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PHOTOELECTRIC EMISSION FROM PHOTOTROPIC MERCURY COMPOUNDS.

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Anaduzzi and Padoa (*N. Cimento*, 1912, **3**, 41), studying the photoelectric emission from benzaldehydephenylhydrazone and other similar phototropic compounds, concluded that the photoelectric current varies with the change in colour. Gallaghere (*Bull. Soc. chim.*, 1921, iv, **29**, 961) obtained similar results with phototropic arylamines. Both authors measured the photoelectric effect by determining the rate of discharge of an electrometer, and thus were unable to detect any rapid changes which might have occurred in the course of their experiments.

We have recently described a number of mercury compounds which exhibit a high degree of phototropic activity (*J. Physical Chem.*, 1928, **32**, 1354) and it seemed possible that these might also have a large photoelectric emission. The method of measuring photoelectric currents described by Toy, Edgerton and Vick (*Phil. Mag.*, 1927, **3**, 482) in which use is made of a thermionic valve appeared very suitable for the purpose, as it is possible by its means to determine the instantaneous current even when very small. Applying this method we have measured the emission from twelve compounds and have found that in nearly every case those prepared in the dark are not photoelectrically active; but after exposure to light, emission of electrons takes place on irradiation with ultra-violet light. A possible explanation is that the light energy is at first expended in effecting a transformation of one form to the other, and it is only when light falls on a transformed particle that an electron can be liberated. This simple hypothesis is, however, not altogether satisfactory in view of the fact that the maximum phototropic activity is found in the visible region while photoelectric activity is confined to the ultra-violet. For the moment no other explanation is forthcoming.

EXPERIMENTAL.

The arrangement of the apparatus is shown diagramatically in Fig. 1. The photoelectric cell A was supported on blocks of paraffin and connected between the grid and plate of the thermionic triode V. Ordinarily 160 volts were applied to the plate and the steady anode current balanced by means of the potentiometer P so that the galvanometers G_1 G_2 showed no deflection. P consisted of a fixed resistance of 700 ohms and variable 12 and 1 ohm resistances in series with it so that a very fine adjustment was possible. G_1 was a pointer galvanometer and G_2 a mirror instrument giving a deflection of 1 cm. for 1×10^{-7} amp. These were fitted with suitable shunts and switches and indicated any change in anode current.

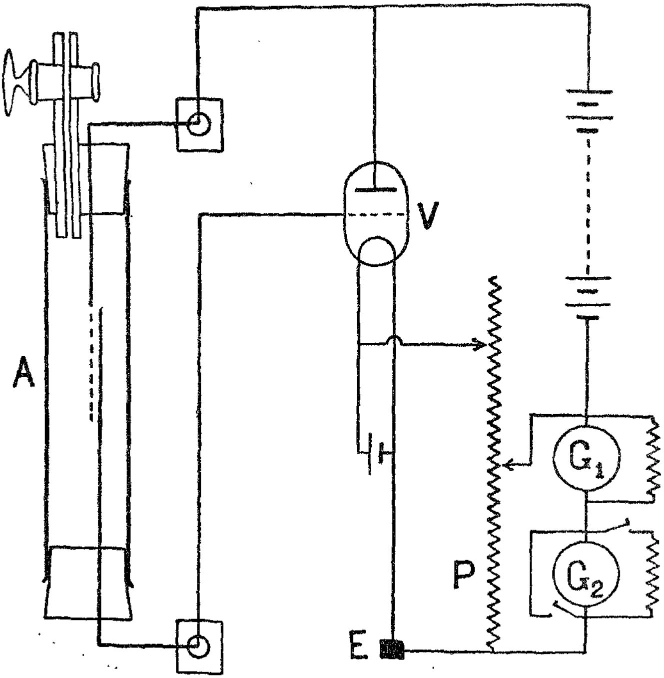

FIG. 1.

The thermionic valve has been used in conjunction with a photoelectric cell by Rosenberg (*Naturwiss.*, 1921, **9**, 359, 389), du Prell (*Ann. Physik*, 1923, **70**, 199) and Ferrie, Jouaust and Mesny (*Compt. rend.*, 1923, **177**, 847). All these authors arranged the cell in such a way that the photoelectric current charged the grid negatively and the system thus behaved as an electroscope of small capacity. Equilibrium was reached when the current from the cell was equal to the leakage, and by improving the insulation it was found possible to obtain effective magnifications of 10^6 and even more. Du Prell investigated the matter in considerable detail and drew attention to the harmful effect of grid current.

In the experiments of Toy, Edgerton and Vick the photoelectric cell charges the grid positively and thus the conditions are different. These authors offer no explanation for the action of the cell and consequently it was considered desirable to ascertain the exact reason for the constancy of the change in anode current for a given photoelectric current and to ensure that the relation between these two quantities was a linear one.

It seemed likely *a priori* that equilibrium would be obtained when the photoelectric current was equal to the grid current. The usual grid current characteristic A, Fig. 2, approaches the axis asymptotically and does not yield much information. The potential of the free grid

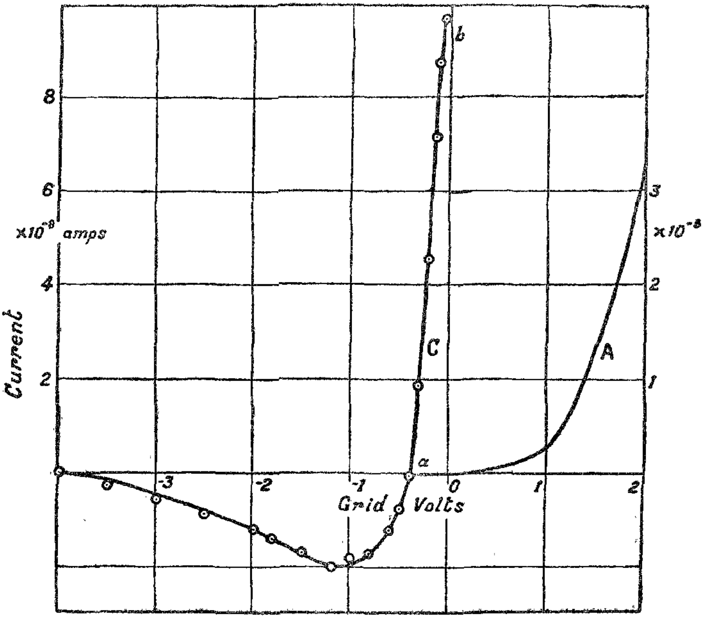

FIG. 2.

was found to be - 0·4 volts and further measurements were made of the very small current in this region by the usual method of biassing the grid through a high resistance (4 megohms), short circuiting the resistance and measuring the change in anode current. The curve obtained is shown in Fig. 2 (*c*), the grid current being reversed in part owing to incomplete evacuation of the valve.

The point *a* where the grid current is zero gives the potential of the 'free' grid, no change in anode current resulting if the grid is disconnected when biassed to this voltage. The slope of the curve from *a* to *b* determines the sensitiveness of the valve. Its value in the neighbourhood of *a* is $1\cdot8 \times 10^{-7}$ amp. per volt and as one volt change on the grid at this point results in a change in anode current of $0\cdot33 \times 10^{-3}$ amp. the current magnification of the system is about 1,800.

As the curve from *a* to *b* is approximately linear and measurements are made over only a small range (1 mv. grid potential) it would be expected that the change in anode current would be proportional to the photoelectric current. This was tested by exposing a silver cell to the mercury arc at different distances and Fig. 3 shows that the assumption is correct within the limit of experimental error.

The actual valve used to which the curves refer was a Cleartron 25B, impedance 33,000 ohms, amplification factor 11. This was selected as being the most sensitive of a number of valves of different types. The suitability of a valve for this purpose has since been investigated in some detail and will form the subject of a separate communication. In making the above calculations the leakage between grid and filament has been neglected. This was measured and found not to influence the results to any appreciable extent.

The photoelectric cell.—The substance to be examined was made into a thin paste with water and floated over a piece of platinum foil measuring 16 × 9 mm. On drying, the coating adhered to the platinum sufficiently to allow handling. Platinum was used as a support as it would not react with the mercury compounds and also because it has been shown by Woodruff (*Physical Rev.*, 1925, **26**, 655) that the photoelectric emission from a platinum surface is negligible under the conditions of our experiments. A piece of nickel gauze the same size as the platinum was used as anode. In order to secure the highest possible insulation, the wires supporting the electrodes were passed through corks in the opposite ends of a quartz tube 1 cm. in diameter, the joints being made airtight with a beeswax-resin mixture. At one end of the tube a small tap was inserted for evacuation. The assemblage is shown in Fig. 1. With this arrangement it was possible

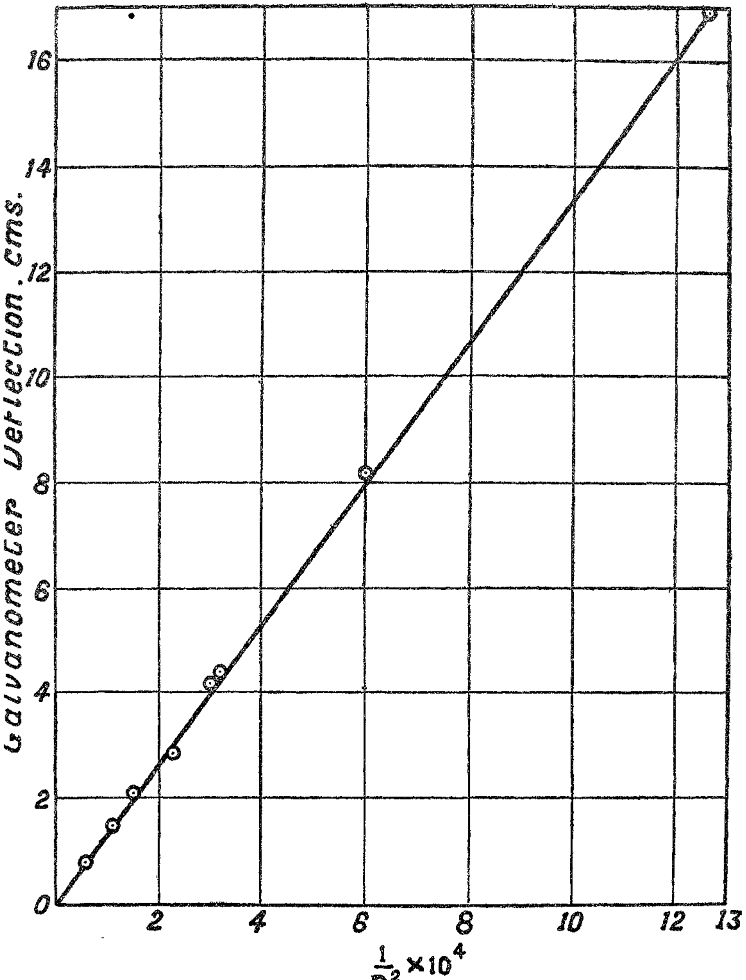
Galvanometer Deflection . cms.
0
2
4
6
8
10
12
14
16
2
4
6
8
10
12
13
$\frac{1}{D^2} \times 10^4$

FIG. 3.

to adjust with sufficient accuracy the distance between the electrodes, normally 0·5 mm. The cell was illuminated by means of a quartz mercury arc lamp working at atmospheric pressure and consuming 2·5 amps. at 92 volts.

Before recording actual measurements a preliminary inquiry was made into the effect of (1) the gas pressure in the cell and (2) the distance apart of the electrodes. Using a sample of the compound HS.Hg.CNS, the galvanometer deflection with air at 1·0 mm. in the cell was 4·9 cm., at 2·0 and 2·5 mm. it was 5·0 cm. and at 3·0 mm. it fell to 4·2 cm. The existence of a maximum value is in accordance with similar observations by Toy, Edgerton and Vick and the order of pressure is the same. In all subsequent experiments the cells were evacuated to 2·0 mm. pressure, a slight variation of pressure in this region having a negligible effect.

Measurements were next made of the photoelectric current when the distance between the electrodes was varied. An increase of the distance from 0·33 to 0·44 mm. reduced the current by 1 per cent. and at 0·59 mm. there was a further reduction of 2 per cent. These changes are almost within the limit of experimental error when all factors are taken into consideration. As far as possible the electrodes were set 0·5 mm. apart. The thickness of the coating might have some influence upon the observed current but comparative experiments indicated that this factor was negligible.

Action of light on different compounds.—Twelve phototropic mercury compounds were studied and it was found that, in general, the initial photoelectric current was small, and that on continued exposure there was an increase until a maximum was reached. Simultaneous darkening of the compound occurred. If the compound was left in the dark overnight and again exposed, the initial photoelectric current was larger than before, but the final current was approximately the same. This result could be repeated on successive days although the initial currents were somewhat irregular, according to the duration of exposure on the preceding day and the exact time allowed for recovery. If the cell was heated to 100° for some hours the initial current was reduced very nearly to that given by the fresh substance. These observations are in agreement with the hypothesis that the compounds when prepared in the dark give rise to little or no photoemission while the blackened forms have considerable activity. If this is the case it is possible to form a quantitative estimate of the relative amount of the two varieties in the surface layer and thus make more accurate estimates of the rate of darkening than is possible by judging the shade. Table I gives a few values for the initial and final galvanometer deflections on different days and illustrates the order of accuracy which may be expected in these experiments. In order to obtain comparable results the apparatus was always adjusted so that a standard cell containing a strip of polished silver gave a fixed deflection on the galvanometer (43 cm.).

TABLE I.

Initial and final photoelectric currents at different periods.

HS.Hg.CNS (*a*)			HS.Hg.CNS (*b*)			I.Hg.CNS			I.Hg CNSe		
Day	Initial	Final	Day	Initial	Final	Day	Initial	Final	Day	Initial	Final
1	0·2	9·4	1	0·5	9·3	1	1·3	3·4	1	3·0	13·0
2	1·6	9·1	2	3·0	9·3	2	1·7	3·3	2	4·0	13·3
7	0·5	9·7	3	3·5	9·5	3	2·3	3·4	3	4·3	13·3
9	2·0	9·3	4	3·0	9·3	4	2·5	3·2	4	4·9	13·4
10	7·0	9·7	5	5·0	9·6	5	2·4	3·4	5	7·5	13·4
12	6·5	9·6				6	2·8	3·3	7	4·5	13·5
13[1]	1·5	9·3									

$2HgS.HgCl_2$			$2HgS.HgBr_2$			$2HgSe.HgI_2$			$2HgS.Hg(CNS)_2$		
Day	Initial	Final	Day	Initial	Final	Day	Initial	Final	Day	Initial	Final
1	0·1	10·5	1	6·5	14·6	1	2·0	6·2	1	0·2	3·4
2	0·6	10·3	2	9·0	14·3	2	4·3	6·0	2	0·8	3·4
3	4·6	10·6	4	7·4	14·5	3	4·2	6·3	3	1·8	3·5
4	7·8	10·5	6	7·8	14·4	4	4·8	6·0	4	2·6	3·4
5	9·0	10·6	7	9·0	14·3	6	3·0	6·1			
8[2]	1·5	10·8				7	3·8	6·4			
9	4·2	10·6				8	3·5	6·3			
10	6·0	10·7									

[1] After heating to 100° for 4 hours.
[2] After heating to 90° for 6 hours.

As already mentioned, the initial currents are somewhat irregular on successive days but there appears to be a distinct tendency towards a steady increase, particularly in the case of the compounds HS.Hg.CNS and $2HgS.HgCl_2$. This suggests that repeated illumination retards the subsequent rate of reversal in the dark. No effect of this nature was observed in the original experiments in which the rate of recovery was measured, but in these the compound was darkened only to a particular shade and not completely as in the present case. There are indications that the compound takes longer to recover after a prolonged exposure to light subsequent to complete darkening, but definite measurements have not yet been made and this aspect of the subject requires further investigation.

It will be observed that in some instances the initial current, even with the fresh substance, is by no means small. Readings taken at short intervals indicate that the initial rate of change is sometimes very rapid and is therefore not easy to determine exactly. The figures in Table I refer to values 5 seconds after exposure to light.

Figs. 4 and 5 show some typical curves obtained by taking galvanometer readings at short intervals after exposure to light. Curves i and ii are for the compound $2HgS.HgCl_2$ freshly prepared and after darkening and recovery overnight. The second curve is one that would be expected for a mixture of the fresh substance with about 10 per cent. of the darkened form. Curve iii is for a fresh sample of HS.Hg.CNS and is of a slightly unusual shape as the rate of emission increases with time instead of remaining constant as in the previous case. Curves of similar shape were obtained with this compound after darkening and recovery. Curves iv and v were obtained with the iodine compounds I.Hg.CNS and $2HgSe.HgI_2$. These differ from the preceding in that they give a definite emission immediately on exposure.

A different type of curve is given by $2HgS. HgBr_2$ (vi). The emission measured as soon as possible after exposure to light is high but is changing so rapidly that an accurate determination is not possible. The shape of the curve indicates that the initial emission might be zero. The case of I.Hg.CNSe shown separately in Fig. 5 is similar, the apparent tendency of the curve to start from zero being more marked as shown in curves vii and viii taken on consecutive days. In curve ix taken a day later, the initial bend appears to be absent. In order to study the initial effect more closely the light was reduced to nearly one-half its original intensity giving curves x and xi on consecutive days. These curves show a distinct tendency to pass through the origin and indicate the rapid formation of an intermediate compound

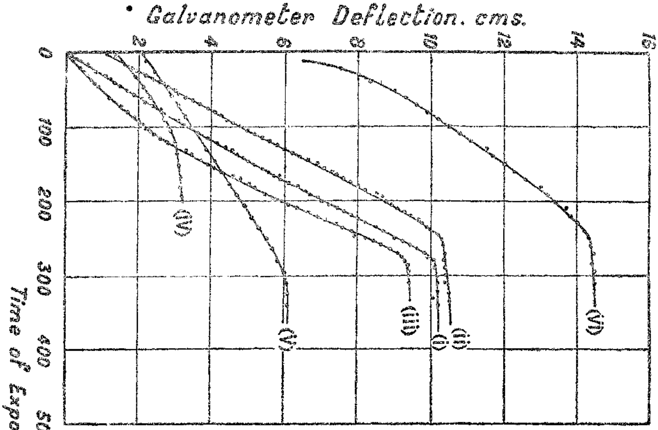

FIG. 4.

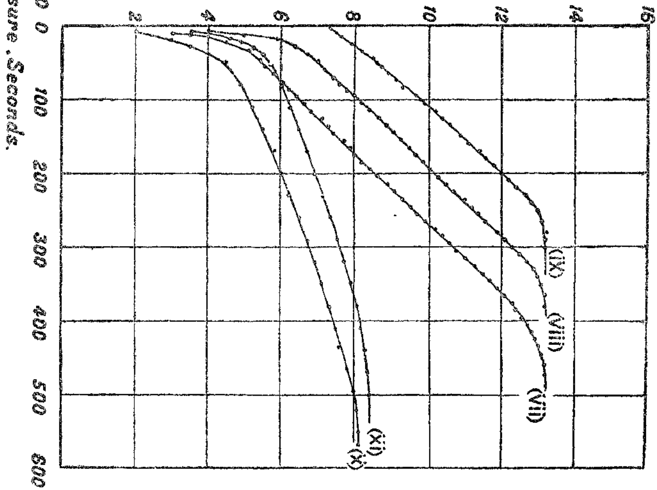

FIG. 5.

having approximately one-half the emissive power of the final product. When the first bend is reached the colour change is only slight, so that the intermediate compound appears to be of the same colour as the original one.

It is possible that action of a similar nature occurs with other compounds, but owing to the rapidity of the first change, measurements are difficult to make.

Wavelength of the active light.—Although the colour change of the compounds under investigation is greatest in the visible region, no photoelectric effect is produced by visible light. The same is the case for ultra-violet light filtered through glass or a solution of cobalt sulphate and nickel chloride transparent to 2600 A. U. It appears therefore that only light of wavelength less than this gives rise to electron emission.

It might be suspected that the ultra-violet light has some specific action on the compounds causing their activity to increase on irradiation. This was tested in the case of the substance I. HgCNSe by darkening it through a green filter and then exposing to the mercury arc. The initial emission was found to be the same as the maximum reached when exposed to the arc without a filter, so that it is the darkened form of the compound which is active irrespective of its method of formation.

A similar experiment was made with the same compound in the stage of the initial rapid change. Exposure through a green screen had the same effect as exposure to the direct arc, so that the formation of the first product is not specific to ultra-violet light.

THE RELATION BETWEEN LIGHT SENSITIVENESS AND PHOTOELECTRIC EMISSION.

As already mentioned, the green region of the spectrum is the most active in producing colour changes in these compounds while only ultra-violet light gives rise to electron emission. If there is any relation between the two properties it would most probably be found by comparing them for light of similar wavelength. In the first paper of this series it was shown that the colour change in ultra-violet light was slow, but the relation to the velocity for the visible region was not determined and it by no means follows that the ratio is constant for different substances.

We have now measured the times taken for darkening to the same shade (*a*) when exposed directly to the quartz arc (*b*) when exposed through an ultra-violet filter which cut out the visible region almost entirely and transmitted the ultra-violet as far as 2800 A. U. The results are shown in Table II and it may be seen that the ratios of the times of darkening vary from 2·0 to 4·2. Much importance cannot be attached to the relation between the figures for different compounds as the shades to which darkening took place are arbitrary and the colours vary for different compounds. It might be expected that a better comparison could be made from the curves showing the photoelectric activity assuming that the compounds are completely darkened when the curves turn over at the top. Figures for this quantity are given in column 3 of Table II, the actual values being multiplied by a factor to make them comparable with those in column 4, light of different intensity having been employed in the two cases. It will be noted that the two sets of figures although somewhat correlated, differ in a marked manner in several cases. It is possible that most of the compounds are slightly transparent to visible light but opaque to ultra-violet light so that the photoelectric effect would reach a maximum as soon as the surface layer of molecules was converted into the darker form. Maximum darkening as judged by eye would require some time longer according to the transparency of the particles. In practice it was difficult to estimate the colour during the experiments on photoelectric emission because of the grid which covered the compound, but as far as could be seen, the colour when the maximum emission was obtained was usually somewhat lighter than the deepest shade which could be reached.

TABLE II.

Light Sensitiveness and Phototropic Activity.

	Compound	Time of darkening, minutes			Ratio		Max. photo-electric current amps. × 10^{-11}
		(*a*) From curves × 2·1	(*b*) Direct arc	(*c*) Through filter	*c* : *b*	*c* : *a*	
1	$HS.Hg.CNS$	9·6	6	25	4·2	2·6	15
2	$Cl.Hg.CNS$	80	95	...	...	...	1·5
3	$I.Hg.CNS$	5·0	20	63	3·2	12·6	5
4	$Br.Hg.CNSe$	8·6	30	72	2·4	8·3	6
5	$I.Hg.CNSe$	14·8	25	70	2·8	4·7	21
6	$I.Hg.CNO$	10·5	30	75	2·5	7·1	1·5
7	$Hg.Cl_2.2HgS$	9·6	12	33	2·8	3·4	16
8	$HgBr_2.2HgS$	8·6	10	29	2·9	3·4	22
9	$HgI_2.2HgS$	7·5	9	24	2·7	3·2	82
10	$HgI_2.2HgSe$	10·5	40	84	2·1	8·0	9
11	$Hg(CNS)_2.2HgS$	9·6	10	30	3·0	3·1	5
12	$Hg(CNSe)_2.2HgS$	...	35	82	2·3	...	1·5
	Ag	..	..	...	...	...	67
	HgS	...	...	...	...	...	62
	HgSe	...	...	...	...	...	5

The times of darkening (*c*), although for ultra-violet light, are for longer wavelengths than those producing the photoelectric effect as there was no emission when the light was passed through the ultra-violet filter. The ratios to the times (*b*) for unfiltered light do not vary very widely and it is possible that darkening times for the extreme ultra-violet would be of the same relative order. The ratios *c* : *a* are much more divergent and it is difficult to say which figures more nearly represent the times of darkening. Whichever are adopted, however, there appears to be no quantitative relationship between the times of darkening and the photoelectric emission. In several cases the phototropic and photoelectric activities run parallel for related compounds, for example the chlorine compound 2 is less active than the iodine compound 3, and the activity rises from chlorine to iodine in the compounds 7, 8 and 9. The selenium compounds 10 and 12 are less active than the corresponding sulphur compounds 9 and 11, but the iodine compounds 3, 5 and 6 appear to be irregular. According to column (*c*) the selenium compound is intermediate in phototropic activity, according to (*a*) it is the least active while its photoelectric activity is the greatest of the three.

Photoelectric fatigue.—None of the substances examined showed any signs of photoelectric fatigue when exposed for 80 minutes. The photoelectric currents remained constant over this period within the limit of experimental error.

SUMMARY.

1. The photoelectric emission from 12 phototropic compounds of mercury has been examined and it is found that in all cases the emission from the compounds prepared in the dark is zero or very small.

2. On exposure to light the emission increases to a maximum and remains steady without any sign of fatigue. The maximum current was 82×10^{-11} amp. in the case of the compound $HgI_2.2HgS$ in air at 2 mm. pressure.

3. In some cases the increase in emission takes place in two stages with different rates of increase pointing to the formation of an intermediate compound.

4. On keeping in the dark or on heating, the photosensitiveness decreases very nearly to that of the freshly prepared compounds.

5. The dark varieties of the compounds give the same emission whether formed by the action of visible or of ultra-violet light.

6. There is no definite relation between phototropic and photoelectric activity although there is some correlation in the case of compounds of the same class.

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