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MAXIMUM EXCURSION OF THE PHOTOELECTRIC LONG WAVE LIMIT OF THE ALKALI METALS

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Abstract

Earlier experiments have shown that the long wave limit of photoelectric action in the case of thin films of the alkali metals varies with the thickness of the film. A maximum value is attained greater than that for the metal in bulk, which for the majority of the alkali metals lies in the infra-red. The wave-length of the maximum excursion of the long wave limit was first studied for Na, K, Rb and Cs. In each case it was found to coincide with the first line of the principal series, i.e. the resonance potential. If this relation holds for lithium, its maximum long wave limit should be greater than that of sodium. This was tested and confirmed by experiments in which red-sensitive lithium films were prepared, sensitive to 0.6708μ. It is suggested that photoelectric emission is caused when sufficient energy is given to the atom, to produce its first stage of excitation. The identity of photoelectric and thermionic work functions suggests that atomic excitation is the initial process in thermionic emission as well.

IN A previous publication,[1] the behavior of alkali metal films deposited slowly in high vacua has been described. The characteristic feature of such a film, as for instance one of sodium on platinum, is that as it accumulates, the photoelectric long wave limit moves from the blue end of the spectrum toward the red, reaches an extreme position and then recedes again to the final position characteristic of a thick layer. The curve showing the final relationship between photoelectric current and wave-length rises much more rapidly toward the short wave-lengths than does the curve with the same long wave limit during the building-up process.

The experimental procedure for studying these films as described in the earlier paper consisted first, of cleaning off a platinum plate in the photoelectric cell bulb by electronic bombardment and collecting the alkali metal on the cold walls of the cell; secondly, in allowing the alkali metal to slowly re-deposit on the platinum plate. In the case of sodium, the process of redeposition occurs quite slowly and the photoelectric behavior of the deposit may be studied over a period of many hours. With the metals potassium, rubidium and caesium, it is necessary to immerse the photoelectric cell in liquid air in order to hold the metal evaporated from the platinum plate on the walls long enough for the properties of the partially covered plate to be studied. The various thicknesses of film may be studied either while they increase in thickness as the bulb is allowed to warm or as they are decreased in thickness by successive warmings of the plate.

Another method of producing thin film cells is to allow the alkali metal to diffuse into the bulb through a side tube of small diameter. We have in

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[1] Ives, Astrophys. J. **60,** 4 (1924).

this way prepared caesium cells with the caesium deposited on platinum, silver, magnesium, and other metals. The procedure is to allow the alkali metal to diffuse in while the cell is illuminated and connected with the galvanometer. When the maximum sensitiveness is reached, the side tube is sealed off. After sealing off, the sensitiveness is apt to continue to change somewhat but may be held more constant by admitting an inert gas such as argon. By properly choosing the time of sealing off the side tube, cells may be produced in which the long wave limit has made good approximation to its maximum position.

It has been a matter of interest to us to know how far the long wave limit travels in this excursion out to a maximum and then back. In the case of sodium, as is shown by Fig. 1, which is reproduced from the earlier paper, this maximum excursion is to a point still in the visible spectrum, somewhere between 0.57μ and 0.60μ. In the case of the other three metals which were studied, however, this maximum wave-length is in the infra-red, beyond the range of the spectrometer which was used in the earlier study. The determination of this maximum therefore awaited opportunity for securing a monochromatic illuminator suitable for near infra-red work.

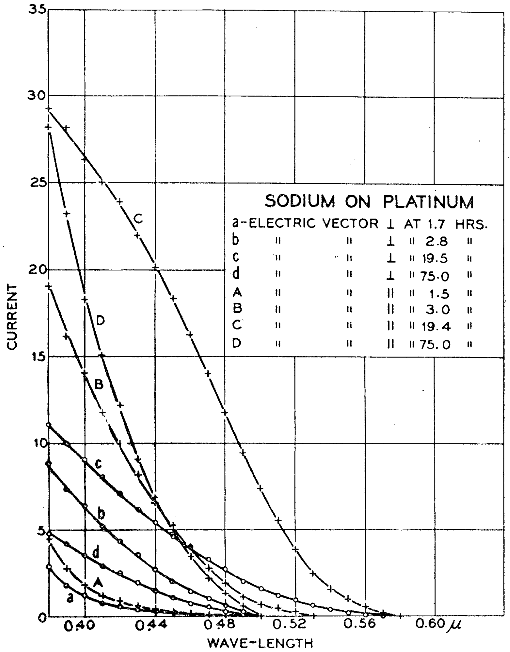

Fig. 1. Progress of photoelectric emission as Na film builds up on Pt plate; exciting light polarized; equal energy spectrum.

APPARATUS

As a monochromatic illuminator for working in the near infra-red, we have taken a Hilger spectrometer of the constant deviation type, and have extended its calibration beyond 1μ. This calibration was effected by the use of a pair of partially silvered glass plates sealed together with a slight separation so as to produce interference bands in the spectrometer which were measured as to position in the visible spectrum, and followed out into the infra-red by means of a sensitive thalofide cell. Using the constant determined from the visual measurements the scale was extended and marked on an addition to the usual wave-length drum of the instrument.

As a light source we have used a coiled tungsten filament. The photoelectric currents were measured with an electrometer by the steady deflection method as described in earlier papers. For the present investigation, it has not been necessary in all cases to reduce the observations to equal energy values.

An adjunct which is absolutely essential to a study of this sort is a series of light filters, each of successively longer wave-length cut-off, to filter out the short wave end of the spectrum. The necessity for these filters arises from the fact that the long wave limit is approached very gradually, in fact, almost asymptotically, and that in all cases the amount of photoelectric action is so much greater from the short wave energy that an exceedingly small amount of scattered light will result in deflections beyond the true long wave limit. It is therefore necessary for the cut-off of the filters used to trail pretty closely behind the long wave limit as it moves out. To meet these requirements we have used a rather complete set of Wratten filters, which give progressively longer wave-length cut-offs from the blue end of the spectrum, well out into the infra-red. These have been employed both as adjuncts to the monochromatic illuminator, and also at times alone, directly in an unresolved beam of light, the wave-lengths transmitted being determined from the transmission data furnished by the makers of the filters.

The cells studied were mostly of the central cathode type. A polarizing voltage of 22.5 was used in all cases, as this produces practically complete saturation, and no shift of the threshold wave-length was found to occur with increased voltage.

RESULTS ON SODIUM

In Fig. 2 are shown a series of curves for a thin film of sodium on platinum as it increases in thickness. Attention is called to the apparent extension of the long wave limit when no filter is used, and its recession toward the blue when such a filter is used that only the tail of the excitation region is exposed.

With the use of a filter, the long wave limit for sodium on platinum comes, at its maximum excursion, very nearly to 0.59μ. We have obtained exactly similar results with a sodium film on clean, thoroughly outgassed, tungsten.

The results with spectrally resolved light shown in the figure have been further confirmed by taking a sodium film on platinum through its complete life history while illuminated by the focussed image of a carbon arc crater, the light from which was passed through a series of Wratten yellow and orange-red filters. For this set of experiments a d'Arsonval galvanometer with a sensitivity of 10^{-10} amperes per mm deflection was used to detect the currents. At the maximum excursion, a detectable current was found with the No. 26 filter (transmission 3.17 percent at 0.59μ) *and no current with filter No. 29* (*transmission 0 at 0.59μ*), showing that the long wave limit at 0.59μ is a real limit to photoelectric response.

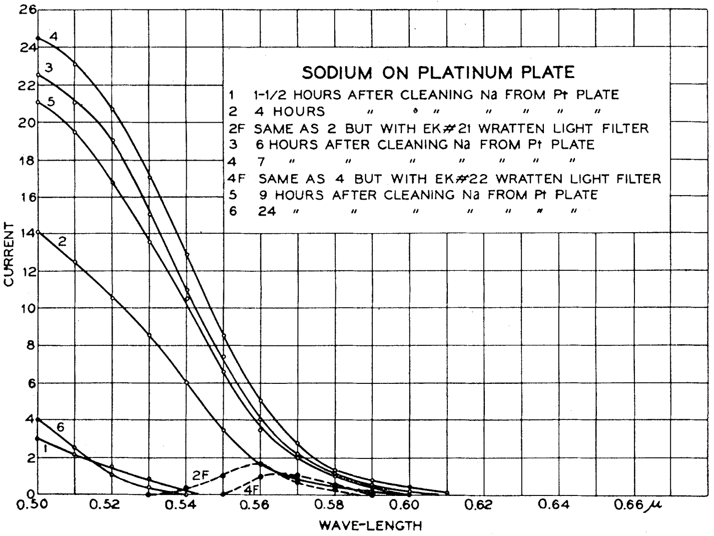

Fig. 2. Photoelectric current vs. wave-length of exciting light, showing excursion of long wave limit for Na film on Pt; critical maximum obtained accurately after eliminating light of short wave-lengths with suitable filters. Values not reduced to equal energy spectrum.

Results on Potassium, Rubidium and Caesium

Of these three metals, the maximum excursion has been determined for films on platinum, and, in the case of caesium, also on silver, as described more in detail below. The results may be summarized as follows: For potassium on platinum, with a Wratten No. 23 filter to cut out stray light, the extreme long wave limit found was 0.77μ. For rubidium, the extreme long wave limit found was 0.795μ. The complete series of curves for this metal are shown in Fig. 3. For caesium, with an extra dark, visually opaque Wratten filter (No. 87) for stray light elimination, the extreme long wave limit found was 0.895μ. Fig. 3 very conclusively illustrates the fact that the change in threshold value produced by varying the thickness of film was an actual shift in wave-length and could not possibly be explained as a general increase in sensitiveness resulting in a rotation of the spectral distribution curve about the maximum threshold as a pivot.

We have, in addition to the caesium-on-platinum, made measurements on two caesium-on-silver cells in which the caesium was deposited up to a maximum sensitiveness and the deposition then stopped somewhat in the manner described in the first part of this paper. Of these, one gave an extreme long wave limit of 0.86μ and the other 0.895μ. In view of the uncertainty of stopping the deposition process at exactly the right point, we believe that these cells confirm the value found in the controlled cells, the significance of which will now be discussed.

Discussion of Results on Sodium, Potassium, Rubidium and Caesium

Examination of the long wave limits for these four metals at their maximum value reveals at once, to the student of spectroscopy, a striking agreement with the wave-lengths of the first line of the principal series of each element, or the chief resonance line. The values of these are, in the several cases[2];—sodium 0.5896μ, potassium 0.7899μ, rubidium 0.7947μ and caesium 0.8943μ. The agreement, considering the difficulties of the experimental procedure, and the order of accuracy of the wave-length calibration, is so close as to leave in our minds little doubt that this coincidence is actually exact. We shall leave until a later section the discussion of the significance of this agreement and confine ourselves for the moment to a discussion of further experiments which are suggested.

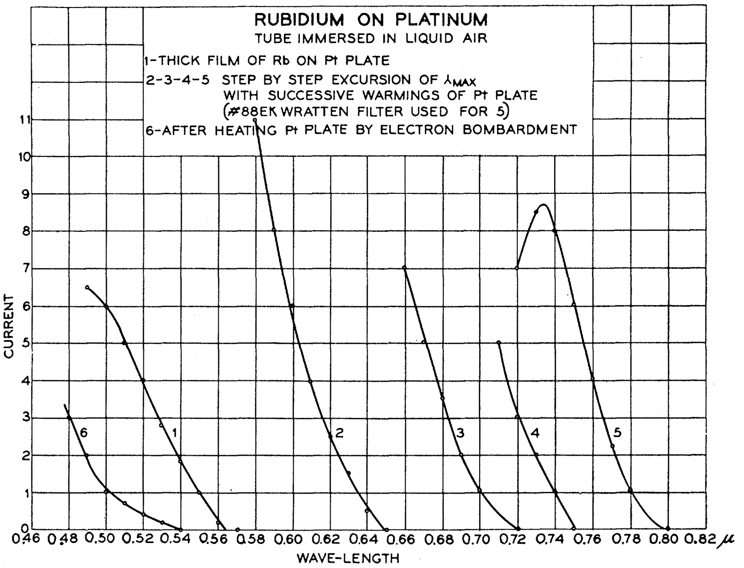

Fig. 3. Photoelectric current vs. wave-length of exciting light, showing excursion of long wave limit for Rb film on Pt; maximum value obtained after filtering our light of short wave-lengths. Values not reduced to equal energy spectrum.

The most significant experiment in our opinion is a search for the same phenomenon with lithium, for although lithium is higher in the periodic table than sodium, the principal resonance line at 0.6708μ is considerably greater in wave-length than the corresponding sodium line. Another experiment or rather series of experiments would be a study of the same phenomena with the alkaline earth metals, of which magnesium, calcium, strontium and barium all have their first resonance lines in the spectroscopic region which is accessible to our apparatus.

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[2] See "Critical Potentials," Bull. Nat. Res. Council **48,** 1924.

EXPERIMENTS ON LITHIUM

In view of the crucial test which lithium affords of the relationship found with the other alkali metals we have delayed publication of our findings with these until, by the development of a method of handling lithium its behavior could be satisfactorily studied. The technique of handling lithium has taken considerable time and effort to master, as it is in a different class, with respect to experimental difficulties, from the other alkali metals. It has considerably higher melting and boiling points, and is commonly believed to attack glass and platinum. The most serious obstacle to its manipulation is presented by the extreme toughness and hardness of the shell of oxide which forms on it in air, coupled with the extreme lightness of the metal. Attempts to melt and distill it in glass from the lump form in which it is obtained commercially have been quite unsuccessful, as the glass blackens and cracks before any lithium metal breaks through its oxide shell. There is reason to believe that the oxide sublimes at a temperature as low or lower[3] than the boiling point of the metal, and the common presence of carbide as an impurity offers a further obstacle to the melting and distilling processes.

The procedure which we have found successful for producing pure lithium metal is best described by reference to a figure showing the photoelectric cell design finally used. This (Fig. 4) consists of two Pyrex glass bulbs *A* and *B*, with a connecting tube *C*. Bulb *A* is provided with a central nickel cup, which stands directly below a long glass tube *T*, through which the lithium is to be introduced. The method of introducing the lithium is as follows: The bottom end of a thin-walled steel tube is turned down to a sharp edge. This tube is then driven down through a piece of lithium metal, [Kahlbaum], so that on withdrawing, the tube contains a cylindrical slug whose sides are protected from the air by the tube walls, and the only oxide present is on the comparatively small areas at top and bottom. The steel tube with its slug of lithium is placed in the glass tube *T*, which is so constructed as to hold the steel tube several centimeters above the nickel cup. Then a long steel rod, loosely fitting in the steel tube, is inserted, resting on top of the lithium, and the end of the glass tube is sealed off. The cell is then exhausted, all the metal parts in the bulb *B* are well baked out, and the cup in *A* is brought to a red heat by a high frequency field.

The next step consists in heating the steel tube, by a high frequency induction furnace, until the lithium melts. When it melts the weight of the steel rod suffices to break the oxide crust, and a globule of clean lithium metal appears at the end of the steel tube, where it may hang, or it may drop into the nickel cup. This globule is then held molten by the induction furnace and gives off metallic lithium which collects on the walls of the bulb *A*. By means of a bunsen flame this metal film is periodically redistilled off the walls and through the connecting tube into the bulb *B*. This bulb, the photoelectric cell proper, has as cathode, a metal plate (e.g. tungsten), behind which is a tungsten filament, to be used for heating the plate by electronic bombardment; and as anode, a nickel cylindrical can, open at

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[3] Lebeau, Compte Rendus **136**, 1256 (1903).

the end toward *A*. As the distillation proceeds the metal parts of *B* become coated with lithium, which in appearance and behavior under the flame is very similar to the other alkali metals. The cathode plate is cleaned off by heating to a white heat several times, and allowed to re-coat. Meanwhile the bulb *A* becomes blackened by what appears to be at first partly carbon from the carbide present in the original lithium and, later by a reaction between the lithium and the glass. When a good supply of lithium is obtained in *B*, the tube is pumped until a high vacuum is obtained, which is assisted by the charcoal tube, later to be placed in liquid air, and the whole cell is sealed off from the pump.

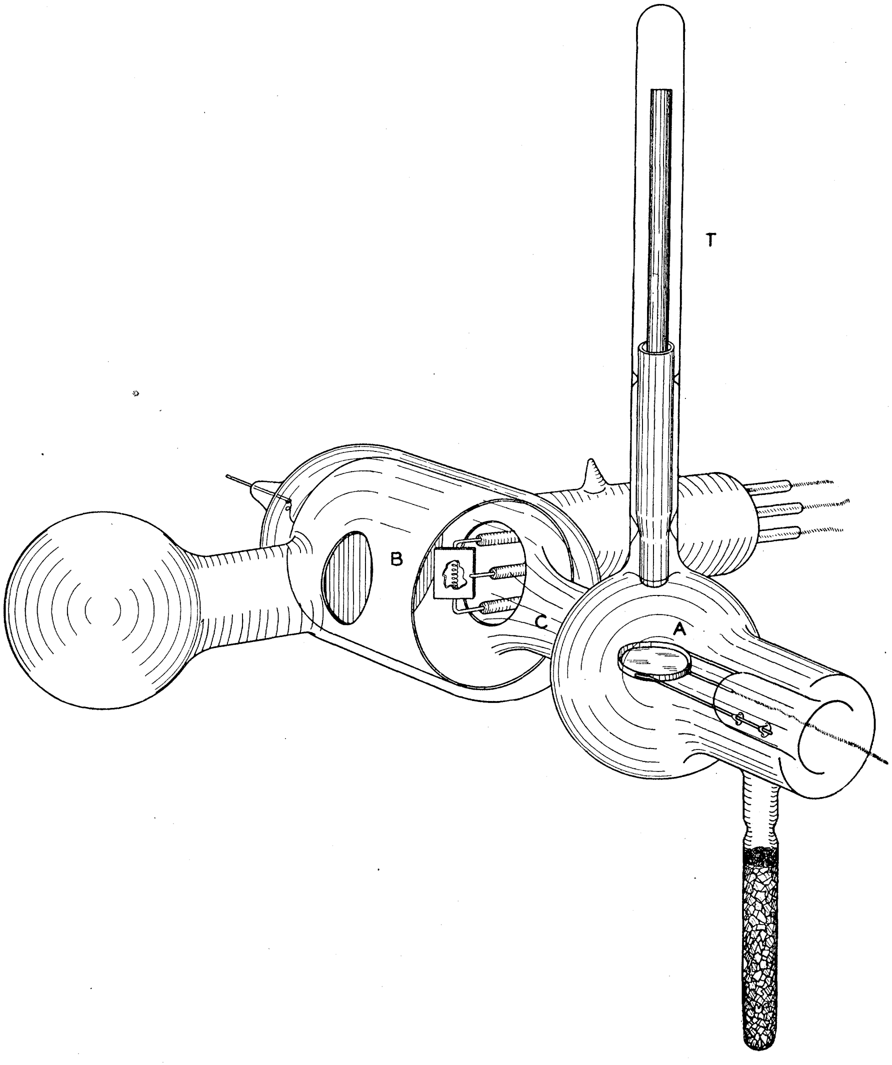

Fig. 4. Type of tube used in preparing pure Li films. Practically oxide-free Li metal dropped from tube *T* to cup of bulb *A*, then distilled into bulb *B* for measurement. (See text.)

The cell thus prepared exhibits, as the tungsten plate is cleaned off, and then recoated, by gentle warming of the metal on the glass in B, *all the characteristic phenomena shown by the other alkali metals.* The cathode first became sensitive to blue light, then as the film increases in thickness, to green, yellow and red; on still further increasing its thickness the red and yellow sensitiveness disappear, and the final thick layer is sensitive only to blue light. *We believe this is the first time that red-sensitive lithium has been observed.*

Measurements through the spectrum of the lithium film on tungsten for all the characteristic stages are shown in Fig. 5. The value of the photoelectric long wave limit for the thick film condition is shown to approach that given by Millikan[4] [0.526μ] and by Pohl and Pringsheim[5] [0.520μ] for lithium metal.[6] In the figure the maximum excursion is shown to a separate scale, as measured through a red filter to block out stray short-wave energy. *It is seen that the wave-length of maximum excursion is again that of the first line of the principal series* (0.6708μ) thus verifying the relationship found with the other alkali metals.

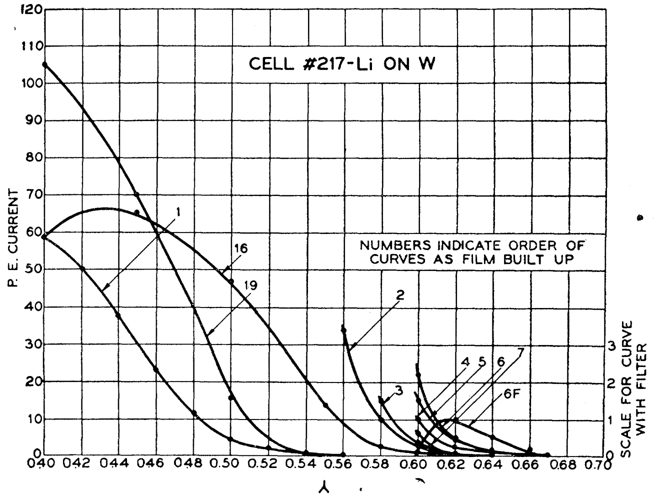

Fig. 5. Photoelectric current vs. wave-length of exciting light, showing maximum excursion to long wave-lengths for a Li film on W. Values not reduced to equal energy spectrum.

We have, by following substantially the procedure above outlined, made several lithium thin-film cells, sensitive to red light. These cells exhibit the characteristic phenomena only for a short time and the conditions for securing red sensitiveness have proved so critical that it is believed worth while to describe some of our experiments in detail. We have made successfully two cells with tungsten plates as the base for the thin films.

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[4] Millikan, Phys. Rev. **7**, 355 (1916).

[5] Pohl and Pringsheim, Verb. D. Phys. Ges. **14**, 46 (1912).

[6] In our earlier attempts to prepare thin films of Li, contamination by the oxide and carbide was visibly evident. In that condition a constant value for λ_o for all thicknesses of film was found. This agreed closely with the long wave limits published by Pohl and Pringsheim and later by Millikan [$0.520\mu - 0.526\mu$].

An exactly similar platinum-plate cell failed to exhibit the characteristic thin-film life history, and red sensitiveness, although a section of platinum wire in a cell used in developing the technique of handling the lithium gave the typical long wave limit very definitely at its most sensitive part. In order to trace this discrepancy a cell was made containing two plates, one of tungsten and one of platinum, capable of illumination separately. This cell was studied on the pump, with color filters interposed before the light, with very interesting results. The first deposit of lithium made both plates sensitive to red light; the platinum plate being approximately three times as sensitive as the tungsten. Both plates were coated until the maximum was passed, and then bombarded until insensitive. On successive re-coatings with lithium the platinum plate became less and less sensitive and soon failed to go through the characteristic thin-film life history at all. The tungsten plate under the same treatment was many times more sensitive, but after several reheatings also failed to become red-sensitive.

Our observations suggest to us that the early failure of platinum as a base is to be ascribed to the alloying of the lithium with the platinum, after the first coating. Similarly the failure of tungsten after a few heatings suggests that it, in time, although more resistant, also takes up lithium to form an alloy, similar perhaps to the alloys of gold with the other alkali metals, which we have previously noted as forming an exception to the usual film-forming behavior. It is possible also that the lithium after having been in contact with the glass of the bulb and having been flamed about the cell is no longer pure enough to form true metallic films. The different behavior of tungsten and platinum plates in the same cell however points rather definitely to a reaction between the lithium and the metal of the plate as playing a predominant role in the character of the lithium film.

Much additional work will be necessary, with various metals as supports for the lithium, to establish the conditions necessary to produce the red-sensitive thin films easily and with assurance of success. For the purposes of the present paper however it is sufficient to have established that ithium films can be made, sensitive up to wave-length 0.6708μ.

Experiments on Barium

We have not as yet made any systematic experiments on the alkaline earth metals. We have, however, had available two Case barium cells[7] on which we have made measurements. In these cells, the barium is evaporated from a filament onto the silvered walls of the cell. Although this process is performed in a manner not known to us in detail, we understand that evaporation is continued until a maximum of sensitiveness is attained. The likelihood that these cells at least approximate to the characteristicl maximum long wave limit is reasonably high.

Measurements which we have made with diffused light on these cells so that their most sensitive spots wherever occurring would be operative gave for one of the cells a long wave limit of approximately 0.70μ and for the other, with a No. 88 Wratten filter, 0.79μ. The long wave limit of the

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[7] Case, Phys. Rev. **17**, 398 (1921).

former lies farther toward the blue than the resonance line of barium (0.7911μ) while that for the latter agrees very closely with this wave-length. These measurements are, of course, not conclusive as we have no guarantee that if the deposition process were followed closely the significant wave-length might not be passed but we believe this to be a strong indication that the resonance frequency plays the same role here.

The Illumination Current Relationship

The idea that the long wave limit should correspond to the resonance frequency has been suggested before, in particular by Kirchner,[8] who in addition has tried to associate the "selective" maximum with the difference between the resonance and ionization potentials. Kirchner points out that if the incident light is responsible for the complete emission of the photoelectrons the process must be in two stages, and as a consequence the photoelectric current should be proportional to the square of the illumination. It is thus important to determine accurately the illumination current relation for the thin films of alkali metal, particularly as close to the long wave limit as possible.

We have made illumination current measurements with an electrometer for the current measuring instrument and with an inverse square law apparatus to vary the light. Illuminating the cells through color filters and taking a number of points we have obtained a close approximation to a rectilinear relation, with no indication of the second power law suggested by Kirchner. These measurements were, however, not entirely satisfactory because they consumed considerable time, in which the cell might change its sensitiveness. Especially does the sensitivity of the cell change when the illuminating source is the crater of an arc. Experiments show that an arc light focussed on a thick potassium film can change the galvanometer deflections for red light fifty-fold in less than ten minutes. We have therefore resorted to a simpler procedure, as follows:

The cells were illuminated by a tungsten lamp, the filament being focussed through a color filter on the cathode of the cell. To vary the illumination a metal plate perforated with many small holes was placed over the image-forming lens. The transmission of the plate was carefully measured in position by means of a potassium hydride cell which had previously been found to have an accurately linear response to illumination. The transmission found (0.38) is independent of the color of the light, as the holes in the plate (1 mm diameter) are too large to introduce any diffraction effects over the wave-length range in question. With this arrangement of apparatus the response of the extreme long wave region of sensitiveness was tested first of all with a sodium-on-platinum cell throughout its whole life history. At each stage such a color filter was selected that the galvanometer deflection was only four or five millimeters, which at the condition of maximum sensitiveness amounted to 1/1000 or less of the deflection with unfiltered light. The currents were then measured with and without the perforated plate. These measurements with the tungsten lamp were supplemented at the

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[8] Kirchner, Phys. Zeits. **25**, 303 (1924).

extreme excursion of the long wave limit by measurements with the crater of a carbon arc, which because of its inferior steadiness and the danger of its heat quickly altering the emission would not alone have been wholly satisfactory.

For all positions of the long wave limit the illumination current relationship was found to be accurately rectilinear. The measurements of the transmission of the perforated plate all lie between 0.36 and 0.45, where the second power law would call for a value of 0.145.

Similar although less extensive measurements were made with a potassium cell immersed in liquid air, and on a caesium-on-silver cell of the permanent type. *The measurements as a group constitute a most perfect confirmation of the generality of the rectilinear illumination current relationship in the thin film cells of all types in all states of film thickness.*

FINAL DISCUSSION

The coincidence of these wave-lengths of maximum excursion of the photoelectric long wave limit with the first line of the principal series, or with the resonance potential, of the various materials investigated points strikingly to the conclusion that when the film is in its most red-sensitive condition, *the process of photoelectric emission occurs when sufficient energy is given to the atom to produce its first stage of excitation.* In the Einstein equation $(1/2)\ m\mathrm{v}^2 = h\nu - p$, as is well known, the term p is to be considered as consisting of two parts, $h\nu_a$ the energy necessary to release the electron from the atom and p', the energy necessary to carry the electron out through the surface of the metal. In the case of the thin films in their condition of maximum sensitiveness, the conclusion above-drawn implies that the photoelectron comes from the atom of alkali metal, that the energy necessary to bring the atom into resonance is sufficient to release the photoelectron, and finally that the term p' is zero.

If we assume that in all cases the photoelectron comes from the alkali metal atom, we may imagine the process of film deposition in general to be one in which up to the condition of maximum sensitiveness the alkali metal only partially covers the surface and the attractive force due to the supporting metal causes the return of the electrons of small energy into the surface. At the condition of maximum emission, the alkali metal is present as individual atoms sufficiently closely spaced so that the attractive action of the underlying metal is inhibited. As the film continues to thicken after the maximum excursion is reached, an alkali metal lattice is built up for which again the retarding forces are greater than for the individual atoms.

This picture of the process of deposition receives support from the differences in the photoelectric emission before and after the maximum is reached. The general slope of the current vs. wave-length curve is comparatively flat before the condition of maximum emission is reached, and steep afterward, indicating a different form of surface force.

Another significant observation is that, with a plane supporting surface, such as a polished platinum plate, the ratios of emissions for obliquely incident light polarized parallel to and perpendicular to the plane of incidence are quite different before and after the condition of maximum emission. In fact, in the earlier stages of film deposition this ratio, which finally may be as high as 20 or 30 to 1, is *unity*, indicating the absence of any regular orientation of the alkali metal atoms. Furthermore, we believe this means that the photoelectric emission must be entirely from the alkali metal atoms, since if the absorptive properties of the platinum entered in, this ratio would be considerably greater than unity. Another reason for believing that the photoelectrons come from the alkali metal atoms is the observation that the maximum long wave limit is the same with different supporting metals.

As already noted the idea that the long wave limit should correspond to the resonance frequency has been previously proposed by others, whose speculations have indicated that the process should consist of two stages, and that the photoelectric current should vary as the square of the illumination. The results of our study of the illumination current relation show this latter conclusion to be contrary to fact. We are therefore of the opinion that while the initial step toward release of the electron is the excitation of the atom by light, its further progress toward emission must be due to other processes, such as collisions. These processes must furthermore be peculiar to the solid, or at least to the thin film condition, as otherwise we would expect photoelectric emission at the resonance frequency from alkali metal vapors.

A matter of considerable interest in this connection is the bearing of this work on thermionic emission. It is very generally held and experimentally[9,10] well established that the photoelectric long wave limit coincides (when expressed in volts) with the thermionic work function. If then the photoelectric threshold is determined by the resonance potential of the atoms, it would appear to follow that thermionic emission is also dependent on the initiation of resonance in the atoms and the phenomenon of thermionic emission is to be associated with electrons belonging to the atoms and not with free electrons, as has been commonly held. As has been shown by Becker,[11] the thermionic work function for thin films of caesium on tungsten makes an excursion toward a low value and back, similar to that made by the photoelectric minimum frequency. It is of considerable significance in this connection that the value Becker finds, from Langmuir's data, for the minimum work function of caesium, is 1.36 volts, where the value from the resonance wave-length is 1.38 volts. The excursion of the work function in the case of barium in a thin film has been studied by Eglin,[12] who gives a minimum value of 1.66 volts, which is to be compared to the resonance potential value of 1.56 volts. It will be profitable to study the minimum thermionic work functions and maximum photoelectric long wave limits together, in the light of the relationship to spectroscopic data here indicated.

We wish to acknowledge our indebtedness to Mr. G. R. Stillwell for assistance in this work, particularly in connection with the method of handling lithium.

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[9] Du Bridge, Phys. Rev. **31,** 236 (1928).

[10] Bridgman, Phys. Rev. **31,** 862 (1928).

[11] Becker, Phys. Rev. **28,** 341 (1926).

[12] Eglin, Phys. Rev. **31,** (1927) (Abstract).