The Cæsium-Oxygen-Silver Photoelectric Cell

An Investigation of the Relations in a Composite Photoelectric Surface

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Technique is described permitting the formation of cæsium-oxygen-silver photoelectric cells under controlled conditions. It is shown that the essential conditions are a quantitative control of the degree of oxidation of the silver cathode base and the amount of cæsium generated together with a regulation of the amount of chemical interaction by a control of the time and temperature of the heat treatment.

Variations in sensitivity to integral light at 2,710° K. color temperature are shown as a function of the initial amounts of oxygen and cæsium and the time of heat treatment.

Small amounts of oxygen were permitted to react with the standard cathode surface. The sensitivity of the cathode fell but recovered due to the diffusion of free cæsium to the surface from the underlying material. The effects are shown in relation to the integral sensitivity and the spectral response from 6,000 Å. to 10,000 Å.

The effects of depositing minute amounts of free cæsium upon the standard cathode surface are also shown in relation to the spectral response.

The active surface of the cathode appears to be a film of free cæsium of atomic dimensions adsorbed upon a matrix of cæsium oxide and silver containing free cæsium and a small amount of silver oxide. The spectral characteristics of the photoelectric response appear to depend largely upon the thickness of the surface film of free cæsium. This film thickness is determined by the cæsium concentration in the underlying matrix and is maintained by a diffusion equilibrium.

INTRODUCTION

EARLY studies of the photoelectric effect were made on pure metals, eliminating, in so far as possible, the effects of absorbed gases. But since the alkali metals alone respond appreciably to visible light, and these only to light at the blue end of the spectrum, the development of photoelectric cells of greater response to ordinary light sources has led to the study of thin films of the alkali metals and of various composite surfaces. The enhanced photoelectric activity of the thin films of the alkali metals was first brought out by Ives [1] who also noted that the maximum response and the greatest extension of sensitivity toward the red end of the spectrum were obtained when the film thickness was of the order of one molecular diameter. Later work [2] has shown that the maximum excursion of the photoelectric threshold of an alkali metal film on a metallic base

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[1] H. E. Ives, *Astrophys. J.*, **60**, 4 (1924).
[2] Ives and Olpin, *Phys. Rev.*, **34**, 117 (1929).

corresponds with the wave-length of the first line of the principal series of the atomic spectrum of the alkali metal.

The first composite surface to attain practical importance was the so-called potassium hydride cell discovered by Elster and Geitel [3] in which a potassium surface is sensitized by a glow discharge in hydrogen. This cell has its maximum response at 4,350 Å. and its photoelectric threshold at 5,900 Å. The response of a good potassium hydride (vacuum) cell to a light source at a color temperature of 2,710° K. is about one microampere per lumen, which is eighty times that obtainable with pure potassium surfaces.

This sensitivity is still below that required for many technological applications. Also, the potassium hydride surface is unstable even at ordinary temperatures and may deteriorate rapidly in use or in storage. So there has been a great demand in engineering applications for both a more stable device, and a cell more sensitive to the red and infra-red light which constitutes the major, part of the emission from common incandescent light sources.

The photoelectric threshold is a direct measure of the work necessary to liberate an electron from a surface, i.e., the "work function" which also figures in the thermionic effect. That is, both red sensitive photoelectric cells and active thermionic filaments possess low values of the work function. The study of the thermionic effect in adsorbed films of cæsium on tungsten and on oxidized tungsten by Langmuir and Kingdon [4] and by Becker [5] have indicated surprisingly low values of the electron work function. It was to be expected that some similar surface should possess a high order of photoelectric response to red light. Research along these lines has resulted in this and other laboratories in the development of the cæsium-oxygen-silver photo-electric cell. Early work on cells of this type is reported by Koller [6] and by Campbell.[7]

For the cells discussed in this paper the active photoelectric surface is formed on a roughened silver sheet. This is slightly oxidized by making it the cathode in a glow discharge in oxygen. Cæsium is then generated by chemical reaction in a pellet enclosed within the photo-electric cell bulb. Finally, by a proper temperature cycle the cæsium is condensed on the silver oxide surface of the cathode and allowed to react with it to form the active photoelectric surface.

[3] Elster and Geitel, *Phys. Zeit.*, **11**, 257 (1910).
[4] Langmuir and Kingdon, *Phys. Rev.*, **21**, 380 (1923) abstr.
K. H. Kingdon, *Phys. Rev.*, **24**, 510 (1924).
Langmuir and Kingdon, *Proc. Roy. Soc.*, 107-A, 61 (1925).
[5] J. A. Becker, *Phys. Rev.*, **28**, 341 (1926).
[6] L. R. Koller, *Phys. Rev.*, **33**, 1082 (1929) abstr. *Phys. Rev.*, **36**, 1639 (1930).
[7] N. R. Campbell, *Phil. Mag.*, **12**, 173 (1931). "Photoelectric Cells and Their Applications" (Phys. Soc. London, 1930), p. 10.

The cells thus obtained are highly sensitive to red and infra-red light. The maximum response is at 8,000 Å., the response is one third as great at 10,000 Å., and the photoelectric threshold is somewhere in the neighborhood of 12,000 Å. Cells are frequently obtained with a vacuum sensitivity of 35 microamperes per lumen to a light at 2,710° K. color temperature, and their useful life is indefinitely long, even at a temperature of 50° C. But such results obtain only if the cells be produced under controlled and definitely specified conditions. It appears that the product is definitely affected by variations in the quantities of cæsium and oxygen. Also, the course of the chemical reactions (still obscure) and the thickness of the final cæsium thin film are very sensitive to slight variations in the process conditions. In the early stages of this work the results were highly erratic; only occasionally was a useful cell obtained. A large amount of development time has been devoted in these laboratories to the isolation and correlation of the various factors which determine the sensitivity of a finished cell. With the technique now available, cæsium-oxygen-silver photoelectric cells are prepared under conditions of quantity production with sensitivities varying within a factor of two and with a process shrinkage no greater than obtained in the production of high quality thermionic vacuum tubes.

The Structural Details and Method of Preparation of the Cells

The structure of the cells used in this study is shown in Fig. 1. The cathode is a semicylinder of silver 99.9 per cent pure. The anode is a nickel wire mounted in the axis of the cylinder. These are mounted on a stem which is sealed into a spherical bulb of soda-lime glass. Around the stem is suspended an open ring of heavy copper wire between the ends of which is crimped a tube rolled from thin sheet molybdenum which carries the cæsium pellet. This structure is adapted to the initiation of the chemical reaction by induced high-frequency currents with a minimum heating of the oxidized cathode. A nickel shield is placed between the pellet sheath and the cathode to protect the latter from radiation and to deflect the hot cæsium vapor evolved by the pellet.

The essential steps in the process of formation of the active cathode surface are:

1. Formation of a silver oxide film on surface of cathode.
2. Preparation of cæsium.
3. Combination of cæsium with silver oxide surface.

1. *Formation of a Silver Oxide Film on Surface of Cathode*

The cells are sealed to a high vacuum exhaust system and baked out at 400° C. The next step is the oxidation of the surface. It was found that oxidation by a glow discharge in oxygen was the most suitable method. This oxidation could not be done quantitatively and uniformly over the front surface of the cathode because of surface irregularities in the silver and because of variations in the physical conditions of the surface. Means were therefore sought to obtain a
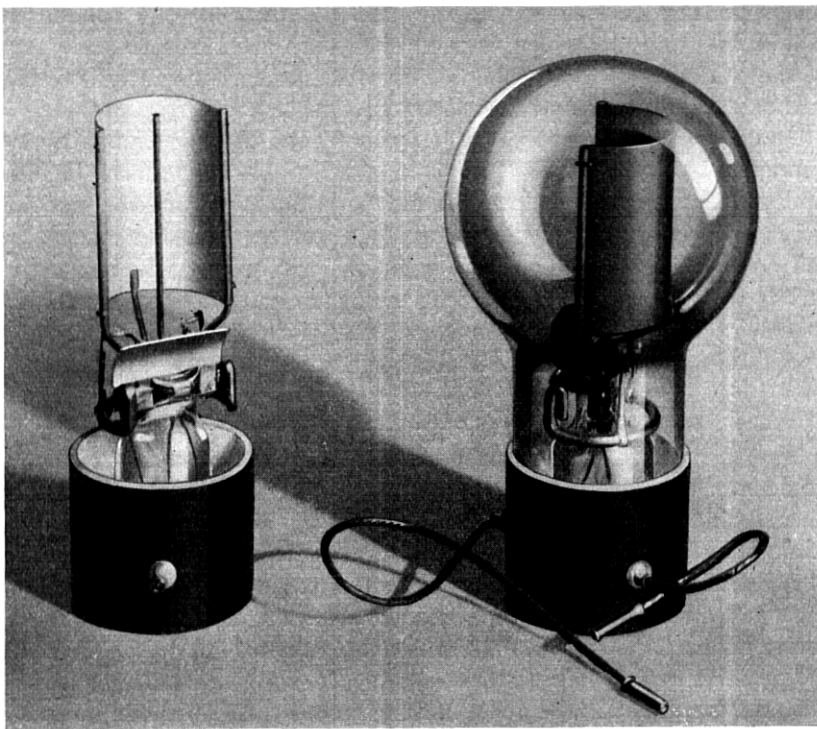

Fig. 1—Western Electric 3A photoelectric cell.

uniform surface and one that would be the same in all cells, independent of irregularities that could not be avoided, which were due to past history.

To accomplish this, electrolytic oxygen is admitted to the exhaust system and the cathode is oxidized by a glow discharge until completely black. Then the circuit is held closed while the cathode is heated by ion bombardment until the silver oxide is decomposed, leaving a bright matte surface. After cooling, this process is repeated.

It is repeated a sufficient number of times to establish a cathode surface that is uniformly rough over its entire front surface and is substantially the same for all cells. The exhaust system is then evacuated and pure oxygen admitted to the optimum pressure for quantitative oxidation.

The quantitative oxidation is accomplished by charging a condenser of known capacity to a definite voltage and then discharging it through the cell in series with a suitable resistance. The discharge is in the proper direction for oxidation of the cathode. A double contact telegraph key is used for charge and discharge of the condenser. The number of taps given to the key is then a quantitative measure of the oxidation of the cathode. After the requisite oxidation of each cathode, the system is again evacuated.

As the oxidation proceeds, the surface goes through characteristic changes in color. At 25 "taps" it is yellow, at 50 red, at 75 blue and at 100 a greenish yellow. If the oxidation is continued, the color goes through another cycle becoming a golden yellow, a deep rose red and an olive green. From then on it is quite dark, but under strong light shows several alternations of red and green before ending in black. As will be seen later an oxide thickness corresponding to about 100 taps is the most suitable for use.

2. Preparation of Cæsium

The early work demonstrated the necessity of a close control of the amount of cæsium made available for the cathode in each cell. After an examination of a number of chemical systems for preparation of cæsium by a high temperature chemical reaction, a pellet composed of a mixture of cæsium chromate, chromic oxide and powdered aluminum was adopted. These materials are thoroughly mixed in quantitative proportions and ground in an agate mortar. A suitable weight of the mixture is compressed in a die. A slight but uniform loss of material is entailed in the pellet making process. Any desired quantity of pellets differing in weight by not more than ten per cent can be made by this process. This pellet is placed in the molybdenum housing described above and after the quantitative oxidation of the surface and removal of excess oxygen the pellet is heated by high-frequency induction to its kindling temperature.

Sufficient aluminum is supplied to completely reduce the cæsium chromate and chromic oxide. Besides permitting a pellet of convenient size, the chromic oxide is instrumental in furnishing, by its reduction, a large amount of heat. The high-frequency heating serves only to initiate the reaction. The exothermic reaction involves a

great rise in temperature and causes the immediate and complete expulsion of all cæsium. This allows the high-frequency heating with the attendant hazard of heating the cathode and reducing a part of the silver oxide to be a minimum. The cæsium travels in straight lines from the pellet housing and is condensed on the glass wall of the bulb. A shield above the housing prevents any cæsium, as it is expelled from the pellet, from impinging on the cathode surface.

3. *Transfer of Cæsium to the Cathode Surface*

The transfer of the cæsium to the cathode surface and its reaction with the silver oxide film to the proper extent is probably the most difficult process to control. The ideal process requires the transfer of the cæsium from the glass wall of the envelope to the cathode surface without the reduction of any of the silver oxide by the heat required to bring about this cæsium transfer, the reaction of the silver oxide with the greater portion of the cæsium and the leaving of a sufficient amount of uncombined cæsium to supply the required volume concentration of cæsium and to cover the entire cathode surface with an equilibrium thin film of cæsium. The practical difficulties in carrying out this process are due to the fact that, at the temperatures required to transfer in a reasonably short time the cæsium from the glass wall to the cathode, the silver oxide has an appreciable rate of decomposition. This difficulty was overcome so far as is possible by heating the glass wall selectively at a controlled temperature. There is a material lag in the cathode temperature in this process. Thus the cathode is kept at as low a temperature as possible while the cæsium is transferred to it at a sufficiently rapid rate.

This is accomplished by surrounding the cell with a stream of hot air for approximately 30 minutes. A glass chimney is placed around the cell. The chimney fits into a transite manifold containing heating coils through which compressed air is fed at the rate of 0.5 liter per second per chimney. The temperature of the air stream is controlled to within 5° C.

If this process is carried on in the usual electric oven where a portion of the winding is exposed, the cathode is heated preferentially due to the radiant heat and it is almost impossible to obtain an active surface due to silver oxide reduction by temperature, as well as to the fact that with the cathode the hottest surface, the cæsium will tend to condense elsewhere. Even with all windings of the oven covered by asbestos sheet so that substantially all heat is due to convection, the process is infinitely more difficult of control than with the hot air stream oven.

It was not found practicable, even with such exact control of the silver oxide film, the amount of cæsium and of the temperatures of the photo-cell parts, to give the cell a definite time-temperature cycle in the transfer process. It is necessary to follow the growth of the photo and thermionic currents as the heating continues. A small tungsten lamp is mounted in a fixed position with respect to the cell and after the heating has progressed for some 20 minutes, observations are made each minute on the total thermionic and photoelectric currents. These currents rise in value as the surface is built up and, by experience, a definite point on the growth curve is found where the hot air stream should be discontinued in order to obtain the optimum surface.

After the cell has cooled it is sealed from the exhaust system if a vacuum cell is desired, or filled to the required pressure with an inert gas, usually argon, if a gass filled cell is desired.

SURFACE STRUCTURE

In the study of the photosensitive cathode surface some information regarding the physical structure and chemical nature of the surface has been gained by direct examination and analysis. The physical nature of the roughened silver may be seen from microphotographs of the cathode taken following the roughening oxidation and reduction which precedes the quantitative oxidation.

Fig. 2a is a plan view taken at 1,530 diameters magnification. Fig. 2b is a transverse section of the cathode supported in a heavy nickel plate taken at 200 diameters. Fig. 2c is a detail view of the front surface of the transverse section taken at 2,450 diameters. It would appear that the effect of the oxidation and reduction is to etch out the polished silver sheet, giving the surface elements a random orientation but not causing any great increase in surface area. If we judge the length of a line element to be doubled, this indicates a four-fold increase in area.

To determine the amount of oxygen entering into combination at each discharge of the condenser, three cells were given 50, 75 and 100 taps respectively of the key controlling the condenser discharge. The excess oxygen was removed and the exhaust manifold trapped off by a mercury seal. Each cathode in turn was then heated by induced high-frequency current till the silver oxide decomposed, and the pressure developed in the exhaust system was measured. The pressures and amounts of oxygen as microgram-molecules of O_2 are given in Table 1.
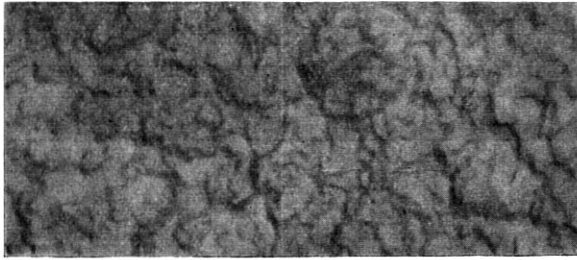
(a)
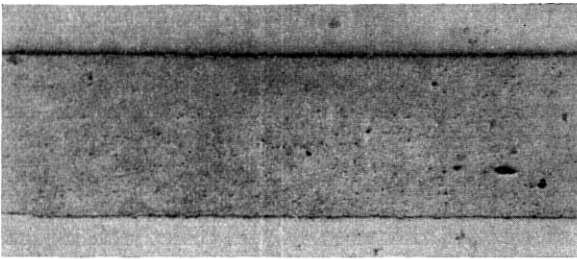
(b)

(c)

Fig. 2—Microphotographs of roughened silver cathode base. (a) Plan view, 1530 diameters. (b) Transverse section, 200 diameters. (c) Transverse section, 2450 diameters.

TABLE 1

No. of Taps	Pressure	Micro-moles of O_2	Micro-moles per 100 Taps
50	0.0179 mm.	2.24	4.48
75	0.0256	3.20	4.27
100	0.0369	4.62	4.62
Weighted average			4.45

This value of 4.45 micro-moles of oxygen per 100 taps corresponds to 1.32 molecules of O_2 or 2.64 atoms per electron equivalent of the charge transported in the glow discharge, assuming complete discharge of the condenser. This value entails a high efficiency in the combination of positive ions with the surface, and also predominantly polyatomic ions at least as complex as O_3^+.

Microchemical analyses were performed on several cells to determine the cathode composition and the final distribution of the cæsium. With an accuracy of about 3 per cent all the initial cæsium was recovered, 68 per cent being recovered from the silver cathode and the rest from the inner surface of the glass bulb. No cæsium was found in the pellet residue. In the cathode surface was also found an average of 0.13 milligram of undecomposed silver oxide. But the actual amount may be greater for we have later evidence that at least 7 per cent of the cæsium on the cathode occurs as the free metal which would reduce silver oxide when the cathode is extracted with water and dilute acid prior to the analysis.

The optimum conditions, as shown later, are obtained with 4.1 milligrams of cæsium chromate in the pellet and a "ratio" of 19 condenser discharges per milligram of cæsium chromate. These are equivalent to 83 micrograms of cæsium and 3.2 micrograms of oxygen (using the factor from Table 1) per square centimeter of the cathode and a ratio of 3.1 atoms of cæsium per atom of oxygen. With 68 per cent retention of the cæsium in the cathode, we obtain 56 micrograms of cæsium per square centimeter and an atomic ratio of 2.1. If we neglect the free cæsium and residual silver oxide in the cathode surface and assume that no oxygen has been lost from the cathode, which implies that the cæsium on the bulb has been oxidized by reaction with water or other constituents of the glass—the atomic ratio of 2.1 suggests that Cs_2O is the main cæsium constituent of the cathode surface. But however probable it may seem, it is not possible to demonstrate this by ordinary analytical means in the presence of free cæsium and residual silver oxide.

These initial and retained amounts of cæsium are equivalent respectively to 910 and 620 atomic layers on the plane cathode surface. If we assume the surface to be increased by a factor of four in roughening, we find the cæsium retained in the cathode surface to be equivalent to roughly 155 atomic layers of free cæsium. This cæsium will, of course, occur mainly as cæsium oxide and be mixed with the finely divided silver from the reduced silver oxide. It would comprise about 50 layers of Cs_2O molecules.

L. R. Koller [6] has given quantitative data on surfaces which were

[6] Loc. cit.

formed by admitting oxygen to a cathode surface covered with a thick adsorbed layer of metallic cæsium. He finds a maximum activity at a cæsium-oxygen weight ratio of 110, which corresponds to 13.2 atoms of cæsium per atom of oxygen. This high value may be due in part to an incomplete yield from his cæsium pellets, but we doubt that the surface structure so obtained can be closely compared with that which we have described. The cells described elsewhere in his paper have much more closely analogous surfaces.

N. R. Campbell [7] has performed experiments in which cæsium is diffused slowly into a cell containing an oxidized silver cathode, all held at 184° C. in an aniline bath. He finds the completion of the reaction corresponds to the formation of Cs_2O, or an atomic ratio of 2.

Kingdon and Thompson [8] also report their cathode surfaces, presumably the same as in the cells described by Koller, to consist of Cs_2O.

A Survey of Macroscope Parameters

With uncertainty as to the microscopic physical structure of this surface, and no adequate theoretical basis for the correlation of photoelectric response to such a detailed structure, a macroscopic frame of reference has been essential to the correlation of data. This has been particularly important in the development phases of the project so that the results obtained should be self-sufficient and the systematic investigation of substances and processes should not be conditioned by the anticipated interpretations. From a thermo-dynamic standpoint, the surface may be considered as a two-dimensional phase or system with two variable components, cæsium and oxygen. If this system were in equilibrium, its properties would depend only on its temperature and the amounts of the components. Since it is far from equilibrium the specification of its condition or "state" requires also its past history, the most vital part of which is the heat treatment.

As the activity of a completed cell is definitely affected by each of the factors controlled in the quantitative technique, it will be seen that the state of the cathode surface is a function of (at least) five parameters, viz: the amount of cæsium, the amount of oxygen, the surface roughness of the silver, and the temperature and time of the heat treatment. Some qualitative experience seems to indicate that variation in surface roughness shows itself chiefly by affecting the efficiency of the glow discharge in the quantitative deposition of oxygen, and to a limited extent involves a greater or less extension

[7] Loc. cit.
[8] Kingdon and Thompson, Physics, 1, 343 (1931).

of the surface. Also, the temperature and time of heat treatment are to a limited extent compensatory. So a more fundamental specification of the active surface would involve the surface concentrations of cæsium and oxygen, and a degree of interaction which is commensurate with the heating time.

The best known thin film phenomena in the past have been of the type of cæsium adsorbed on tungsten, a single component film under essentially equilibrium conditions. At least the film is reversibly adsorbed for it may be condensed or evaporated at will by varying the tungsten temperature or the cæsium vapor pressure. Cæsium on oxidized tungsten is again a two-component film. The cæsium is reversibly adsorbed and, after the cæsium is removed, it appears that the adsorption of the oxygen is reversible at a considerably higher temperature.

Langmuir and Villars [9] have published curves showing the thermionic activity of tungsten filaments with varying amounts of adsorbed cæsium and oxygen. Due to the lack of an independent measure of the amount of adsorbed oxygen the data have been presented from a different point of view, resulting in a determination of the heat of adsorption of the oxygen. But we may point out the obvious though tacit assumption that the thermionic and other properties of the surface are uniquely determined in terms of the amounts of adsorbed oxygen and cæsium (and the temperature). This is equivalent to the presumption that the filament is under equilibrium conditions.

In contrast, the two-component film of cæsium and oxygen on silver which comprises the photoelectric cathode is formed by essentially irreversible processes. No cæsium atom which has combined with oxygen can be released, and no oxygen atom split off from the silver surface may be recombined. And the reaction is stopped long before any equilibrium is reached.

To obtain definite knowledge of the relations in the neighborhood of the optimum conditions we have prepared cathode surfaces under carefully controlled conditions. Two different amounts of cæsium were used and the oxygen-cæsium ratio (the number of "taps" per milligram of cæsium chromate) and the time of hot air heating were systematically varied. The first series of cells was made with pellets containing approximately 5 milligrams of cæsium chromate. The oxygen-cæsium ratio was varied from 15 to 30, and three groups heated for 15, 30 and 60 minutes respectively at 220–225° C. In each case, as shown in Fig. 3, the activity as measured with a light source at a color temperature of 2,710° K. goes through a maximum

[9] Langmuir and Villars, *J. Amer. Chem. Soc.*, **53**, 486 (1931).

in the neighborhood of the 20 ratio.   Also, the maximum activity is significantly higher for the 30-minute heat treatment than for either 15 or 60 minutes.   The second series of cells was made with pellets containing 3 milligrams of cæsium chromate.   The oxygen-cæsium ratio was varied from 10 to 30 and three groups baked for 7.5, 15 and 30 minutes, respectively.   In this series the maximum activity occurs
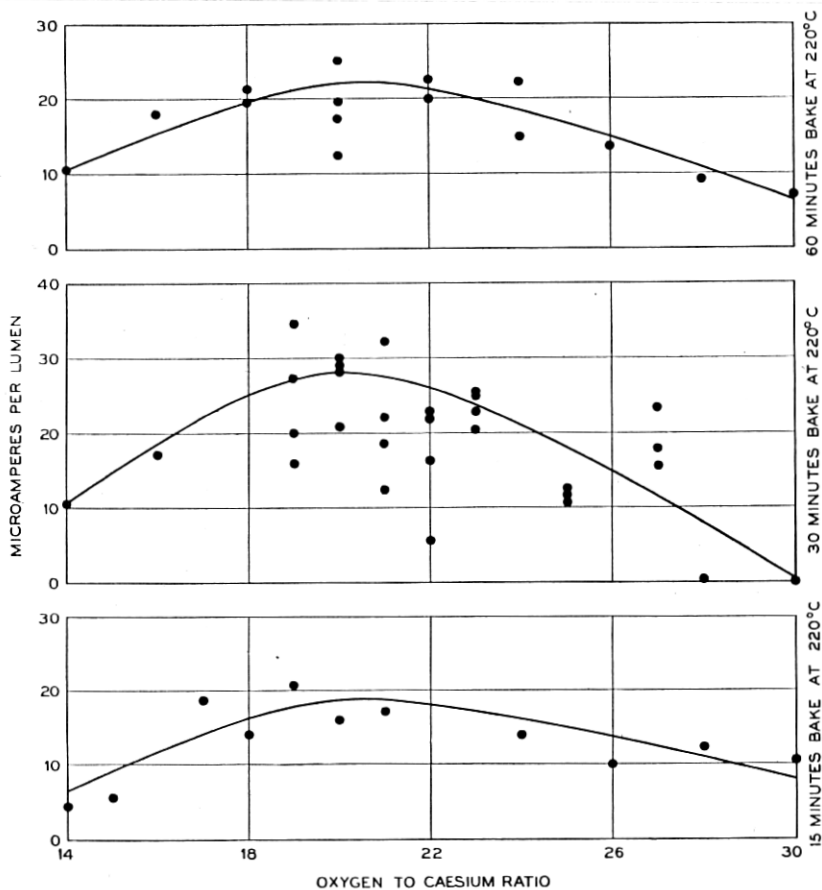

Fig. 3—Integral sensitivity as a function of oxygen-cæsium ratio for 5 mg. pellets.

at a ratio of 17 and with a heat treatment of 15 minutes as shown in Fig. 4.   One additional point of interest is that with the light pellets the cells have still fair activities at the high ratios for the short heat treatments but are destroyed by the 30-minute heating.   This is most probably due to the oxidation of free cæsium by residual silver oxide.

It is also significant to compare the coordinate effects of both oxygen-cæsium ratio and weight of cæsium chromate upon the activity. To this end in Figs. 5 and 6 for the 15 and 30-minute heat treatments, the ratio is plotted as abscissa, the weight of cæsium chromate as ordinate, and a circle is drawn about each point whose diameter is proportional to the observed activity. It is apparent that the 3-milligram pellets give superior results for the 15-minute heat treatment, and the 5-milligram pellets for the 30-minute treatment. Also the 5-milligram pellets seem to be the better, each considered under
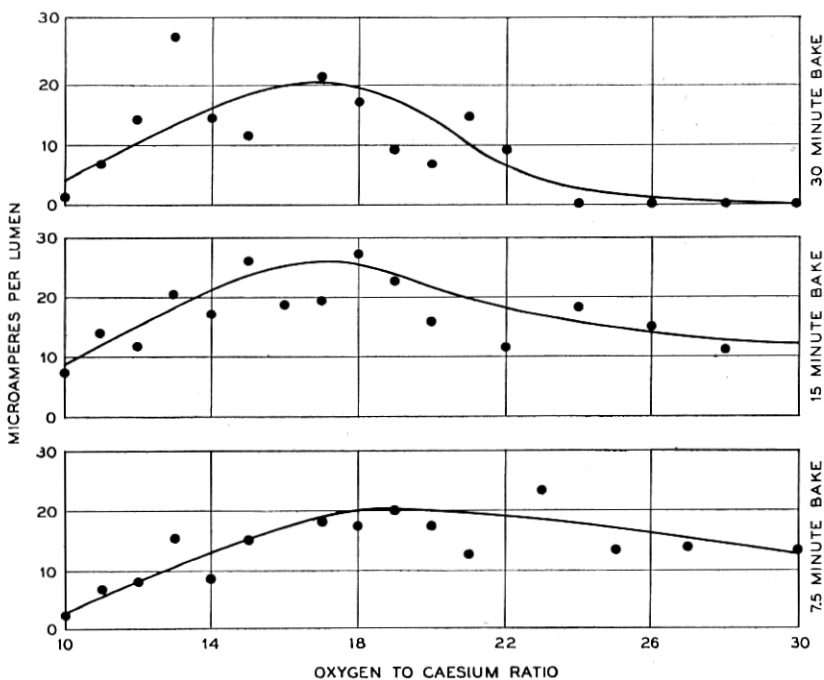
Fig. 4—Integral sensitivity as a function of oxygen-cæsium ratio for 3 mg. pellets.

its optimum conditions. The 5-milligram pellets also seem to yield cells more stable with respect to excessive heating, cf. Figs. 3 and 4. The pellet weights were in general quite uniform, but due to temporary difficulties the weights of the 5-milligram pellets used in the 30-minute heat treatment scattered considerably as is shown in Fig. 6. Fortunately, this scattering furnishes some detailed evidence as to the relation between activity and pellet weight. The locus of highest activity appears to be an oblique line as expressed in the coordinates of Fig. 6. One might predict that the highest activities would be
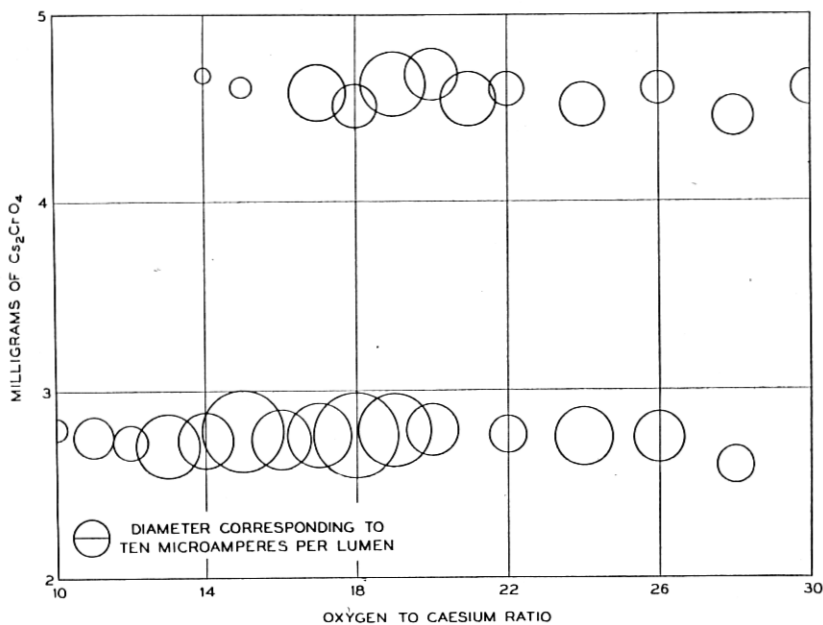
Fig. 5—Integral sensitivity as a function of ratio and weight of cæsium chromate for a 15-minute heat treatment.
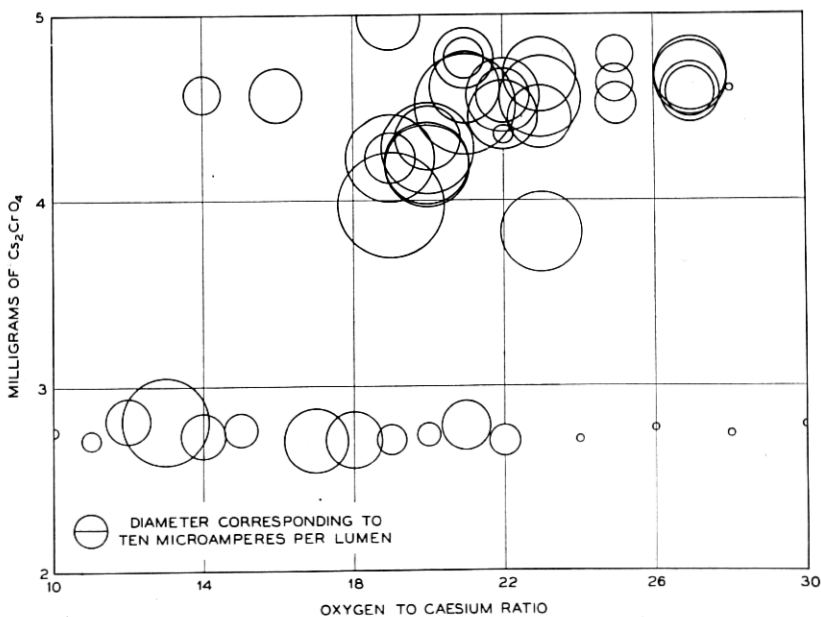
Fig. 6—Integral sensitivity as a function of ratio and weight of cæsium chromate for a 30-minute heat treatment.

obtained by specifying a pellet containing 4.0 to 4.2 milligrams of cæsium chromate, an oxygen-cæsium ratio of 19, and a heat treatment at 220° C. for 25 to 30 minutes. It should be noted, of course, that the above are initial specifications. Two thirds of the cæsium goes to form the matrix and active film of the cathode surface, while the remainder is deposited upon the inner surface of the glass bulb.

Studies of the Cæsium Thin Film

These cells show small fluctuations in sensitivity and shifts in spectral response with time and with the temperature of the surroundings. Even cells prepared under the optimum conditions take several days to stabilize. The integral sensitivity often changes by 5 or 10 per cent, usually to higher values. But further changes occur with changes in temperature. A number of cells aged at 50° C. increased in sensitivity by about 10 per cent in a few days, and then fell to their former stable values after operation for a few days at room temperature. In particular, cells made with large ratios of cæsium to oxygen and short heat treatments, which should be conducive to the presence of small residual amounts of free cæsium, tend to be the least stable, and to decrease rather than gain in integral sensitivity. Such cells are apt also to have low insulation resistance which tends to be unstable in value as compared to the normal cell which has a high and relatively stable insulation resistance.

Since the changes in sensitivity at 50° C. or below are generally reversible, they can not be due to chemical reactions of the irreversible type by which the cells are prepared. These changes seem most easily explicable as due to changes in thickness of a thin film of free cæsium reversibly adsorbed upon the matrix of gross material, many molecules thick, which has been formed upon the silver cathode surface. According to this view it should be possible to correlate the observed fluctuations in sensitivity with variations in film thickness as the free cæsium diffuses in and out of the underlying matrix, or evaporates and recondenses upon the various surfaces of the photoelectric cell interior.

Now it is impossible to differentiate between cæsium adsorbed on the surface, absorbed in the matrix, or in chemical combination, by the type of quantitative data considered in the previous section, for all are placed simultaneously in their appropriate places and in proper amounts by the processes described. Neither is it possible to build up a matrix alone and subsequently place the film upon it with any assurance that the final state shall be comparable to that found in the cells already described. So resort has been had to a variational method of studying the surface film.

We have wished to obtain information regarding the amount of cæsium in the surface film, the amount of free cæsium in the underlying body of the matrix, to check up on the possibility of the diffusion of free cæsium between the surface and body of the matrix and to study the relation between film thickness and the spectral response of the cathode surface. To this end we conducted one series of experiments in which known quantities of oxygen were admitted to cathode surfaces prepared in the standard fashion, following the course of recovery in response with time at various temperatures. In further experiments cæsium vapor was allowed to deposit continuously upon the active surfaces of several cathodes of the same type, while observations were made of the resulting changes in spectral response.

Special cells were made and pumped under as nearly as possible the optimum conditions. The first series of cells were similar in structure to that shown in Fig. 1, except that to the upper end of the bulb was sealed a short glass tube. Within this tube and attached to its upper end was a thin-walled glass bulb containing oxygen at reduced pressure. A steel ball was also included within the tube which could be made to break the glass bulb of oxygen by agitation of the cell. The second series of cells were constructed as shown in Fig. 7. In each cell was supported a glass cylinder closed except for a small orifice pointing obliquely towards the cathode surface. Within this cylinder were a thin-walled bulb of soda-lime glass containing free cæsium and a steel ball with which the bulb could be broken as before.

Monochromatic light was obtained from a Bausch and Lomb No. 2700 glass spectrometer fitted with two slits and calibrated by the makers to 10,000 Å. The light source was a lamp with a helical tungsten filament operated at a color temperature of 2,710° K. Readings were corrected to an equal energy scale using the relative energy curve for tungsten and the dispersion curve of the spectrometer. At the blue end of the spectrum readings were very small due to the low intensity of the light, the low response of the cell, and the wide dispersion of the spectrometer. The values presented are from 6,000 Å to 10,000 Å. The measurements were made with 90 volts across the cells and the photoelectric currents were amplified on a vacuum tube bridge circuit so as to be rapidly readable on a micro-ammeter.

In Table 2 are presented data from four cells to which oxygen was admitted, giving the amounts of oxygen, the equivalent number of atomic layers of cæsium oxidized, the various aging and heat treatments, and the integral sensitivities obtained after the several treat-

ments.   In the second row of Table 2 the equivalent layers of cæsium are computed as upon a smooth cathode surface.   To obtain actual layers upon the roughened cathode these values must be divided by a factor which we have judged to be approximately four.   In addition, since the oxygen flowed freely into the whole structure of the cell,
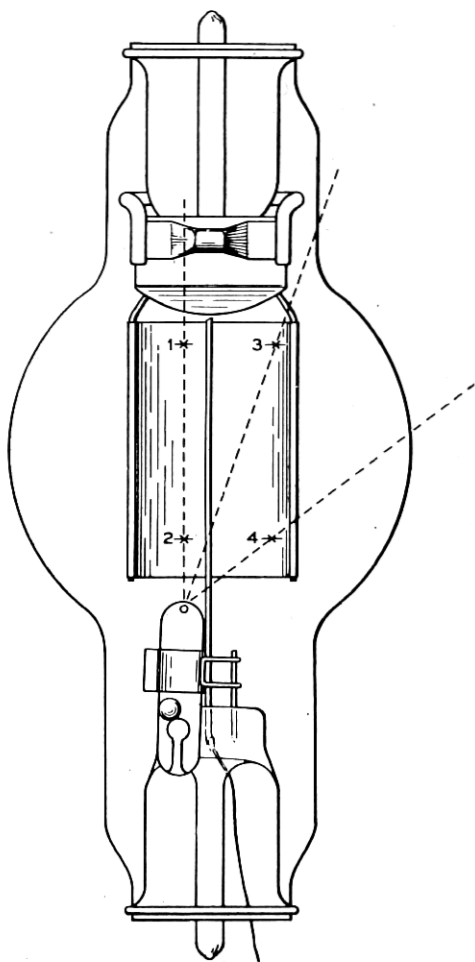

Fig. 7—Cell design for the deposition of cæsium on a cathode surface.

we must consider a film (probably monatomic) of free cæsium adsorbed on the inner surface of the glass bulb which has about four times the area of the cathode.   This film must be present since the bulb itself is appreciably photosensitive.   In cell *A* the oxygen, calculated as

TABLE 2

	Cell A		Cell B		Cell C		Cell D	
Moles of O₂		2.36·10⁻⁸		5.27·10⁻⁸		17.5·10⁻⁸		29.2·10⁻⁸
Equivalent layers of cæsium on smooth cathode		4.01		8.95		29.7		49.7
Estimated layers of free cæsium oxidized on roughened cathode.		0.5		1		6		11
	Time of Treatment	Integral Sensitivity	Time of Treatment	Integral Sensitivity	Time of Treatment	Integral Sensitivity	Time of Treatment	Integral Sensitivity
		$\frac{34.7\ \mu \text{ amps.}}{\text{lumen}}$						
Initial sensitivity..............		34.7		25.4		26.4		29.1
After releasing oxygen.........	48 hours	16.2	68 hours	4.20	0.5 hours	0.25	3 hours	0.10
After aging at 22° C...........	1.7	20.3	8.7	6.83	11.5	1.22	1.0	0.41
After aging at 75° C...........	3.0	28.8	5.0	14.3		0.93	5.0	0.91
After further aging at 75° C....		30.8	5 minutes	15.3	5 minutes	23.4	5 minutes	0.82
After aging at 200° C			10	13.1			5	1.00
After further aging at 200° C...				21.1			10	1.00 / 19.9

equivalent to four layers of cæsium upon a smooth cathode, would be sufficient to oxidize either the monatomic film of cæsium on the bulb, or one atomic layer upon the cathode. We have therefore supposed that about half an atomic layer upon the surface of the cathode was actually oxidized. With the other three cells we have subtracted four "layers" for the bulb and divided the remainder by four to obtain a rough estimate of the actual number of atomic layers of free cæsium upon the cathode surface which were oxidized. These values are shown in the third row of Table 2.

Each cell was first baked for 30 minutes at 75° C. to insure that the surface was in substantial equilibrium. No integral sensitivity changed by more than 10 per cent, and changes in the distribution of spectral response were inappreciable. These results are in agreement with our general experience that these cathodes are stable at 75° C.

All four cells were radically affected by the introduction of oxygen, but none were made entirely inactive. All recovered somewhat at room temperature but the rate of recovery slowed down rapidly. After the recovery had flattened out at room temperature the cells were baked at 75° C. The process of recovery was much accelerated so that cell *A* recovered most of its initial sensitivity, but cells *B*, *C* and *D* did not recover a high sensitivity until after a short heat treatment in an oven at 200° C. Cell *A* losing half a layer of cæsium upon the introduction of oxygen fell to 47 per cent of its initial sensitivity. It recovered to 59 per cent after 48 hours at room temperature, and to 89 per cent after 3 hours at 75° C. Cell *B* losing one layer fell to 16.5 per cent, recovered to 27 per cent after 68 hours at room temperature, to 60 per cent after 14 hours at 75° C., and to 83 per cent after 15 minutes total at 200° C. Cell *C* losing six layers fell to 0.95 per cent, recovered to 3.5 per cent after 12 hours at 75° C., and to 89 per cent after 5 minutes at 200° C. Cell *D* losing eleven layers fell to 0.3 per cent, recovered to 1.4 per cent after 7 hours at room temperature, to 2.8 per cent after 6 hours at 75° C., and to 68 per cent after 20 minutes total at 200° C.

The heat treatment at 200° C. was kept short as reaction between free cæsium and silver oxide and evaporation of cæsium oxide both occur at this temperature and in time would destroy even a normal cathode surface. In the five-minute heat treatments the maximum cathode temperature was doubtless considerably less than 200° C. and the increased effects of the ten-minute treatments which followed are probably due more to the enhanced cathode temperature than to the longer time. The observed recovery must be due to the migration of free cæsium already present as there is no chemical reaction possible

under these conditions by which free cæsium could be obtained from the cæsium oxide present.

This recovery of sensitivity has every appearance of accompanying a diffusion process by which cæsium in the matrix is brought to the surface of the cathode. Initially the concentration is uniform throughout the matrix. As soon as the oxygen is released it oxidizes the cæsium on and near the surface until the oxygen is exhausted. The cæsium oxide formed is identical with that already present. The resulting condition will be a matrix with a very sharp gradient from outer surface inward in cæsium concentration. This will cause a rapid initial rate of outward diffusion. But as soon as diffusion occurs the concentration gradient is decreased and the rate of transfer is less rapid since the cæsium is transported over a constantly greater distance under a decreasing diffusion pressure. As the temperature is raised the mobility of the cæsium is greatly increased but the essential nature of the process is the same.

It does not appear that any conclusion can be drawn from these data as to the thickness of the surface film of cæsium. Even in cell *D* with oxygen equivalent to eleven atomic layers of cæsium there was still a finite residual activity immediately after the oxygen reacted, which was not far different in value from that obtained with the six equivalent layers in cell *C*. It seems probable that the matrix is sufficiently spongy that there is a rapid diffusion of oxygen into it and immediate interaction of oxygen with the absorbed cæsium, preventing a complete clean-up of all cæsium on the surface with the amounts of oxygen used. Cell *D* is also noteworthy in that the oxygen used was equivalent to 7 per cent of the total cæsium found on such a cathode. And after the oxidation of this amount of free cæsium it was still possible to develop from this surface a high sensitivity equal to two thirds that of the initial state. So the initial amount of free cæsium must be still greater than 7 per cent of the total cæsium on the surface.

But it is not necessary to suppose a much greater amount since it is known that monomolecular films have a great tendency to form. This may resolve the difficulty in understanding why, after the equilibrium is reestablished, so large a change in volume concentration involves so slight a change in the surface condition. While the thickness of a surface film in equilibrium with a gas or vapor is a definite function of the pressure, the film thickness changes much less rapidly than the pressure when the film is in the neighborhood of one molecule thick. The same type of functional relationship may also obtain when the surface concentration is determined as a function

of an underlying volume concentration. Langmuir [10] has shown by the use of the Gibbs adsorption isotherm that in the case of solutions where the solute greatly lowers the surface tension, there is a layer of solute at the surface which is approximately a monomolecular film under a wide range of concentrations in the body of the solution. The same type of relationship may well obtain in the system under discussion, and the concept of a surface film merges into that of a limiting concentration at the surface of the matrix.

Measurements of spectral response were taken with the light
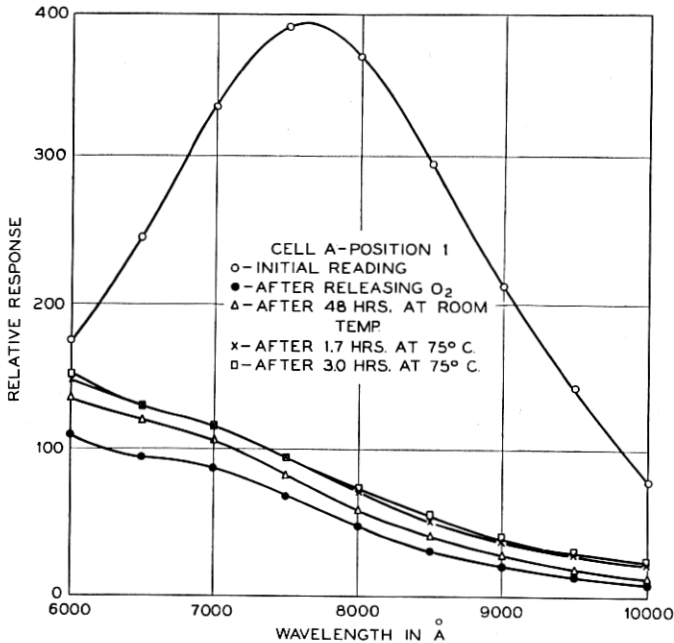
Fig. 8—Relative spectral response to equal energy for cell *A*, position 1.

incident upon four different positions on the cathode surface. The relative positions are the same as shown in Fig. 7. The effects were quite similar for positions 1 and 3 and again for positions 2 and 4, so curves are shown only for positions 1 and 2 for cells *A* and *B* to illustrate the effects at opposite ends of the cathode. In cells *C* and *D* the results were so similar for all four positions that curves are shown only for position 1.

In Figs. 8 and 9 are shown the effects upon cell *A* of the admission of oxygen equivalent to half an atomic layer of free cæsium. Position

[10] Irving Langmuir, *Proc. Nat. Acad. Sci.*, 3, 251 (1917).

1 was nearer the end of the bulb at which the oxygen was introduced and was apparently more oxidized than was position 2. The characteristic spectral maximum for position 1, Fig. 8, is completely suppressed and has not reappeared after 4.7 hours of baking at 75° C. At position 2, Fig. 9, the height of the spectral maximum is greatly reduced but recovers considerably on baking, moving towards the longer wave-lengths, and accompanied by an increase in response at 10,000 Å. till it exceeds that of the initial state. In this final state
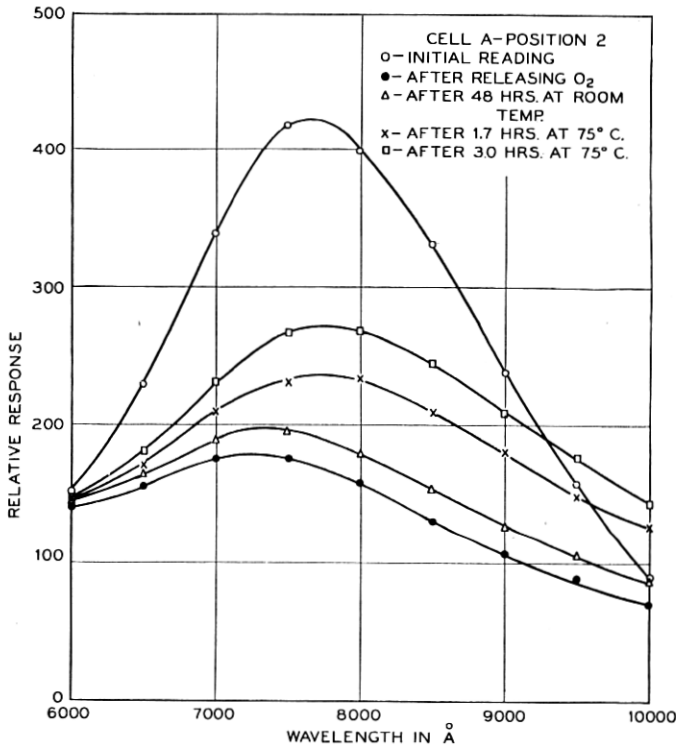
Fig. 9—Relative spectral response to equal energy for cell *A*, position 2.

the integral sensitivity of the cell as a whole had nearly recovered its initial value. The large difference in behavior of the two ends of the cathode is doubtless due to the fact that the oxygen was insufficient to oxidize even the superficial layer of free cæsium and reacted wherever it first struck the cathode. The difference between opposite ends of the cathode is less pronounced in the other cells treated with more oxygen.

In cell *B*, Figs. 10 and 11, which we have estimated to be treated

with enough oxygen to oxidize a complete atomic layer of cæsium, the selective maximum disappeared at both ends of the cathode and only reappeared as a slight indication in Fig. 11 after prolonged heating at 75° C.   On baking for five minutes at 200° C. the selective response reappeared prominently with a maximum at 7,330 Å. but with a loss in response at 9,000 Å. and 10,000 Å. sufficient to involve a decrease in integral sensitivity as shown in Table 2.   Further baking
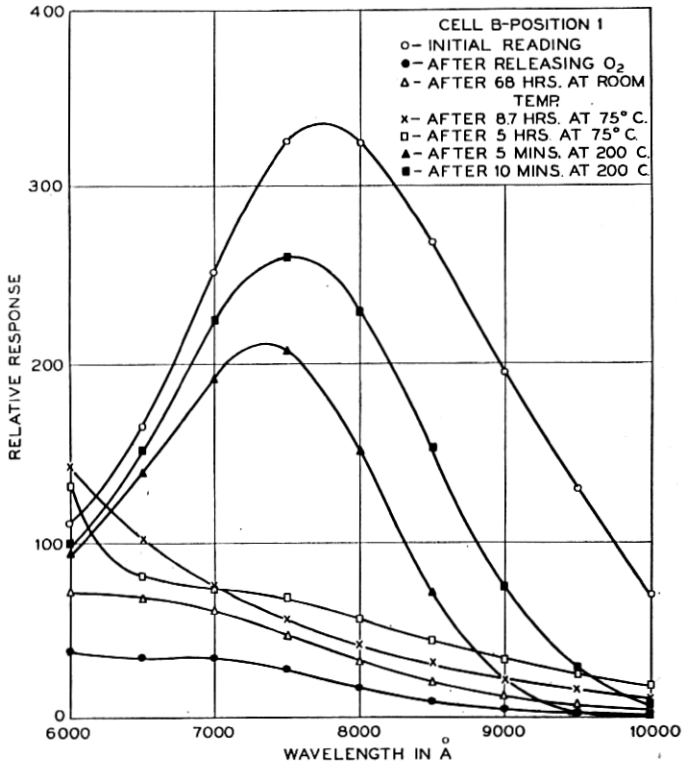

Fig. 10—Relative spectral response to equal energy for cell *B*, position 1.

involved a further rise in the maximum and a considerable increase in response at 9,000 Å.

In cells *C* and *D*, Figs. 12 and 13, which were treated with large amounts of oxygen, the response fell to very low values, rising only slightly on baking at 75° C.   But on baking at 200° C. the selective maximum reappeared but at a longer wave-length than in the initial state, and the spectral response at 10,000 Å. was higher than it was at the beginning.

In all cases the recovery is easily interpreted as attendant upon a diffusion of free cæsium from the matrix to the surface film, furnishing a sequence of states with increasing film thickness, and approaching the initial state of each cell, but we can not estimate the quantitative differences in film thickness from state to state on account of the uncertain nature of the oxidation and diffusion processes.
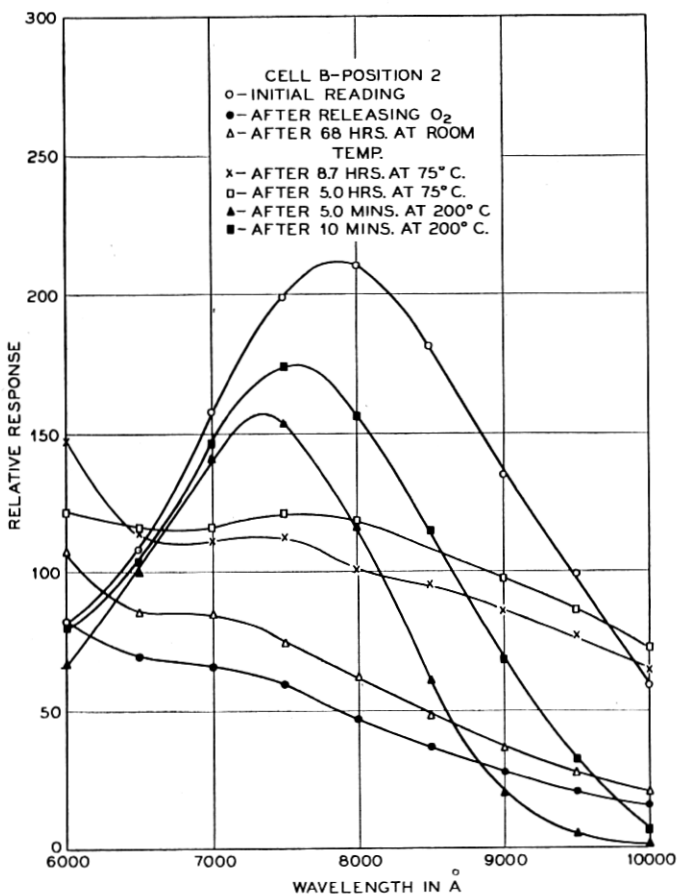

Fig. 11—Relative spectral response to equal energy for cell *B*, position 2.

The extension of this sequence of states to those with film thicknesses greater than that of the initial state was made by the deposition of cæsium upon the cathode surfaces of cells constructed as already shown in Fig. 7. When the cell was shaken and the steel ball made to break the glass bulb containing cæsium, cæsium vapor filled the glass cylinder and diffused slowly through the orifice. Data on three

cells are presented in which rates of deposition of free cæsium differing by a factor of 700 were obtained. The sizes of the orifices differed and positions on each cathode at different distances from the orifice were observed. Measurements of spectral response were made with the light incident upon each of the four positions on the cathode shown in Fig. 7.

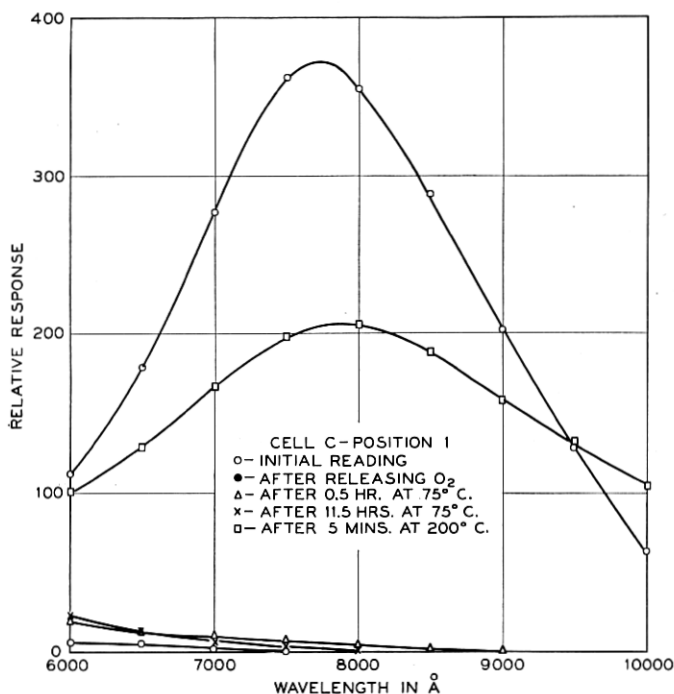From simple kinetic considerations we may derive a formula for

Fig. 12—Relative spectral response to equal energy for cell *C*, position 1.

the rate of deposition upon a surface of the vapor effusing from the orifice:

$$W = 0.01857\sqrt{M/T}\frac{\sigma p_{mm.}}{r^2}\cos\theta\cos\Psi,$$

where W is the weight deposited per cm.^{2} per second (in grams), M is the molecular weight of the vapor, σ is the area of the orifice, $p_{mm.}$ is the pressure within the cylinder in millimeters of mercury (i.e. the vapor pressure of cæsium [11]), r is the distance from the orifice to the surface, θ is the angle between r and the normal to the plane

[11] Int. Crit. Tables III, 205.

TABLE 3

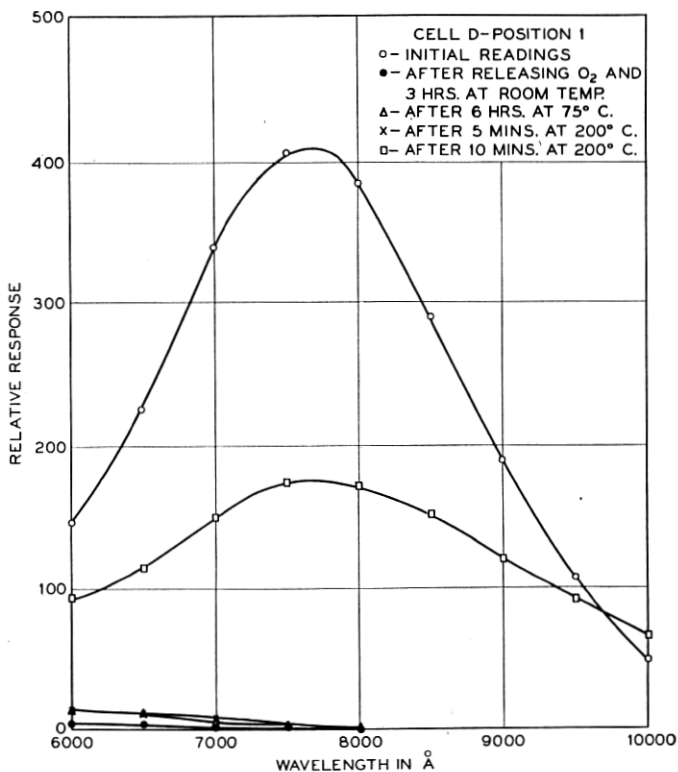| Cell Number	σ	t	Position	W_{Cs}	Layers/Hour
E	0.0107cm.^{2}	29.0° C.	2	0.285μgm. cm.$^{-2}$ hr.$^{-1}$	3.15
F	0.000396	28.0	1	0.000407	0.00450
			2	0.0082	0.0906
G	0.00155	31.0	1	0.00218	0.0242
			2	0.044	0.487

Fig. 13—Relative spectral response to equal energy for cell D, position 1.

of the orifice, and Ψ is the angle between r and the normal to the surface. The constants for the three cells presented and the rates of deposition of cæsium at the various positions are shown in Table 3, where t is the mean temperature during the time of observation, and W_{Cs} is the rate of deposition of cæsium in micrograms per square centimeter per hour. In the last column are shown the equivalent number of atomic layers of cæsium that would be deposited per hour upon a plane surface. As before, these values must be divided by

approximately four to correct for the increase in surface on roughening, but it seems preferable to present the experimental results in terms of measured rather than estimated quantities, so numbers of layers of cæsium deposited will be presented as upon a smooth surface.

In cell E, which had the largest orifice, the changes were so rapid that only one position could be followed. In Fig. 14 the response at each wave-length is plotted against the time on a logarithmic scale.
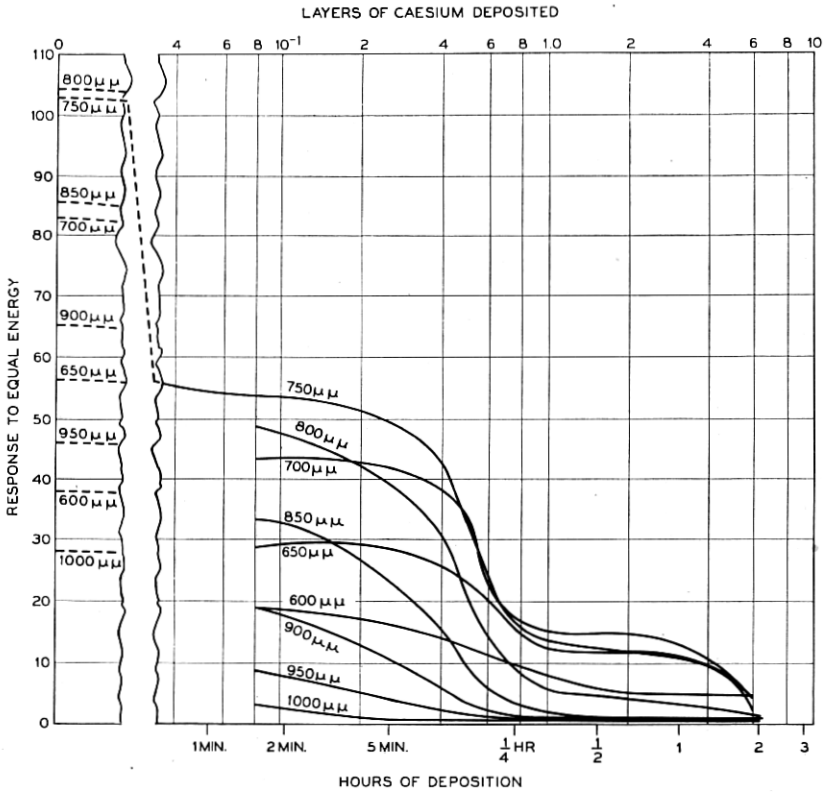

Fig. 14—Spectral response changes in cell E.

The response decreased at all wave-lengths, but the effect increased progressively with increasing wave-length. After two hours the wave-length of maximum response had shifted from 7,750 Å. to 6,000 Å.

With slower rates of deposition, initial effects become apparent. In Fig. 15 are shown the results for position 1 of cell F which involved the slowest rate of deposition. For wave-lengths shorter than 9,000 Å. there is first a rise in response to a maximum at between 10 and 20

hours of deposition which is most pronounced at 7,500 Å. This is followed by a decay which is again most rapid for the longer wavelengths. The responses for 9,500 Å. and 10,000 Å. show no rise and decrease steadily after 10 hours. The responses at these wavelengths were probably at their maxima initially, while the responses at all shorter wave-lengths reach their maxima with increasing time in the order of a progression of wave-lengths from infra-red to visible light. Calculation from the constants in Table 3 shows the maximum
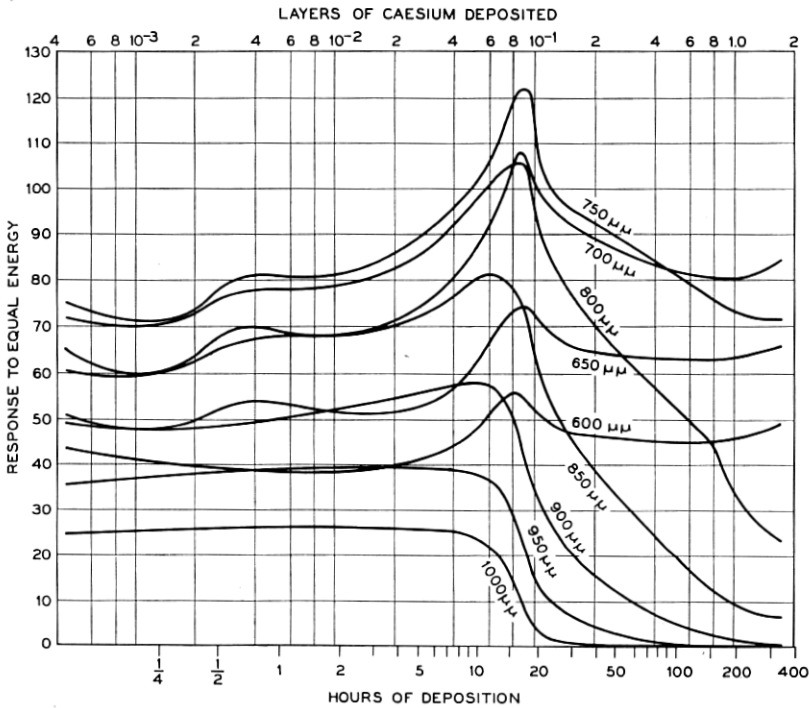
Fig. 15—Spectral response changes in cell *F*, position 1.

response at 7,500 Å. to correspond to the deposition of approximately one tenth of an atomic layer, as may be seen from the scale of abscissæ at the top of the figure.

For position 2 of this same cell, where the deposition was 20 times as rapid, the curves show a great similarity in every respect including the proportionality of the time scales up to the point corresponding to one tenth of a layer, as may be seen in Fig. 16. Then the maxima spread out and the falling off of response is relatively slower than that found in Fig. 15 as expressed in terms of layers deposited. In

fact the two sets of curves become more comparable as expressed in terms of the time scale until after 400 hours the two distributions of spectral response are nearly identical. This final identity may be interpreted in view of the fact that position 2 has received roughly 30 atomic layers of cæsium. For such a thickness the vapor pressure would be expected to approach that of bulk cæsium. At this temperature the rate of vaporization from a bulk cæsium surface would
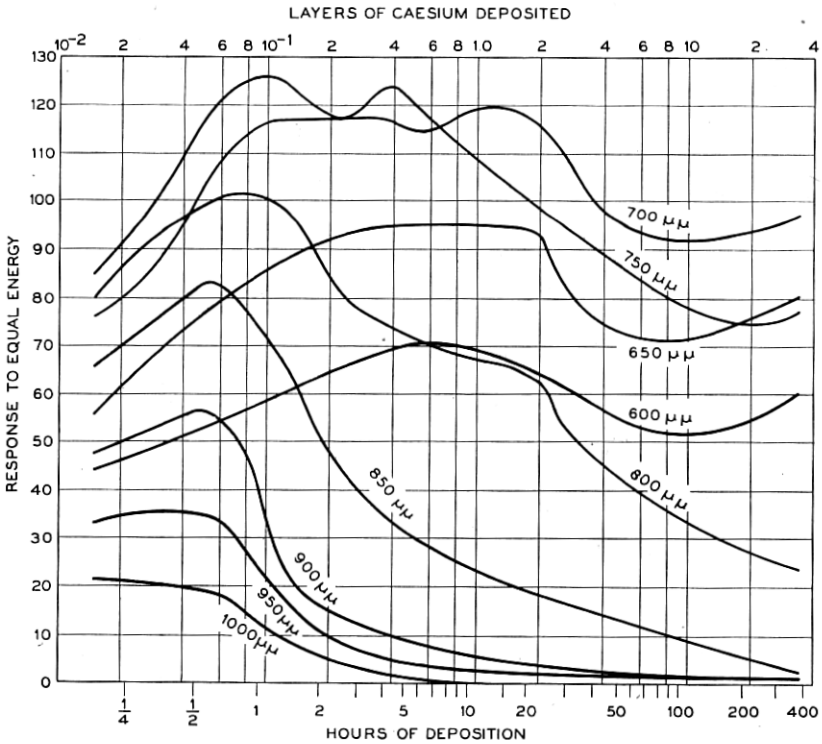

Fig. 16—Spectral response changes in cell *F*, position 2.

exceed the rate of deposition at this point from the orifice. So cæsium should obviously evaporate from position 2 and condense on the less saturated areas such as position 1. Eventually the thickness of the deposited layer should be equalized over the entire surface.

The same qualitative description covers the phenomena observed at the other two positions of the same cell which are not shown. The rate of deposition was slow at position 3 and rapid at position 4. The behavior of all four positions fits into a coherent scheme where the initial sections of the four groups of curves are similar with respect

to the amount of cæsium deposited and the final sections approach similarity with respect to the elapsed time.

In cell *G* similar qualitative results are apparent. The cell was not as active initially as cell *F*, and the rises in response are not so prominent. For the slow position 1, Fig. 17, the maxima in the response curves are lower and broader than for the slow position of cell *F*, Fig. 15. But the maximum response for a wave-length of 7,500 Å. occurs again after the deposition of approximately one tenth of a layer of cæsium, though in Fig. 17 the maximum response at 8,000 Å.
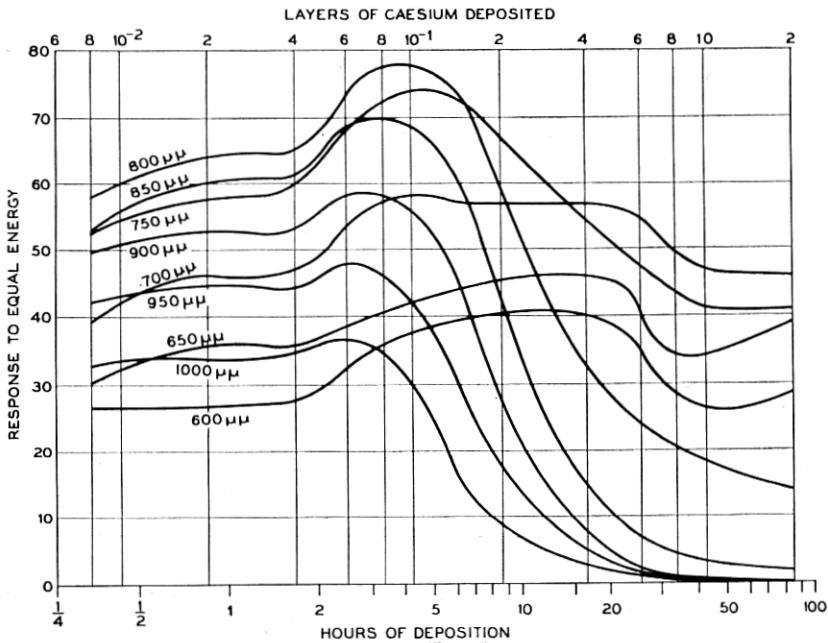

Fig. 17—Spectral response changes in cell *G*, position 1.

is greater than the maximum response at 7,500 Å. In position 2, Fig. 18, which had the fastest rate of deposition the maxima are either entirely absent or else displaced to a position corresponding to about 0.5 of an atomic layer where there are slight indications of maxima for the wave-lengths 7,500 Å. to 6,000 Å.

If we again refer to Fig. 14, which shows curves for the very rapid deposition of cæsium, it appears in this case that after the deposition of one tenth of a layer the response has decreased markedly for light of all wave-lengths. There appears to be a systematic variation of behavior in that the maxima are very sharp for the slow rates of

deposition and are progressively wider and less prominent as the rate of deposition is increased until for very rapid deposition the response for all wave-lengths decreases rapidly from the beginning. In this connection we may recall from the oxidation experiments that a slight amount of diffusion or surface rearrangement may occur in such time intervals as are available in the experiments involving slow deposition of cæsium.

But the behavior of the different cells and even different positions in the same cell may not be closely compared, for their initial states were by no means identical. In each of these cells there was a difference in the colors of the two ends of the cathode due to a distortion of the glow discharge in the quantitative oxidation step of their preparation which was due to the special geometry of these cells
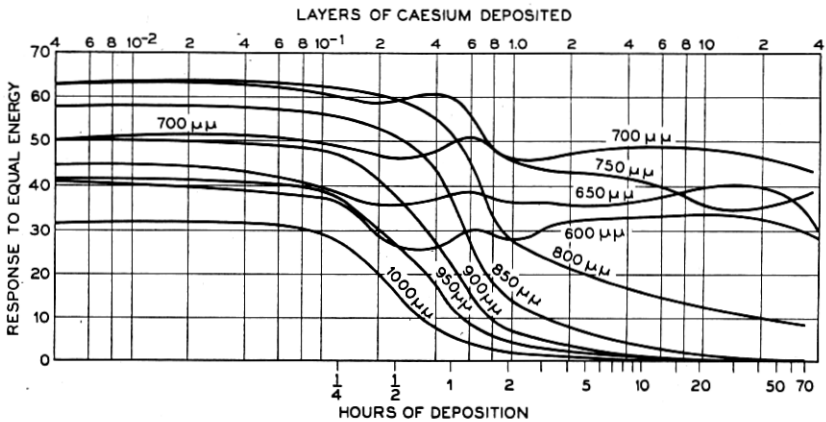

Fig. 18—Spectral response changes in cell *G*, position 2.

But certain gross conclusions may be drawn. In all cases the addition of a few tenths of a layer of free cæsium caused profound modification in the spectral response characteristics. If we regard the results for the slower rates of deposition as more typical of steady state conditions of the cathode surface, it appears that we may increase the response in the region about 7,500 Å. at the expense of the response at and beyond 10,000 Å. by the addition of a few tenths of a layer of free cæsium. It should be remarked again, however, that in view of the roughness of the surface these quantities should be reduced by a factor of four, and the critical amount of cæsium may well be less than even a tenth of a layer on the actual surface. Further addition of cæsium causes a decrease in sensitivity at all wave-lengths, and this effect is increasingly pronounced towards the infra-red end of the spectrum.

In Fig. 19 are shown spectral distribution curves of the response to equal energy with different amounts of deposited cæsium selected from the data shown in Fig. 15. These curves show in more conventional fashion the shift in the position and height of the spectral maximum. This illustrates the general behavior of the equilibrium surface upon the addition of further cæsium. There is an increase in response at the spectral maximum upon the addition of approximately
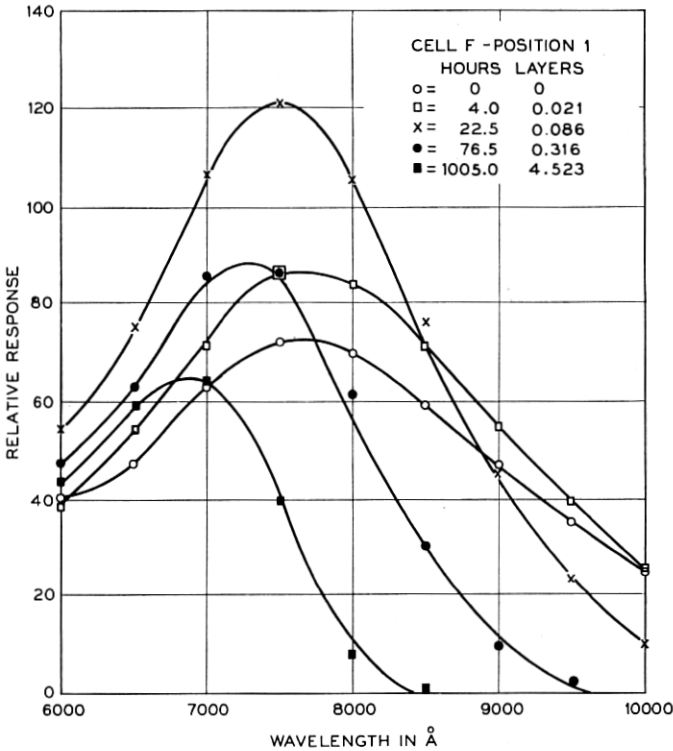

Fig. 19—Relative spectral response to equal energy for cell *F*, position 1.

one tenth of a layer of cæsium. As further cæsium is added the height of the spectral maximum progressively decreases. The wavelength of the maximum spectral response and the wave-length of the photoelectric threshold both recede progressively toward the ultraviolet upon the addition of free cæsium to the normal surface.

Combining the results from the experiments where oxygen was admitted to the cells and those where additional cæsium was deposited upon the cathode, we have a sequence of states with increasing thickness of the cæsium thin film upon the cathode surface. If we take

curves for the spectral response of various states obtained by oxidation followed by diffusion at room temperature and at 75° C., and then include curves for the spectral response of various states obtained by the slow deposition of cæsium we may obtain a composite family of curves such as are sketched in Fig. 20 to show the whole sequence of response characteristics whose parameter is the thickness of the surface film of free cæsium. In obtaining curves for this composite progression of states we have not considered surfaces after they were
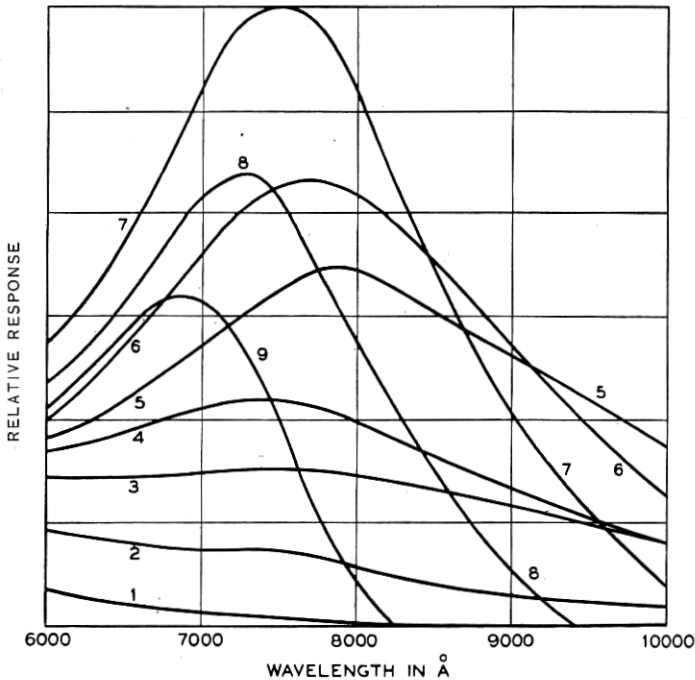

Fig. 20—Relative spectral response to equal energy of a cæsium-oxygen-silver cell as an idealized function of film thickness.

baked at 200° C. because of the likelihood at this temperature of surface changes other than in cæsium concentration alone.

When the amount of cæsium in the surface is far below the normal (as after admitting oxygen equivalent to six layers of cæsium) we have a spectral response which decreases continuously with increasing wave-length, as shown in curve 1 of Fig. 20. This is the same type of response as obtained by Koller [6] from cells prepared by treating with cæsium a silvered bulb with an adsorbed film of oxygen which gave a type of surface designated by him as "Cs–O–Ag." With increasing film thickness the response increases at all wave-lengths

[6] Loc. cit.

and a selective maximum appears as in curves 3 and 4. Then its height rises and its position moves to longer wave-lengths until the maximum occurs at 8,000 Å. as in curve 5, and the response at 10,000 Å. attains its highest value. From a consideration of prevalent concepts of thin-film effects in thermionic and photoelectric phenomena one should expect the surface in this state, which has apparently the maximum value of the photoelectric threshold, to be covered with a monatomic film of free cæsium. As we continue increasing the amount of cæsium in the film, the height of the maximum still rises but its position recedes to 7,500 Å. and the response at 10,000 Å. falls as represented in curves 6 and 7. In the transition from curve 5 to curve 7 the gain in response at 7,500 Å. is offset by the loss in response at and beyond 10,000 Å. As a result the integral sensitivity to tungsten light is sensibly constant and the optimum states for maximum integral sensitivity lie within this range. With further increase in cæsium film thickness the height of the maximum drops, and the positions of both the selective maximum and the photoelectric threshold recede towards shorter wave-lengths as in curves 8 and 9. Eventually we should doubtless approach the spectral response curve for bulk cæsium [12] with the selective maximum at 5,400 Å. and the photoelectric threshold at 7,100 Å.

The large changes in spectral response following the deposition of minute amounts of cæsium upon the cathode surface are further evidence that the photoelectric effect is a phenomenon of the superficial surface only and is conditioned mainly by the thickness of the surface film of free cæsium. Although the cathode surface as a whole is prepared by irreversible chemical reactions which are arrested before their completion, the film thickness of the standard surface is determined by the concentration of free cæsium in the underlying matrix and is maintained by a diffusion equilibrium. In the preparation of the standard surface this partition is first determined at 220° C. in the heat treatment. Stabilization involves a readjustment of the surface to equilibrium with the adjacent portion of the matrix at room temperature. But the attainment of complete equilibrium at room temperature takes so long that many fluctuations of the ambient temperature intervene and the actual history of such a photoelectric surface involves a long series of diffusion waves accompanied by small fluctuations in the thickness of the surface film which determines its photoelectric behavior.

[12] Miss Seiler, *Astrophys. J.*, **52**, 129 (1920).