

THE  
PHYSICAL REVIEW.

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A STUDY OF THE TRANSMISSION SPECTRA OF  
CERTAIN SUBSTANCES IN THE INFRA-RED.

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WITHIN a few years the study of obscure radiation has been greatly advanced by systematic inquiry into the laws of dispersion of the infra-red rays by Langley,<sup>1</sup> Rubens,<sup>2</sup> Rubens and Snow,<sup>3</sup> and others. Along with this advancement has come the more extended study of absorption in this region. The absorption of atmospheric gases has been studied by Langley<sup>1</sup> and by Ångström.<sup>4</sup> Ångström<sup>5</sup> has made a study of the absorption of certain vapors in relation to the absorption of the same substances in the liquid state, and the absorption of a number of liquids and solids has been investigated by Rubens.<sup>6</sup>

In the present investigation, the object of which was to extend this line of research, the substances studied were: plate glass, hard rubber, quartz, lamp-black, cobalt glass, alcohol, chlorophyll, water, oxyhæmoglobin, potassium alum, ammonium alum, and ammonium-iron alum.

<sup>1</sup> Report on Mt. Whitney Expedition, Profess. Papers, U. S. Signal Service, XV.

<sup>2</sup> Annalen der Physik und Chemie, N. F. XLV., p. 238.

<sup>3</sup> Annalen der Physik und Chemie, N. F. XLVI., p. 529.

<sup>4</sup> Bihang till K. Svenska Vet.-Akad. Handlingar, Band 15, Afd. 1, No. 9.

<sup>5</sup> Ofversigt af Kongl. Vetenskaps-Academiens Forhandlingar, 1890, No. 7, Stockholm.

<sup>6</sup> Annalen der Physik und Chemie, N. F. XLV., p. 258.

*Apparatus Used.*

The galvanometer used was similar in many respects to the instrument described by B. W. Snow,<sup>1</sup> though designed and built independently and used several months before the description referred to appeared. The aggregate weight of the moving parts of the galvanometer was 48 mgs. Throughout the work the four coils were connected in multiple with a resistance of 9.3 ohms. The sensitiveness was varied from time to time for convenience, but for the measurement of energy in the weaker parts of the spectrum deflections corresponding to currents of  $10^{-10}$  ampère were read.

In circuit with the galvanometer was a thermopile, made up of ten bismuth-antimony junctions arranged in a line 15 mm. long, the line being filed until the exposed surface was less than a milli-

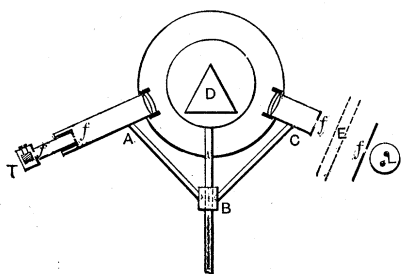


Fig. 1.

meter in width. The arrangement of the entire apparatus for the study of the infra-red spectrum is given in Fig. 1. The whole is a modified spectrometer. *L* is a fifty-volt Edison incandescent lamp, the spectrum of which was used as a basis for determining the transmission of the various substances; *f*'s are diaphragms, *D* the prism, *ABC* a device for automatically maintaining minimum deviation, *E* a track on which layers of the substances under examination could be passed between the lamp and the first lens, and *T* is the thermopile, interchangeable with the cross-wires of the eyepiece of the observing telescope. The apparatus was arranged in two rooms; the lamp *L* and the track *E* in one, and the remaining parts of the spectrometer in the other. A small hole in the partition, which could be closed at will by means of a shutter, served to connect the two rooms. The room containing the thermopile and prism

<sup>1</sup> Annalen der Physik und Chemie, N. F. XLVII., p. 213.

was kept dark, and all draughts excluded. It was entered only once or twice a day to change the spectrometer setting. The glass lenses of the spectrometer were retained. It is easily seen that their absorption could not enter as an error in the present investigation; for if the energy of the lamp at any wave-length be taken as unity, and the lamp be allowed to shine on the thermopile so that it receives this wave-length only, with nothing between but a system of plates transmitting a percentage  $a$  of the energy they receive, the galvanometer deflection will then be proportional to  $a$  or  $ka$ . If now another body, which transmits a percentage  $b$  of the energy received by it, be placed between the lamp and the plates, then the energy which reaches the thermopile will be  $ab$ , and the galvanometer deflection  $kab$ . The ratio of the second deflection to the first is  $b$ , the percentage of transmission of the body in question.

A carbon bisulphide prism served for dispersion; that substance was selected because it is known that carbon bisulphide at a temperature of fifteen degrees follows the well-known Cauchy formula for dispersion:  $N = a + \frac{\beta}{\lambda^2}$  where  $N$  is the refractive index and  $\lambda$  the corresponding wave-length.

Rubens<sup>1</sup> has investigated experimentally the law of dispersion of bisulphide of carbon out to wave-length  $2\ \mu$ , and has found it to agree very closely with this law, and further, from the near agreement between the square root of the dielectric constant and the index of refraction for infinite wave-lengths computed from the Cauchy formula, it is probable that the dispersion follows Cauchy's law throughout the whole spectrum. The carbon bisulphide used in the present study was obtained by double distillation, and the variation of its indices of refraction with temperature was carefully studied at various wave-lengths. The results were found to agree very closely with similar results obtained by Wüllner.<sup>2</sup>

A comparison of the two is given in Table I.

<sup>1</sup> Annalen der Physik und Chemie, N. F. XLV., 1892, p. 256.

<sup>2</sup> Annalen der Physik und Chemie, Band CXXXIII., 1868, p. 16.

TABLE I.

C. LINE.			F. LINE.		
Temperature.	Wüllner.	Nichols.	Temperature.	Wüllner.	Nichols.
18.2		1.6202	19.25		1.65335
18.25	1.6198		19.3	1.6530	
18.55	1.6196		19.42		1.6532
18.58		1.6198	19.6	1.6530	
18.6	1.6196		19.70	1.6529	
18.91		1.6197	19.76		1.6530
19.0	1.6193		20.18		1.6528
19.10	1.6192		20.25	1.6525	
19.14		1.6194	20.5	1.6522	
19.45	1.6189		20.54		1.6524
19.46		1.6192	21.08		1.6520
20.15	1.6183	1.6186	21.1	1.6517	
20.55	1.6181		25.27		1.6485
21.80		1.6181			
22.1	1.6169				
22.32		1.6170			
22.83		1.6166			
23.02		1.6164			
23.4	1.6159				
24.20		1.6156			
25.24		1.6147			
26.08		1.6142			

The temperature change in the indices of refraction is seen to be sufficiently large to make it necessary to correct all observations for temperature. The temperature coefficients of indices of refraction for the various Fraunhofer lines are given in Table II.

If  $N_t$  is the index of refraction for a wave-length  $\lambda$  at a temperature  $t^\circ$ , and  $a$  is the temperature coefficient for that wave-length, then the index of refraction  $N_{t'}$  for  $t'^\circ$  will be  $N_{t'} = N_t - a(t' - t)$ .

The temperature coefficients gradually diminished as the wave-length increased through the visible spectrum, and a similar decrease was assumed through the infra-red. In the temperature corrections made to observations,  $t' - t$  was never greater than  $3^\circ$ . The temperature taken for the standard to which all observations were reduced was  $23^\circ.5$ . The prism was calibrated by the

TABLE II.

	A		C		D	
	Range	$a$	Range	$a$	Range	$a$
Wüllner <sup>1</sup>			$t = 7^\circ$ $t' = 23^\circ$	.00078		
Nichols	$t = 20^\circ$ $t' = 25^\circ.4$	.000759	$t = 18^\circ.2$ $t' = 26^\circ$	.000763	$t = 19^\circ.8$ $t' = 26^\circ.1$	.000768
	F		G		LINE BEYOND G, N $23^\circ.5 = 1.6782$	
	Range	$a$	Range	$a$		
Wüllner	$t = 7^\circ$ $t' = 23^\circ$	.00082	$t = 7^\circ$ $t' = 23^\circ$	.00085		
Nichols	$t = 19^\circ.2$ $t' = 26^\circ.2$	.000805			$t = 21^\circ.2$ $t' = 26^\circ.2$	.000858

Fraunhofer lines, and the Cauchy constants computed. The equation to the calibration curve of the prism was  $N = 1.5772 + \frac{.01681}{\lambda^2}$ . The values  $a = 1.5772$  and  $\beta = .01681$  were obtained by observing the indices of refraction for the Fraunhofer lines  $b$ ,  $C$ ,  $B$ , and  $A$ , and substituting these indices in turn with their corresponding wavelengths into the general formula  $N = a + \frac{\beta}{\lambda^2}$ .

The indices of refraction observed and computed were:—

TABLE III.

	OBSERVED.	COMPUTED.
$b$ .	1.6398	1.6398
$C$ .	1.6156	1.6162
$B$ .	1.6123	1.6128
$A$ .	1.6063	1.6063

The prism on two angles of its base carried conical points. The point beneath the refracting angle fitted into a corresponding

<sup>1</sup> Annalen der Physik und Chemie, Band CXXXIII., 1868, p. 16.

pit; the other point into a groove in the table of the spectrometer. This device made it possible to take the prism off the spectrometer to allow a zero reading at any time, after which the prism could be accurately replaced. For calibration the ordinary spectrometer slit was used with an eye-piece cross-wire, but in the energy measurements, in order to get an intense source, a straight portion of the filament of the incandescent lamp was substituted for the slit, and the rest of the filament screened by diaphragms. To change from the slit to the filament, and from the cross-wire in the eye-piece to the thermopile, without disturbing the calibration, the spectrometer was set at zero reading, the eye-piece carefully focussed on the slit and the observing telescope clamped. The slit tube was then removed and the lamp filament put in the exact place where the slit had been, as determined by its image in the eye-piece. Then the eye-piece was taken out and a slit a millimeter wide was put in the plane of the cross-wires and moved from side to side until the image of the filament fell in the middle of the slit. The line of junctions of the thermopile was fitted accurately to this opening. After these changes the prism could be replaced on the spectrometer, the telescope carrying the thermopile could be unclamped, and by means of the calibration curve the thermopile could be set to receive radiations of any desired wave-length.

The width of the line of thermo-junctions in angular measure was  $10'$ . Because of this width and the increasing condensation of rays by the prism as the wave-length increased, measurements beyond  $\lambda = 2.46$  were of little value. The wave-lengths given in the tables correspond to the wave-lengths received by a line through the middle of the face of the thermopile.

#### *Method of Observation.*

Before beginning a set of readings, the galvanometer circuit was closed once for all. When the galvanometer needle was quiet, the shutter between the lamp and prism was opened, and the lamp allowed to shine on the thermopile until the needle had reached the end of its first swing: the shutter was then closed and the

return swing observed. The mean of the reading from which the needle started and the reading to which it returned was taken as the zero reading. Any uniform change in the zero point of the galvanometer during the ten or twelve seconds required to get the two swings was thus eliminated.

The percentage of energy of a given wave-length transmitted by any one of the substances was estimated as follows: 1st, The energy of the bare lamp was measured. 2d, The lamp energy transmitted through the substance. 3d, The energy of the bare lamp again. The ratio of the second reading to the mean of the first and third was taken as a transmission percentage. The use of the mean of the first and third for the lamp reading obviates the error which might otherwise enter from a uniform change in the constant of the galvanometer. Since the glow lamp was fed from a storage battery, the source of radiant energy was very nearly constant. From three to five determinations of this transmission percentage were made for each of the substances at all observed points. The mean of these readings is in each case the transmission percentage given in the tables. The probable error in the transmission percentages in no case exceeds  $\pm 4\%$ , and in most cases is less than  $\pm 1\%$ .

#### *The Results.*

Table IV. contains the transmission percentages in the infra-red spectra of a piece of French plate glass 8.3 mm. thick, and of a sheet of black hard rubber .2 mm. thick. The transmission spectra of these two substances were examined at nine different points and the corresponding wave-lengths are given in  $10^{-6}$  meters at the heads of the columns.

TABLE IV.

$\lambda$	0 <sup>u</sup> .775	.862	.940	1.19	1.41	1.58	1.85	2.37	2.90
Plate glass . . .	82.4	76.9	77.5	71.7	83.7	82.1	82.5	75.1	76.7
Hard rubber . .	30.7	54.1	58.9	65.0	58.4	58.9	58.1	52.0	56.6

The results in this table are shown graphically in Fig. 2, in which wave-lengths are plotted as abscissæ, and the corresponding percentages of transmission as ordinates. The parallelism of the curves beyond  $\lambda=0^{\mu}.862$  seems to show that if the rubber

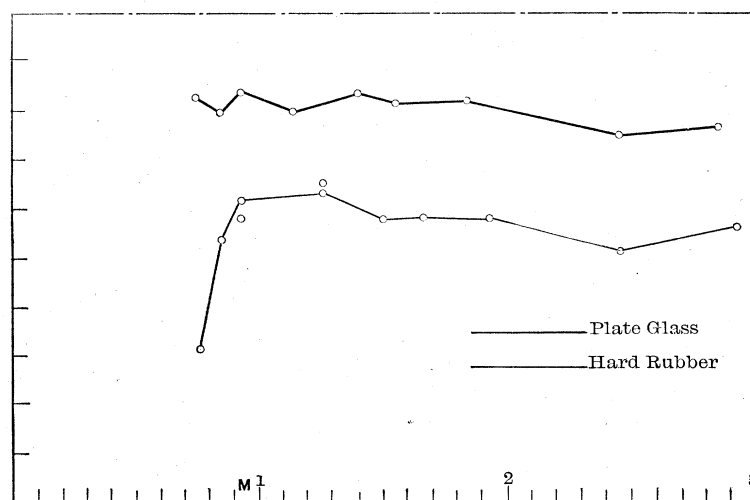


Fig. 2.

had been thinner or the glass thicker, the two spectra beyond this point might have been identical within the limits of probable error.

Figure 3 shows the same results in a slightly different way. The upper curve in this figure shows the distribution of energy in the normal spectrum of the glow-lamp used.<sup>1</sup> Wave-lengths are plotted as abscissæ, and corresponding intensities of radiant energy as ordinates. The distribution of energy in the prismatic spectrum was obtained by the same apparatus as that used in getting the transmission percentages, consequently the radiant energy before reaching the thermopile passed through two glass lenses, the glass sides of the prism, and the bisulphide of carbon. Because of the lack of selective absorption in glass in this region of the spectrum and the almost perfect diathermancy of carbon bisulphide

<sup>1</sup> Obtained by a method to be described in an article on Distribution of Energy in the Spectrum of the Glow-Lamp, by Dr. E. L. Nichols.



(Rubens,<sup>1</sup> Knut Ångström<sup>2</sup>), the only effect of this transmission is that all the ordinates of the curve in Fig. 3 are less than the true values by a constant percentage.

The distribution of energy in the normal spectrum is obtained from the distribution in the prismatic spectrum by correcting for the increasing condensation of rays in the direction of the longer wave-lengths.<sup>3</sup>

The ordinates of the middle curve are obtained by taking the product of the transmission percentage of glass for each wave-

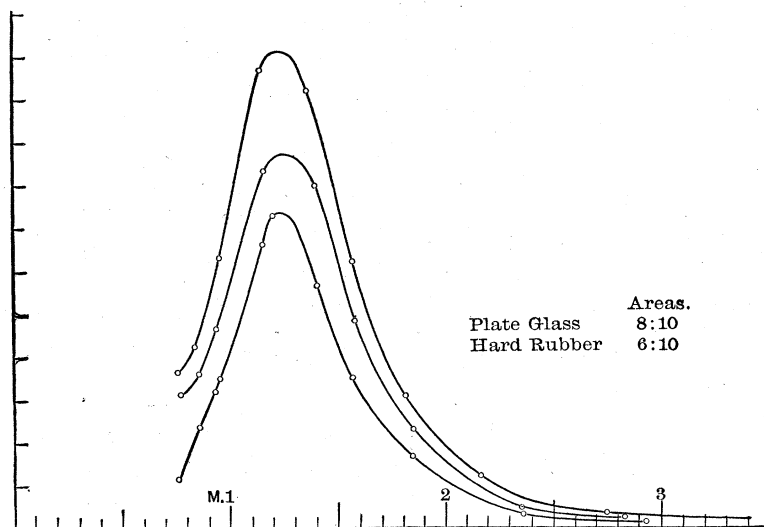


Fig. 3.

length and the ordinate of the energy curve of the lamp at that wave-length. The lower curve shows the distribution of energy in the transmission spectrum of hard rubber. From the way in which these curves are plotted the total infra-red energy transmitted by the substances varies as the areas included between the curves and the base line. In the case of glass and hard rubber the percentages of transmission for the different wave-lengths observed

<sup>1</sup> *Annalen der Physik und Chemie*, N. F. XLV., p. 260.

<sup>2</sup> *Ofversigt af Kongl. Vetenskaps-Academiens Forhandlingar*, 1892, No. 7, Stockholm, p. 345.

<sup>3</sup> *Report on Mt. Whitney Expedition*, p. 231; also Draper, *American Journal of Science*, 1872.

were so nearly constant that the observed points on the diagram were connected by a curve similar to the energy curve of the source.

Table V. contains the transmission percentages for quartz and lamp-black.

TABLE V.

$\lambda$	.778	.971	1.14	1.33	1.55	1.78	2.14
Quartz . . . . .	81.2	88.7	90.0	91.9	90.9	92.8	94.5
Lamp-black . .	Too small to measure.	Too small to measure.	Too small to measure.	01.5	02.5	01.5	01.0

The quartz was an unusually clear plate of rock crystal 6.8 mm. thick, cut perpendicular to the optical axis of the crystal. The lamp-black was a deposit formed by smoking a plate of the glass described in Table IV. In this way a known medium was intro-

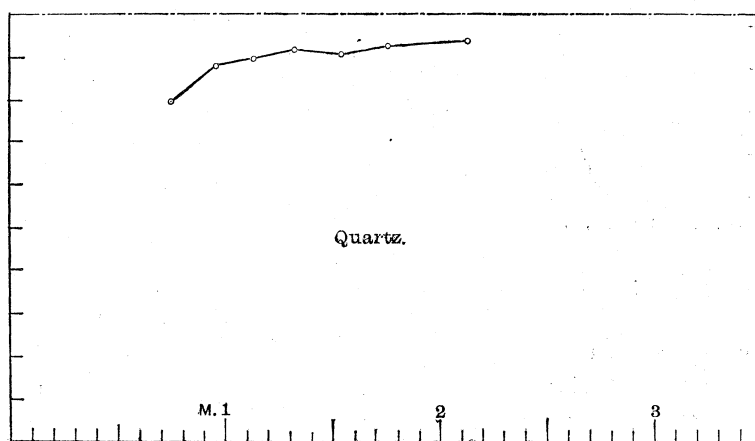


Fig. 4.

duced as a carrier for the smoke film. The film was thickened until a square centimeter of area was obtained. It was uniform and just heavy enough so that the outline of the filament of a glow-lamp at normal candle power was barely visible through it, when the lamp was held 30 cm. away from the eye in a dark room.

Figures 4 and 5 show these results plotted according to the conventions explained for Figs. 2 and 3. It will be noticed that the diathermancy of quartz increases with the wave-length as far,

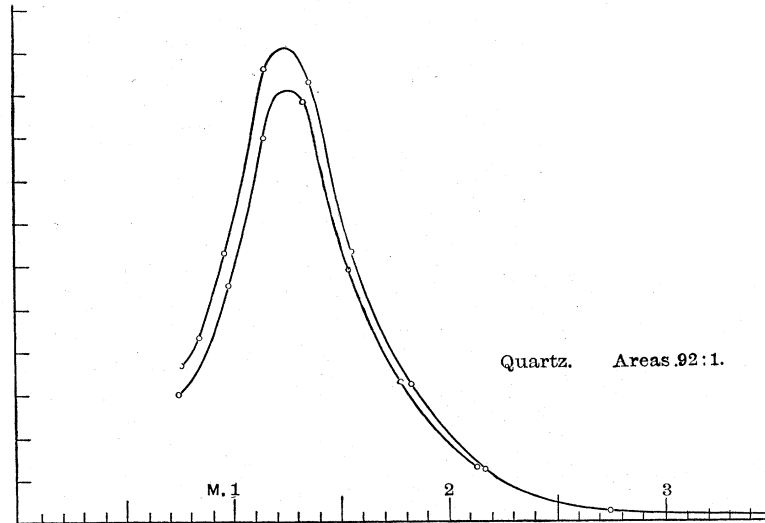


Fig. 5.

at least, as  $\lambda = 2^{\mu}.14$ . The results for lamp-black are not shown graphically.

Table VI. gives similar results for cobalt glass.

TABLE VI.

$\lambda$	.775	.862	.940	1.19	1.41	1.58	1.86	2.37	2.86
Cobalt glass . . .	79.6	80.1	66.7	20.0	20.7	22.6	45.7	55.4	52.9

The plate was 2.8 mm. thick. In the visible spectrum cobalt glass shows a number of absorption bands, and Table VI. shows the presence of a deep band in the infra-red beginning at  $\lambda = 0^{\mu}.862$ . At  $\lambda = 1^{\mu}.86$  the diathermancy has increased somewhat from the lowest values, but it does not, within the region studied, reach its former value again. Figures 6 and 7 show the results for cobalt glass graphically.

Table VII. shows the transmission percentages for absolute alcohol and a solution of chlorophyll in alcohol. These percentages are for layers of alcohol and chlorophyll solution 1 cm. thick,

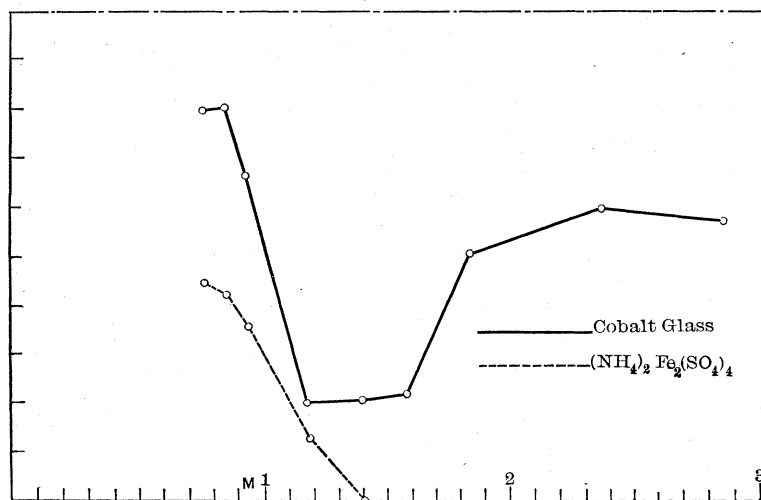


Fig. 6.

contained in a flat cell with thin glass walls. The percentages are computed on the basis of energy transmitted through glass sides and all. The same cell was used for both solutions, so the results are comparable.

TABLE VII.

$\lambda$	.776	.863	.941	1.19	1.41	1.58	1.85	2.32	2.83
Alcohol ( $C_2H_6O$ )	75.9	77.3	75.8	40.2	01.8	01.5	too small to measure	too small to measure	too small to measure
Chlorophyll . . .	66.1	77.1	70.3	32.1	01.9	too small to measure	"	"	"

At  $\lambda = 0.863$  and  $\lambda = 1.41$  the solutions were equal in absorbing power. The transmission spectra for both liquids came to an end near  $\lambda = 1.4$ . These results are shown graphically in Figs. 8 and 9.

Table VIII. contains the transmission percentage for the empty cell; for water; for a solution of oxyhæmoglobin, made up of 5 cc. cat's blood and 2cc. chloral in a liter of water; for a solution

of commercial potassium aluminium sulphate in water, saturated at  $0^{\circ}$ ; and for a solution of commercial ammonium aluminium sulphate in water, saturated at  $0^{\circ}$ . Centimeter layers of all these

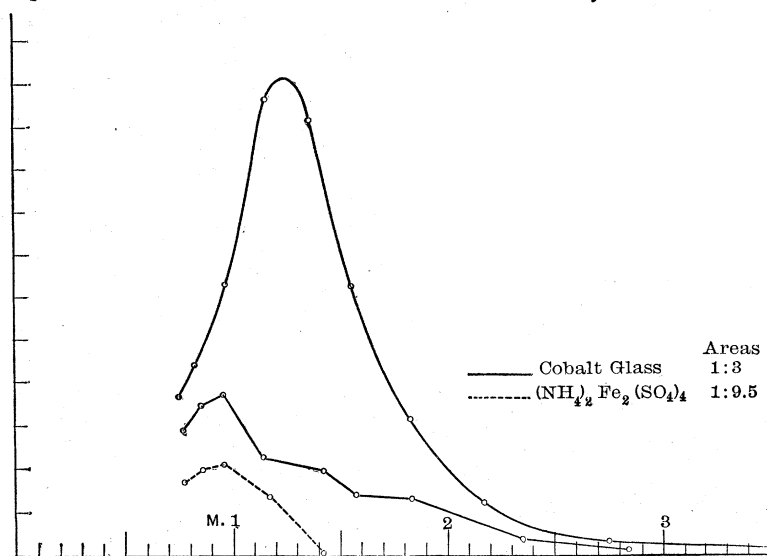


Fig. 7.

solutions were examined in the same cell, which was similar in every respect to the one used for alcohol and chlorophyll. These results are shown in Figs. 10 and 11.

TABLE VIII.

$\lambda$	.779	.865	.945	1.19	1.41	1.59	1.89	2.29	2.82
Empty cell . . . .		72.	73.	73.					
Water . . . . .	76.2	74.4	58.4	14.4	too small to measure	too small to measure	too small to measure	too small to measure	too small to measure
Blood . . . . .	68.9	74.7	55.6	16.0	"	"	"	"	"
$K_2Al_2(SO_4)_4$ . . .	73.6	72.2	51.3	16.2	"	"	"	"	"
$(NH_4)_2Al_2(SO_4)_4$	73.8	76.2	54.8	14.7	"	"	"	"	"

For  $\lambda=0.865$  the transmission of the empty cell is seen to be a trifle less than that of the cell filled with the several solutions. This is not an impossible relation, because the reflection from the inner surfaces of the cell is cut down considerably when the cell is

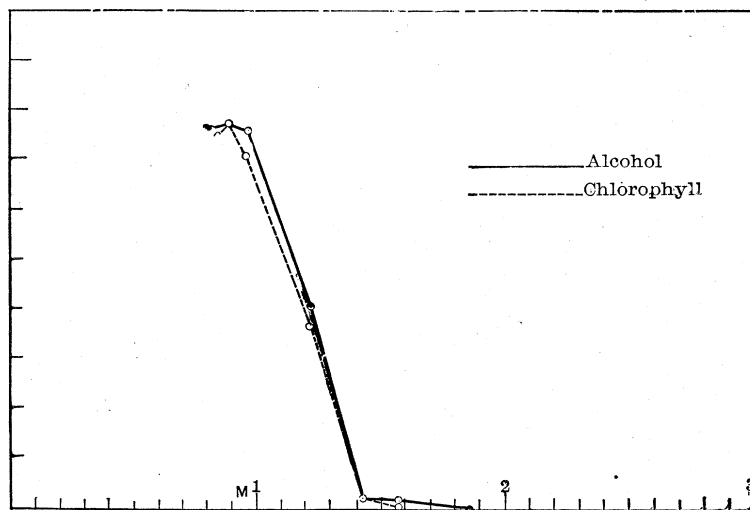


Fig. 8.

filled with the solutions, and the solutions were found highly diathermous at this point. The transmission spectra of these three solutions look very much like the spectrum of pure water. This seems to show that in alum solutions, commonly used to cut out dark heat, the alum is inactive. Whether alum in solution absorbs more radiant heat than distilled water has been questioned before, and H. N. Draper asks in "Nature,"<sup>1</sup> "Why use alum dissolved in water instead of water alone, to cut off obscure radiation?" In the next issue of that periodical he is answered on *a priori* grounds by Ch. Ed. Guillaume, that solid alum in its absorption occupies nearly the same place in the scale of solids that water does among liquids; consequently, if there be any difference in the selective absorption of the two substances, the alum solution will naturally be expected to cut out more radiation than the water alone.

<sup>1</sup> Vol. 44, p. 446.

Melloni,<sup>1</sup> using an Argand lamp with a glass chimney as a source, found that a layer of alum solution 9.21 mm. thick trans-

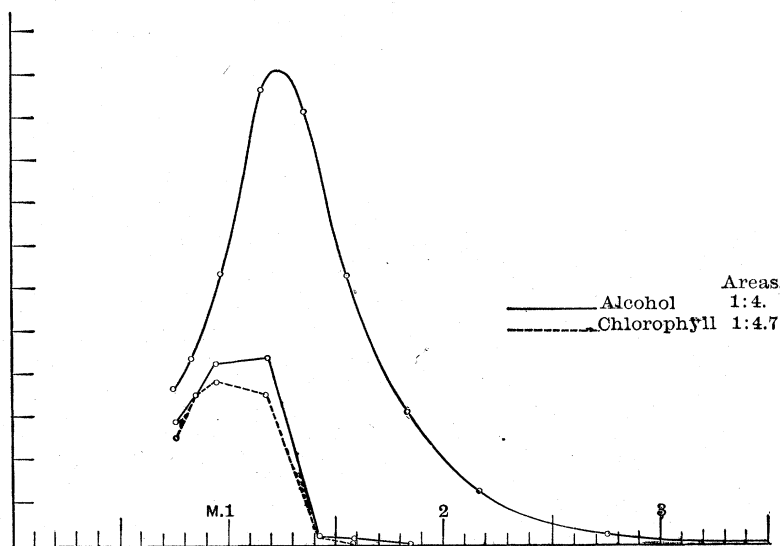


Fig. 9.

mitted 12% of the total incident radiation, and that distilled water under like circumstances transmitted only 11%.

Shelford Bidwell,<sup>2</sup> using a paraffine lamp as a light source and the thermopile, obtained the following results:—

SOLUTIONS.	DIATHERMANCY.
Empty cell . . . . .	1000
Water, distilled . . . . .	197
Tap water . . . . .	200
Alum, saturated solution . . . . .	204

F. C. Porter,<sup>3</sup> using the electric arc at 40 volts and 6.4 ampères, as a source and the Crooks radiometer, reached the following results:—

<sup>1</sup> Thermochrose, p. 165.

<sup>2</sup> Nature, Vol. 44, p. 565.

<sup>3</sup> Nature, Vol. 45, p. 29.

	No. of revolutions of radiometer arms.	Time in half-seconds.
1. Unimpeded radiation . . . . .	25	160
2. Through empty cell . . . . .	25	254
3. Unimpeded radiation . . . . .	25	152
4. Cell + water . . . . .	25	820
5. Unimpeded radiation . . . . .	25	164
6. Cell + water (second experiment) . .	25	832
7. Unimpeded radiation . . . . .	25	160
8. Cell + alum solution . . . . .	25	43,200
	(time of two revolutions actually taken)	
9. Unimpeded radiation . . . . .	25	160

The spectra of all these solutions stopped before wave-length  $\mu.41$  was reached. It was thought that possibly the quantity of alum in a centimeter layer of the solutions was not enough to pro-

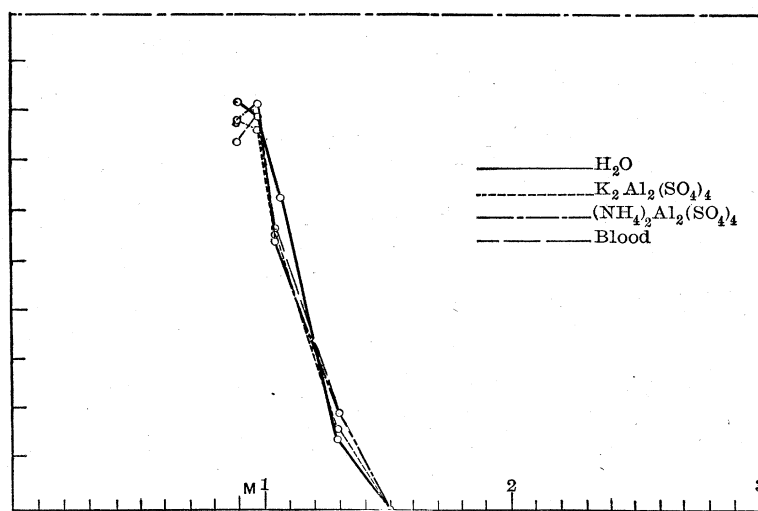


Fig. 10.

duce a noticeable effect ; consequently layers two centimeters thick were examined under like circumstances. The results appear in Table IX.



TABLE IX.

$\lambda$	.779	.865	.945	1.19	1.41	1.59	1.89	2.29	2.82
Water . . . .	77.1	71.7	44.2	03.7	too small to measure	too small to measure	too small to measure	too small to measure	too small to measure
Blood . . . .	72.0	68.4	42.3	05.1	"	"	"	"	"
$K_2Al_2(SO_4)_4$ . .	74.1	69.5	39.5	03.9	"	"	"	"	"
$(NH_4)_2Al_2(SO_4)_4$	75.8	69.6	42.6	05.4	"	"	"	"	"

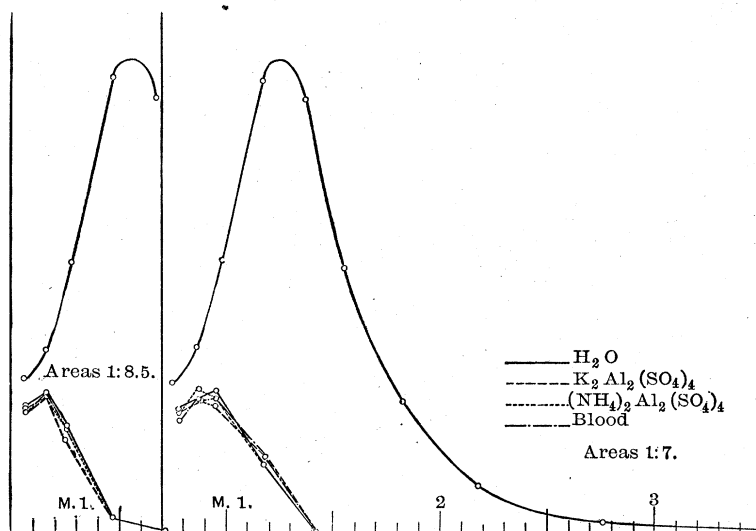


Fig. 11.

Table X. gives the transmission percentages for a centimeter layer of water solution of commercial ammonium-iron alum saturated at 0°. The cell was the one used for the other alum solutions.

TABLE X.

$\lambda$	.777	.863	.943	1.19	1.41	1.58	1.88	2.30	2.80
$(NH_4)_2Fe_2(SO_4)_4$	45.0	42.9	35.5	12.5	too small to measure	too small to measure	too small to measure	too small to measure	too small to measure

The contents of this table are shown graphically in Figs. 6 and 7.

*Summary of Results.*

1. The diathermancy of plate glass is fairly uniform through the infra-red down to  $\lambda=3$ . The highest and lowest percentages of transmission are 82 and 72.

2. The diathermancy of hard rubber rises very rapidly just beyond the limits of the visible spectrum reaching the percentage 59 of transmission at  $\lambda=0^{\mu}.940$ . It does not rise above 65% nor fall below 52% between  $\lambda=0^{\mu}.940$  and  $\lambda=3^{\mu}$ .

3. The diathermancy of quartz increases with the wave-length from the limit of the visible spectrum to  $\lambda=3^{\mu}$ .

4. Lamp-black absorbs almost non-selectively throughout the region studied.

5. Cobalt glass has a wide absorption band between  $\lambda=0^{\mu}.862$  and  $\lambda=1^{\mu}.85$ .

6. The diathermancy of alcohol is nearly constant between  $\lambda=0^{\mu}.776$  and  $\lambda=0^{\mu}.941$ . Beyond the latter wave-length it decreases rapidly and ceases at  $\lambda=1^{\mu}.4$ . Chlorophyll in solution does not decrease the diathermancy of alcohol at  $\lambda=.863^{\mu}$  and at  $\lambda=1^{\mu}.41$ .

7. Neither potassium alum nor ammonium alum in solution alters the diathermancy of distilled water in the region studied.

8. Ammonium-iron sulphate in solution decreases the diathermancy of distilled water.

The work described in the foregoing paper was done in the Physical Laboratory of Cornell University during July and August, 1892, under the direction of Dr. Edw. L. Nichols, to whom I take pleasure in acknowledging my indebtedness for assistance and many important suggestions. I am indebted to Mr. E. S. Ferry also for help in making some of the observations preliminary to this study.