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ON THE ELECTRICAL RESISTANCE OF THIN FILMS.

By Isabelle Stone.

THE discrepancy between the resistance of a film of given thickness measured directly by the Wheatstone bridge, as compared with the resistance calculated from its weight, density and dimensions, suggested the present investigation. As shown farther on by tables and curves, the calculated resistance is but a small fraction of the initial resistance of the film, when measured directly. The process of experimenting, however, revealed the fact that the initial resistance was not constant, but decreased with time, reaching its lowest value only after an infinite time. Films have not been preserved for longer intervals than three or four months; but the values of the resistance at the end of this length of time, while only approximately constant, nevertheless compare very favorably with the calculated values for the same thickness. This paper makes no pretensions of giving an exhaustive account of the subject under consideration. Many lines of research are only touched upon; none are worked out fully. The only metal studied is silver. The other metals, as well as the entire subject of films deposited in a vacuum, have not yet been touched upon. Investigation in all these directions, which is needed in order to have a good conception of the action of films, will be taken up at a future time.

As before stated, the metal chosen for experiment was silver deposited by the "Rochelle Salt Process." The silver was deposited on glass plates which were weighed before and after the silvering. From the weight of the silver and the dimensions of the glass plate, the surface density was calculated. The glass plates were 8 × 0.8 centimetres in dimensions and were laid face downward in such a way that the ends rested on a packing of silver leaf over the copper terminals. Good contact between the glass and terminals was insured by covers of fibre screwed down above and below the glass plate. Too great pressure, which would break the glass or tear the film, was avoided by cushions of paper at either end of the covers.

It was at once noticed that the resistance of the same film was not constant, but varied from hour to hour. Consecutive readings showed a steady decrease in resistance, the fall being more marked the higher the original resistance. The following table illustrates this fact.

TABLE I.

Film.	Weight.	R_0	Successive Readings of R directly after silvering.	R after 24 hours.
(a)	.24 mg.	1372	1261, 1239, 1166, 1097	550, 543, 530
(b)	.27 mg.	628	480, 338, 290	203
(c)	.36 mg.	93	78, 77.5, 77	44.1 43, 42.4
(d)	1.44 mg.	5.9	5.9	5.6

Thinking that this decrease might be due to moisture, the films were kept in dessicators except when taking measurements, but the same regular fall of resistance with time was observed.

After it was discovered that the resistance of a film at any time was a function of the age of the film, an attempt was made to find out the rate of fall. Readings of the resistance of a new film were taken at intervals, fifteen minutes apart, for several hours, and consecutive readings taken on the same film after an interval of sixteen or twenty-four hours. A film whose initial resistance was 528 ohms, fell in 4½ hours to 404 ohms. The first half of the time the average fall was 6 ohms every 15 minutes, and the last half 4 ohms in the same interval. After 16 hours the resistance of the film was 225 ohms, and in the next 30 minutes the fall was 3 ohms. It was found that the greatest fall in resistance occurred in the first 24 hours. Also, that the higher the original resistance of the film, the greater the fall in the first 24 hours. The curves show this very clearly.

Experiments were tried to show the effect of heat on the films. It was found that heat accelerated the time effect. To show this, the comparison of a heated and unheated film is annexed.

TABLE II.

		R_0	After 5 minutes heat.	After 5 hours heat.	After 24 hours.
Thick film.	heated.	(a) 130	8.9	4.8	4.9
	not heated.	(b) 88	72	50	38
Thin film.	heated.	35566	223	87	89
	not heated.	35000	35000	31252	14614

Two similar films (*a*) and (*b*) were taken ; (*a*) was heated for five minutes and (*b*) not heated. A comparison of the resistances of both (*a*) and (*b*) was made after (*a*) was removed from the oven ; (*a*) was then heated for five hours, and another comparison between resistances made. A thin film shows the fall of resistance as effected by heat in an even more marked degree.

To find the effect of moisture on a film, a film was heated in an oven which also contained a vessel of boiling water. A comparison unheated film was made and its fall of resistance compared with that of the heated film.

TABLE III.

		R_0	After 5 minutes heat.	After 5 hours heat.	24 hours after silvering.
Thick film.	heated with moisture.	193	10	5.4	6
	not heated.	90	—	52	40
Thin film.	heated with moisture.	3380	254	35500	—
	not heated.	2164	—	761	—

(It is to be noticed that the thin film failed to hold after 5 hours of heating.) Any differences between a film heated with dry heat or in the presence of moisture could not be detected.

A series of experiments was undertaken to find how much heating was necessary to lower the resistance of a film to its minimum value, and if less than this period of heating was allowed, to see whether the film continued to fall with time or not. Also, at what point in the curve illustrating the fall of resistance with time, the heat when applied would have the greatest effect in lowering the resistance. The experiments were conducted according to the following methods :

Comparison unheated films were kept for each heated film.

A. (*a*) The film was not disturbed for one hour after silvering. Readings of its resistance having been taken initially and at the end of the hour it was put in the oven and heated one minute, removed, measured and left undisturbed afterward.

(*b*) A new film was treated similarly, except that it was heated for 2 minutes.

(*c*) A new film was treated similarly, except that it was heated for 3 minutes, etc.

B. (*a*) After measurement the film was not disturbed for 5 hours. It was then measured, heated one minute, measured again and put aside.

(*b*) A new film was left undisturbed for 5 hours, and heated 2 minutes.

(*c*) A new film was left undisturbed for 5 hours and heated 3 minutes, etc.

C. (*a*) After measurement the film was not disturbed for 16 hours. It was then measured, heated one minute, measured again and put aside.

(*b*) A new film was left undisturbed for 16 hours and heated 2 minutes, etc.

Each of the above series of experiments was carried out for a thick film and also for a thin film.

By consulting these tables, it can be seen that

(1) Heat accelerates the time effect.

(2) The greater the age of the film, the less the effect produced on it by heat.

(3) In general, the longer the heat is applied, the greater the fall in the resistance.

TABLE IV.

		R_0	After 1 hour.	Heated ½ min.	Fall in R.	After 48 hrs.	R_0	After 1 hr.	Heated 1 min.	Fall in R.	After 48 hrs.	R_0	After 1 hr.	Heated 2 min.	Fall.	After 48 hrs.
Thick film.	heated.	22	19.8	16.4	3.4	12	42.2	37.7	19.9	17.8	10.8	18	16	7	9	7.2
	not heated.	14.2	12.1	11	1.1	9	56.4	48	46	2	14	15	13	13	0	11
Thin film.	heated.	1616	1488	1102	386	503	2542	2116	813	1303	420	1018	920	190	730	134
	not heated.	2088	2088	1987	101	527	914	882	800	82	538	6089	3746	—	—	734

TABLE V.

		R_0	After 1 hour.	Heated 3 min.	Fall.	After 48 hrs.	R_0	After 1 hr.	Heated 4 min.	Fall.	After 48 hrs.	R_0	After 1 hour.	Heated 5 min.	Fall.	After 53 hrs.
Thick film.	heated.	15.5	13.4	7	6.4	7.2	13.4	13.1	7.2	5.9	8.1					
	not heated.	15	14	—	—	12.6	13.6	13	—	—	12					
Thin film.	heated	1204	1014	133	881	94	1015	939	170	769	128	2390	1456	336	1120	271
	not heated.	567	482	474	8	65	266	251	—	—	111	510	347	—	—	126

TABLE VI.

		R_0	After 1 hour	Heated 6 min.	Fall	After 1 hour	R_0	After 1 hour.	Heated 7 min.	Fall	After 1 hour	R_0	After 1 hour	Heated 8 min.	Fall	After 1 hour
Thin film.	heated	1155	780	47.5	732.5	42	1933	1262	101.8	1160.2	94.7	3413	2831	86.4	2744.6	84.2

TABLE VII.

		R_0	After 5 hrs.	Heated 3 Min.	Fall	After 53 hrs.	R_0	After 5 hrs.	Heated 4 min.	Fall		R_0	After 5 hrs.	Heated 5 min.	Fall	After 24 hrs.
Thick film.	heated						53	40	35	5		61	27	11.5	15.5	9.7
Thin film.	heated	1293	624	470	154	462										

TABLE VIII.

		R_0	After 5 hrs.	Heated 6 min.	Fall		R_0	After 5 hrs.	Heated 7 min.	Fall		R_0	After 16 hrs.	Heated 5 min.	Fall	After 10 hrs.
Thick film.		92	46.8	15.9	30.9		155	80.5	14.7	65.8		30	22.7	21.7	1	17.9
Thin film.												1135	128	61.7	66.3	58

TABLE IX. (Thick film.)

R_0	After 16 hrs.	Heated 6 min.	Fall	After 5 hrs.	R_0	After 16 hrs.	Heated 7 min.	Fall	After 5 hrs.
34.5	16.4	8.4	8	8.3	33.4	16.7	8.7	8	8.9

(4) A certain period of heating reduces the resistance of each film to its lowest value.

(5) This period of heating, necessary to produce the minimum resistance, is greater, the greater the initial value of the film.

(6) After the minimum value of the resistance is reached, further heating has no effect upon the film.

(7) When not reduced to its minimum resistance by heat, the film continues to decrease with time in the ordinary manner.

(8) When the lowest value of the resistance is produced by heating, there seems to be a certain increase in the resistance, when measured after a number of hours.

To find whether heat produced any effect on comparatively thick films, a plate was placed in the silver bath three or four times and a heavy coating of silver thereby secured. The initial resistance was 5 ohms. After one half hour, it had fallen to 4.9 ohms. On heating it for 5 minutes the resistance fell to .98 and when measured after a rest of 72 hours, its resistance was .97 ohms. It would thus seem to be true that heating produces an effect upon films of all thicknesses.

Experiments were tried to see if an electric current would have the same effect as heat upon a film. Many experiments were tried to determine the proper current which would have an effect upon the film without destroying it. The results roughly obtained were not entirely satisfactory. The fall in resistance of a film as an effect of current was in excess of the corresponding fall as an effect of time in the comparison film; but it was not proved that this excess of fall was due to the electric current and not to the heating effect of the current. It was also noticed that with films of high resistance, the short currents sent through the film, while a bridge balance was being obtained, lowered the resistance noticeably. The question as to whether this change was due to heat or electric current demands a separate investigation.

In taking consecutive readings of the resistance of a film, it was noticed that the slamming of a door or other violent vibration produced a small but instantaneous decrease in the resistance. A few experiments were made by placing a film on the resonator of a tuning fork in vibration and measuring its resistance before and after, also by striking the table on which the film lay. The results seemed to confirm the fact that shocks hastened the fall of resistance; but the experiments were not carried further.

It was decided to take films varying in initial resistance from 5 to 100,000 ohms, observe the resistance from day to day and construct curves for each film, taking times as abscissæ and resistances as ordinates.

A and *B* are the bottom and top clamp of fibre, screwed together by screws through the four holes; *d*, *e*, *f*, *g* are cushions of tissue paper; *m* and *n* are copper terminals over which silver leaf is

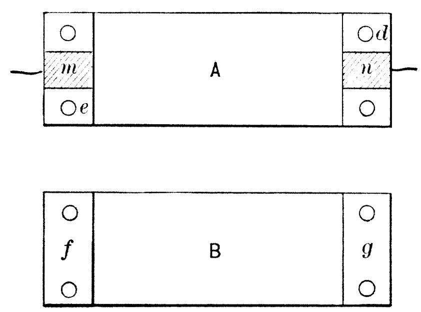

Fig. 1.

placed. The glass plate is the length of the clamp and the width of the terminals. It rests silvered face downward, upon the silver leaf. Twelve covers of hard rubber were made for the twelve films to be experimented upon. Sheet rubber was used as an insulator, and to prevent the breaking of the glass by pressure from the hard rubber covers. A sulphide was formed on the silver, due to the sulphur from the rubber. The effect was much more noticeable in those films which were heated. When kept in a dessicator, the sulphide continued to form on the films, though not so rapidly as when they were kept in the air. The presence of the sulphide manifested itself sooner on the thin than on the thick films by an increase in the resistance. The rubber covers and cushions were, therefore discarded. Fibre covers were tried with cushions of tissue paper. A set of curves recorded in the tables as films set up between December 19, 1896, and January 7, 1897, were the result of a fairly good set of readings. The effect of the sulphide in increasing the resistance did not manifest itself except on the two films of highest initial resistance and even in those cases not till after a month had expired.[1] It was noticed that temperature had an appreciable effect on the resistance, the effect of cold being to retard and of heat to accelerate the decrease in the resistance.

A new series of experiments was undertaken, aiming to carry out three precautions.

(1) To avoid a sulphide formation.

(2) To keep the film at a constant temperature.

(3) To use the same silvering solution for all the films.

Having found that sulphide was formed in the presence of air it was decided to isolate the films as much as possible. Each terminal containing the film to be examined was placed in a glass jar, known to contain air as pure as possible. A tin cover was screwed down upon the top of the jar, the only openings being two small holes to allow the wires passage. These jars, twelve in number, were placed in a box completely enclosed and lined with felt. The box was placed in a constant temperature room and removed for a few minutes only each day in order to take the necessary measurements and note any changes in temperature given by a thermometer placed in the box. The three series of curves for the films set up on March 2, March 4 and March 11, show the effect of these conditions.

The reason for setting up three distinct series of films from the same solution was to try to ascertain whether the age of the solution had an effect upon the fall of resistance. Observations were made on films of initially the same resistance, set up from the same solution; but at intervals of several days apart. By comparison of the resistance readings, it was concluded that the age of the solution had to do with the fall of resistance, the fall in the first forty-

[1] Due probably to escape of illuminating gas.

eight hours being much less the older the solution. An analogous phenomenon was observed in the heat experiments. However, films of less than 100 ohms initial resistance did not show this characteristic.

In order to prevent completely the formation of the sulphide on the silver film, the terminal, enclosing the film to be observed, was placed in a glass tube, connected with a mercury air pump, the air exhausted and the tube sealed off. The results are given in tables under films set up on March 26, 27 and 30.

Under these circumstances a film of initially very high resistance, 144,000 ohms, decreased for a few days in resistance to 80,000 ohms and then increased indefinitely. As this could not now be due to the formation of the sulphide, it was concluded that the preservation of films of an initial resistance above 50,000 ohms was impossible with the methods of experimentation hitherto used.

TABLE X.

First Series. Films kept in dessicator.

Curves.	Date.	Solution.	C_1	C_2	$C_1 + C_2$	n	k	Temp.	Weight in mg.	Time.
(d)	Dec. 19.	B	291	27280	27571	.43	.52		.12	53 days
(m)	Jan. 7.	C	386	5403	5789	.43	.40		.22	34 days
(g)	Dec. 21.	B	87	1073	1160	.43	.28		.38	51 days
(b)	Dec. 22.	B	26	160	186	.43	.19		.62	50 days
(j)	Dec. 22.	B	8.4	28.6	37	.43	.18		1.52	48 days
(k)	Dec. 23.	B	4.3	5.2	9.5	.43	.12		1.61	49 days
I	Nov. 7.	D	84	1202	1286	.43	.30			17 days
II	Nov. 5.	D	16	512	528	.43	.34			27 days

$$y = c_1 + c_2 e^{-kt^n}$$

$$c_1 = y \text{ when } t = \infty.$$

$$c_1 + c_2 = y \text{ when } t = 0.$$

Time means period during which observations were taken.

Table XI.

Second Series. Films in glass cans kept in felt-lined boxes.

Curves.	Date.	Solution.	C_1	C_2	$C_1 + C_2$	n	k	Temp.	Weight.	Time in days.
(d)	Mch. 2.	A.	992	31538	32530	.43	.85	21°		48
(m)	"	"	416	18984	19400	.43	.80	"		"
(i)	"	"	260	7140	7400	.43	.75	"		"
(g)	"	"	123	2447	2570	.43	.60	"		"
(h)	"	"	24	408	432	.43	.44	"		"
(c)	"	"	19.2	11.97	31.13	.43	.19	"		"
(k)	"	"	5.6	12.14	17.7	.43	.18	"		"
(b)	Mch. 4.	"	1821	42379	44200	.43	.76	20.5		40
(f)	"	"	600	13940	14540	.43	.60	"		"
(a)	"	"	415	6185	6600	.43	.37	"		"
(j)	"	"	156	1894	2050	.43	.30	"		"
(e)	"	"	41	711	752	.43	.55	"		"
O	Mch. 11.	"	938	31162	32100	.43	.51	19°3		65
R	"	"	642	25995	26098	.43	.43	"		"
L	Mch. 10.	"	370	9730	10100	.43	.42	"		"
P	Mch. 11.	"	320	4550	4870	.43	.52	"		"
T	"	"	190	3384	3574	.43	.43	"		"
Q	"	"	190	2170	2360	.43	.34	"		"
S	"	"	159	651	810	.43	.36	"		"

Table XII.

Third Series. Films kept in vacuum tubes.

Curves.	Date.	Solution.	C_1	C_2	$C_1 + C_2$	n	k	Temp.	Wgt.	Time in days.
(9)	Mch. 27.	F	1600	42800	44400	.43	.25	19.°3		50
(7)	"	"	19090	5510	24600	.43	.11	"		"
(10)	"	"	450	15550	16000	.43	.26	"		"
(6)	Mch. 26.	"	233	4677	4910	.43	.23	"		"
(8)	"	"	90	954	1044	.43	.25	"		"
(2)	Mch. 27.	"	80	710	790	.43	.23	"		"
(5)	Mch. 30.	E	869	9001	9870	.43	.23	19.°3		"
(11)	"	"	2248	3052	5300	.43	(.68)	"		"
(3)	"	"	106	1324	1430	.43	.44	"		"
(1)	"	"	85	196	281	.43	.28	"		"

(11) increased in resistance after the fourth day. The value of k therefore could be obtained only approximately. From an analogy with (5) it was concluded that the value of k should be nearer .5. The fall of (7) was noticeably small.

The connection between the initial resistance of a film and its thickness is shown in the following table:

TABLE XIII.

	Thickness in centimeters.	R_0 Resistance of a film 10×1 cm.	R Calculated resistance.	$\frac{R_0}{R}$ Ratio of experimental to calc. R.	Thickness in centimeters.	R_0 Resistance of a film 10×1 cm.	R Calculated resistance.	$\frac{R_0}{R}$
Solution A. Dates, June 21 and June 22.	.0000013	435284	8	54410	.00000096	1188470	11.3	105174
	.0000019	13733	5.6	2452	.0000021	15176	4.7	3229
	.0000032	3545	3.1	1143	.0000019	12765	5.4	2364
	.0000036	1043	3.0	348	.0000029	1356	3.7	367
	.0000085	198	1.2	165	.0000108	170	1.0	170
	.0000088	194	1.1	161	.0000157	67	.6	111
	.0000192	33	.5	66				
	.0000224	19	.4	47				
Solution B. Dates, June 25 and June 26.	.0000035	10157	2.8	3627	.0000019	141833	5.4	26265
	.0000037	4423	2.9	1525	.0000030	13937	3.4	4037
	.0000045	1010	2.2	463	.0000037	2935	2.7	1083
	.0000083	344	1.2	286	.0000041	1173	2.4	488
	.0000156	132	.6	220	.0000056	537	1.8	301
	.0000173	47	.5	94	.0000081	234	1.2	195
					.0000239	55	.4	137

TABLE XIV.

	Thickness in centimeters.	R_0	R.	$\frac{R_0}{R}$
Solution C. Date, June 29.	.0000026	260855	4.2	62108
	.0000037	16215	2.8	5836
	.0000054	2744	1.9	1506
	.0000075	260	1.5	178
	.0000123	127	.9	142

Density of silver, 10.53.

The second column gives the experimental value of the resistance of a film of known thickness, ten centimeters in length and one centimeter in width. The calculated resistance is found by dividing the specific resistance in ohms times the length by the thickness times the width. The thickness was calculated from the weight of the film by dividing the weight in grams by the area times the density. Curves were drawn taking the thicknesses, estimated in millionths of a centimeter, as abscissæ and the ratio $\frac{R_0}{R}$ as ordinates.

The calculated resistance for a given thickness is but a small fraction of the experimental value for the same thickness.

Three different solutions were used in this set of experiments. It can be seen from the curves that two series of weighings made on two successive days; but from the same solution agree closely, while there is a difference in the form of the curve for different solutions.

Having drawn the curves given by the experimental values of the film at times when observations were taken, the theoretical curve, to which each experimental curve most closely corresponds, had to be deduced. The theoretical curve given by $y = C_1 + C_2 e^{-kt^n}$ corresponds most closely with the experimental curves. The tables give the calculated values for the constants C_1, C_2 and k, taking n throughout the same for each curve. The agreement between the experimental and theoretical curves was very close.

From an observation of the curves and the values of k corresponding to the curves it is apparent that the lower the value of k the slower the fall of resistance. Hence it can be seen at a glance, in the second series, by comparison of the values of k, that the fresher the solution the more rapid the fall. For any one of the three sets of curves in this series, the decrease in k as the initial resistance decreases follows approximately the experimental law $r = ce^{km}$ where values of $c_1 + c_2$ are taken as abscissæ and corresponding values of k as ordinates, the constants being c and m. For the curves drawn from films kept in a vacuum, a somewhat different order holds. For each curve, no matter what the initial value of the resistance, k is approximately the same, *i. e.*, the law $y = c_1 + c_2 e^{-kt^n}$ is very closely followed as $y = 42 + 958e^{-.25t^{.43}}$. On looking at the tables, it is seen that the curves for the vacuum films are distinguished from the others by the slowness with which they fall. The higher the value of k the more rapidly the resistance falls. For vacuum films k is approximately .25, whereas, in other cases, the value varies from .85 to .18. Curve (7) $R_0 = 24600$ exhibits a

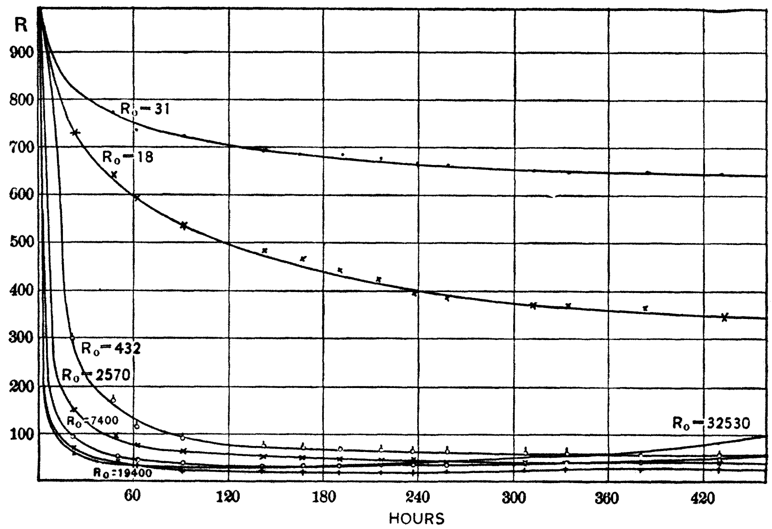

Fig. 2.

curious exception to the law and curve (3) $R_0 = 1430$ shows that the tube was not properly exhausted.

Fig. 2 shows seven curves, known in the tables as Series II, Mch. 2. For all but $R_0 = 31$ and $R_0 = 18$ the law $y = 37 + 963e^{-.69t^{.43}}$ holds. $R_0 = 31$ descends too slowly for the compari-

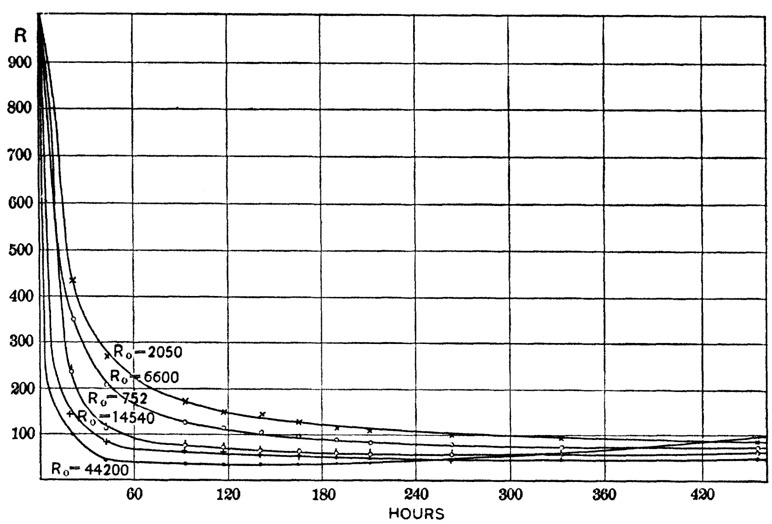

Fig. 3.

son, the higher the initial resistance the more rapid the fall. The two curves $R_0 = 32530$ and $R_0 = 19400$ rose in resistance after a few days.

Fig. 3 shows five curves, known in the tables as Series II, Mch. 4. The higher the resistance the more rapid the fall. $R_0 = 752$ is an exception. The approximate law followed is $y = 56 + 944e^{-.51t^{.43}}$. k in this case is less than k for the fresh solution, showing that the older the solution the slower the decrease.

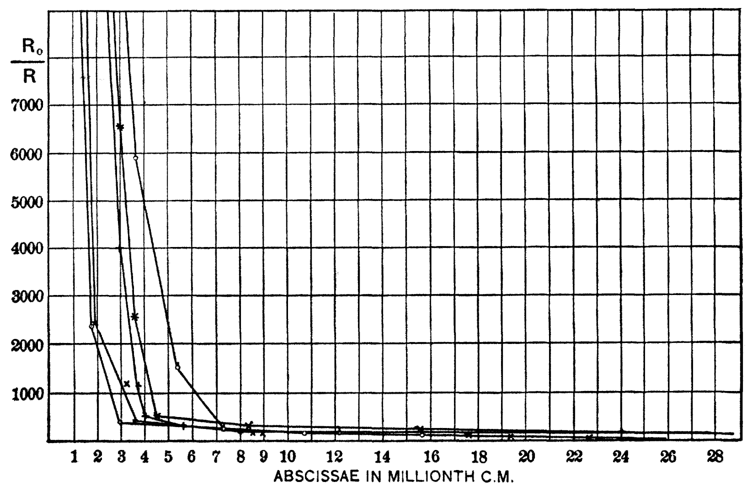

Fig. 4.

Fig. 4 shows the lack of agreement between the calculated and experimental value of the resistance for the same film. The abscissæ are thicknesses given in millionth centimeters. The ordinates are the ratios of the experimental to the calculated resistance. Just why the films kept in a vacuum decrease in resistance more slowly than those exposed to the air is not clear. In case of films between 20,000 and 50,000 initial resistance exposed to the air it was noticed that the more rapid the fall of resistance in the first forty-eight hours the more certainly could a uniform and considerable rise in resistance be expected after a few days. (*d*) and (*m*) of Mch. 22 and (*b*) of Mch. 4 are examples.

It would seem that the rearrangement of the molecules of the silver is carried on more slowly and uniformly when air is excluded, the process being completed theoretically after an infinite time. Films kept for three months were found still falling in resistance. It certainly cannot be said that the sulphide formed on the silver due to the presence of air, retards the fall of resistance, since the resistance of films in a vacuum falls much more slowly than that of those films exposed to air. It is possible that the quicker the rearrangement takes place, the less enduring the film. There may be a greater accumulation of the silver particles in some regions than in others and a space practically free from silver particles may exist. At all events, it was noticed that films of 30,000 or more initial resistance, when heated a few minutes, showed a greater decrease of resistance, but when heated several hours increased in resistance to values higher than the initial reading. Similarly, high films as (*b*), (*d*) and (*m*) show k equal to .76, .85 and .80 respectively, as compared with ordinary values of from .2 to .5. This means a rapid decrease in the first twenty-four hours and is followed by an enormous increase within a week after silvering. The films which behaved in this manner were formed from fresh silver solutions.

In general, then, the decrease of resistance with time is caused by a gradual settling down of the silver molecules into a more and more compact mass. Heat accelerates this action, bringing in a few minutes the film into that condition which time acting alone accomplishes only after months. Preliminary experiments indicate that electric currents and shocks produce a similar effect upon a film as that produced by heat.

I wish to express my gratitude to Professor A. A. Michelson, who suggested this subject for research and who has forwarded its accomplishment in all ways and not least by the untiring patience and interest which he has ever shown.

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