THE EFFECT OF TEMPERATURE ON FLUORESCENCE AND ABSORPTION.

By R. C. Gibbs.

III. Absorption of Various Specimens at High Temperature.

THE effect of high temperature on the absorption of the specimens described in this paper is a continuation of the work done on uranium glass at high temperatures[1] and at low temperatures.[2] The substances investigated consisted of various colored glasses of unknown composition, a few cubes, the composition of which was partially known, and a cube of fluorite. Only a few of these specimens showed any fluorescence.

Apparatus.

The specimen G was placed inside a hollow iron cylinder, as indicated in Fig. 16. On the outside of the cylinder was wound a few layers of iron wire and heating was secured by sending an electric current through this wire. The temperature of the specimen was measured by an iron constantan thermo-junction J. For convenience in inserting the specimen into the furnace, it was first placed inside of a cylindrical iron case C. This case fitted rather closely into the opening in the iron cylinder and was pushed into place by another hollow iron tube T, the inner cross section of which was slightly smaller than that of the case. In order to prevent internal reflection as much as possible, iron washers W_1 and W_2 were placed at each end of the iron case. To prevent air currents and therefore unequal heating, two mica windows were placed in positions indicated by M_1 and M_2. A hole was drilled in the side of the furnace for the purpose of observing the effect of high temperature on the fluorescence of the specimens studied and was filled with a plug P when the intensity of transmitted light was

[1] Gibbs, R. C., Phys. Rev., Vol. XXVIII., No. 5, p. 361.
[2] Gibbs, R. C., Phys. Rev., Vol. XXX., No. 3, p. 377.

being measured. Some of the specimens were thin pieces of glass and in order to hold them in position, they were ground to very nearly the same diameter as that of the iron case and inserted be-

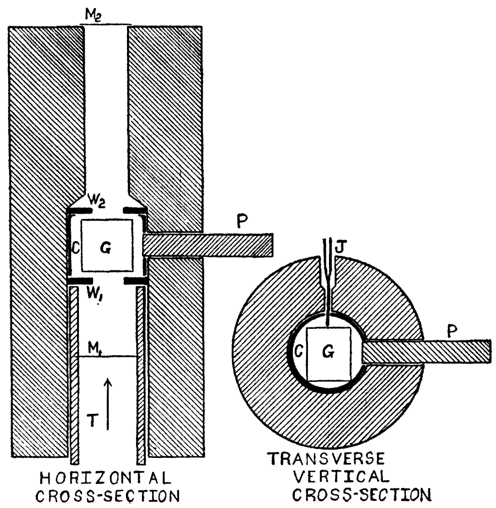

Fig. 16.

tween it and the washer W_1. The intensity of transmitted light was measured by means of the Lummer-Brodhun spectrophotometer. The arrangement of the apparatus is shown in Fig. 17.

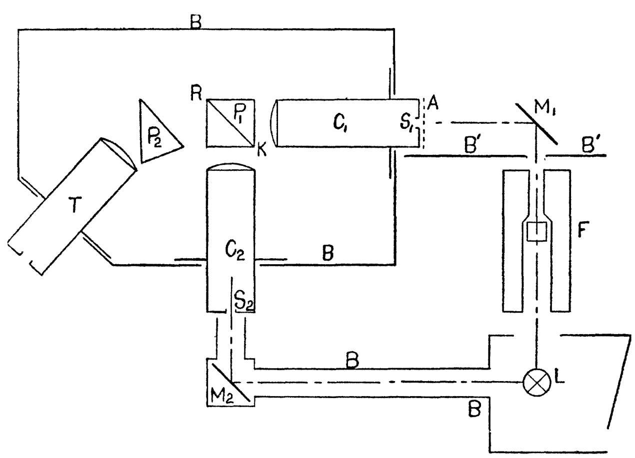

Fig. 17.

F represents the furnace, L the acetylene flame, M_1 a glass mirror and M_2 a block of magnesium carbonate, B screens covered with black paper, B' several layers of asbestos, covered with black paper on the side of the mirror, to prevent undue heating of the mirror, and A a ground glass screen to secure uniform intensity of field. Slit S_1 was set to a constant width in most of the observations and the intensity measured by varying the width of slit S_2. A set of observations throughout the spectrum was made with the glass removed from the furnace, and the intensity of the light thus measured was regarded as that of the incident light subject to corrections for reflection which will be mentioned later. The specimen was then inserted into the furnace and a set of observations made throughout that part of the spectrum where sufficient light was transmitted to be measurable. The temperature was then raised and a set of similar observations made at 100°, 200°, 300°, and 400° C., at which temperatures sufficient time was given to let the temperature inside of the furnace become uniform. After the measurements had been made at the highest temperature, the furnace was allowed to cool off and observations were made again at room temperature on the following day. This procedure seemed justifiable because the same acetylene flame served both for the source of incident light and that of the comparison light.

Correction for Reflection.

The ratio of the intensity of the transmitted light to that of the incident light measured, as mentioned above, would be the percentage transmission if it were not for the reflection at both surfaces of the specimen. In the case of normal incidence, about four per cent. of the light falling upon the glass surfaces is reflected. This is computed on the assumption that in the Fresnel formula $[(n-1)\div(n+1)]^2$, we use 3/2 for the index of refraction. This same percentage will be reflected at the second surface, so that if we regard I as the intensity of the light striking the first surface $.96I$ will actually get into the specimen. If we designate the observed transmitted light by T, the amount of light which reached the second surface of the specimen would be $T/.96$ and we should then have $T/I(.96)^2$ as the ratio of the intensity of the light reaching the second surface to that of the light which entered the specimen, or in other words $T/I(.96)^2$ is the percentage transmission. Attention is here called to the fact that Kayser, in his Handbuch der Spectroscopie, Vol. III., p. 12, has failed to take account of the reflection at the second surface in the case of normal incidence. In the following results, the percentage transmission was computed

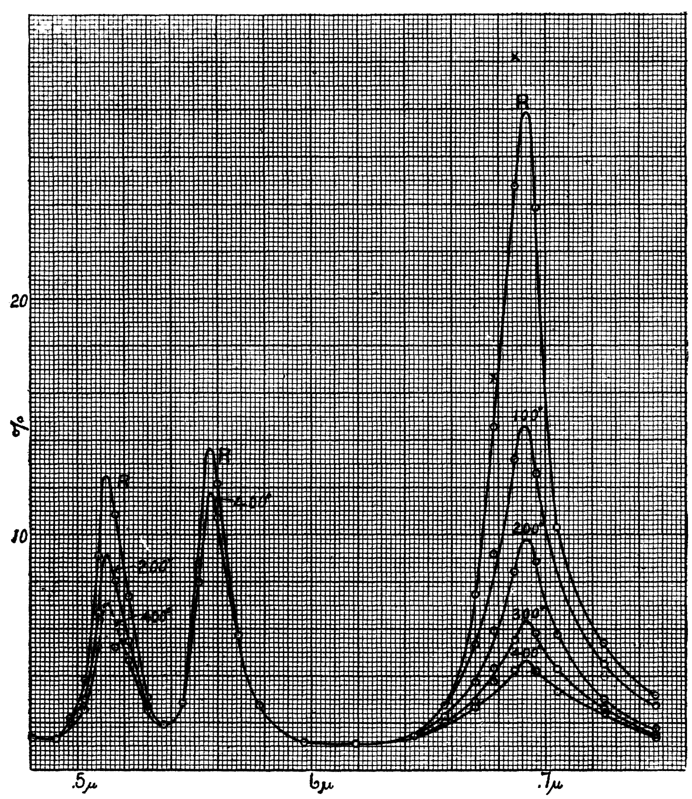

Fig. 18.

Showing the percentage transmission of erbium glass at various temperatures. Thickness = 1.451 cm.

according to the above formula with the full realization that the light did not strike all parts of the surface at normal incidence, and that the index of refraction is not 3/2 for all wave-lengths, but the error thus introduced is probably negligible.

Coefficient of Absorption.

The coefficient of absorption β, shown in the following curves, was computed from the formula

$$\beta = \frac{\log_e 1/D}{x},$$

where D represents $T/I(.96)^2$ and x the thickness of the specimen. The computations for the numerator of this formula were made graphically by referring to a curve which was secured by plotting between percentage transmission and the $\log_e 1/D$, the curve extending from small percentages up to 100.

Erbium Glass.

A specimen of glass found in the laboratory, which showed when viewed through a pocket spectroscope practically a line transmission spectra, was for various reasons thought to contain erbium, and its percentage transmission for various temperatures, is shown in Fig. 18. Inasmuch as the transmission bands are very narrow and the absorption bands so great, it was necessary to use a variable slit width and below is a table of the slit width in millimeters for the various wave-lengths.

Table IV.

λ	Slit Width.	λ	Slit Width.
.481μ	1.0	.578μ	.6
.491	1.0	.597	1.0
.497	.6	.691	1.0
.503	.6	.644	1.0
.509	.3	.657	1.0
.516	.3	.670	1.0
.522	.3	.678	.5
.530	.6	.687	.5
.537	.6	.696	.5
.545	.6	.705	.5
.552	.3	.725	1.0
.560	.3	.747	1.0
.569	.6		

Below is a table showing width of slit in terms of wave-lengths at various parts of the spectrum for a slit width of .7 mm.:

.450μ	7+μμ	.600μ	21+μμ
.500	11+	.650	27−
.550	16−	.700	35

The above slit widths were used for high temperatures except that for 300° and 400° the slit width was kept at 1 mm. throughout the red band. In computing the percentage transmission,

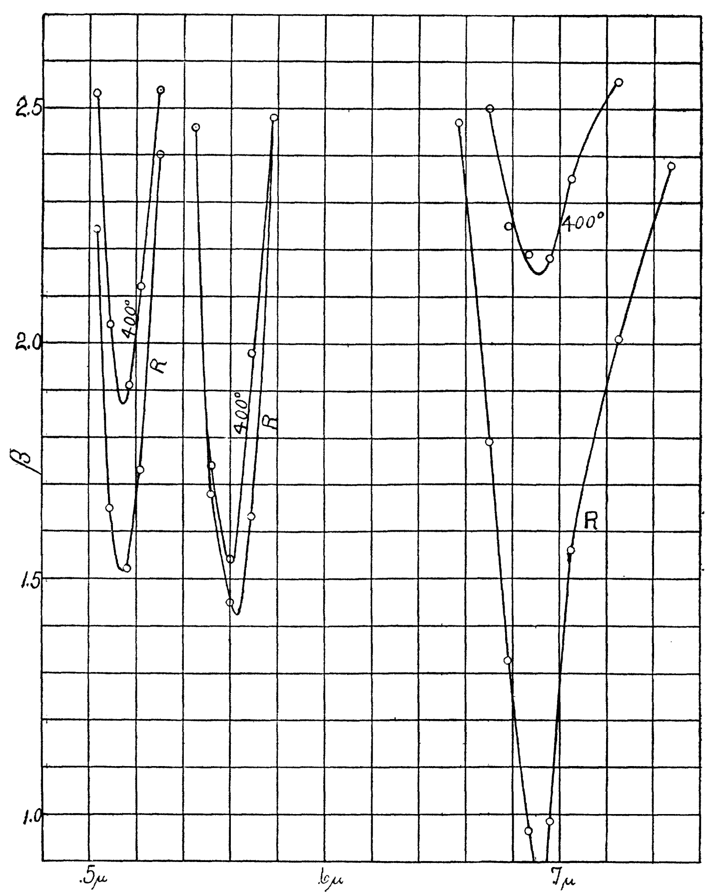

Fig. 19.

Showing coefficient of absorption of erbium glass.

the observed intensities of transmission were reduced to a standard slit width by assuming a strict proportionality between intensity and slit widths which in several cases is probably far from true. It is however to be noticed that exceptionally smooth curves were obtained as the result of such procedure. Of course the small percentage transmission between the bright bands has no very great significance, as considerable of the light there measured might have been due to stray light, and in plotting the coefficient of absorption for this specimen, as shown in Fig. 19, only those bands which lie near the brighter regions of the spectrum have been indicated. With narrow bands of this sort considerable error is made, due to the width of the slit and two points are shown in Fig. 18 by crosses which indicate the nature and magnitude of the correction to be made, because of this error. The location of these points was determined by reference to the formula derived by Nichols and Merritt.[1] The luminescence curve of the comparison source necessary for computing this correction was obtained from data given by Abney and Festing.[2] In deriving the general formula for slit correction, a small mistake was made in the computation, and the authors have asked the writer to call attention to the error. On page 342 of this article, the coefficients of f and f'' were added and one of the coefficients $(c - a)^3/3$ was omitted. When this is introduced- the value of k_1 becomes $c(a^2 + c^2)/3$ when $a < c$, the same value as when $a > c$.

The intensity of the transmitted light decreases considerably in both the red and green bands, but shows a very slight decrease in the yellow band. On cooling back to room temperature, the intensity of transmitted light was the same as before heating. There seems to be no shift of the bands on heating and the coefficient of absorption curves serve to emphasize the narrowness of these transmission bands.

Sapphirin Glass.

In Fig. 20 is shown the percentage transmission for various temperatures on first heating this specimen. Up to 300° there is a slight increase in transmission in the neighborhood of the absorption band, especially on the side of the shorter wave-lengths, and a slight decrease in the transmission in the blue end of the spectrum. At

[1] Nichols and Merritt, Phys. Rev., Vol. XXX., No. 3, p. 343.

[2] Abney and Festing, Phil. Trans., 1886, II., p. 542.

400° the transmitted light had increased considerably at the red end of the spectrum, but decreased considerably in the region from the crest of the absorption band to the shortest wave-length measured. On cooling back to room temperature, the broken line in

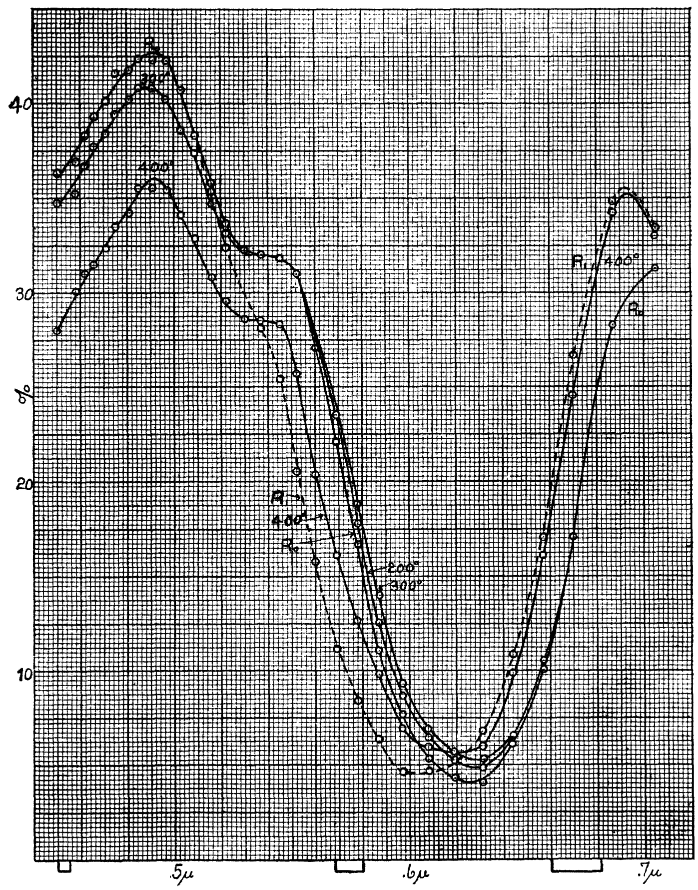

Fig. 20.

Showing the percentage transmission at various temperatures of sapphirin glass on first heating. R_0 = room temperature before heating. R_1 = room temperature after heating. Thickness = 1.344 cm.

Fig. 20 indicates the percentage transmission showing a considerable shift of the absorption band toward the shorter wave-lengths, a slight decrease in the maximum of the absorption and an almost complete disappearance of the irregularity in the neighborhood of .54μ. The intensity was measured at room temperature on three successive days and it was found that the change above noted was a permanent one, at least for that length of time. The specimen was

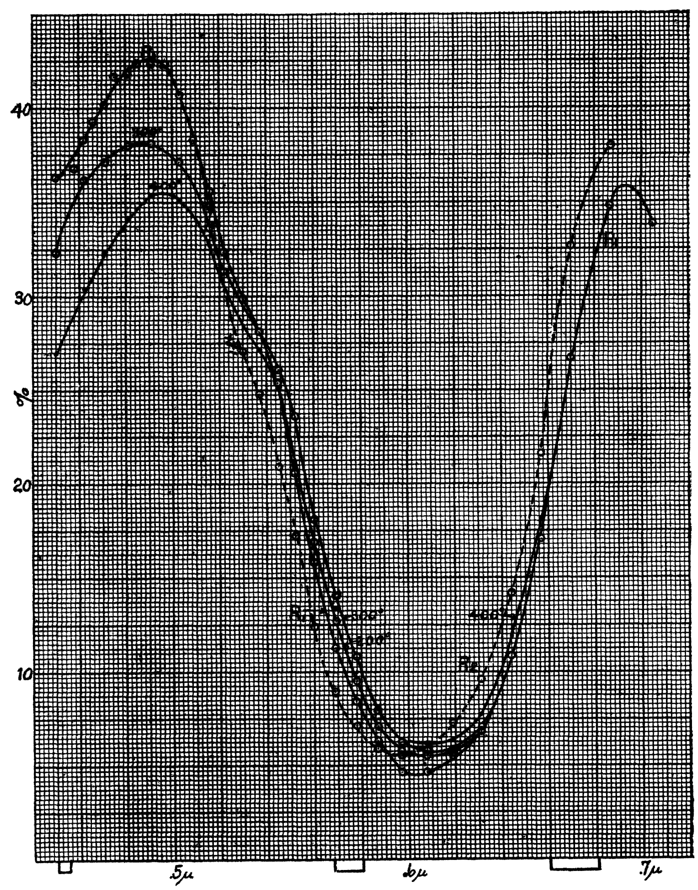

Fig. 21.

Showing percentage transmission of sapphirin glass at various temperatures on second heating. R_1 = room temperature before second heating. R_2 = room temperature after second heating.

again heated and in Fig. 21 are shown the corresponding changes which were very similar in nature to those on the first heating, but somewhat smaller in magnitude. The permanent shift was again observed after cooling back to room temperature, although it was not so much as in the first case. The three room temperature curves are shown in Fig 22 and they seem to indicate that the glass on heating was undergoing some change analogous to annealing and would

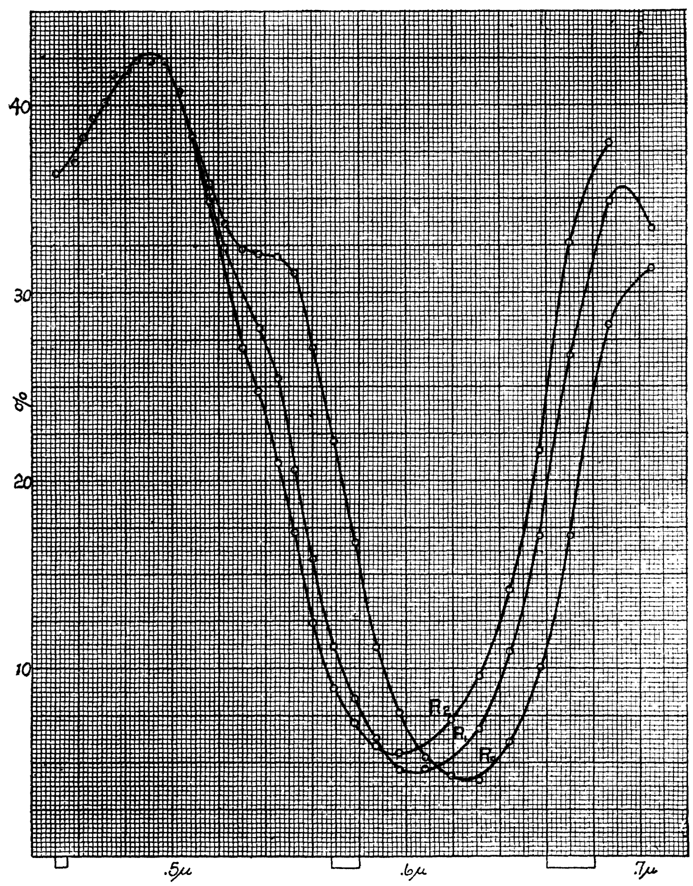

Fig. 22.

Showing percentage transmission of sapphirin glass at room temperature at three different times. R_0 = room temperature before heating. R_2 = room temperature after first heating. R_2 = room temperature after second heating.

probably reach a steady state after several heatings. Looking at the specimen directly with the eye, small colored streaks could be seen in the glass due to irregularities, and these show quite a different color after heating. This specimen shows a brick red fluorescence particularly when excited by daylight, but a very small amount of fluorescence, if any, when excited by the light of the mercury arc. The effect of heating on the fluorescence seemed to

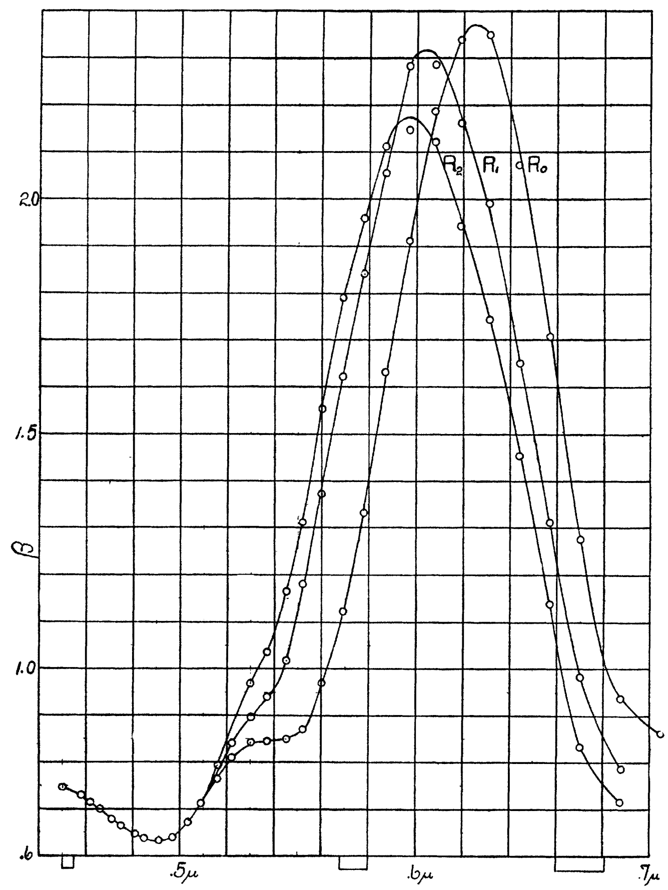

Fig. 23.

Showing coefficient of absorption of sapphirin glass at room temperature. R_0 = room temperature before heating. R_1 = room temperature after first heating. R_2 = room temperature after second heating.

increase its intensity. This was, however, determined by looking at this specimen directly with the eye through the hole made in the side of the furnace, and is not to be regarded as very accurate.

In Fig. 23 is shown the coefficient of absorption for the three room temperature measurements. In the last four figures, as well as in the figures that follow, the little rectangles at the bottom indicate the width of slit in wave-lengths.

COBALT GLASS NO. 1.

In the curves in Fig. 24 it will be seen that on heating cobalt glass, an increase in the transmission resulted, except in the extreme red end of the spectrum where there was a continual decrease. This

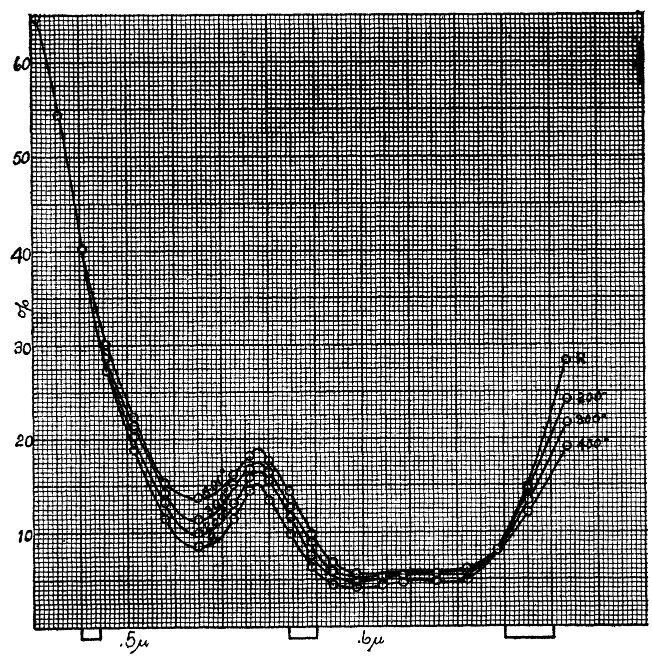

Fig. 24.

Showing percentage transmission of cobalt glass no. 1. Thickness .181 cm.

specimen absorbed considerable light, and consequently rather wide slit widths had to be used in order to measure the light transmitted in the main absorption band. On account of the wide slit width, it is impossible to bring out, very much, the narrow absorption bands, one of which lies in the region .595μ and the other at about .6μ. These are easily discernible with a pocket spectroscope and with some other arrangement whereby more intense light could be secured, these narrow bands could be defined. On the whole there seems to be a slight general shift of the curve toward the red end of the spectrum. In Fig. 25 is shown the coefficient of absorption for the highest and lowest temperatures measured. If these curves be

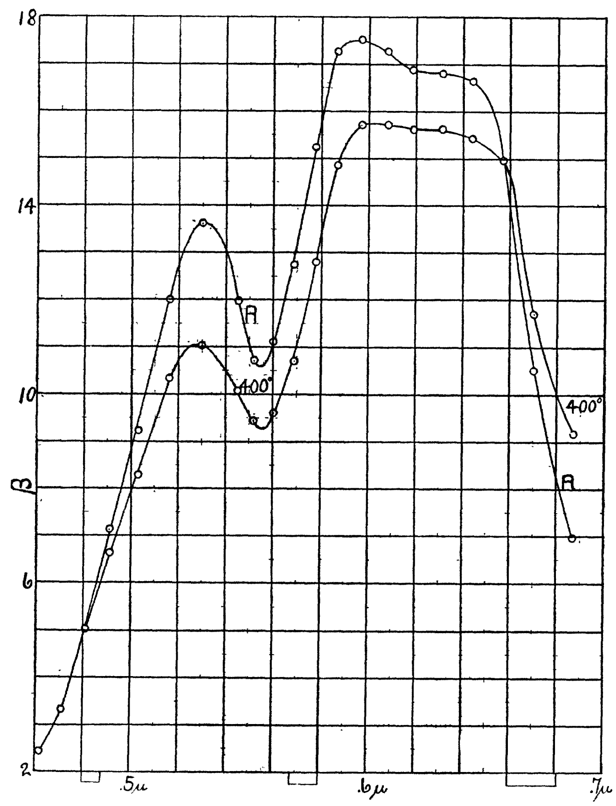

Fig. 25.

Showing the coefficient of absorption of cobalt glass no. 1 at room temperature and at 400°.

compared with the curves shown by Houstoun,[1] it will be found that there is quite a close agreement between the results secured. Houstoun shows by tables and curves in the case of several solids and liquids the values for what he calls the index of absorption

[1]Houstoun, Ann. der Phys., 21, p. 535, 1906.

computed according to a formula due to J. Ehlers. The writer has been unable to make the curves agree exactly with the tables, particularly in the case of the cobalt glass mentioned above.

Cobalt Glass No. 2.

In Fig. 26 is shown the effect of heating on the transmission of another specimen of cobalt glass, and in Fig. 27 is shown the corresponding coefficient of absorption. These curves indicate the

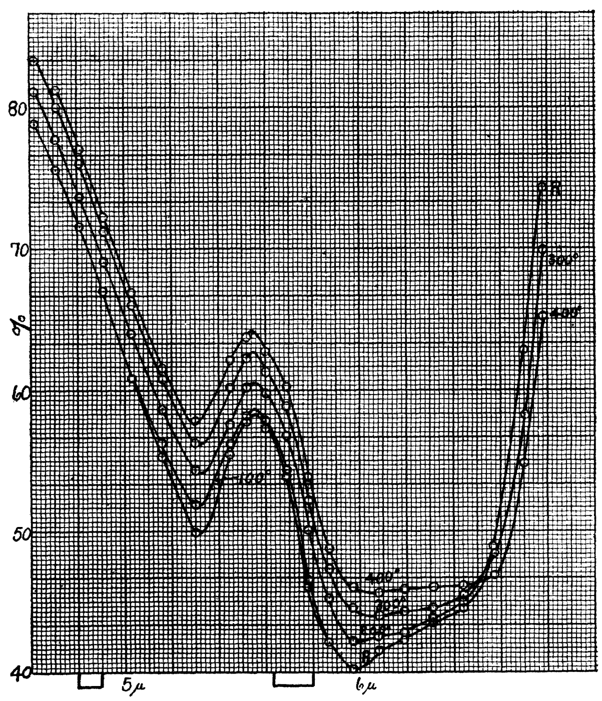

Fig. 26.

Showing the percentage transmission of cobalt glass no. 2 at various temperatures. Thickness = .206 cm.

same effect as was secured with the other specimen of cobalt. A much narrower slit might have been used with this specimen, inasmuch as the absorption was not so large.

Green Glass No. 1.

From Fig. 28 it can be seen that the transmission of this specimen decreases considerably on heating. There is a considerable shift of

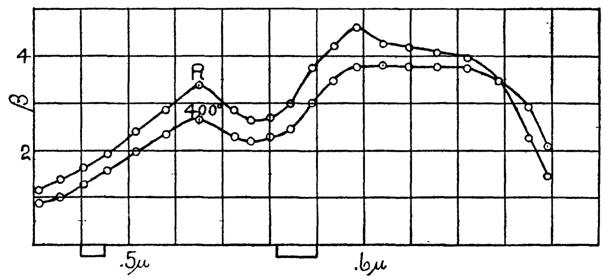

Fig. 27.

Showing coefficient of absorption of cobalt glass no. 2.

the maximum toward the longer wave-lengths, indicating that the absorption band in the violet is either shifting toward the red or is

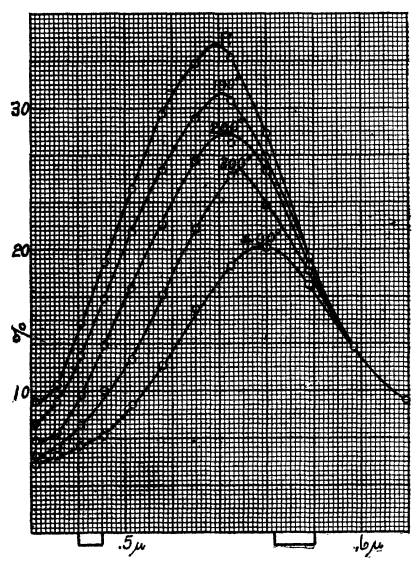

Fig. 28.

Showing the percentage transmission of green glass no. 1 at various temperatures Thickness = .208 cm.

simply becoming broader on that side. Fig. 29 shows the corresponding curves for the coefficient of absorption.

GREEN GLASS NO. 2.

The changes in transmission and coefficient of absorption for green glass no. 2 due to heating are very similar to those mentioned for green glass no. 1, as can be seen by reference to Figs. 30 and 31.

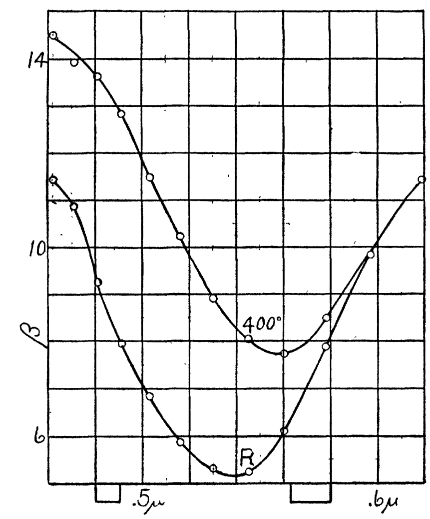

Fig. 29.

Showing coefficient of absorption of green glass no. 1.

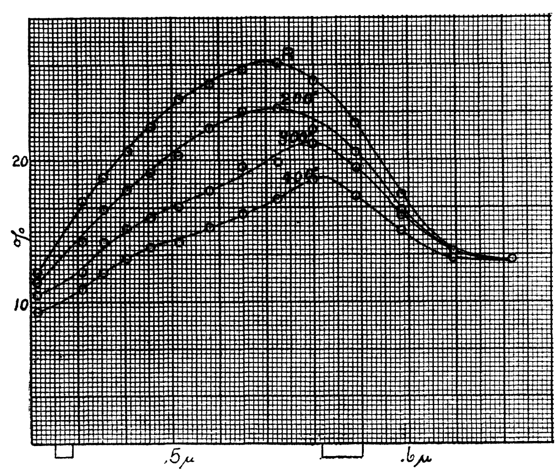

Fig. 30.

Showing percentage transmission of green glass no. 2 at various temperatures. Thickness = .186 cm.

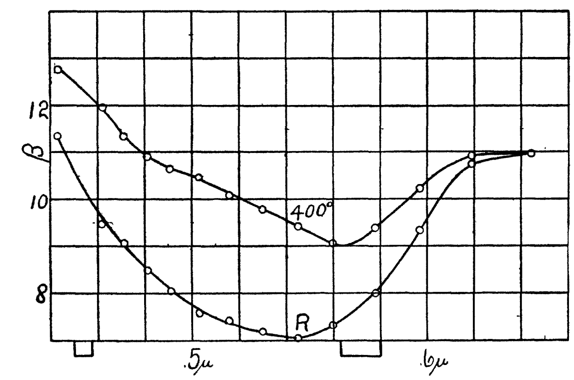

Fig. 31.
Showing coefficient of absorption of green glass no 2.

Blue Glass.

The amount of light transmitted by this glass decreased with rise of temperature as shown in Fig. 32. The absorption was quite

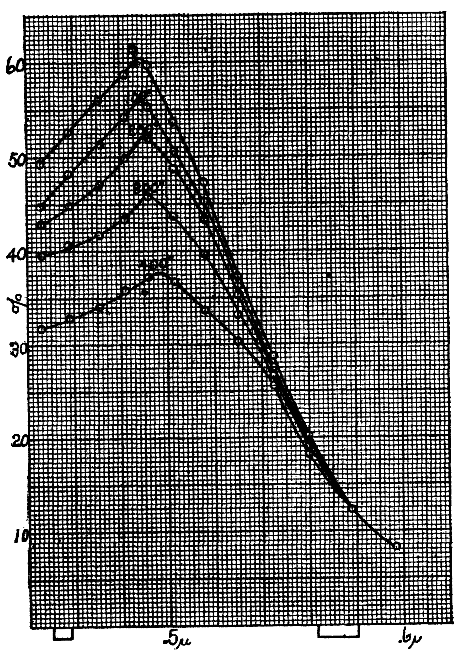

Fig. 32.
Showing percentage transmission of blue glass at various temperatures. Thickness = 226 cm

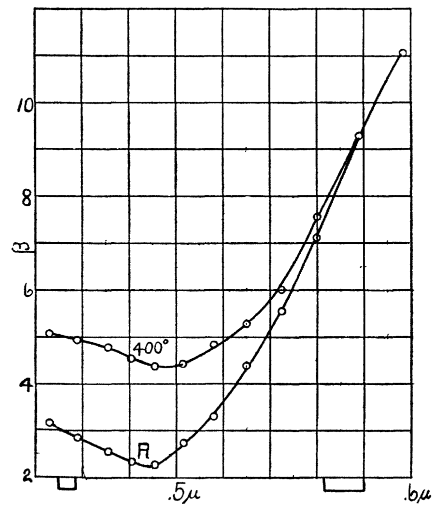

Fig. 33.

Showing coefficient of absorption of blue glass.

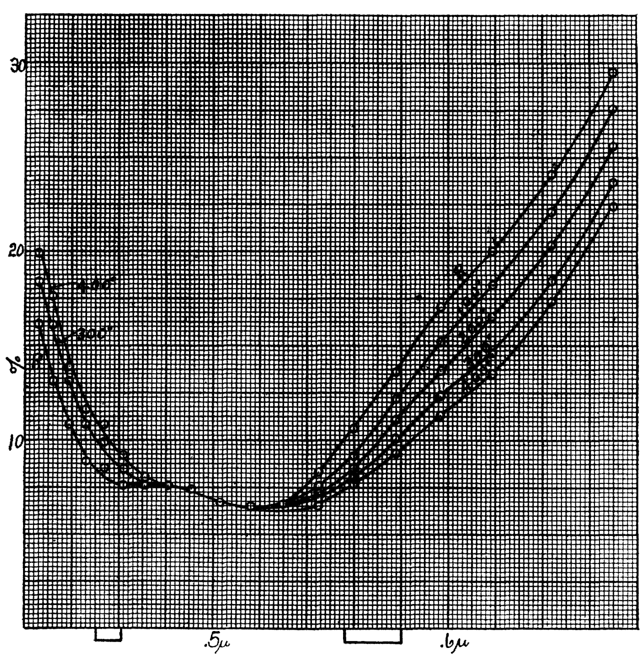

Fig. 34.

Showing percentage transmission of purple glass at various temperatures Thickness = .155 cm.

complete at .6μ, and on heating was very little affected in that region. The maximum for the transmission seems to have shifted slightly toward the longer wave-lengths with increasing temperature and, on the whole, the changes were very similar to those found in the case of the two green glasses. In Fig. 33 are shown the corresponding changes in the coefficient of absorption.

Purple Glass.

On heating the purple glass the transmission for the longer wave-lengths decreased, but increased for the shorter wave-lengths with the result that the absorption band was shifted toward the red.

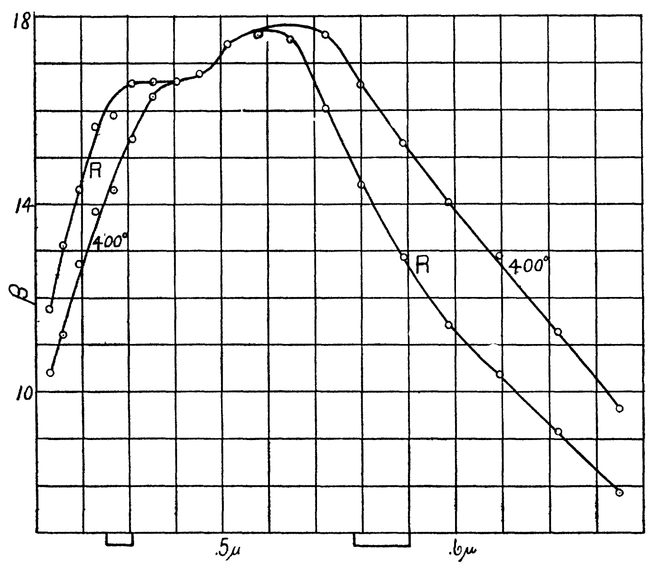

Fig. 35.

Showing coefficient of absorption of purple glass.

In the region of .5μ there was no measurable change. The corresponding changes in the coefficient of absorption are shown in Fig. 35.

Amber Glass.

The curves in Fig. 36 show a gradual increase in the absorption of amber glass with increasing temperatures. The change extends over the entire range of the spectrum measured, and indicates either a shift of the absorption band toward the red, or what is more likely a broadening of the band on that side. In Fig. 37 are shown the corresponding changes in the coefficient of absorption of amber glass.

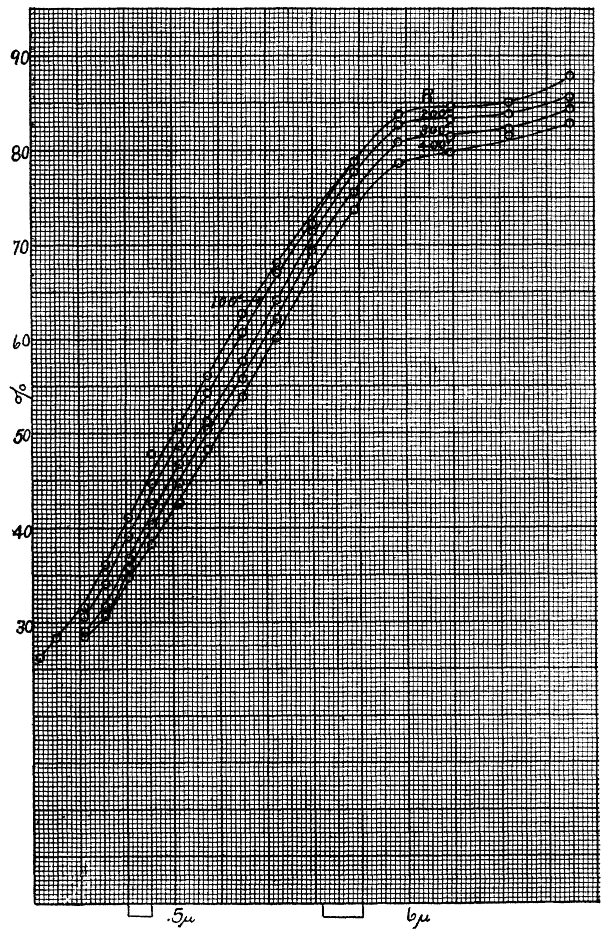

Fig. 36.

Showing percentage transmission of amber glass at various temperatures. Thickness = .155 cm.

URANIUM GLASS.

The curves in Fig. 38 are introduced merely to call attention to a peculiar surface effect which developed on heating and from the standpoint of changes in the internal absorption they have no meaning. The large changes in the transmission were very surprising

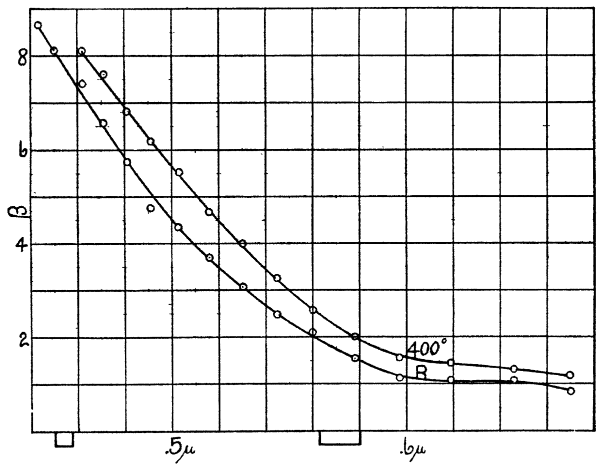

Fig. 37.

Showing coefficient of absorption of amber glass.

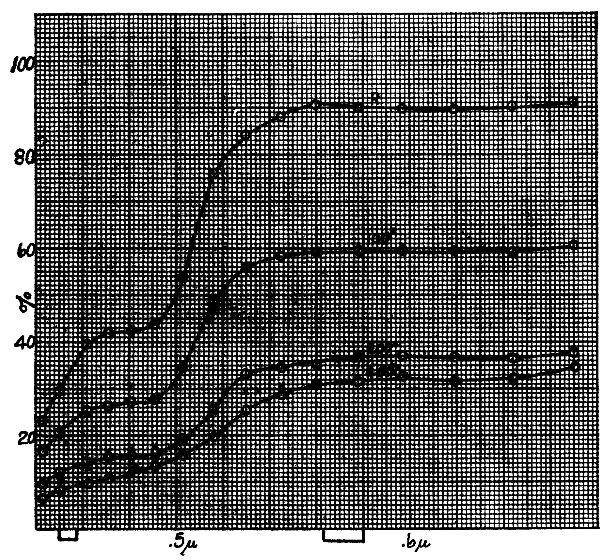

Fig. 38.

Showing percentage transmission of uranium glass at various temperatures with changing surface conditions. Thickness = 1.506 cm.

and, after cooling, another set of observations was made at room temperature, the results of which are indicated by crosses. On removing the specimen from the furnace, the entire surface of the glass was found to be covered with what appeared to be a white powder, but which in reality consisted of small flakes of the glass. These were easily rubbed off, leaving the surface not very unlike that of ground glass. Polishing showed that the effect was entirely a surface one. The exact cause of the flaking has not been determined. The curve marked out by the crosses indicates, in a rough way, that

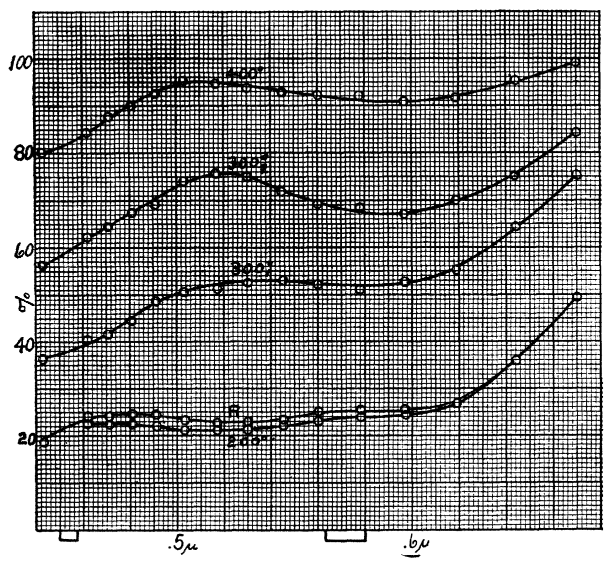

Fig. 39.

Showing percentage transmission of fluorite at various temperatures. Thickness = 1.322 cm.

the internal absorption was increased slightly by heating, although it is not absolutely certain that such is the case. This specimen showed the green flourescence so characteristic of uranium compounds.

FLUORITE.

A cube of fluorite showing purple fluorescence decreased its transmitting power up to about 200° C., and then suddenly began to become more transparent, as shown in Fig. 39. The curve marked

$300°_1$ is the result of observations made very soon after 300° had been reached, the observation being made through the spectrum from blue to red. A few observations were then repeated in the middle of the spectrum, but the settings did not agree at all with those previously made at the same wave-lengths. The transmission was increasing, although the temperature had been uniform for over an hour. Even then the rate of change was so large that one would hardly make a setting and record it before the fields in the telescope would show a contrast. The temperature was kept at 300° and this change watched. The rate of change slowly decreased, and at the end of an hour and a half the intensity had very nearly reached a constant value. Another set of observations was then made through the spectrum with the result shown in curve marked $300°_2$. The fact that the two 300° curves are closer together in the red than in the blue indicates that considerable change occurred while the first observations were being made. The settings for the 400° curve were begun about an hour after reaching that temperature, and at that time the transmission was practically constant. Having become almost perfectly transparent no great amount of further change could be expected. On cooling back to room temperature, the transmission remained practically the same as that shown for 400°. The cube then had been permanently changed from a muddy specimen to a clear one by heating to 400°. Viewing it directly with the eye, one would hardly recognize it as the same specimen. Another fluorite cube had been previously tried, but it broke, due to too rapid heating. The observations, however, had been carried far enough to show that its transmission was changing in a way very similar to the one here described.

Ruby Glass (Surface Film).

A piece of glass covered with a film on one side such that practically only the red of the spectrum is transmitted is called ruby glass. The film of glass no. 1 was thought to contain copper and that of no. 2 gold, and the two specimens may be designated as copper ruby glass and gold ruby glass. In Figs. 40 and 41 are shown the changes in transmission due to the heating of these specimens. The absorption for both specimens increases with rise of temperature and to about the same extent. On cooling back to room temperature, the intensity of transmission returned to its former values.

Amber Glass (Surface Film).

A piece of glass covered with a film of unknown composition, giving an amber colored transmission spectrum, was also studied at various temperatures with results as indicated in Fig. 42. The absorption, however, decreased on heating, a result which is in direct contrast with the behavior of the ruby specimens. On cooling

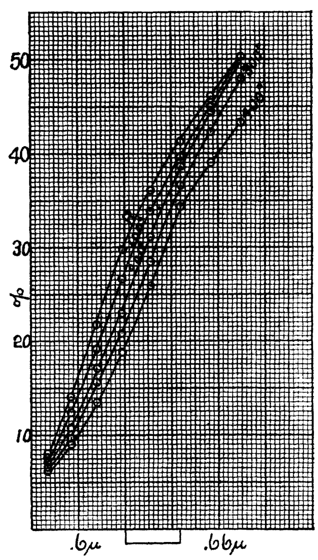

Fig. 40.

Showing the percentage transmission for ruby glass no 1 at various temperatures.

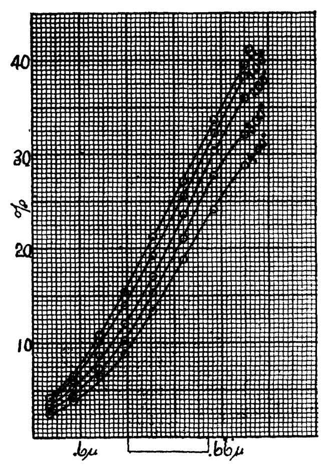

Fig. 41.

Showing the percentage transmission for ruby glass no. 2 at various temperatures.

back to room temperature, the absorption did not quite recover its previous value. A second heating showed again the same changes due to increasing the temperature, and on cooling, a more complete return to the previous room temperature curve.

Theoretical Considerations.

It is generally accepted that absorption of the kind here studied is due to either of two rather closely related though quite distinct phenomena or a combination of the two. Every substance may be regarded as made up of free electrons and molecules or atoms or groups of atoms with attached electrons, the attached electron together with its atom being commonly called an ion. The relative number of the free and attached electrons varies with the substance,

Fig. 42.

Showing percentage transmission of amber glass (surface film) at various temperatures.

and in all likelihood depends on the temperature. A good electrical conductor may be regarded as containing a large number of free electrons, while an insulator has relatively few of these electrons. The free electrons being very light are capable of being set into vibration by disturbances covering a rather wide range of frequencies, whereas the heavy ions can be caused to vibrate only when the conditions for resonance are secured.

The result of increasing the temperature may be and in most cases probably is, to increase the number of free electrons on account of the more violent vibrations of the molecules. But there may be other factors not as yet very well understood which would tend to decrease the number of free electrons on heating. In fact it is not at all improbable that these factors predominate in some substances, over certain ranges of temperature at least, and that in consequence some substances become more transparent as the temperature is raised.

The shifting of absorption bands to different wave-lengths as the result of heating may be accounted for by assuming that the groups of ions break up into simpler groups with slightly different natural periods of vibration. These simpler groups of ions may again combine forming still other groups. The natural frequency of the newly formed groups may be higher or lower than that of the original group, and the absorption band is accordingly shifted toward the shorter or longer wave-lengths.

Summary.

The essential results of these observations taken as a whole may be briefly stated as follows:

1. Heating sometimes increases the absorption and sometimes decreases it. Although the former may occur in the majority of cases, yet the existence of the latter has been amply proven.

2. The selective absorption bands are shifted by heating in some cases toward the longer wave-lengths but in others toward the shorter wave-lengths. The latter phenomena has not, to the knowledge of the writer, been noted by other investigators.

3. In the case of certain specimens a permanent change in the absorption has been found.

The writer hopes to investigate in the near future the effect of low temperatures on the absorption of these same specimens.

The author wishes to acknowledge the many helpful suggestions made by Professors Nichols and Merritt in connection with the investigations here described.

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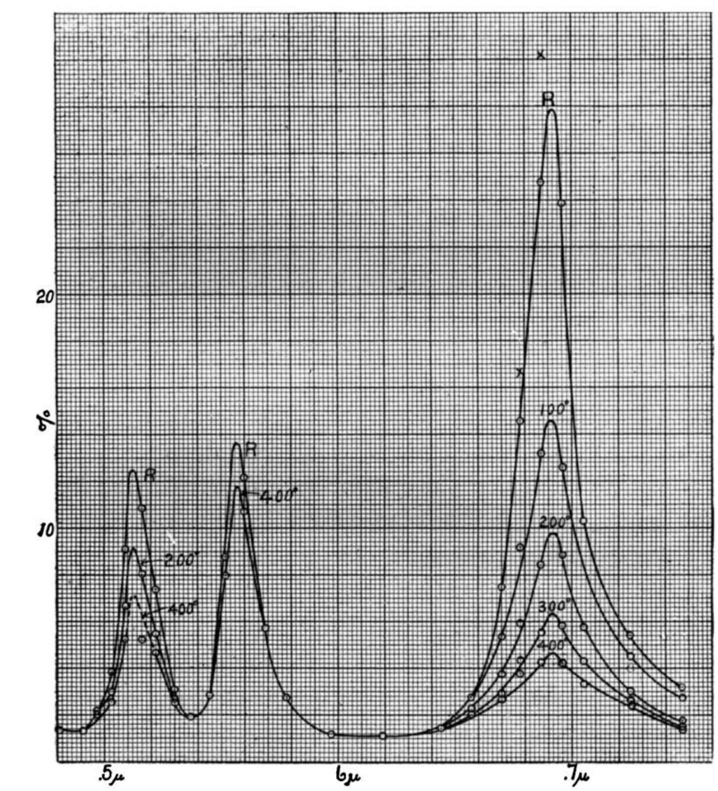

Fig. 18.

Showing the percentage transmission of erbium glass at various temperatures. Thickness = 1.451 cm.

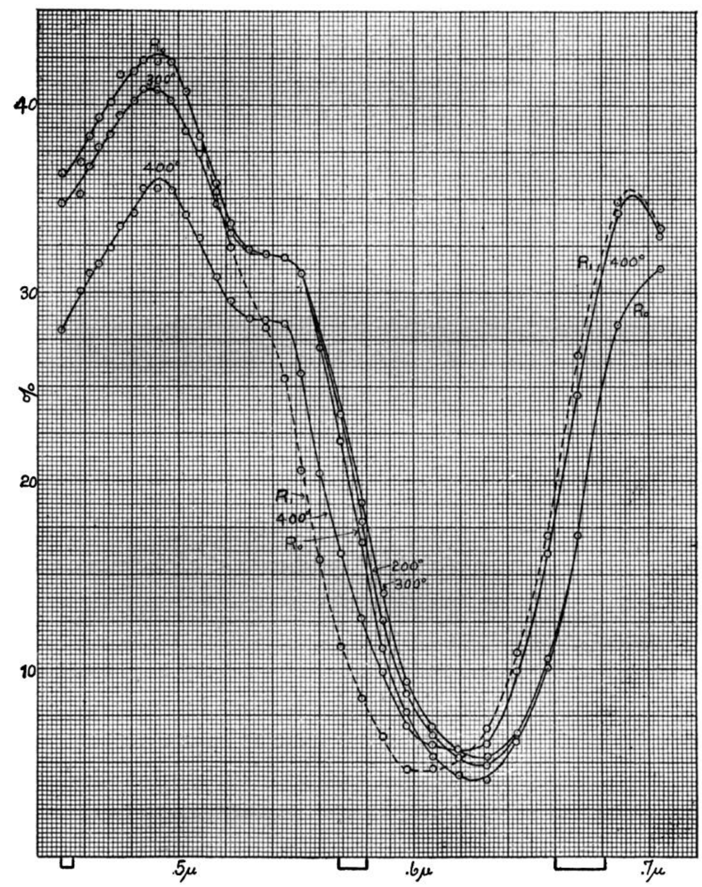

Fig. 20.

Showing the percentage transmission at various temperatures of sapphirin glass on first heating. R_0 = room temperature before heating. R_1 = room temperature after heating. Thickness = 1.344 cm.

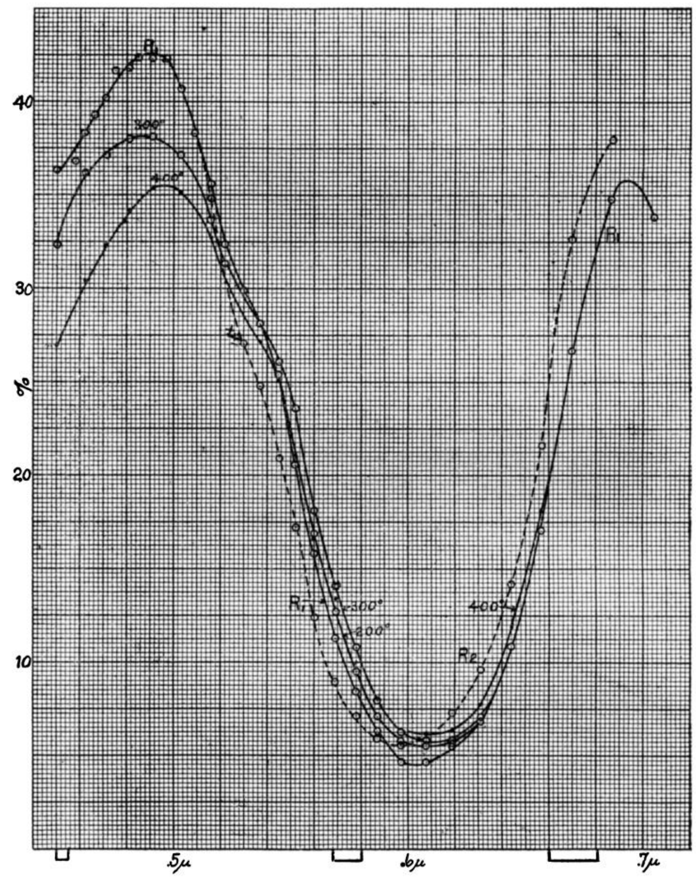

Fig. 21.

Showing percentage transmission of sapphirin glass at various temperatures on second heating. R_1 = room temperature before second heating. R_2 = room temperature after second heating.

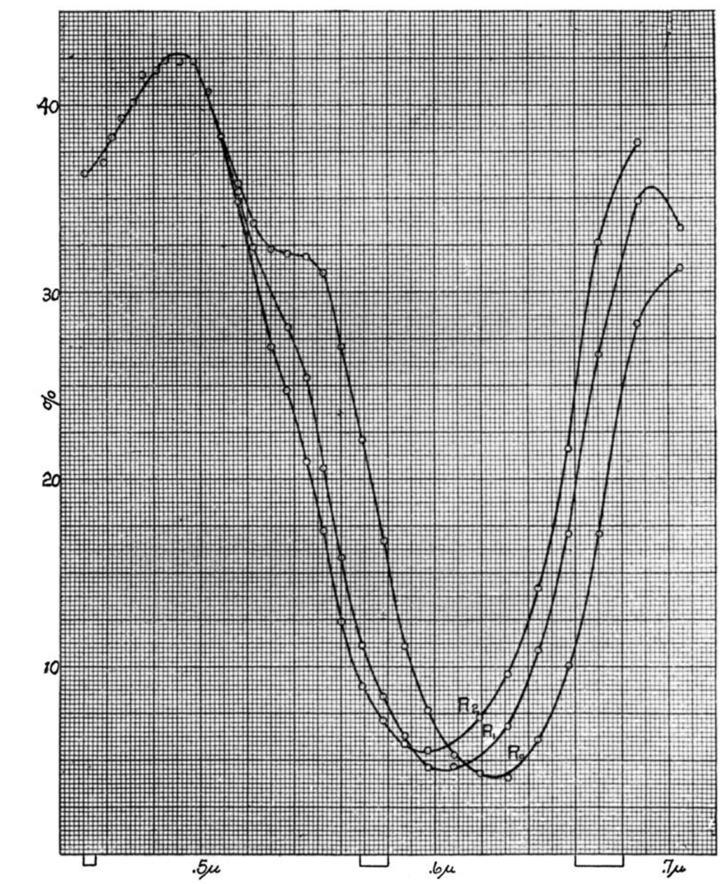

Fig. 22.

Showing percentage transmission of sapphirin glass at room temperature at three different times. R_0 = room temperature before heating. R_2 = room temperature after first heating. R_2 = room temperature after second heating.

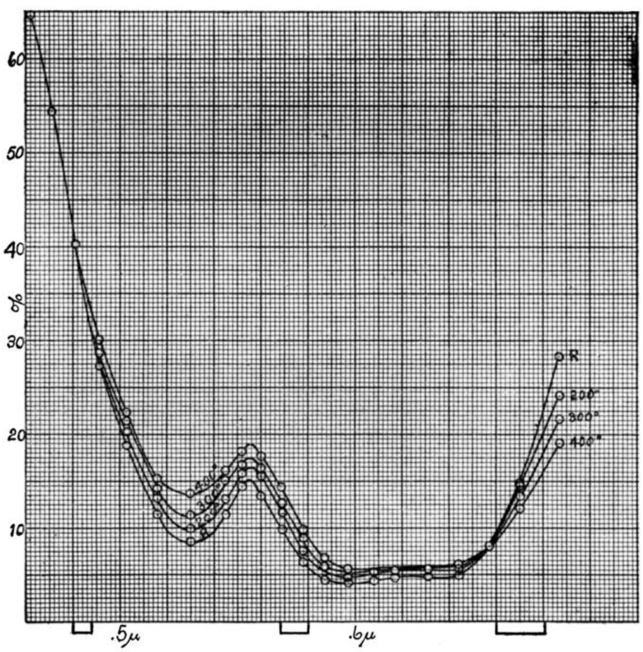

Fig. 24.

Showing percentage transmission of cobalt glass no. 1. Thickness .181 cm.

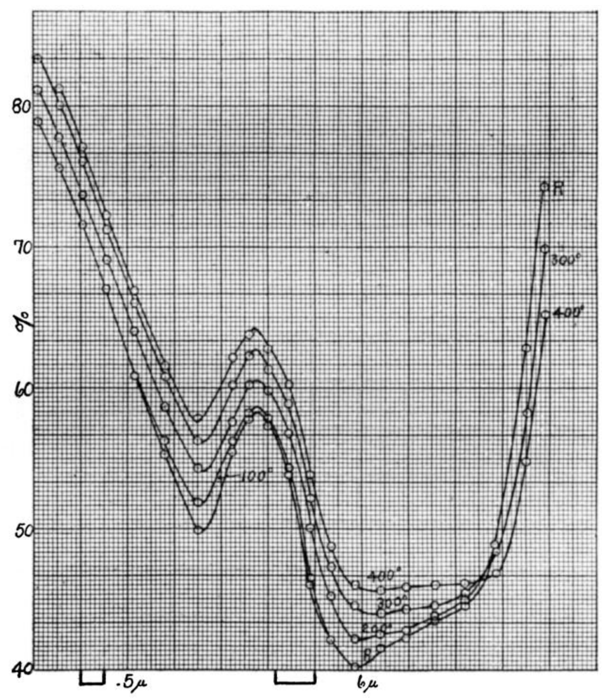

Fig. 26.

Showing the percentage transmission of cobalt glass no. 2 at various temperatures. Thickness = .206 cm.

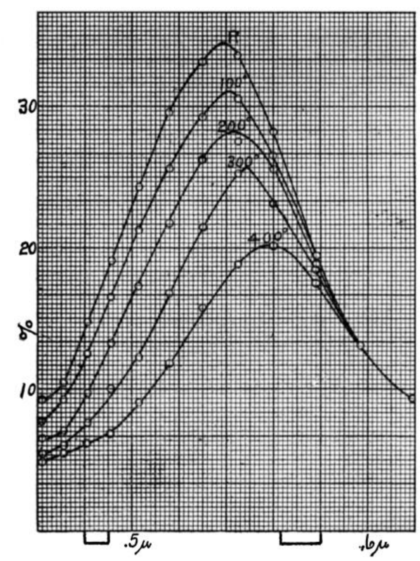

Fig. 28.

Showing the percentage transmission of green glass no. 1 at various temperatures Thickness = .208 cm.

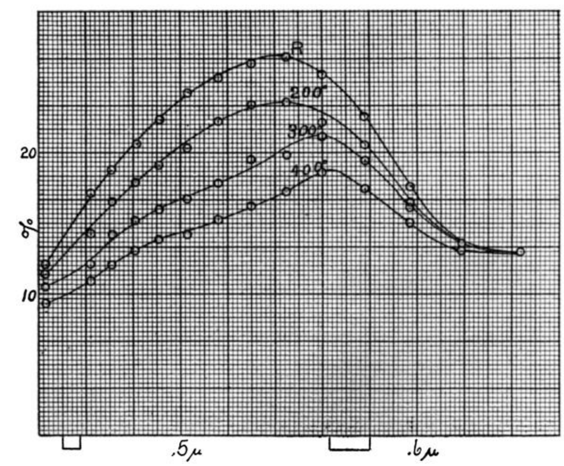

Fig. 30.

Showing percentage transmission of green glass no. 2 at various temperatures. Thickness = .186 cm.

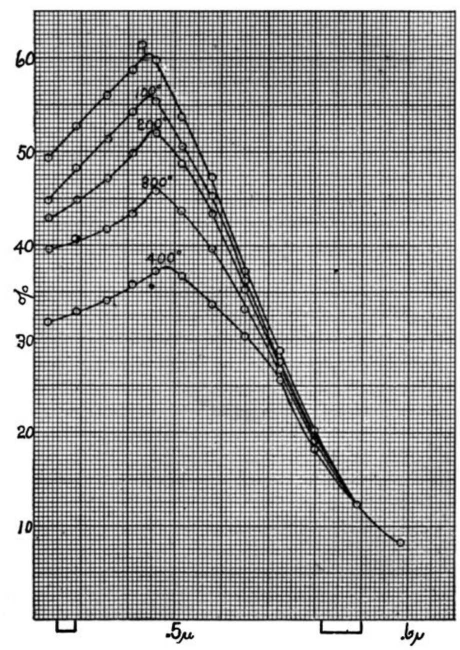

Fig. 32.

Showing percentage transmission of blue glass at various temperatures. Thickness = 226 cm

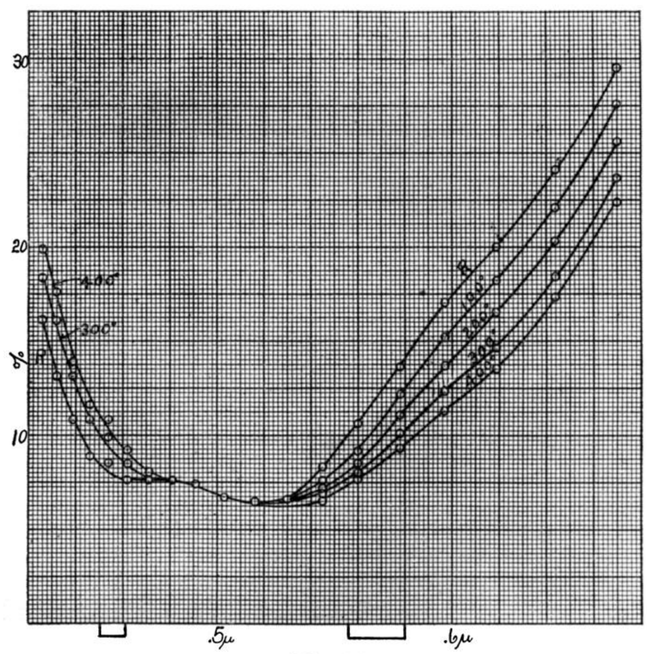

Fig. 34.

Showing percentage transmission of purple glass at various temperatures Thickness = .155 cm.

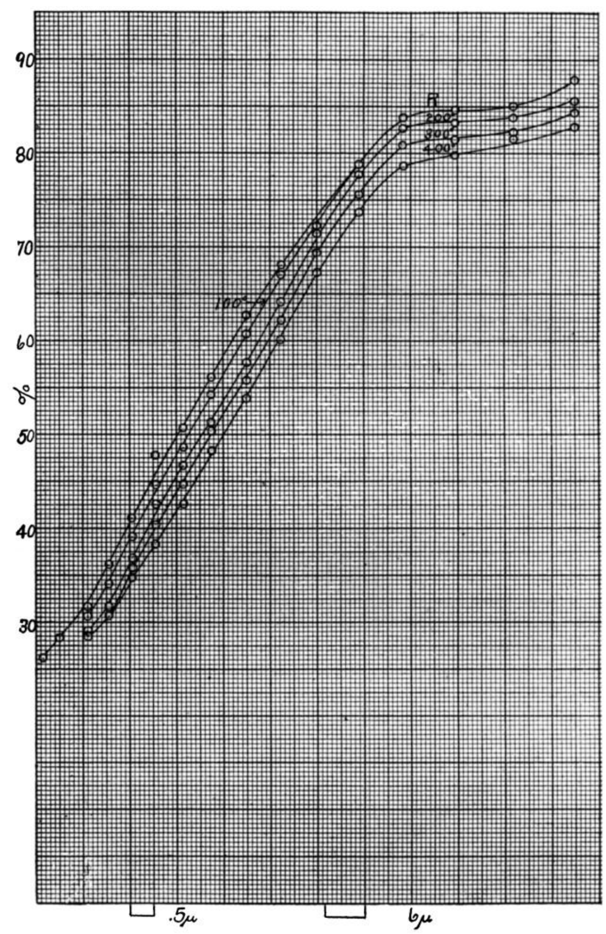

Fig. 36.

Showing percentage transmission of amber glass at various temperatures. Thickness = .155 cm.

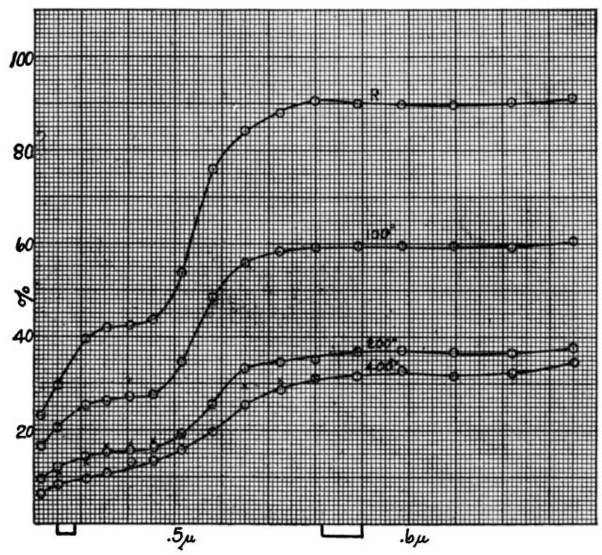

Fig. 38.

Showing percentage transmission of uranium glass at various temperatures with changing surface conditions. Thickness = 1.506 cm.

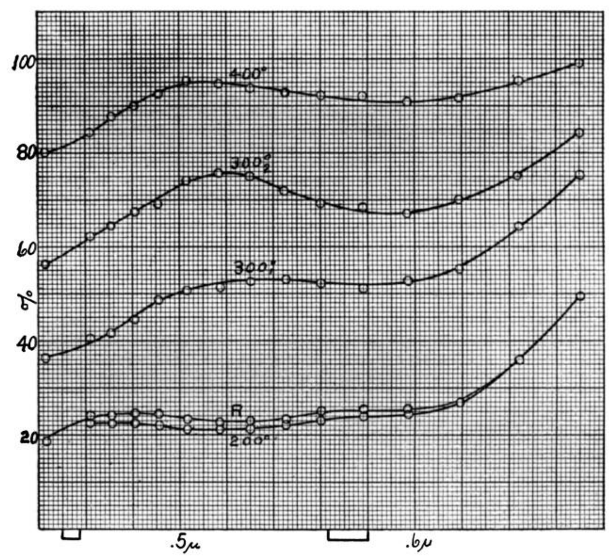

Fig. 39.

Showing percentage transmission of fluorite at various temperatures. Thickness = 1.322 cm.

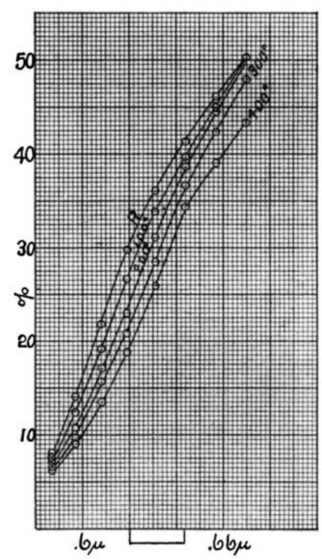

Fig. 40.

Showing the percentage transmission for ruby glass no. I at various temperatures.

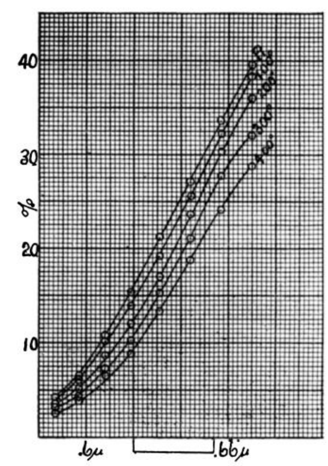

Fig. 41.

Showing the percentage transmission for ruby glass no. 2 at various temperatures.

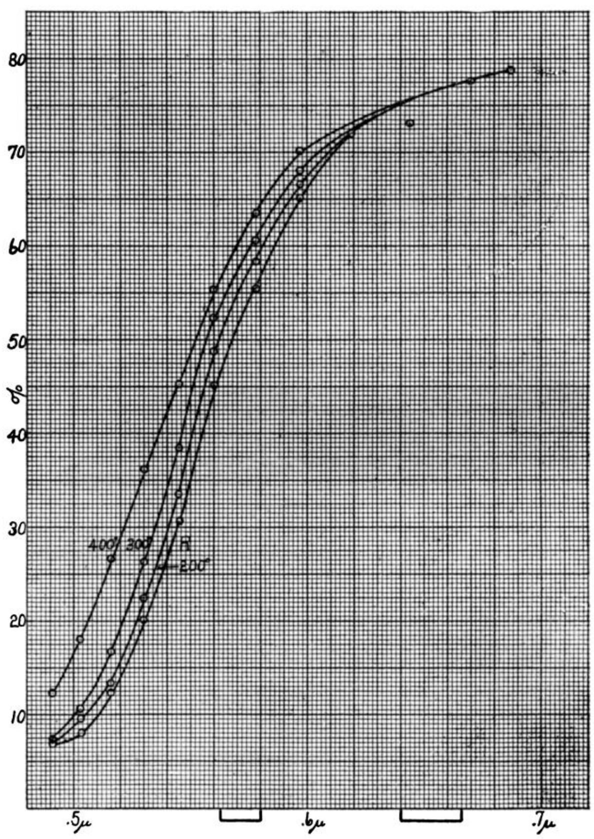

Fig. 42.

Showing percentage transmission of amber glass (surface film) at various temperatures.