THE PHOTOLUMINESCENCE AND KATHODO-LUMINESCENCE OF CALCITE.

By E. L. Nichols, H. L. Howes and D. T. Wilber.

THAT calcite is luminescent has been known for many years. E. Becquerel[1] mentioned it among the numerous substances whose phosphorescence of short duration was revealed by the use of his phosphoroscope. He gave the duration as half a second.

While Stokes[2] found calcite devoid of fluorescence, von Lommel[3] described all the specimens examined by him as showing a fine red glow in the path of a beam of sunlight transmitted through the crystal.

Sohncke[4] in his study of polarized fluorescence found spar from Iceland active, but crystals from Cumberland, England, inactive, a fact which doubtless explains the discrepancy between the observations of Stokes and of von Lommel.

G. C. Schmidt[5] confirmed the experiments of Sohncke and shared his view that the luminescence is not inherent in calcite but due to traces of foreign substances in solid solution.

Pochettino,[6] who more recently has examined many minerals under the action of kathode rays, finds calcites from some fourteen localities to possess phosphorescence of considerable duration and always with the same spectral distribution. It is however easy by a cursory examination of any considerable collection of calcites with the light of the iron spark, to confirm the statements of Sohncke and of Schmidt as to their varied behavior.

In a recent inspection by this means of the specimens available in the mineralogical laboratory of Cornell University we found many which showed the brief but vivid red glow typical of the calcites from Franklin Furnace, N. J.; others emitted a white phosphorescence, not brilliant but of long duration, an effect apparently common among stalagmites from various localities. A few pieces were pale green, a few amethystine

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[1] E. Becquerel, La Lumiere, I., p. 354, 1867.

[2] Stokes, Phil. Trans., XI, p. 516, 1852.

[3] v. Lommel, Wiedemann's Annalen, XXI., p. 422, 1884.

[4] Sohncke, Wiedemann's Annalen, LVIII., p. 425, 1896.

[5] Schmidt, Wiedemann's Annalen, LX., p. 740, 1897.

[6] Pochettino, Il Nuovo Cimento (5), XVIII., p. 260, 1909.

in the color of their fluorescence, as though by the combination of a red and a blue band. One small crystal exhibited a strikingly brilliant and persistent blue phosphorescence, which came chiefly from a small portion, not as though a foreign particle were embedded there but rather as though some substance had gone into solution and filled a portion of the crystal bounded by growth planes which separated it from the remaining parts. Many of the calcites in this collection did not respond perceptibly to the light of the spark.

It is obvious that in the luminescence of calcite we have to do with phenomena as complicated as those found in the case of the phosphorescent sulphides and like the latter dependent upon the nature and amount of the dissolved material and upon treatment by heat. In contrast to the brilliant but brief phosphorescence noted by Becquerel, Headden[1] described calcites from Joplin, Mo., which after exposure to sunlight continued to glow with a reddish color for at least 14 hours and others from Fort Collins, Colo., the phosphorescence of which had a duration of several hours. The Joplin calcites were strongly thermoluminescent. Headden made a careful analysis of his material and found in addition to small amounts of Mn, Fe and Zn, measurable quantities of the rare earths. He was inclined to attribute the phosphorescent properties to the presence of yttrium.

Since a specimen of calcite from Lowville, N. Y., showed the reddish phosphorescence in the metamorphosed rock calcite and none in the "nail head" calcite-crystals—presumably recrystallized from solution—and since in general stalagmitic calcite did not show the red color, it was assumed that heat might be requisite to the production of this property. Accordingly a piece of calcite having a faint whitish glow was heated white hot and on cooling the calcined tip showed the red glow. To ascertain whether a chemical impurity was also necessary to produce the phosphorescence—as suggested by the work of Crookes[2] on the yellow phosphorescence of calcium oxide containing traces of yttrium—some of Kahlbaum's reprecipitated calcium carbonate was ignited but only the faintest white phosphorescence was obtained. A small amount of manganese chloride was added and the red phosphorescence showed at once. Some difficulty was experienced in reproducing this result until it was found hat a proper atmosphere is required during the ignition to prevent the manganese from turning black, presumably because of oxidation.

The best results were obtained by adding to one gram of calcium

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[1] Headden, Am. Jour. of Science (4), XXI., p. 301, 1906.

[2] Crookes, Proc. Roy. Soc., 42, 115, 1887.

carbonate 1 c.c. of 1/50 molar manganese chloride solution, evaporating to dryness on a water bath, adding 50 mg. of oxalic acid crystals and grinding to a powder. The mixture was then ignited to a white heat. Ammonium chloride and sodium bicarbonate gave nearly as good results as oxalic acid, using the same weight.

The product obtained by this method glows with a reddish phosphorescence similar to that of the calcites when excited by ultra-violet light. It is, however, calcium oxide, the loss in weight being due to the loss of carbon dioxide. It deteriorates rapidly, ceasing to give any glow after standing a few weeks in the air, presumably due to the formation of calcium hydroxide.

This leads to the possibility that the phosphorescent centers are actually calcium oxide, with manganese or other oxide attached in a special manner produced by the heat treatment, and that the calcium carbonate in the calcite crystals is a matrix which holds these few scattered luminescent particles. It is conceivable that a metamorphosed calcite could be heated to a temperature at which the carbon dioxide would slowly be driven off, leaving a small per cent. of calcium oxide dissolved in the calcite.

A strong blue phosphorescence was obtained by using bismuth chloride as an activator in the place of the manganese chloride, and faint pinkish phosphorescence by employing antimony, copper, and uranium. These specimens were all strongly thermoluminescent.

Our interest in the luminescence of calcite originated in the desire to determine the law of decay of substances of brilliant but brief phosphorescence for comparison with that of the uranyl salts recently studied.[1]

A sample from Franklin Furnace appeared to suit our purpose. It showed the fine red after-glow characteristic of the calcites of that locality and although the duration of visibility (one half second), was about one hundred times that of the uranyl salts it was much too brief for examination by the method of single excitation. The fact that this calcite under the action of the kathode rays showed brilliant phosphorescence lasting several minutes added greatly to the interest of the comparison since, as has very recently been discovered by Misses Wick and McDowell,[2] certain uranyl salts at the temperature of liquid air likewise have phosphorescence of long duration when excited by the kathode discharge.

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[1] Nichols and Howes, Phys. Rev. (2), IX., p. 292, 1917.

[2] Wick and McDowell, Phys. Rev. (2), XI., p. 421, 1918.

PHOTO-LUMINESCENCE

For the study of the brief photo-luminescence of the calcite a special phosphoroscope of the disk type was constructed, the chief novelty of which lay in the method of indicating the speed of revolution. It consists essentially of a drum *D* (Fig. 1) mounted upon a vertical shaft and driven by a small electric motor. It could be belted direct to the motor from any one of the three pulleys at the base of the shaft or, for low speeds, to a large pulley driven by worm gearing on the motor shafts. Thus the very great range of speeds necessary in phosphoroscopic measurements was readily obtained.

For the indication of speeds a brass disk was mounted on the shaft of the phosphoroscope below the drum. This passed between the poles of a little electromagnet *M*. Brushes *B*, *B* on the periphery of the disk and on the shaft *S* conveyed the current generated by this disk dynamo to the circuit of a d'Arsonval mirror galvanometer *G*. Adjustments of the resistance of the galvanometer circuit afforded deflections through the same range for the various speeds employed and enabled us to follow all changes in the rotation of the phosphoroscope regardless of the slip of the belt or of fluctuations in the current supply of the motor. Constancy of the field of the disk dynamo was secured by the use of storage cells and precautions were taken to eliminate thermal E.M.F.'s at the brushes. The phosphorescent material, in powdered form was mixed with white zapon varnish and applied with a brush to the outside of a brass collar *P* which fitted snugly over the slightly tapered drum of the phosphoroscope. A number of these collars, which were readily interchangeable, were provided to facilitate the examination of one substance after another.

Excitation was by means of an iron spark actuated by the convenient form of transformer devised for this purpose by Mr. W. S. Andrews,[1] or sometimes by means of a mercury arc in quartz, the tube of which was brought as close to the drum of the phosphoroscope as possible.

With the simple instrument just described exceedingly interesting and instructive observations of phosphorescence having a visible range between 1/100 seconds and 3 or 4 seconds may be made. The color-changes in the phosphorescence of bodies whose spectra have two or more bands which differ in wave-length and persistence are beautiful and most striking.

To determine the curve of decay a photometer of the type described in previous papers was employed. The eye piece *E* was usually directed to the rim of the drum 180° from the region of excitation (see Fig. 1), so that the spark would be hidden by the body of the drum.

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[1] Andrews, General Electric Review, April, 1916.

A light filter *F* was interposed between the comparison lamp *C* and the Lummer-Brodhun cube. Before taking measurements, however, elaborate screening was employed to exclude stray light coming from the exciting source.

The usual method was to maintain a constant angle as above between points of excitation and of observations, varying the speed of the motor for successive settings. An assistant would adjust the motor speed, then move the comparison lamp along the bar until the observer announced a match. He would then immediately read the speed from the galvanometer scale which was mounted above the bar, and subsequently read the photometer setting. Thus the observer's eyes were spared, which is an important precaution in the readings at low speeds for which the brightness drops to less than 1/1,000 of the initial brightness. Occasional interchanges between observer and assistant in these experiments tended to eliminate the bias of both and check the results.

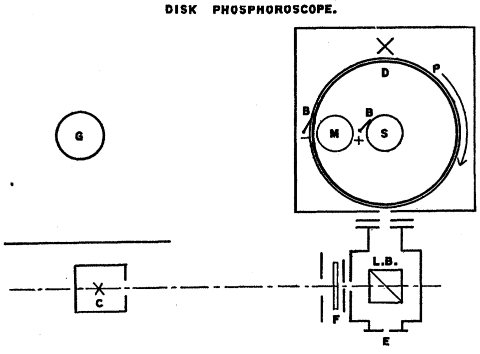

Fig. 1.

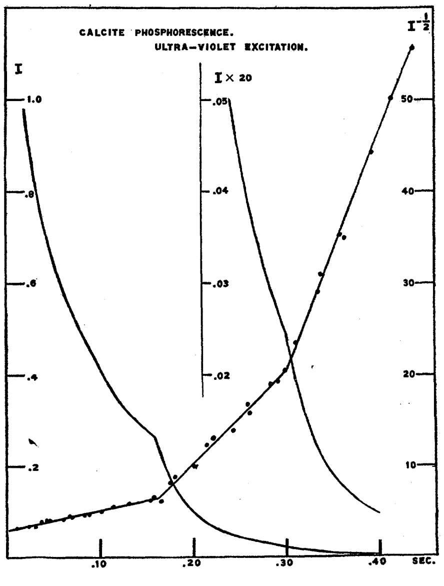

Fig. 2.

The curves thus obtained were of the form shown in Fig. 2. Plotted with the reciprocal of the square root of intensity as ordinates they indicate three successive linear processes with increasing rates of decay, a type hitherto supposed to be peculiar to the phosphorescence of the uranyl salts.[1]

In the use of the disk photometer, as with any method in which periodically repeated exposures to excitation occur, results are comparable only throughout the range of speeds for which saturation is obtained. For the calcite under observation and with the intensity of excitation available, saturation was found to exist for all speeds of the disk less than that corresponding to .02 second decay. Any measurements in which the time interval from the close of excitation was not greater than .02 second were accordingly rejected.

Curves of the type shown in Fig. 2 differ so fundamentally from those universally associated with phosphorescence that one is at first inclined to question their validity and to ascribe their form to the methods necessarily employed in the study of phosphorescence of short duration. We went into this question very carefully in our investigation of the photophosphorescence of the uranyl salts and convinced ourselves by varying the form of apparatus, and the mode of excitation that the new curves were correct. In a recent paper on types of phosphorescence[2] we have indicated certain fundamental distinctions between the curves of decay of persistent phosphorescence and those characteristic of vanishing phosphorescence and have shown that the latter cannot be regarded as the first stages of curves of persistent phosphorescence.

There is indeed good reason to believe that we have in the two cases distinctly different effects. That both types can be produced in a single substance by varying the mode of excitation has been demonstrated for the uranyl salts, in the investigations already cited. It will be seen from the results to be given in the present paper that the same is true of calcite.

KATHODO-LUMINESCENCE.

To determine the law of decay of the phosphorescence produced by kathode rays a crystal *P* was placed in the bottom of a V-shaped vacuum tube, Fig. 3, and was viewed directly through the transmitting zone of the Lummer-Brodhun cube of the photometer. The comparison light for the reflecting zone was transmitted through a screen of ground glass or milk glass from a small tungsten lamp mounted upon a long photometer bar.

The approximate color match was obtained by the use of a suitable orange-yellow color screen. The excitation was produced by means of a large motor-driven influence machine.

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[1] Nichols and Howes, *l. c.*

[2] Nichols and Howes, Proc. Nat. Acad. of Sci., 1918.

The time of close of excitation was automatically recorded on a chronograph; the subsequent times when the brightness of phosphorescence matched that of the comparison light placed at previously selected stations along the bar was indicated upon the same chronograph sheet by tapping a key in the chronograph circuit. The first observation was made as soon as practicable, *i. e.*, about .4 second after the close of excitation and readings were continued for about 300 seconds. The range of intensities was so great that the farther end of the bar was reached some time before the run was completed and the subsequent observations were obtained by substituting the milk glass screen for that of ground glass. The ratio of transmission of the two, which was about 1 : 80, was carefully measured.

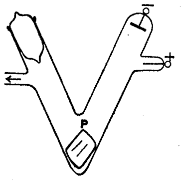

Fig. 3.

The curve in Fig. 4 is characteristic of the kathodo-phosphorescence of these calcites, but as in the case of the curves of decay of the persistent phosphorescence of other substances the first two linear processes tend to merge, giving curves of the form shown in Fig. 5. This occurs, as has been pointed out in a previous paper[1] whenever various portions of the substances are subjected to excitation of widely different intensity.

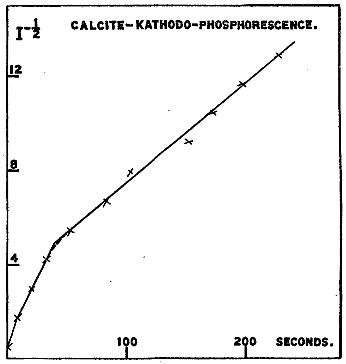

Fig. 4.

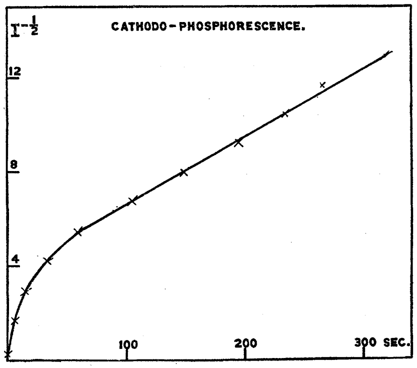

Fig. 5.

In photo-luminescence this is due to the penetration of the exciting light to the inner layers of a crystal;—in the case of kathodo bombardment it may also be due in part to the existence in the kathodo stream of particles having different velocities. It appeared that the colored film on the surface of calcite, due to prolonged exposure to kathode rays was conducive to the type of curve in Fig. 5 whereas the simpler form with well defined knees was characteristic of crystals with fresh unmodified surfaces.

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[1] Nichols and Howes, *l. c.*, p. 301.

Shorter runs in which the stations along the bar were placed nearer together allowing just sufficient time to make the successive observations, served to establish more conclusively the linear character of the earlier processes. Fig. 6 gives the results of such a run. The initial observation in this and in the two preceding curves, is located at the origin of the time ordinate. Such readings were made before the close of excitation. The initial position is such as to indicate even more rapid decay of phosphorescence during the first half second than subsequently, but, by this method, it was impossible to obtain readings lying within this interval.

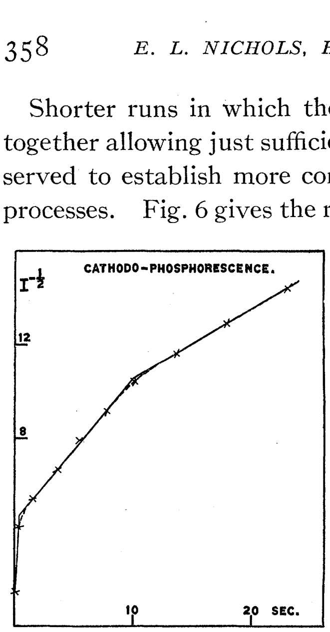

Fig. 6.

Since the whole of the visible processes of decay in the case of the *photo-phosphorescence* of these calcites occurs during this first half second of time it was deemed of interest to determine, if possible, what takes place during this interval when the excitation is by kathode bombardment. To this end we constructed a phosphoroscope capable of running in vacuo.

The disk, which was 4.2 cm. in diameter and which carried a flat periphery as in the instrument already described, was mounted at the upper end of vertical steel shaft 115 cm. in length. This passed coaxially through an iron tube 1.3 cm. in diameter. At the upper end this tube was threaded with a circular iron plate *N*, see Fig. 7, upon which a vacuum tube *V* with flanged lip was mounted.

The kathode *K* was in a side tube. It faced the periphery of the disk at a distance of about 0.5 cm. The iron plate served as anode.

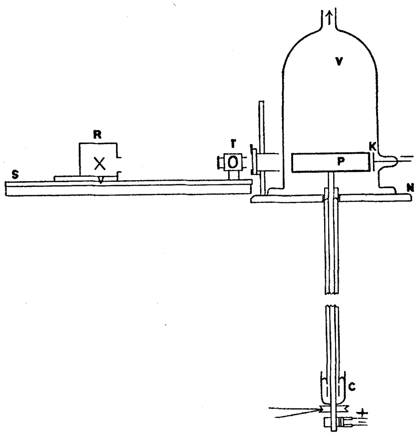

Fig. 7.

The iron tube within which the steel shaft revolved was provided with a deep iron cup *C* at the bottom, like the cistern of a barometer and the shaft passed through a mercury-tight stuffing box in the base of this cistern. The shaft was motor driven at various speeds from pulleys attached below the stuffing box. When the cistern was filled with mercury and the vacuum tube exhausted with a Gaede pump, the mercury rose around the shaft, as in a barometer tube and a good kathode ray discharge was readily obtained and maintained. By means of countershafts and reduction gears, the speed of the disk could be varied from twenty or more revolutions a second to one revolution in one hundred seconds.

The intensity of the phosphorescence was measured by reading the position of the comparison lamp *R* on the bar *S* when the two fields were of equal intensity in photometer *T*. The range of the measurements made with this instrument is so great that they cannot adequately be represented in a single diagram. Indeed it was not found advantageous to make a detailed and continuous study of the entire range upon a single specimen because calcite, which is one of the most stable of luminescent substances under *photo-excitation*, becomes rapidly fatigued when exposed to kathode rays, with permanent discoloration of the surface layers.

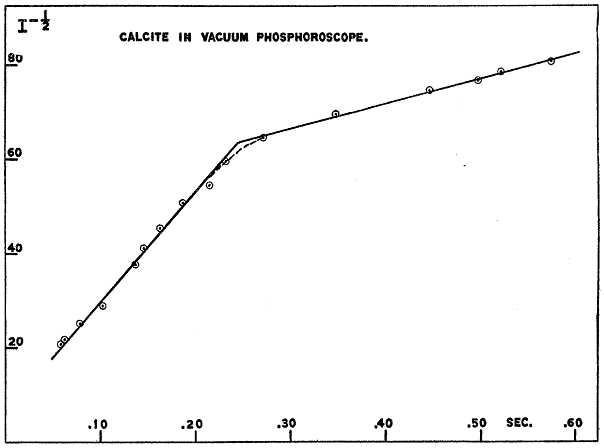

Fig. 8.

Three sets of experiments were therefore made, using freshly prepared coatings of the powdered crystals:

1. *From .06 Second to .60 Second.*—A typical curve for this range is shown in Fig. 8. The whole of this curve lies within the time interval between the close of excitation and the first observation made by the method of single excitation already described (see Figs. 4, 5 and 6).

Like the curve for the vanishing phosphorescence produced by photo-excitation (Fig. 2) it is made up of sharply separated linear processes, but of the opposite type (*i. e.*, that usually associated with persistent phosphorescence).

It is clear therefore that so far as the law of decay is concerned the beginnings of persistent phosphorescence are *not* like the curves for vanishing phosphorescence. It is also evident that the *first process observable by the method of single excitation is not the initial process* in the case of persistent phosphorescence but is preceded by an earlier and more rapid decay lasting less than half a second.

2. *From .60 Second to 20 Seconds.*—This interval corresponds approximately to that covered by Fig. 9. Like the curves which had been obtained over this interval of time by the method of single excitation these resulting from measurements with the revolving disk in vacuo are characterized by a well-defined knee at about 10 seconds, separating two linear processes. The results of the two methods are identical as to type, as may be seen by comparing Fig. 9 with Fig. 6.

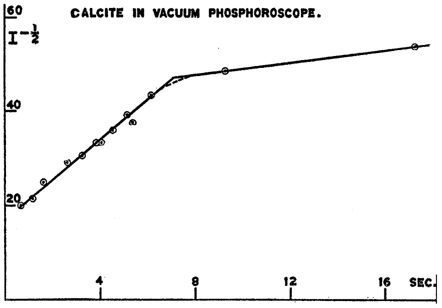

Fig. 9.

3. *From .6 Second to 300 Seconds.*—For this great range the difficulties of maintaining a constant vacuum and kathode discharge were such that we contented ourselves with establishing the existence of a knee in the curve at about 40 seconds corresponding to that obtained by the method of single excitation (Fig. 4), and of a linear process beyond.

The Effects of Temperature.

When a crystal of calcite from Franklin Furnace is heated certain changes in its photo-phosphorescence are noticeable. The after-glow, which is ruddy at + 20°, becomes reddish yellow and at higher temperatures a paler yellow. Before a red heat is reached phosphorescence becomes extinct, but the luminescent power returns on cooling. When excited at temperatures approaching that of liquid air the phosphorescence appears to be of a deeper, more intense, red than that produced at room temperature.

The temperatures at which the color changes noted above occur seem to correspond in general to those related to the production of thermoluminescence in calcites from Joplin, Mo. Dr. Headden found that specimens from that locality began to glow at + 60°, were most brilliant at about + 180° and were not extinct at + 200°. We were able to confirm these observations in this regard in the case of a large crystal kindly furnished us by Professor Headden. Upon heating slowly one end of the crystal in the Bunsen flame thermo-luminescence first appeared at the hot end, then receded gradually from the flame. The luminescence was confined to a rather narrow band which moved through the crystal with the conduction of heat, showing that the effect occurred between fairly well defined limits of temperature. The appearance after several minutes was as follows. The tip of the crystal, within the flame, appeared faintly red hot; then a dark non-luminescent zone below the red heat, but above that of thermo-luminescence, appeared; then the narrow thermo-luminescent belt,—very brilliant in the center and dying away more gradually toward the cooler end of the crystal. Our Franklin Furnace calcites, although strongly photo-luminescent, showed no trace of thermo-luminescence, and strangely enough, we could not excite to phosphorescence the crystals sent us by Professor Headden either by prolonged exposure to sunlight or by the action of the iron spark, although they were of the stock examined by him in 1906, at which time they exhibited the remarkably persistent phosphorescence after solar excitation described in his paper. The explanation of this loss in the phosphorescent properties of these calcites has not yet been found.

To determine more exactly the effects of temperature on the phosphorescence of our Franklin Furnace calcites the disk of the phosphoroscope used in the determination of photoluminescence was heated from below by means of a circle of minute gas jets *J*, *J*, Fig. 10—surrounding the shaft below the disk. The temperature of the ring on which the powdered calcite was mounted was measured by means of a Pt-Cu thermojunction *T* which could be inserted in a drill-hole in the metal of the ring.

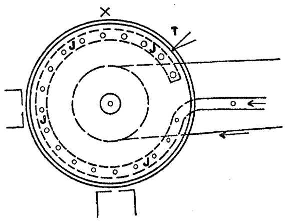

Fig. 10.

The phosphoroscope was driven at a constant speed and the brightness of the coating at various temperatures between + 20° C. and 350° was measured by means of a Lummer-Brodhun spectrophotometer, one collimator of which was directed towards the coating of the phosphorescent calcite. The other collimator was illuminated by the comparison lamp. Slit widths were maintained equal and constant and measurements were made by moving the comparison lamp along a photometer bar. Readings were made in the red of the spectrum (.65 μ) and in the green (.52 μ).

Accurate determinations by this method are difficult since they involve constant intensity of excitation and constant speed of the phosphoroscope throughout the run. Both conditions were hard to maintain with our apparatus. Fair control of the speed could be only had by continual attention to the lubrication, particularly at the higher temperatures, where castor oil had to be substituted for the more volatile lubricants. This trouble could have been completely overcome by suitable reconstruction of the phosphoroscope but it seemed hardly worth while on account of the uncertain behavior of the iron spark. This source of excitation is altogether unsatisfactory where intense and really constant intensities are demanded. We have not as yet found an adequate substitute however for strong excitation by ultra-violet radiation.

At the higher temperatures the heated air greatly interfered with the action of the spark. To obviate this a quartz window was mounted between the disk and the spark, but we were greatly surprised to find that the excitation was reduced to a small fraction of its former intensity.

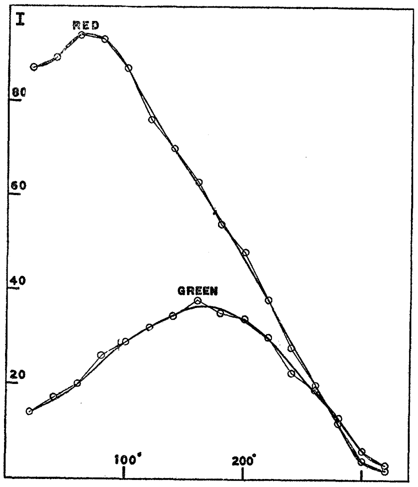

Fig. 11.

It appears that the luminescence of these calcites is chiefly produced by rays which are of shorter wavelength than those transmitted by quartz. This almost precluded the use of a mercury arc in quartz for these observations, although we did make several sets of spectrophotometric measurements with this source by way of a check.

The curves in Fig. 11 show the variations in the red and green throughout the range of temperatures mentioned above. Ordinates are intensities—referred to that of the corresponding region in the spectrum of the comparison light, and the readings are numerically comparable only if reduced to terms of energy. For the present purpose—which is to depict the relative effects of temperature, the curves in their present form will suffice. It will be noted that in both of these regions the brightness increases with the temperature. The red however reaches a maximum at about 70°, whereas the green continues to rise to about 160°. After passing the maximum the fall of both curves is continuous and rapid and they approach extinction;—*i. e.*, become too feeble for measurement, at about 350°.

The marked change in color is indicated by the fact that whereas if at 20° the region at .52 μ be made as bright as the corresponding region in the spectrum of the comparison source, the red would be about 50 times as bright as the red of the comparison; while above 250° the relative brightnesses become nearly equal. At these higher temperatures, indeed, the distribution of intensities in the spectrum of the phosphorescence differs but little from that of a tungsten lamp up to about .5 μ. Its spectrum extends but little beyond that wave-length towards the violet, however, and the color is accordingly a fine luminous yellow.

Spectrophotometry of the Phosphorescence at + 20° and + 200°.

The differing effects of temperature upon the two regions of the spectrum, as just described, are indicative of the presence of more than one band in the phosphorescence of these calcites. The components of the spectrum overlap, however, to such an extent as to be indistinguishable by spectroscopic inspection. We, undertook, therefore a detailed spectrophotometric study, making measurements every 50 Ångströms from .66 μ to .50 μ.

It was easier to ascertain the deviations from constancy of the phosphorescent surface, due to irregularities in the iron spark or fluctuations in the speed of the disk than it would have been to control these conditions throughout an entire spectrophotometric experiment. To this end a photometer was mounted so as to follow the fluctuations. The arrangement of the apparatus is indicated in Fig. 12.

The disk phosphoroscope *D*, already described, is driven by the motor *M*. The spark gap is within the enclosure *S*. The collimator *A* of the spectrophotometer *H* receives light from the phosphorescent ring on the disk, 180° from the point of excitation. The photometer *P* is so placed as to permit observations of the brightness of the ring at a point 90° beyond *A*. The comparison lamps C_1 and C_2, mounted on photometer bars as shown, serve respectively the collimator *B* and the photometer. The comparison lamps are similar 6-volt tungsten lamps in multiple on a circuit supplied by a suitable storage battery.

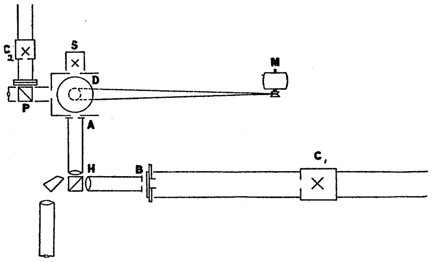

Fig. 12.

The method requires two observers—one at the eyepiece of the spectrophotometer, the other at the photometer. The latter follows the fluctuations of the phosphorescence and records its brightness at the instant when each spectrophotometric setting is made. It was thus possible to eliminate, with a fair degree of accuracy, all errors due to changes in the excitation or speed.

Spectrophotometric measurements were made with this apparatus with the disk at + 20° and + 200°. The results are shown in the two curves in Fig. 13 in which ordinates are φ_λ/C where φ_λ is the intensity

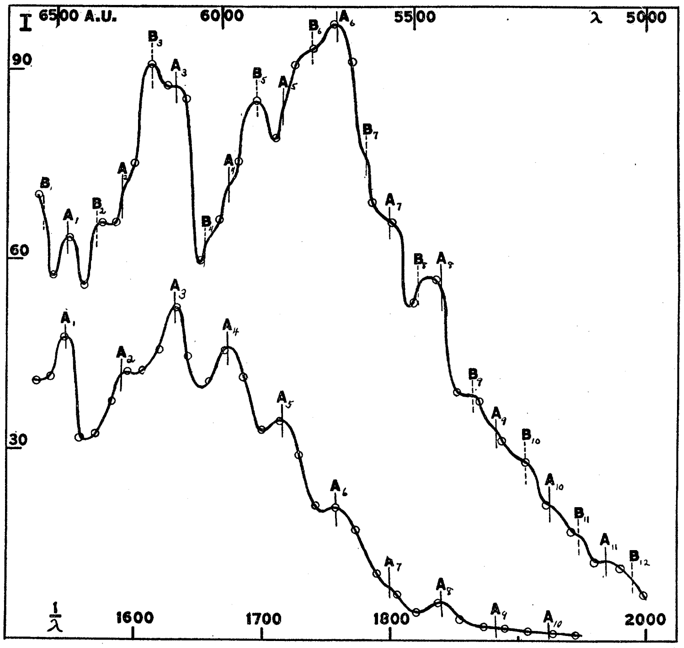

Fig. 13.

of the phosphorescence spectrum at wave-length λ and C is the intensity of the spectrum of the comparison lamp at the same wave-length. Abscissæ are frequencies, or $1/\mu \times 10^3$. The lower curve in the diagram is for 20° and the upper curve for 200°.

The curve for + 20° shows the phosphorescence spectrum to be complex, consisting of numerous overlapping components grouped about the main crest at $\lambda = 6131$ $(1/\lambda = 1631)$. If we assume that the components form a series with equal frequency differences, which is a common if not universal characteristic of luminescence spectra,[1] and take 42 units as the approximate interval, assigning one member of the series to the peak of the principal crest as above, we get the following series of components:

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[1] Nichols and Merritt, PHYS. REV. (1), XXXIII., p. 354, 1911, and subsequent papers. Nichols, E. L., Proc. Am. Philos. Soc., LVI., p. 258, 1917.

TABLE I.

Series A. (*Interval 42.*)

Band.	λ.	$1/\lambda \times 10^3$.	Band.	λ.	$1/\lambda \times 10^3$.
A_1	.6464	1547	A_7	.5559	1799
A_2	.6293	1589	A_8	.5432	1841
A_3	.6131	1631	A_9	.5311	1883
A_4	.5977	1673	A_{10}	.5195	1925
A_5	.5831	1715	A_{11}	.5084	1967
A_6	.5692	1757			

TABLE II.

Series B. (*Interval 42.*)

Band.	λ.	$1/\lambda \times 10^3$.	Band.	λ.	$1/\lambda \times 10^3$.
B_1	.6545	1528	B_7	.5618	1780
B_2	.6369	1570	B_8	.5488	1822
B_3	.6203	1612	B_9	.5365	1864
B_4	.6046	1654	B_{10}	.5247	1906
B_5	.5896	1696	B_{11}	.5133	1948
B_6	.5754	1738	B_{12}	.5025	1990

These frequencies coincide in position with the subordinate crests that are visible as ripples in the curve in Fig. 13. Their positions are indicated by the short vertical lines marked *A* which cross the curve.

There are suggestions of a secondary or accompanying series, but the indications of it in the curve for 20° are not sufficient to establish its position or interval. In the curve for 200°, however, which is likewise plotted in Fig. 13, this secondary series (*B*) is strongly developed and becomes quite as prominent as series *A*. The strongest crest is now found at $\lambda = 5692$ ($1/\lambda = 1757$) and is broadened as if due to the presence of an unresolved doublet. Its edge towards the violet coincides in position with A_6 in the 20° curve. Its edge towards the red may be regarded as due to the outcropping of a member of series *B*,—the location and interval of which can be pretty definitely established from the crests B_3 and B_5. This series in both curves is indicated by short broken vertical lines (B_2, B_3, etc.). Its interval is also approximately 42 units of frequency.

The structure of the spectrum of this calcite resembles that of the phosphorescent sulphides which, as has been shown in a recent paper,[1] is made up of one or more series of overlapping components. The luminescence of this calcite however differs in at least one important respect from that of the sulphides. The light from the sulphides, as is

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[1] Nichols, E. L., Proc. Am. Philos. Soc., LVI., p. 258, 1917.

well known is quenched by exposure to infra-red. The glow of the calcite is not appreciably affected by such radiation either during or after excitation. Of this we assured ourselves by careful observations.

To determine whether the Franklin Furnace calcite, which has been subjected to kathodo-bombardment acquires, even temporarily, the power of photo-phosphorescence a crystal was mounted in the V-shaped kathode ray tube already described (Fig. 3). A quartz lens was cemented over the open end of the tube, in place of the ground glass plug. The crystal glowed in the usual manner after excitation by the kathode rays.

Exposure to radiation from an iron spark mounted just above the quartz window produced the same brief, red after-glow, whether applied before, during, or after kathodo-excitation. The two effects appeared to be quite independent and could be simultaneously produced and superimposed.

It was in connection with these experiments that the following tentative observations on the effect of low temperatures were made.

The knee of the V-tube was submerged in liquid air and kathodo excitation was used. The luminescence seemed to the eye redder than at room temperature and very bright. The increase in intensity may, however, have been due to improvement in the vacuum due to cooling and a consequent change in the kathode discharge.

Photo-excitation gave the same brief ruddy afterglow as at room temperature, seemingly of a deeper red. No notable change in duration was observed. No quantitative measurements, of color, intensity or duration were made at these temperatures.

SUMMARY.

1. Samples of calcite from Franklin Furnace were subjected to excitation with the iron spark and to kathode bombardment.

2. The phosphorescence under photo-excitation is of the vanishing type, color ruddy, duration about .4 second.

3. Decay curves of the photo-phosphorescence are of the type characteristic of vanishing phosphorescence, previously recorded only in the case of certain uranyl salts. These curves show three "linear" processes.

4. The phosphorescence under kathodo-excitation is of the persistent type, red in color, measurable at 300 seconds after excitation.

5. Decay curves of kathodo-phosphorescence are of the more usual type, *e. g.*, that of the sulphides. These curves exhibit a series of linear processes.

6. The red and green regions of the spectrum are both affected by rising temperature, the red attaining a maximum intensity at about 70°

and the green at about 160°, while both become too dim to measure at about 350°.

7. An analysis of the spectrum reveals two series of overlapped bands, spaced equally in frequency units.

8. The Franklin Furnace calcites are not affected, as to the rate of decay of their phosphorescence, by the application of red or infra-red radiation.

9. Their characteristic ruddy phosphorescence appears to be due to the presence of traces of manganese. Calcium carbonate artificially prepared is rendered similarly phosphorescent by the addition of a manganese salt and subsequent heat treatment.

10. The action of kathode rays does not render these calcites even temporarily capable of persistent phosphorescence under photo-excitation.

11. The vanishing phosphorescence due to photo-excitation may be superimposed upon the persistent phosphorescence of kathodo-excitation either during or after exposure to the kathode rays.

Physical Laboratory,
Cornell University,
June 19, 1918.