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Influence of annealing on the characteristics of light-sensitive selenium

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THE INFLUENCE OF ANNEALING

on the

CHARACTERISTICS OF LIGHT-SENSITIVE SELENIUM.

by

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The Influence of Annealing on the Characteristics of Light-sensitive Selenium.

The explanation of the light sensitiveness of selenium in one of its allotropic modifications, the grey metallic form, has long been an attractive problem to physicists. The question may be attacked in two ways, and in the past both methods have been fruitful of results.

One method consists in varying the conditions under which the selenium is crystallized, and, from a study of the samples resulting, formulating an explanation of the nature of the action of various agencies, such as light, heat, pressure, X rays, and other radiations, on selenium. Here may be mentioned the exhaustive researches of Bidwell, Ries, Marc, and Pfund. Bidwell[×] investigated the effect of the addition of impurities on the sensitiveness of selenium in the form of selenium cells, and showed that a small percentage of impurities, in the form of metallic selenides, increased the sensitiveness of the cells; a large amount, however, decreased the sensitiveness. Marc[*] and Pfund[+] verified the observations of Bidwell with respect to the effect of impurities on the sensitiveness. Pfund further investigated the variation of the sensitiveness of selenium throughout the spectrum, finding maximum sensitiveness at $700 \mu\mu$. He also observed that the nature of the selenide added did not influence the position of the maximum.

× Phil. Mag. XL, p. 233, 1895.
+ Phil. Mag. VII, p. 26, 1904.
* Die Physikalisch-chemischen Eigenschaften des Metallischen Selens, 1907.

Marc studied the influence of annealing on the resistance and sensitiveness of selenium, and made a general investigation of the processes taking place during crystallization. Ries[+] investigated in great detail the temperature coefficient of selenium, and found it to be positive at high temperatures, negative at low temperatures. He also studied the effect of annealing on the resistance and sensitiveness of selenium cells.

The other method of attacking the problem is to study the effect of the various agencies on commercial selenium cells, the method of preparation of these being unknown, and from the observations deducing an explanation of the nature of the action of light sensitive selenium. For this purpose, cells made by Giltay and Ruhmer have been extensively used. The process of making these is a trade secret, and, thus, unknown to the investigators. Among the latter researches may be mentioned the recent work of Brown[×], Stebbins[*], Miss McDowell[#], and Nicholson[ª]. The variation of the conductivity with temperature, pressure, etc., were studied and the wave-length sensibility curves for Giltay and Ruhmer cells obtained.

The investigations have led to two theories as to the action of light sensitive selenium, which, however, are not essentially unlike. Thus, Marc proposes the following explanation: in selenium there are two components present, A and B, in equilibrium under different conditions of temperature, illumination, pressure, etc. He assumes that component A is practically a non-conductor

+ Die Elektrischen Eigenschaften und die Bedeutung des Selens für die Electrotechnik, 1908.
× Phys. Rev., XXXIII., p. 1; p. 403, 1911.
* Phys. Rev., XXVI., p. 273, 1908., Astrophys. Journ., 27, p. 183,
# Phys. Rev., XXIX., p. 1, 1909., XXXI., p. 524, 1910.
ª Phys. Rev., N. S., III., p. 1, 1914.

of electricity, while B conducts, and that under the influence of light the equilibrium is displaced, component A changing into B, the amount transformed depending upon the intensity of the light. When the light is removed, the action proceeds in the opposite direction, thus decreasing the conductivity of the cell. Brown[×] has proposed essentially the same theory, except that he assumes the presence of three components in equilibrium according to the reaction, $A \rightleftarrows B \rightleftarrows C$. He has put this theory in mathematical form and derived equations expressing the transformations that take place under various conditions in certain types of cells studied.

The other theory, proposed by Pfund[+], and adopted by Ries[*] and Nicholson, assumes the expulsion of low velocity electrons from the atoms of selenium under the influence of light, thereby rendering the selenium a better conductor than in the dark. It is assumed that the velocities of the electrons are not great enough to carry them outside of the element, hence, they serve only to increase the conductivity. Nicholson[#] has developed this theory mathematically, and applied it to explain the action of a certain type of cell.

× Loc. cit.
\+ Phys. Rev., XXVIII., p. 324, 1909.
* Die Ursache der Lichtempfindlichkeit des Selens, 1911.
\# Loc. cit.

The recent work of Pfund[×] in analysing selenium cells by means of the spectrum opens up a new field in which comparatively little has as yet been done. The results of experiments along this line must materially influence the theories as to the reason for the action of light sensitive selenium. Earlier investigations of the same nature were very incomplete and unsatisfactory. Among them may be mentioned the work of Ries, Marc and Berndt. Marc[+] tested the effect of blue-green, yellow and red light on Ruhmer cells and on some of his own manufacture. He, however, does not describe the conditions of experiment accurately, and it is not at all certain that monochromatic light was used in the results recorded, nor even that the light used was of the same energy in the various colors. Neither is the wave length given. In order to obtain monochromatic light he employed a prism for part of the observations and colored plates for others. It is well known, however, that colored plates do not yield monochromatic light. Of three cells recorded, two showed maximum sensibility to the blue-green light, and one to the red. Under varied conditions of temperature the maximum sensibility of the first two cells shifted from the blue to the red.

Berndt[*] tried to simplify the conditions of experiment somewhat by using as a source of light the lithium, sodium and thallium lines, and also by reducing the light to equal intensity by comparison with a standard by means of the Bunsen grease spot photometer. This is hardly a satisfactory method of comparison

× Phys. Rev., XXVIII., p. 324, 1909, XXXIV., p. 370, 1912, Phil. Mag., VII., p. 26, 1904.
+ Zeitschr. Anorg. Chem. XXXVII., 3, p. 459, 1903.
* Phys. Zeitschr. V., p. 121, 1904.

of energy, however, when lights of different colors are used. Berndt's results, on cells of his own construction, showed that the sensibility decreased with a decrease in the wave length of the incident light.

The work of other earlier observers was along the same lines and need not be given here, since it is open to the same objections as given above.

Pfund, in his work obtained monochromatic light by the use of a prism and adjusted the energy of the exciting light by means of a sensitive thermopile. He further simplified conditions of experiment by making the periods of exposure equal, 12.5 sec., instead of waiting for equilibrium to be reached in the light. In his first series of observations, made on cells of his own construction, he found the maximum sensibility to be at 700$\mu\mu$. Later investigations by him consisted in the extension of this work to the problem of the optical properties of selenium, and the probable application of selenium to photometry. In his later experiments he made use of Giltay cells; however, with all the cells recorded by him the maximum senitiveness remained at 700$\mu\mu$, and seemed inherent in the selenium itself, and not due to impurities.

Stebbins[×] analyzed cells, made by Giltay and Ruhmer, according to the method followed by Pfund. He found one Giltay cell to possess a maximum sensibility at 600$\mu\mu$, and at 700$\mu\mu$. A re-annealed Giltay cell showed a maximum at 710$\mu\mu$, and the Ruhmer cell was recorded as having a maximum at 710$\mu\mu$.

The work of Pfund was further extended by Brown and Sieg[+]

× Loc. cit.
+ Phys. Rev., N. S., II., p. 487, 1913.

who investigated a Giltay cell and found that the wave-length sensibility curve showed a sharp maximum at 800μμ, a broad maximum in the region 540μμ to 600μμ, and a minimum at 640μμ.

Nicholson[+], working in Pfund's laboratory, records the wave-length sensibility curve for a Giltay cell, and finds a sharp maximum at 700μμ, also a broad maximum in the shorter wave lengths, and aminimum about 650μμ.

The above is a brief resumé of the analysis of selenium cells by light, and represents the most important work done along this line up to the present time, with the exception of the last contribution of Brown and Sieg.[×] Of course, the exact measurements of the observers following the method outlined by Pfund are more valuable than the earlier experiments. In the latter, without exception, it was found that the maximum sensibility of the cells to light lay in the red end of the spectrum, at 700μμ to 800μμ.

None of the writers above mentioned, however, have taken into account the probable effect of annealing on the wave-length sensibility curve. In each case in which "home-made" cells were analyzed the process of crystallization was the same throughout the investigation.

In a later investigation by Brown and Sieg, they made use of some cells prepared by the author. Contrary to the usual results, sensibility curves were found in some cases in which the maximum instead of being in the red end of the spectrum showed in the blue. An analysis of the data covering the method of making these cells revealed the fact that the crystallization of the selenium took place under different conditions in the different

\+ Loc. cit.
× Phys. Rev., N. S.,

samples. This immediately suggested the possibility that a better knowledge of the conditions governing the construction of light sensitive selenium cells might be of assistance in explaining the action of light sensitive selenium. With this purpose in view, the following investigation was carried out.

It will be shown in this paper that the resistance, sensitiveness, and shape of the wave-length sensibility curve of selenium cells can be controlled by varying the process of annealing. A simple explanation for the different types resulting will also be offered.

METHOD OF MAKING.

The cells, of which about 40 were constructed for this investigation, were all of the Bidwell type, i. e., two parallel wires were wound spirally around an insulating form, and the spaces between the wires were filled with selenium.

The selenium used was some in stick form from Merck. No steps were taken to further purify it, since it is , according to other observers, quite pure. Moreover, Pfund[×] has shown that the presence of metallic selenides does not affect the shape of the wave-length sensibility curve. A few samples were made in which rather impure selenium was used, and the cells resulting were not as satisfactory as those made from selenium from Merck. The resistance of these was in general high, and they were sluggish in action, although they had essentially the same characteristics as those made from the purer element. It has been observed by Marc[+] that impure selenium crystallizes less completely in a given time than pure selenium. To this fact the unsatisfactory action of the samples made with impure selenium is ascribed.

As insulating forms soapstone was used. At first glazed porcelain was tried ,but proved unsatisfactory on account of the difficulty of working into forms. The advantages of the talc over the porcelain are evident. It is much softer, and can therefore, be easily machined. It is also a very good insulator.

Several kinds of wire were tried as electrodes; copper, German silver, nickel, platinum, and Advance wire. Again, although selenides are formed during the crystallization process, due to

× Loc. cit.
\+ Loc. cit.

the high temperature, the shape of the wave-length sensibility curve will not be changed, although the sensitiveness and the resistance of the cell will be affected. These points are to be verified in some later work. Copper, German silver, and Advance wires have this disadvantage that, at the temperature of annealing, a film of oxide covering the wire is readily formed. This so materially increases the resistance of the cell as to make it practically useless for investigation except with very sensitive apparatus. Nickel wire is much less easily oxidized, and proved as satisfactory as platinum wire, besides being less expensive, and was used in all except the first few cells.

The first cells had a sensitive surface about 1×3 in. in size, but since only a few square millimeters are necessary for investigation, the size was reduced to about 1×3 cm. The distance between the electrodes in these smaller cells was a little less than 1 mm.

In applying the selenium to the form the following method was adopted as being the most satisfactory. The form was heated, on a hot plate, to a temperature just above the melting point of selenium, 217° C, and then the selenium, in stick form was rubbed over the heated surface immediately on removing from the hot plate. As is well known, with this treatment the selenium at once changes, on solidifation, to the grey metallic variety and is conducting and light sensitive. This method was found to be superior to melting the selenium on the form as far as obtaining smooth, thin films was concerned. However, in all cases in which the samples were tested out immediately on making, the resistance was found to be very high, of the order of 10^8 ohms, and the sensitiveness, even under intense illumination, in no case greater than 5 to 1. (By sensitiveness is meant the ratio of the resistance of the cell in the dark to that in the light.) Upon making, therefore, the cells were "annealed", the process taking place in an electric oven whose temperature could be quite accurately controlled. It is in this "annealing" process, which consists merely in keeping the cells for some time at a high temperature, or in gradually changing the temperature, that the changes which impart different characteristics to the cells take place. This will be described in greater detail in a later paragraph, since it is varied from cell to cell.

In general, all the samples received the same treatment after annealing. They were allowed to come to a temperature of 170°C while in the oven, then removed and placed in small glass tubes which had been thoroughly cleaned and dried. They were then sealed to prevent the access of moisture and other vapors and allowed to come to room temperature. Usually, they were allowed to rest for 24 hours before being investigated, being kept in a light tight box in the meanwhile. With these precautions, all the samples were found to be permanent, with respect to light sensitiveness, at least throughout the duration of this investigation, and quite stable.

CHARACTERISTICS OF THE CELLS.

The cells were investigated with respect to resistance, sensitiveness, shape of wave-length sensibility curve, and permanence.

The method generally described for crystallizing the selenium, namely, heating for some time at about 180°C was at first followed. The first cell made by this method had a high sensibility, but was not permanent. The next few samples were not at all satisfactory, so the method was abandoned. Instead, the cells were annealed at higher temperatures and a longer time was taken for the process. By this method samples were obtained which were quite satisfactory.

RESISTANCE.

The resistance of the cells was measured by means of a Wheatstone bridge. Since the resistance varies with the voltage impressed upon it, the same E. M. F., 16 volts, was used throughout.

Here the observations of Ries × in regard to the variation of resistance with annealing were verified. Thus, Ries records two samples which were heated at different temperatures, and shows that the higher the temperature to which the cell was heated the lower its resistance. His method, however, differs from that employed in this investigation in that he subjected the individual cells to a series of temperature changes, heating them first to a moderately high temperature, then cooling and measuring the resistance and sensitiveness; again heating to a slightly higher temperature than previously, cooling, and test-

× Loc. cit.

ing again, proceeding in this manner until a temperature of 215°C had been reached. In these experiments each cell was subjected to a high temperature but once, but the results were the same as far as resistance is concerned as those of Ries. The following table gives some typical results:

Table 1.

No. of cell.	Temp. of annealing.	Time of annealing.	Resistance.
23	210-200°C	6 hrs.	233000 Ohms
22	210°C	4 hrs.	358000 Ohms
28	210°C	5 hrs.	490000 Ohms
16	180°C	3 1/2 hrs.	1400000 Ohms
15	190°C	2 hrs.	3690000 Ohms

The above table shows the influence of annealing on the resistance of the cells. What is true of the cells in this table was found , almost without exception, to be true of all; i.e., the higher the temperature of annealing and the longer the time, the lower the resistance.

Table 2 shows this same thing in a slightly different manner. It was found that if the cells were heated for only a short time at a high temperature and the annealing completed at a lower temperature the resistance in all cases was also low. Thus, cells No. 18 and 19 were given exactly the same treatment, except that cell No. 18 was given a preliminary heating of half an hour at 210°C. The resistance of No. 18 is seen to be less than 1/40 that of No 19. The same is true of No. 20 and 21.

Table 2.

Cell	Temp. of annealing.	Period of annealing.	Resistance.
18	210°C 180°C	1/2 hr. 9 hrs.	976 000 Ohms
19	180°C	9 hrs.	40 000 000 Ohms
20	210°C 180°C	1/2 hr. 14 hrs.	250 900 Ohms
21	180°C	14 hrs.	9 500 000 Ohms

The resistance of a few samples was measured while the temperature was falling from 170°C to room temperature, immediately after annealing. Here the observations of Marc[×] and Ries[+] were confirmed; viz., that above a certain temperature selenium has a positive temperature coefficient, while below this temperature the coefficient is negative. The temperature at which selenium possesses the maximum conductivity was not determined, however.

The resistance of the freshly made cells was, in general, low, but increased gradually with time, reaching a constant value about two weeks after making. This gradual, permanent increase of resistance is no doubt due to the contraction of the selenium and its tearing away from the electrodes. The resistance of the various samples ranged from 12 000 Ohms to 42 000 000 Ohms.

× Loc. cit.
\+ Loc. cit.

LIGHT-SENSITIVENESS.

The sensitiveness of the cells was measured by observing the change in conductivity, rather than the change in resistance, on illumination. For this purpose the cell was connected in series with a dry battery and a portable galvanometer. The sensitiveness of the galvanometer was 10^{-7} amps. As source of illumination a 110 volt, 16 c.p. light at a distance of about 30 cms. was used. The sensibility of the different samples ranged from 5/1 to 20/1. An increase in sensitiveness with increasing age was also noted. Table 3 shows a typical example.

Table 3.

Cell.	Date.	Conductivity in the dark.	Conductivity under intense illumination.	Sensitiveness.
8	Dec. 10	4.0 (2 volts)	20.0	5/1
	" 13	.5		15/1
	" 15	.6	10.5	17/1
	" 16	.6	14.2	23/1
	" 17	.4	11.2	28/1
	Feb. 5	1.3 (8 volts)	49.0	38/1

With regard to the effect of annealing on the sensitiveness of the cells not much can be said as a result of these experiments. The first cell made had a remarkably high sensitiveness, 70/1 in ordinary daylight, but it was not permanent. In fact, 24 hours after making its sensitiveness had decreased to 5/1. Nor was it possible to duplicate it. Another sample, No. 14, in the apparatus used for investigating the wave-length sensibility curves, had an effective sensibility about ten times that of the best Giltay cell in the possession of this laboratory. This cell, also, was not permanent, its sensibility having decreased to 1/5 the original value in one month. Now, as far as is known to the author, the high sensitiveness of these two cells was due only to a variation in the conditions of annealing, the exact circumstances being unknown at the present time. That phase of the subject is under investigation at the time of writing, nothing definite having been discovered thus far.

Mention should be made of the instability of the cells immediately on making. This is shown by the fact that the sensitiveness of cell No. 1 was not permanent but disappeared within a few hours of making. Cell No. 5, which was tested out immediately on taking from the oven, while cooling from 90°C to room temperature was found to be strongly light negative during part of the cooling process. In his theory of the action of light sensitive selenium, Ries attributes the light negative effect to the presence of moisture. It is quite unlikely, under the conditions, that moisture could have been present in this sample while cooling from the temperature of annealing, at which it had been kept for some hours, to room temperature. Moreover, in that case it should have remained light negative at the lower temperature. However, this cell was the only one investigated in this manner in which this behavior was noticed, and it is not safe to assume, from this one isolated experiment that the light negative effect is inherent in selenium. The data mentioned above is given in table 4 , below.

Table 4.

Conductivity in Dark.	Time.	Conductivity on Illumination.	Sensitiveness
34	8:02	16	- 2.1/1
39	8:03	16.8	- 2.2/1
23.2	8:04	17.5	- 1.3/1
40	8:05	18.2	- 2.2/1
15	8:06	18.5	+ 1.2/1
14.8	8:07	19.0	+ 1.2/1
14.2	8:09	18.9	+ 1.3/1

THE WAVE-LENGTH SENSIBILITY CURVES.

In order to determine the wave-length sensibility curves the same method of procedure as outlined by Brown and Sieg* was followed and the same apparatus was used. The apparatus is shown in diagram in Fig. 1. Light from a Nernst glower(I) is focussed by means of lens(L) upon the slit(S_1) of a Hilger monochromatic illuminator(P), and passes through slit(S_2) in a box, blackened on the inside, where it falls upon a concave mirror (M). This mirror can be rocked so that the beam of light can be made to fall either upon a thermopile(T) or upon the selenium cell(Se) placed at its focus. The illuminator was calibrated between 380$\mu\mu$ and 800$\mu\mu$, so that the prism could be set at any desired wave length in this region by turning the prism by means of a screw head.

The thermopile used was by Coblentz, of the Rubens type, with wires of Bi and an alloy of Bi and Sn. It had a resistance of 2.25 ohms, and was used in connection with a galvanometer of the Thomson type, made by Siemens and Halske. The resistance of this with its coils in parallel was 1.35 ohms, and its sensibility, with a period of 6 sec., was about 10^{-10} amps. However, in this investigation, it was not necessary to know the absolute sensibility so long as it remained constant. This it was found to do.

The Nernst glower was kept at constant intensity by using a battery of storage cells as the source of current and was overvolted to 120 volts to increase the brilliancy of the light.

* Phys. Rev., N. S., 1914.

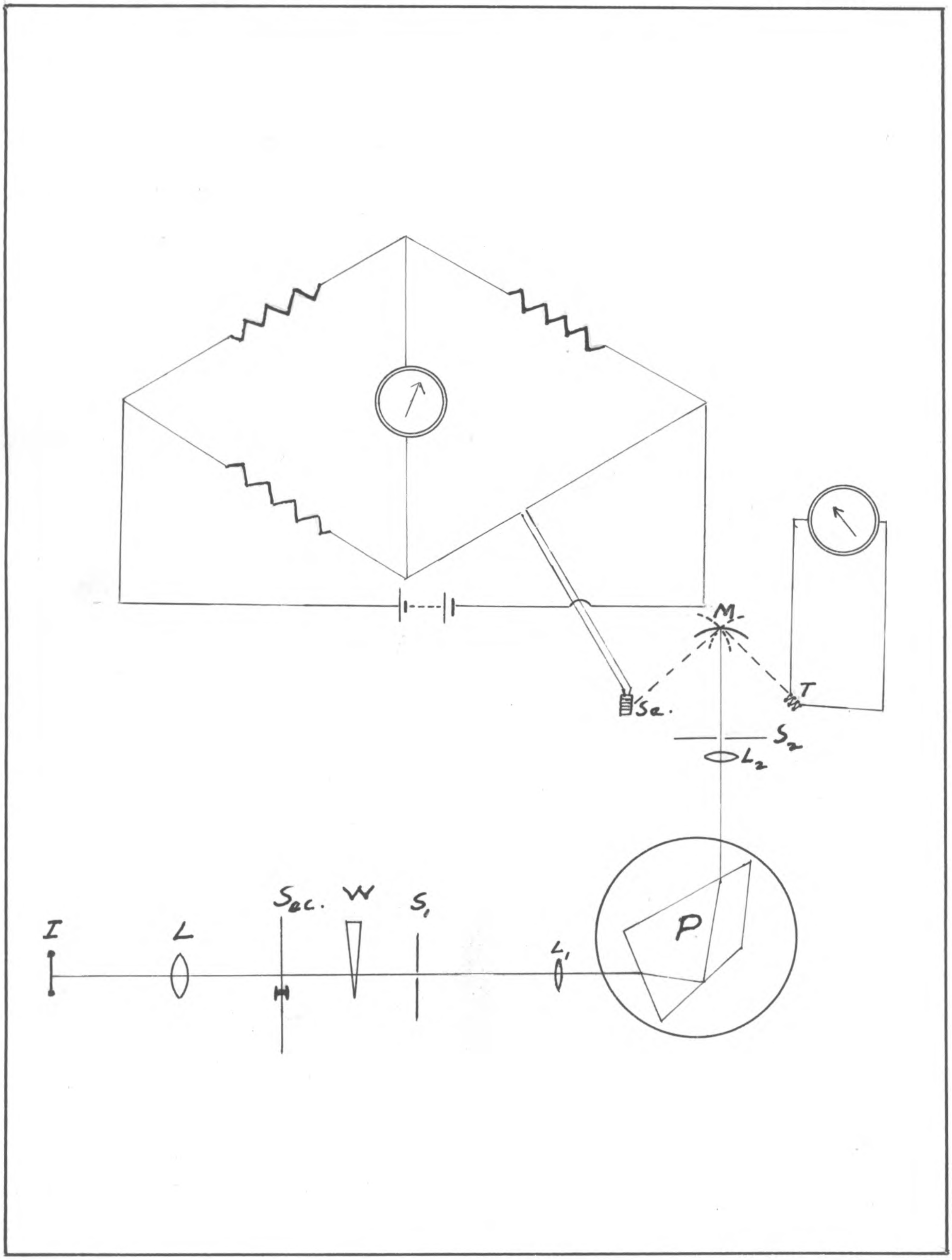


Fig. 1.

The optical wedge(W), made by gradually drawing an ordinary photographic plate out of its envelope, was placed in front of slit(S_1) to cut down the intensity of the light incident on the selenium cell. The sector(Sec.), attached to a fan motor, served the same purpose.

The selenium cell was made one arm of a Wheatstone bridge, which included a 16 volt battery of dry cells and a D'Arsonval galvanometer whose sensibility was of the order of 10^{-8} amps. Three periods of exposure of the cell to light were used, 10 sec., 30 sec., and .4 sec. For the .4 sec. exposures the method of Brown and Clark* was used. A pendulum opened the shutter in front of slit S_1, thereby exposing the cell to the light. At the same instant it closed the key K_1, Fig. 2, throwing the galvanometer in the Wheatstone bridge into circuit. .4 sec. later the pendulum struck key K_2, opening it, thereby throwing the galvanometer out of circuit. Thus, the deflection for an exposure of .4 sec. could be read. For the longer exposures the galvanometer circuit was kept closed, and the time of exposure determined by means of an ordinary stop watch.

In obtaining a curve the following method was followed: The energy of the wave length at which the curve was started was measured by means of the galvanometer connected to the thermopile, and adjusted to the desired value by use of the optical wedge or rotating sector. This same energy was then allowed to fall upon the selenium cell, and the deflection of the galvonometer, used in connection with the Wheatstone bridge, recorded. The illuminator was then set at the next wave length desired,

* Phys. Rev., XXXIII., p. 53, 1911.

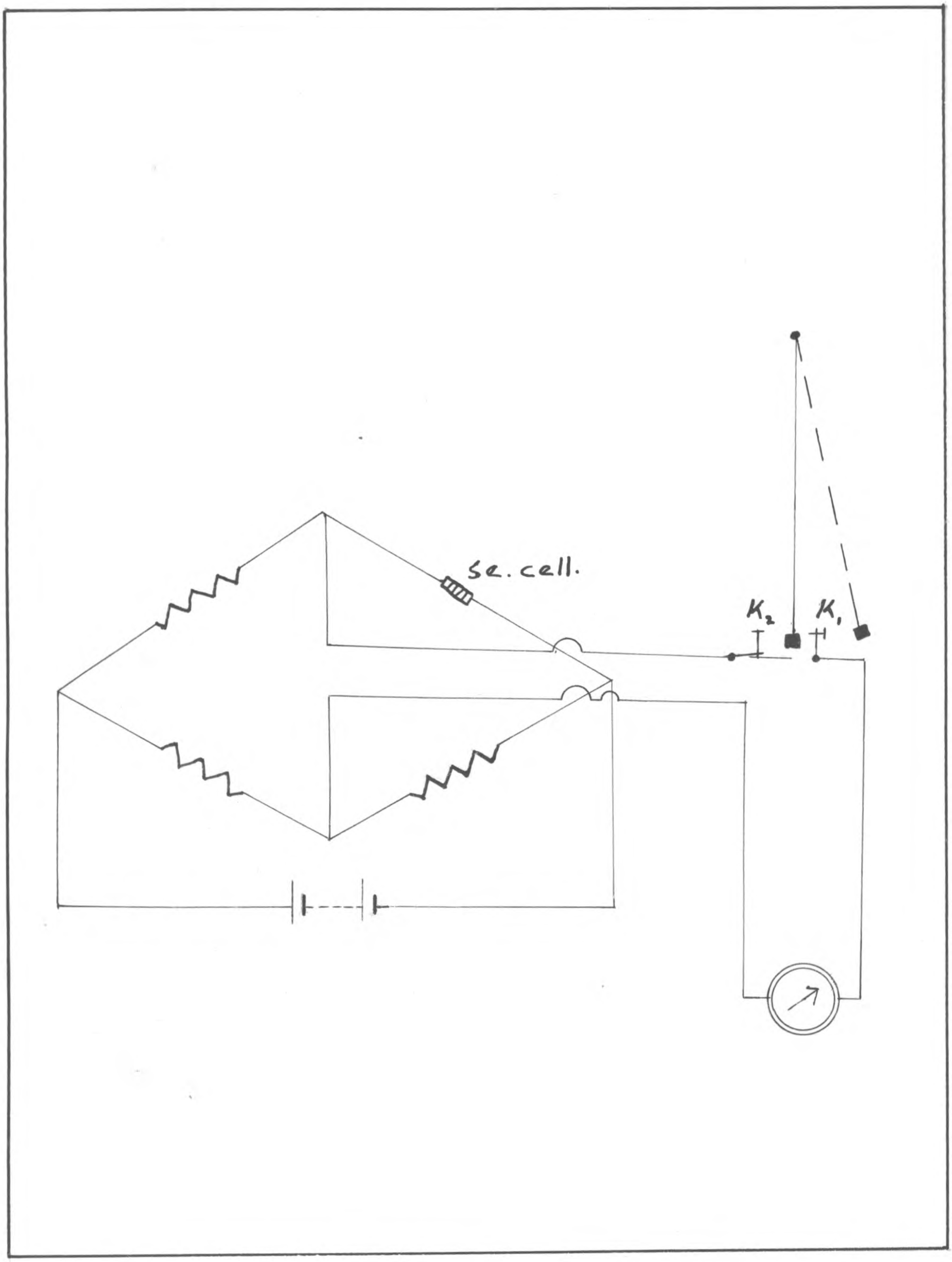
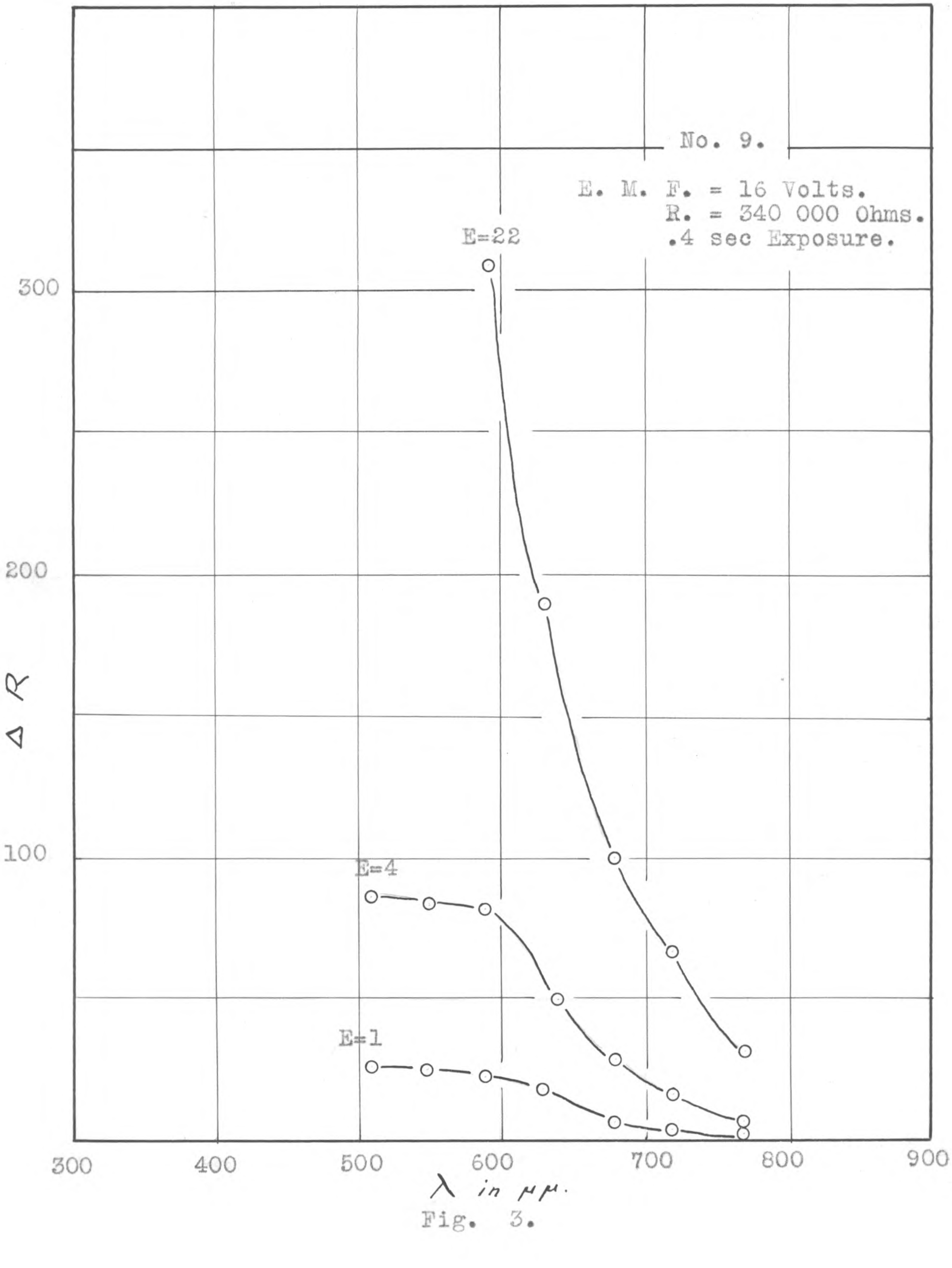


Fig. 2.

and the energy adjusted as before; then, when the cell had recovered its original dark resistance, it was again exposed. In this manner it was proceeded until the entire curve had been determined. The range, in general, was from 460 μμ to 800 μμ, since at values lower than 460 μμ the energy of the source was not sufficiently great to be measured accurately. The exposure always took place in the order from short to long wave lengths, since Brown and Sieg have shown* that the order of exposure does not influence the shape of the curve. This procedure also has the advantage that the energy of the succeeding wave lengths must be cut down instead of increased, since the energy at the shorter wave lengths is very low. The slit width was kept constant throughout the investigation, and the other factors were also kept constant as much as possible.

It was found that, except in a few cases, the shape of the wave-length sensibility curve did not change, whether the intensity of the incident light were high or low, or whether the cell were exposed short or long intervals. This is shown by the curves in Fig.3. Here the wave lengths are plotted as abscissae, and the change in resistance, which is proportional to the deflection of the galvanometer, as ordinates. Fig. 3 shows that the curves retain the same essential characteristics when the energy of the incident light is varied by a factor as great as 22. Fig. 4 shows that the type of curve remains the same for different periods of exposure. Fig.5 gives one type of curve in which a change in the energy of the light incident on the cell changes the shape of the curve. This last curve

* Loc. cit.



No. 9.
E. M. F. = 16 Volts.
R. = 340 000 Ohms.
.4 sec Exposure.
E=22
E=4
E=1
300
200
100
ΔR
300
400
500
600
700
800
900
λ in μμ.

Fig. 3.

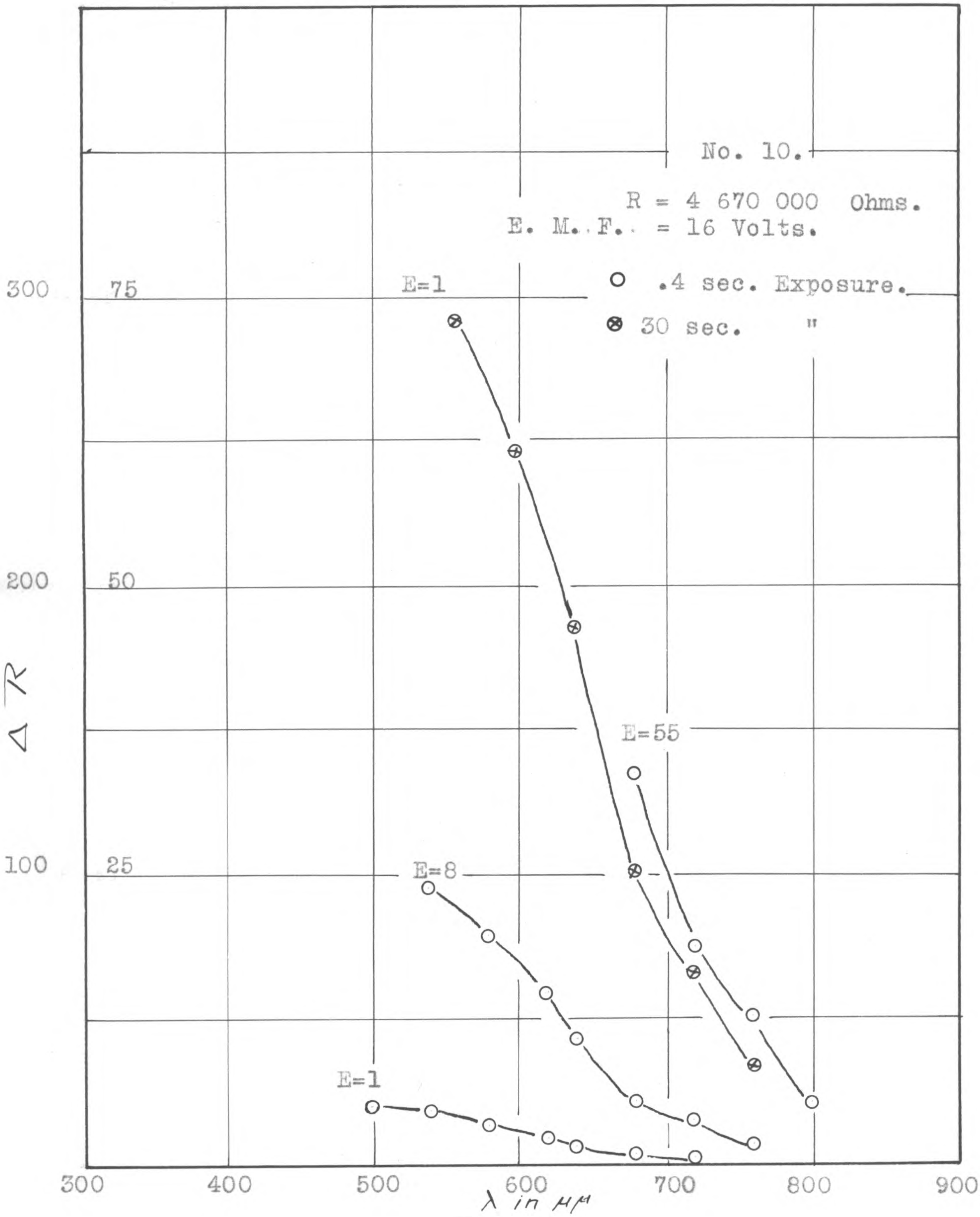
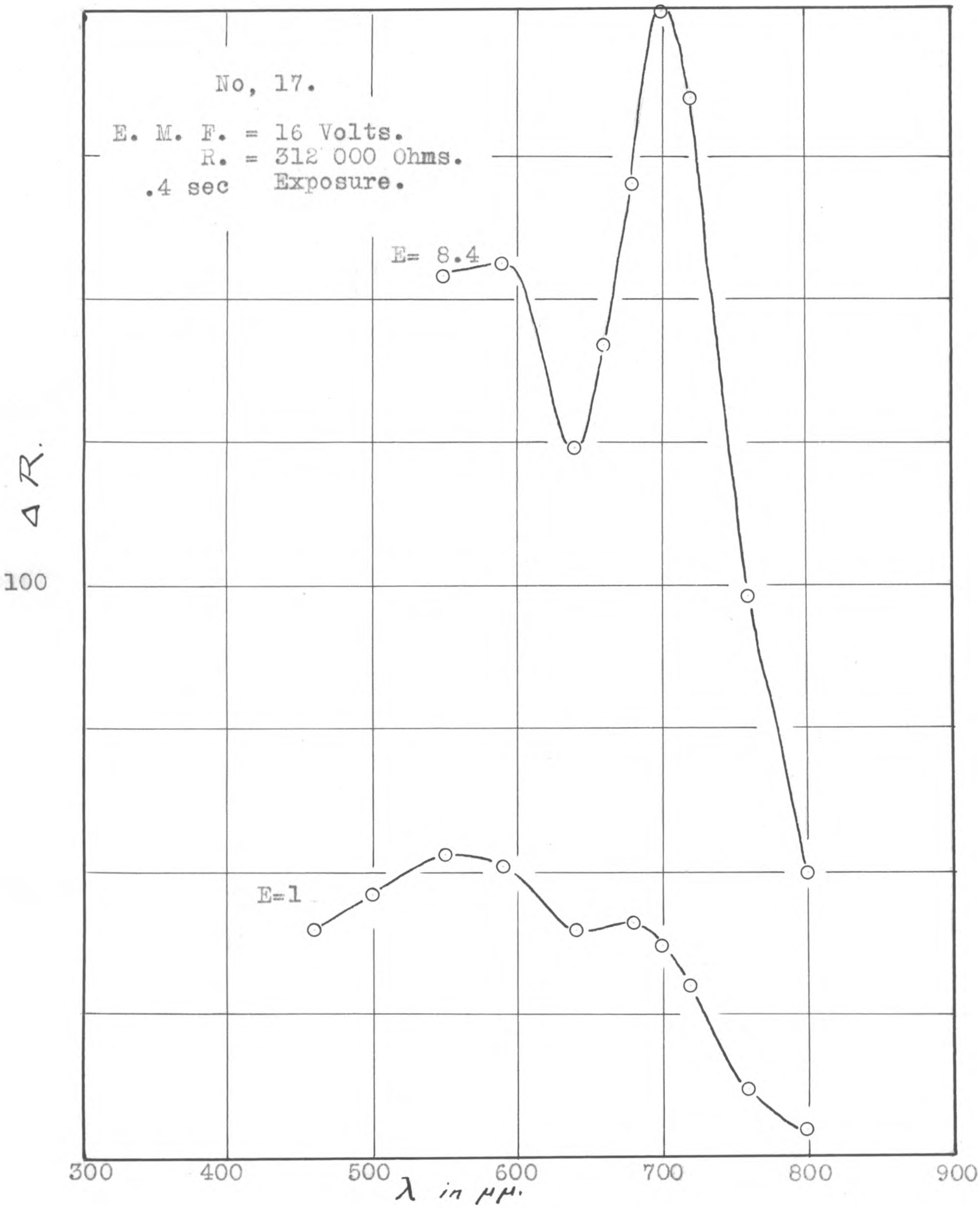

No. 10.
R = 4 670 000 Ohms.
E. M. F. = 16 Volts.
○ .4 sec. Exposure.
⊗ 30 sec. "
E=1
E=55
E=8
E=1
300
200
100
75
50
25
Δ R
300
400
500
600
700
800
900
λ in μμ

Fig. 4.



No, 17.
E. M. F. = 16 Volts.
R. = 312 000 Ohms.
.4 sec Exposure.
E= 8.4
E=1
Δ R.
100
300
400
500
600
700
800
900
λ in μμ.

Fig. 5.

is the typical curve obtained by observers for the Giltay type of cells. Whenever possible, therefore, on account of the sensitiveness of the apparatus, the exposures were taken for .4 sec.

The results obtained showed a wide variety of types of sensibility curves. The curves show maxima at wave lengths not previously recorded. Fig. 6 shows the curves obtained for different types. The curves are all plotted on an arbitrary scale which is so chosen that the maximum ordinate is the same for the different curves. They, therefore, do not show the relative sensitiveness of the cells. It is seen from this figure that maxima occur at wave lengths ranging from 440$\mu\mu$ to 800$\mu\mu$, and this most probably does not represent the entire range. These curves merely show the location of the most prominent maxima developed in this investigation. They are found at 440$\mu\mu$, 500$\mu\mu$, 550$\mu\mu$, 700$\mu\mu$, 720$\mu\mu$, and 800$\mu\mu$.

From Fig. 6 it is seen that the cells can be divided, in general, into two groups, viz., those which have their maximum sensibility at wave lengths greater than 640$\mu\mu$, and those in which the maximum occurs at wave lengths shorter than 640$\mu\mu$. There is one type of cell, however, which is an exception to the above statement, in that it has two maxima which are both very sharp and of about the same magnitude, one in the red at 700$\mu\mu$ or 720$\mu\mu$, and one in the violet at 440$\mu\mu$. The curves for this type are shown below in Fig.7. This type of cell is obtained when, after applying the selenium to the form in the manner previously described, it is heated for about 10 hours

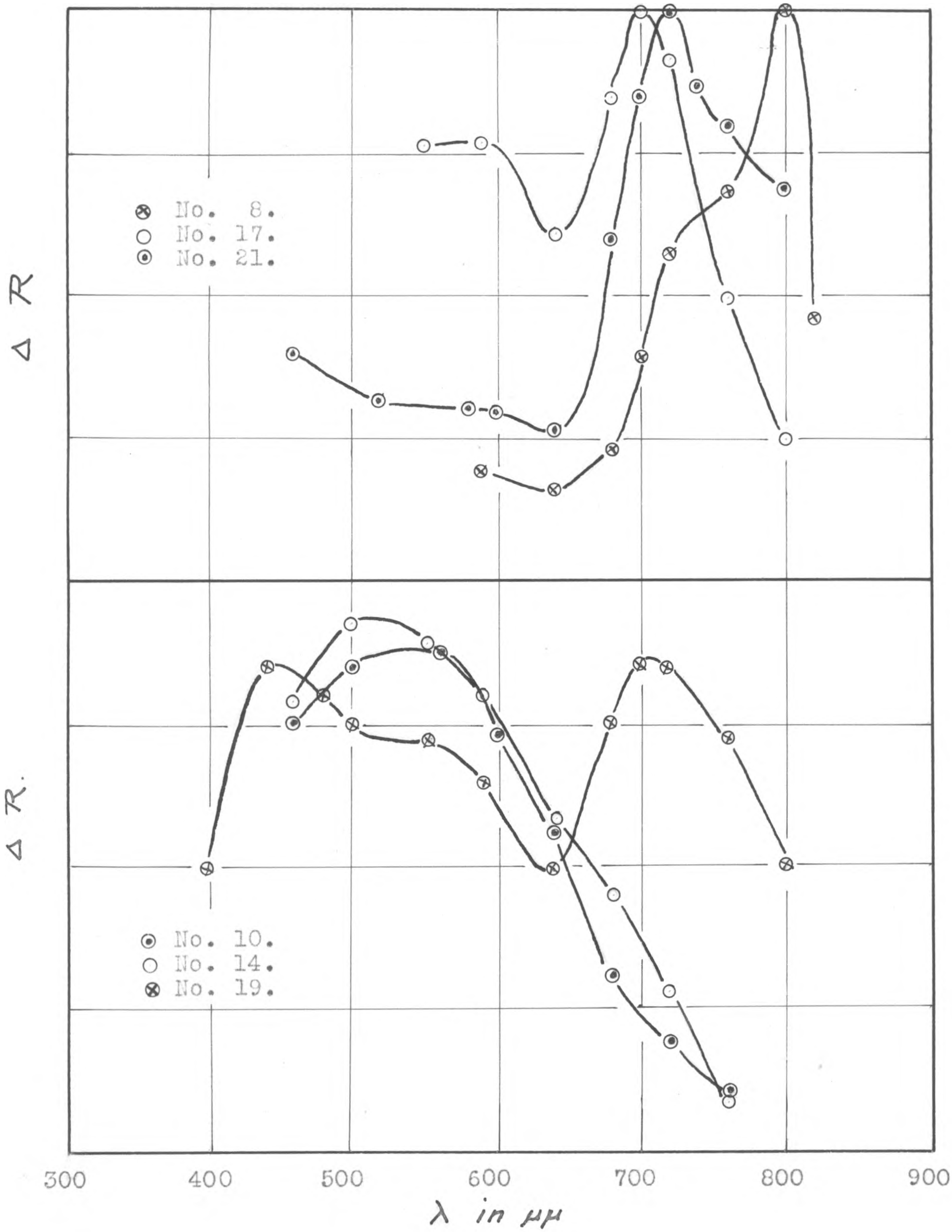

No. 8.
No. 17.
No. 21.
Δ R
No. 10.
No. 14.
No. 19.
Δ R.
300
400
500
600
700
800
900
λ in μμ

Fig. 6.

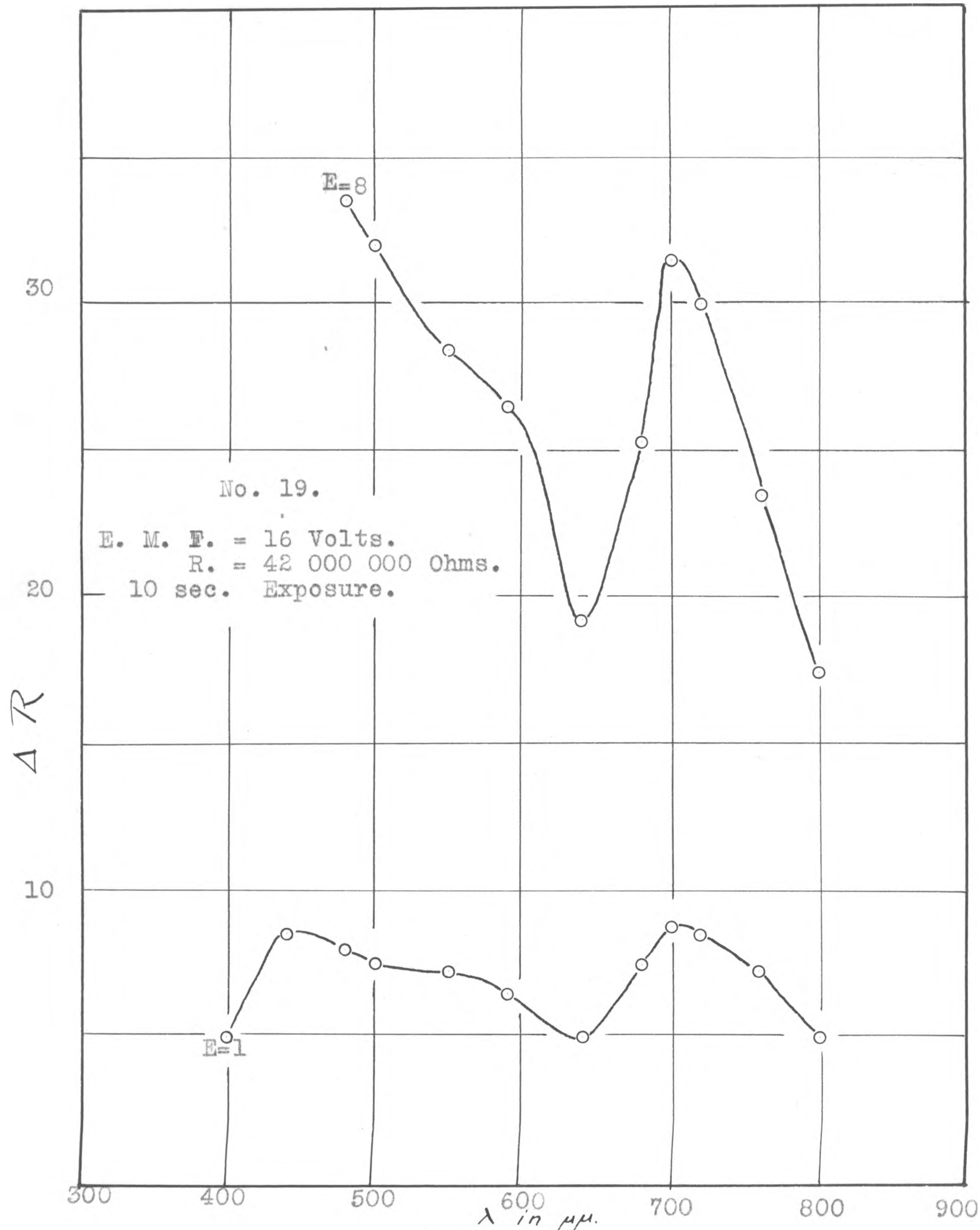

E=8
E=1
No. 19.
E. M. F. = 16 Volts.
R. = 42 000 000 Ohms.
10 sec. Exposure.
30
20
10
ΔR
300
400
500
600
700
800
900
λ in μμ.

Fig. 7.

at 180°C. In no case,,however, has a maximum been found at 640$\mu\mu$, nor has the author been able to find one recorded at this point.

Fig. 8 shows clearly the effect of variation in the conditions of annealing on the shape of the wave-length sensibility curve. This set of curves is typical of a large number obtained when conditions of temperature were the same as those represented here. With the same heat treatment, maxima have appeared at the same points as indicated in this figure, with but few exceptions. In the cases of exceptions the temperature control was found to be at fault.

Fig. 8, (A) represents the type of curve obtained when the cell, immediately after making, is subjected to a temperature of 210°C for some time, in this case 4 hours. This type shows a maximum about 500$\mu\mu$, and very little sensitiveness above 640$\mu\mu$.

Fig. 8, (B) represents the type obtained when the cell on making is subjected for a short time to a temperature of 210°C, in this case 1 hour, then allowing the temperature to fall gradually to 200°C, and keeping it constant at this point for four hours. Here is seen a change in the shape of the curve and a hint of a maximum in the red.

Fig. 8, (C) represents the type obtained when the cell was heated at 210°C for 30 min., the temperature allowed to fall to 190°C and kept constant there for 6 hours.

Fig. 8, (D) represents the type resulting when the cell was heated for 30 min. at 210°C and then at an average temperature of 170°C.

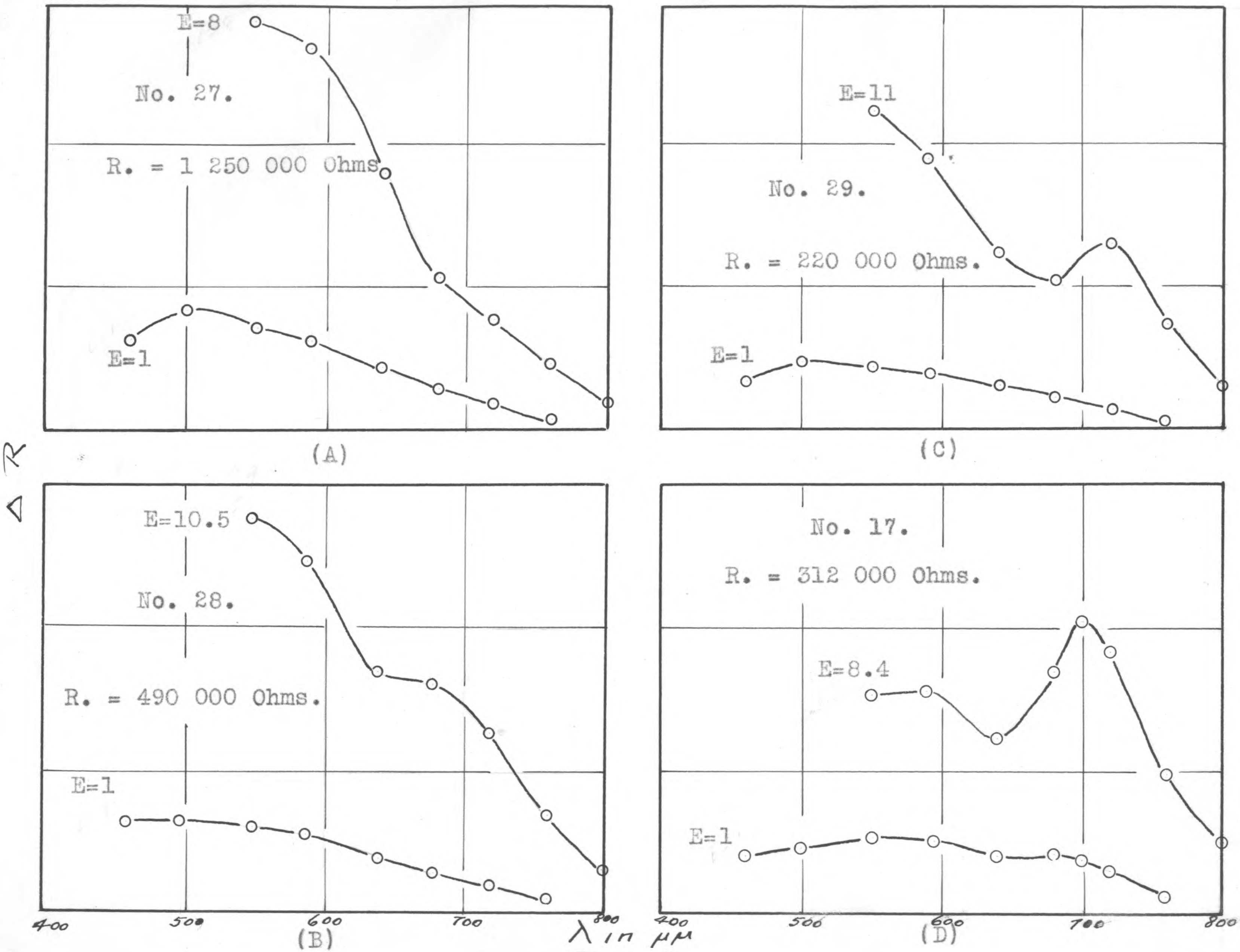

E=8
No. 27.
R. = 1 250 000 Ohms
E=1
(A)
E=11
No. 29.
R. = 220 000 Ohms.
E=1
(C)
ΔR
E=10.5
No. 28.
R. = 490 000 Ohms.
E=1
400
500
600
700
800
(B)
No. 17.
R. = 312 000 Ohms.
E=8.4
E=1
400
500
600
700
800
(D)
λ in μμ

Fig. 8.

In each case the preliminary heating at 210°C was given in order to lower the resistance of the cell, as was shown to be the case earlier in this paper. This was done in order to increase the accuracy of the measurements, for the arrangement for obtaining the wave-length sensibility curve is more sensitive, and hence, more accurate, the lower the resistance of the cell measured.

The control of the maximum in the red is clearly shown by Fig. 8. As the temperature of annealing becomes lower, the maximum in the red, relative to that in the blue, becomes gradually higher, until in the type shown in (D) it exceeds that in the blue.

The most obvious explanationof the variation found in the various types of selenium cells, in the light of recent work on selenium, rests on the probable difference in the crystals composing the various types of cells. As we have seen, a rough classification into two general types can be made, those most sensitive to red light and those most sensitive to blue. Dr. Brown has succeeded in producing several new forms of selenium crystals by sublimation. A cell made by depositing one variety of these on a form, such as has been previously described, was found by him to have a maximum at 780$\mu\mu$. It is not improbable that the maximum sensitiveness of a cell composed of crystals of another variety should lie in the blue end of the spectrum. Nor is it inconceivable that the location may change due to a variation of the pressure at the time of formation of the crystals. These assumptions would find confirmation or contradiction in work done on single crystals. Drs. Brown and Sieg in some very recent investigations, the results of which have not yet been published, have found the maximum sensitiveness of a single crystal to lie in the red end of the spectrum. An extension of this work, it is hoped, will further confirm the assumptions made above.

The explanation of the different types of cells on this basis, then, is simple. A cell, such as is represented by (A), Fig. 8, may be thought of as containing crystals which are sensitive to a great extent only to blue light, and few or none at all of those sensitive to red light. In other words, the temperature at which this type is annealed is too high to favor the formation of crystals sensitive to red light. Proceeding to another type, (C) in Fig. 8; this could be assumed to contain a mixture of the two varieties, the amount of the red crystals present not being sufficient to overcome the effect of the blue crystals. The type represented in Fig. 7 might be explained on the same basis, i. e., a mixture of red and blue crystals, in which the point of maximum sensibility to light has been shifted towards the ultra-violet, due to a variation in some one or more of the conditions governing the formation of the crystals.

If the conclusions given above are correct, the problem of the explanation of the light sensitiveness of selenium reduces to the explanation of the changes taking place in the single crystals under the influence of light and other agencies. This problem is now being investigated by Drs. Brown and Sieg.

PERMANENCE OF THE CHARACTERISTICS.

As to the permanence of the characteristics of the different types evidently no definite statement can be made, as the time elapsing between the production of the first cell and the present is hardly long enough to warrant any such statement. Fig. 9 shows the characteristic curves of two cells taken at different time intervals. It is seen that they are essentially the same.

It has been mentioned that the sensitiveness of two of the cells was not permanent, but decreased rapidly in value. With these two exceptions, the sensibility of the samples showed a gradual increase for a few weeks after making, just as the resistance did.

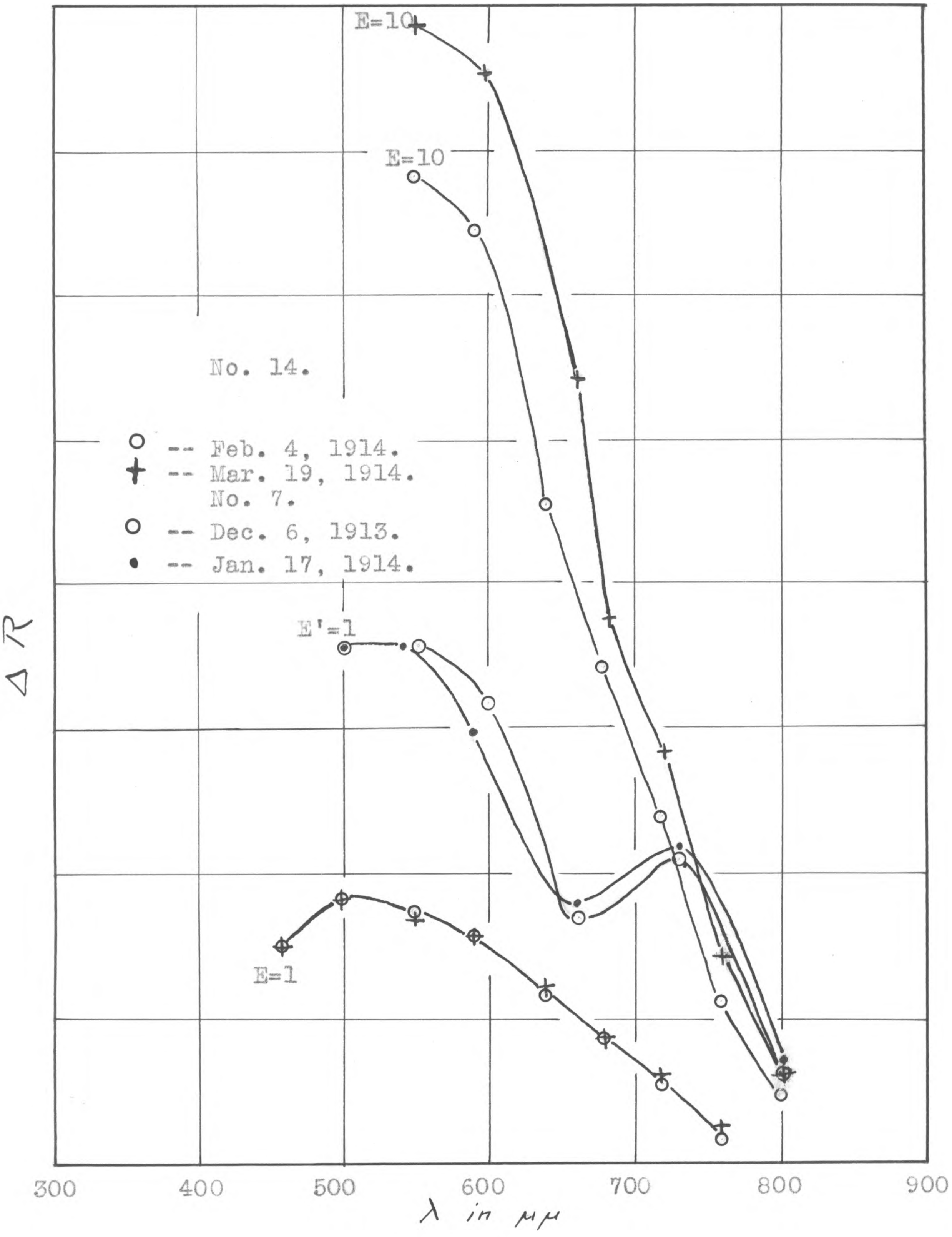

E=10
E=10
No. 14.
O -- Feb. 4, 1914.
+ -- Mar. 19, 1914.
No. 7.
O -- Dec. 6, 1913.
• -- Jan. 17, 1914.
E'=1
E=1
ΔR
300
400
500
600
700
800
900
λ in μμ

Fig. 9.

SUMMARY.

In this paper has been shown:

1. That the resistance of selenium cells depends to a great degree upon the treatment to which they have been subjected while annealing them.
2. That the heat treatment probably determines the sensitiveness of the cells. Definite proof was not obtained on this point, however, although this conclusion is indicated by results obtained in two cases.
3. That the location of the maximum in the wave-length sensibility curve can be controlled by a variation in the conditions under which the selenium in the cell is crystallized. It was shown that the temperature variations play the most important part.
4. That the various types of cells produced in this investigation can be explained by assuming the presence of various kinds of crystals in the cell. The temperature at which one kind is formed may not be favorable for the formation of another variety, hence, the production of the different types of cells.