent. reflection at each surface. This method also neglects any change in the index of refraction of the glass with rise of temperature.

For trials in which the furnace was heated it was found that beyond 2.0μ the radiation from the furnace and the specimen was an appreciable factor. For example, as seen from Table I. for the red glass at 4.0μ d_1 , the galvanometer deflection caused by the radiation, when the tungsten lamp was sending radiation through the glass, was 145 mm. and the corresponding deflection d_2 when the glass was removed was 167 mm. For the same wave-length the deflection d_3 , taken when the tungsten lamp was turned off, was 90 mm. with the glass in the center of the fur-

¹ Wied. Ann., 53, p. 276, 1894.

nance and the deflection d_4 taken when the glass was removed and the lamp off was 80 mm. Thus between 2.0μ and 4.0μ the order of taking observations was as follows: The drum was set at a certain wave-length, the shutter closed and the zero of the galvanometer determined. With the lamp turned off a deflections d_3 was taken with the glass in the center of the furnace. The slide V was then quickly moved to the other side and galvanometer deflection d_4 read. The zero was again determined and the deflection d_1 and d_2 taken as previously described. The transmittance was then calculated from the expression

$$T = \frac{d_1 - d_3}{0.96^2 (d_2 - d_4)} \times 100.$$

DISCUSSION OF RESULTS.

A table of observed and computed data is shown in Table I. The effects are shown diagrammatically by the figures Nos. 2, 3, 4, 5 and 6.

Glass No. I.
Temperature 440°C .

μ .	d_1 , mm.	d_2 , mm.	d_3 , mm.	d_4 , mm.	$\frac{d_1 - d_3}{d_2 - d_4} \times 100$.	Av. %.	Trans.
.65	3	20	0	0	15	15	16.2
	3	20			15		
	3	20			15		
.75	50	65	0	0	77.0	76.7	83.0
	50	65			77.0		
	47	62			76.0		
1.0	81	102	0	0	79.4	79.3	85.9
	81	102			79.4		
	80	101			79.2		
1.5	121	148	0	0	81.8	81.3	88.0
	120	149			80.6		
	120	147			81.6		
2.0	150	185	2	2	81.0	81.0	87.7
	150	185	2	2	81.0		
	150	185			81.0		
2.5	157	189	13	11	81.0	80.8	87.5
	157	190	13	11	80.4		
	155	186			81.2		
	159	192			80.6		
3.0	139	192	41	38	63.6	63.1	68.4
	139	195	41	38	62.5		
	139	192			63.6		
	139	194			62.8		
3.5	169	213	85	73	60.0	60.3	65.3
	169	212	85	73	60.4		
	169	212			60.4		
4.0	145	167	90	80	63.2	63.2	68.4
	145	167	90	80	63.2		
	145	167			63.2		

Fig. 2 indicates for the red glass the same shift in the visible region as was found by Gibson. This sample shows a decrease in absorption with rise of temperature throughout the whole range except for wave-lengths

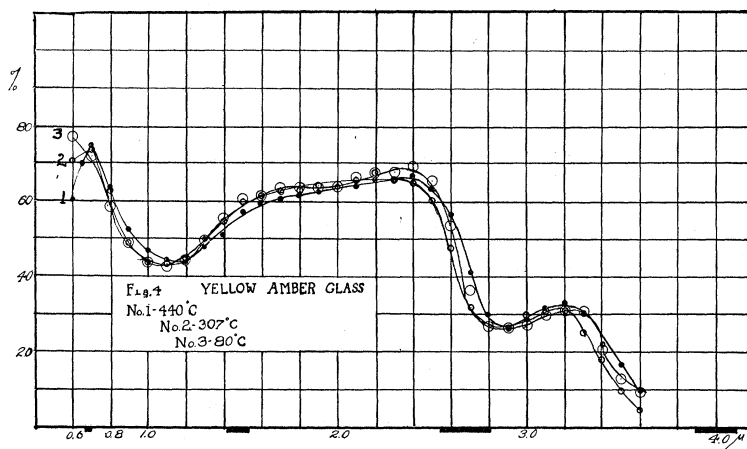


Fig. 4.

less than 0.75μ when the absorption increases with a rise of temperature. There is evidence of a shift of the whole transmission band, extending from about 0.7μ to about 2.7μ , toward the less refrangible portion of the

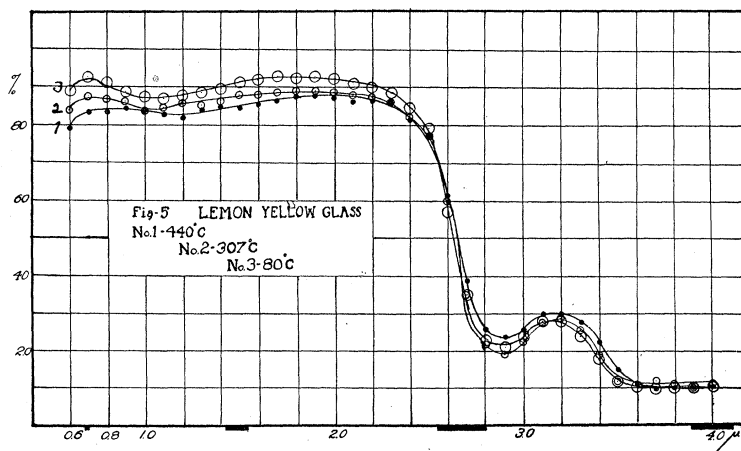


Fig. 5.

spectrum. The absorption band at 1.0μ is less marked at higher temperatures. The absorption band at 3.35μ although less prominent than the band at 1.0μ is modified so as to make the percentage of trans-

mittance more uniform in this region. This specimen exhibited no sharp absorption bands in this region.

The percentage transmittance for the orange glass is shown in Fig. 3. There is indication of a slight shift with a rise of temperature of the transmission band extending over about the same region as the transmission band for the red glass. There is also a very slight increase in transmittance throughout this transmission band. At the 3.3μ absorption band there is a marked increase in the transmittance with rise of temperature. Fig. 4 shows a shift of the whole transmission band toward the longer wave-lengths with a rise of temperature and a slight decrease of transmittance except in the region of absorption bands, when the transmittance increases. The absorption band at 1.1μ shows evidence of a shift toward the longer wave-lengths.

Fig. 5 shows unmistakably, at higher temperatures, a decrease of transmittance throughout the range from about 0.6μ to 2.4μ with the highest temperature in the region of the absorption band at about 2.9μ the transmittance is higher than at lower temperatures.

With a specimen having sharp absorption bands, as shown in Fig. 6,

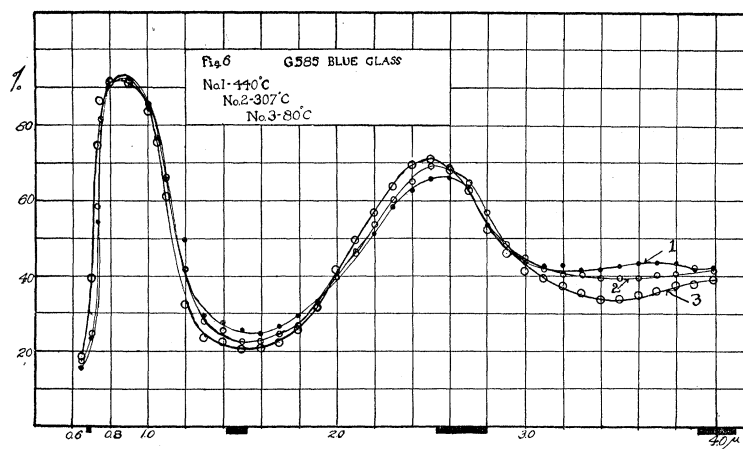


Fig. 6.

there is further evidence that an increase in temperature produces a decrease in absorption in the region of absorption bands in the infra-red. The peaks of the transmission bands are shifted toward the longer wave-lengths at higher temperatures. This is brought about by an increase in absorption on the long wave-length side of an absorption band and a decrease of absorption on the short wave-length side of an absorption band. The net result of this is to broaden the absorption band without

any apparent shift in the peak of an absorption band. This applies particularly well to the absorption band having a maximum between $1.3\ \mu$ and $1.8\ \mu$.

In general the following conclusions may be drawn regarding the effect of a rise of temperature upon the absorption spectra of these glasses.

1. Rise of temperature decreases slightly the absorption in the region of an absorption band.
2. There is a shift of the transmission bands toward the longer wavelengths, which is greater on the more refrangible edge than on the less refrangible.
3. The same results are obtained whether one observes a series of ascending or a series of descending temperatures.

This investigation was suggested by Professor R. C. Gibbs; I am indebted to him for many helpful suggestions throughout the work. I am also indebted to my wife, Margaret Grantham, for assistance in taking the data and computing results.

CORNELL UNIVERSITY,
ITHICA, N. Y.