

ON THE VARIATION OF THE CONDUCTIVITY OF ALUMINIUM ANODE-FILMS WITH TEMPERATURE.

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In a previous Paper* it was shown that in the few cases tried, and there mentioned, the variation of the leakage current of Al anode-films with temperature followed an exponential law, *i.e.*—

$$i = A e^{a\theta}$$

or—

$$\log i = \log A + a\theta$$

the curves obtained by plotting $\log i$ to θ being straight lines over the whole range of temperature from ordinary temperature to the boiling-point of the electrolyte. It was also shown that a was independent of the formation period.

A more extended investigation having proved that this law is obeyed in a very large number of cases, it would seem to demonstrate the fact that the law has some electro-chemical or perhaps physical significance, and is not merely an empirical relationship. It is therefore thought worth while to give an account of these more complete experiments.

The chief variables that may influence these results are :—

1. The time of formation ;
2. The electrolyte ;
3. The voltage of formation ;
4. The concentration of the electrolyte ,
5. The voltage used during the test ;

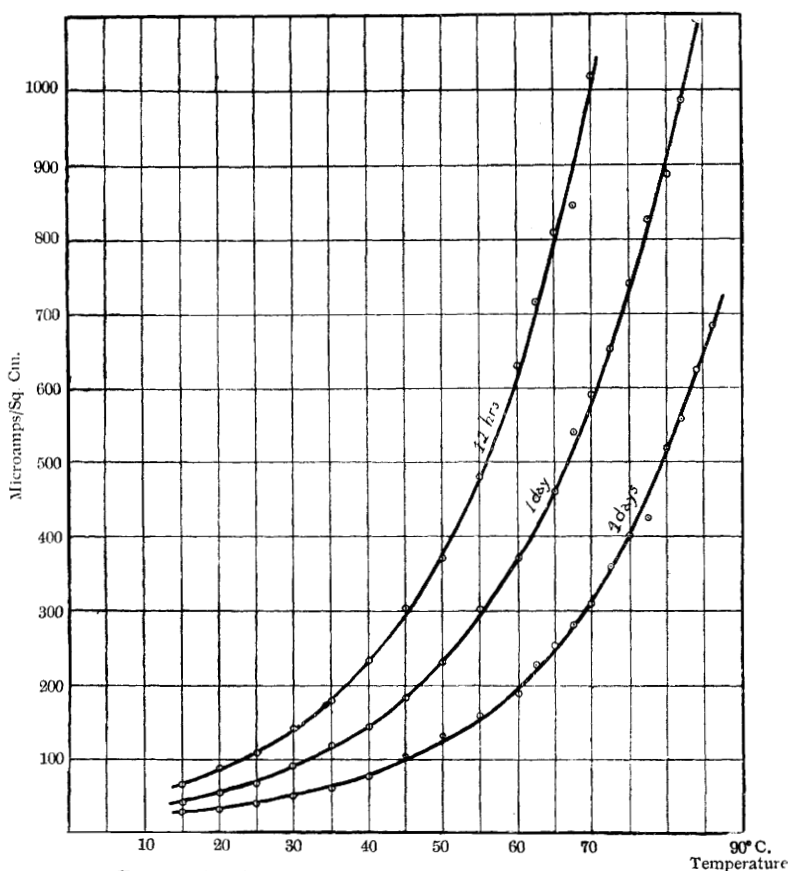
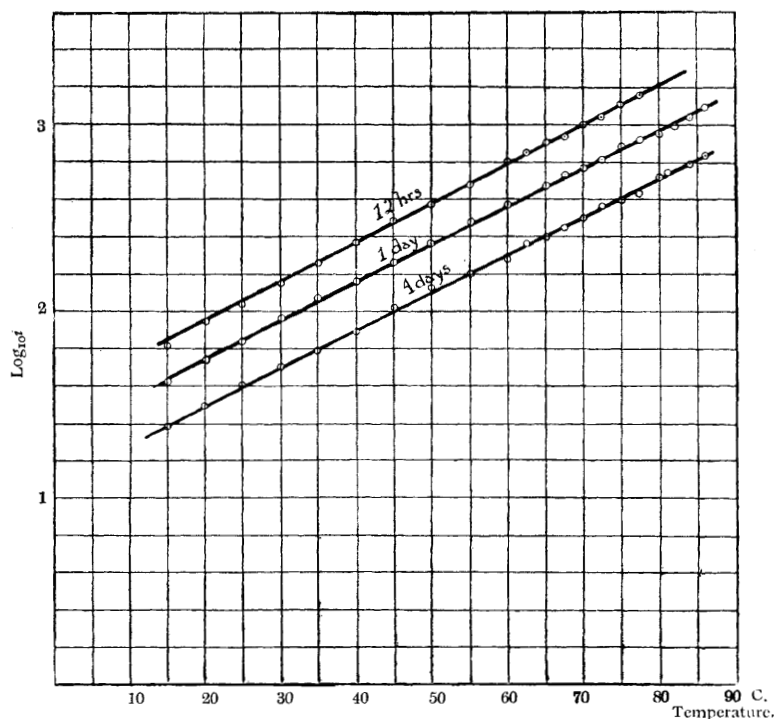
and we will now consider them in turn.

1. The Influence of the Time of Formation.

Fig. 1 and Table I. give the results obtained for saturated Am_2HPO_4 for three different formation periods, viz., twelve hours, one day, and four days respectively. The curves show a rapid increase of the current with temperature. Fig. 2 gives the same results with $\log i$ plotted to the temperature. It will be seen that they give very good straight lines, and moreover the lines are all parallel with one another, the actual values of a and A being :—

	Am_2HPO_4 , 100 Volts.		
	12 Hours	1 Day	4 Days
a	0·0622	0·0612	0·0612
A	33·9	20·9	11·7

* *Trans. Faraday Soc.*, vol. vii., 1911, p. 1.

FIG. 1.— Am_2HPO_4 , 100 Volts for various Formation Periods.FIG. 2.— Am_2HPO_4 , 100 Volts for various Formation Periods.

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TABLE I.
 Am_2HPO_4 . 100 *Volts*.

Temp. ° C.	Half Day.		One Day.		Four Days.	
	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$	$\text{Log}_{10}i$.	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$	$\text{Log}_{10}i$.	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$	$\text{Log}_{10}i$.
15	66	1·82	41·8	1·62	23·8	1·38
20	87	1·94	55·4	1·74	31	1·49
25	108	2·03	69	1·84	40	1·60
30	141	2·15	91	1·96	49·5	1·70
35	179	2·25	119	2·07	61	1·79
40	233	2·37	144	2·16	77	1·89
45	303	2·48	183	2·26	104	2·02
50	372	2·57	232	2·36	132	2·12
55	480	2·68	303	2·48	159	2·2
60	630	2·80	372	2·57	189	2·28
62·5	716	2·85	—	—	228	2·36
65	810	2·9	461	2·67	253	2·40
67·5	847	2·93	542	2·73	281	2·45
70	1,020	3·01	592	2·77	310	2·5
72·5	1,190	3·04	653	2·82	360	2·56
75	1,290	3·11	740	2·88	400	2·6
77·5	1,440	3·16	827	2·92	425	2·63
80	—	—	888	2·95	520	2·72
82	—	—	985	2·99	560	2·75
84	—	—	1,095	3·04	625	2·8
86	—	—	1,250	3·09	685	2·84

TABLE II.
 $(\text{Am}_2\text{O})_{3/7}(\text{MoO}_3)$. 25 *Volts*.

Temp. ° C.	Half Day.		One Day.		Four Days.	
	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$	$\text{Log}_{10}i$.	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$	$\text{Log}_{10}i$.	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$	$\text{Log}_{10}i$.
20	20·1	1·30	13·2	1·12	9·0	0·95
25	28·8	1·46	18·6	1·27	13·2	1·12
30	38·5	1·59	26·8	1·43	18·3	1·26
35	52·5	1·72	—	—	26	1·41
40	81·2	1·91	52	1·72	39·4	1·62
45	115	2·06	76	1·88	55	1·74
50	163	2·21	102	2·01	88	1·89
55	238	2·38	144	2·16	105	2·02
60	322	2·51	202	2·31	147	2·17
62·5	384	2·58	—	—	169	2·23
65	442	2·65	285	2·45	195	2·30
67·5	529	2·72	348	2·54	240	2·38
70	655	2·82	417	2·61	292	2·47
72·5	798	2·90	510	2·71	390	2·59
75	962	2·98	615	2·79	472	2·67
77·5	1,130	3·05	745	2·87	605	2·78
80	—	—	850	2·93	—	—

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that is to say, while the effect of increasing the time of formation is to decrease the initial value A , in the expression $i = Ae^{at}$, it has no influence on a .

Table II. and Fig. 3 give the results for $(Am_2O)_37(MoO_3)$ for the same three periods of formation, but for a much lower voltage, viz. 25. As before, a is independent of the time of formation, being 0.0910, 0.0895, and 0.0910 respectively.

2. The Influence of the Electrolyte.

Fig. 4 shows how the various electrolytes that were tried follow the exponential law. The experimental results are given in different tables, and the curves, with the exception of the $Am_2C_2O_4$, all refer to one particular voltage and period of formation, viz., 100 volts and one day respectively.

The only exception to the exponential law is in the case of $AmHCO_3$, the anomalous behaviour of which electrolyte is considered later on.

The values of a for the five electrolytes are as follows:—

Electrolyte (Saturated)	Value of a in Ae^{at}
$Am_2B_4O_7$	0.1090
$AmHCO_3$	0.09255
$(Am_2O)_37(MoO_3)$	0.0890
$Am_2O_2O_4$	0.0865
Am_2HPO_4	0.0612

3. The Influence of the Voltage of Formation.

Table IV. and Fig. 5 give the results obtained with Am_2HPO_4 for a formation period of one day, but for different voltages of formation. The lines are practically parallel with one another, the actual values of a being 0.0610, 0.0608, and 0.0612, for 25, 50, and 100 volts respectively, showing that a is independent of the voltage of formation.

Table V. and Fig. 6 give a similar set of results for $(Am_2O)_37(MoO_3)$. Again we have nearly parallel straight lines, the values of a being 0.0895, 0.0880, and 0.0890.

Finally, in Table VI. and Fig. 7 are given the results for $Am_2C_2O_4$, which is an electrolyte with a low critical voltage, and a very considerable leakage current. Since its critical voltage at ordinary temperatures is in the neighbourhood of 100, and an Al anode-film formed in it would therefore fail as the temperature rises, the 100-volt curve it is impossible to give, but even at 50 volts it will be seen that the line is straight, and even in this case the value of a is independent of the voltage of formation.

The exception to the general law mentioned in section 2, *i.e.*, $AmHCO_3$, will now be considered. In Table VII. are given the results for saturated $AmHCO_3$ for the three different voltages, and for a formation period of one day and the log curves are depicted in Fig. 8. It will be noticed that these are straight lines up to a temperature of about 55°, at which point there is an abrupt change, and the curve proceeds along another straight line which is not as steep as in the first stage. The initial lines for the three voltages are, nearly parallel to each other, but not so closely parallel as in the previously mentioned examples— a in fact decreases as the voltage increases (as shown in the following table (p. 240).

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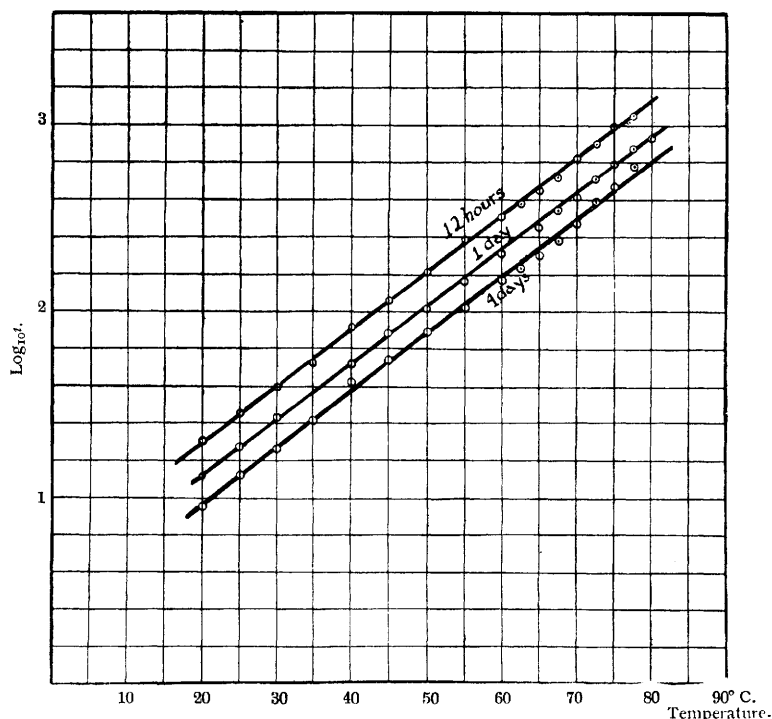
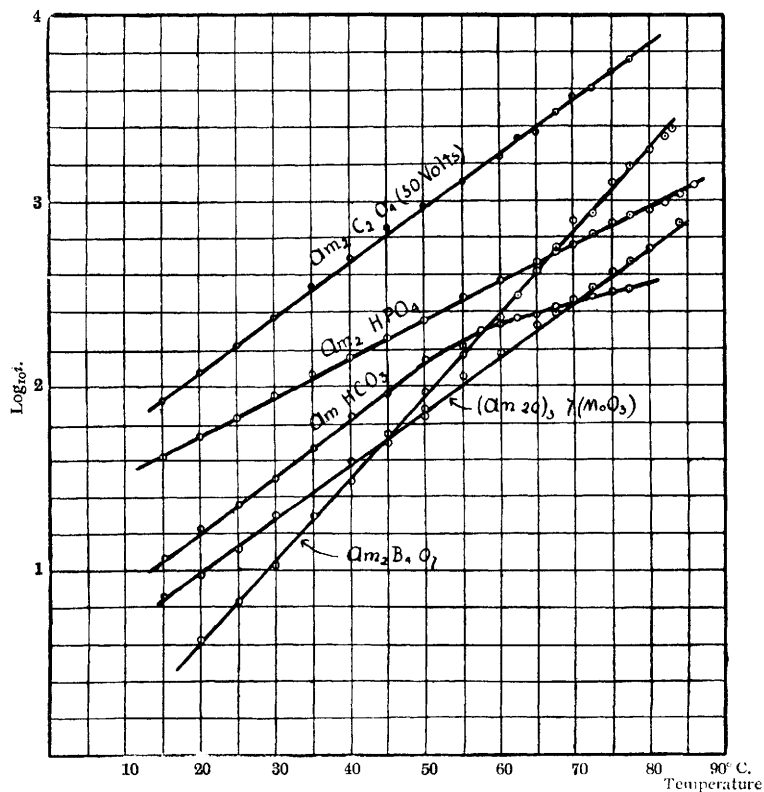
FIG. 3.— $(\text{Am}_2\text{O})_{3.7}\text{MoO}_3$, 25 Volts for various Formation Periods.

FIG. 4.—100 Volts, 1 Day's Formation, various Electrolytes.

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TABLE III.
Formation Period 1 Day. 100 Volts.

Temp. °C.	(Am ₂ O) ₃ 7(MoO) ₃ .		Am ₂ B ₄ O ₇ .	
	Microamps Sq. Cm.	Log ₁₀ i.	Microamps Sq. Cm.	Log ₁₀ i.
15	7.1	.85	—	—
20	9.35	.97	4.3	.63
25	13.2	1.12	6.65	.82
30	19.8	1.3	10.8	1.03
35	—	—	21	1.30
40	39.2	1.6	30.7	1.49
45	56	1.75	50.2	1.70
50	78.2	1.88	94	1.97
55	111.5	2.05	147	2.17
60	151	2.18	233	2.37
62.5	—	—	306	2.49
65	213	2.33	416	2.62
67.5	247	2.39	562	2.75
70	290	2.46	780	2.89
72.5	349	2.53	845	2.93
75	408	2.61	1,260	3.10
77.5	465	2.67	1,560	3.19
80	543	2.74	1,910	3.28
82	—	—	2,250	3.35
83	—	—	2,470	3.39
84	765	2.88	—	—

TABLE IV.
Am₂HPO₄. Formation Period 1 Day.

Temp. °C.	25 Volts.		50 Volts.	
	Microamps Sq. Cm.	Log ₁₀ i.	Microamps Sq. Cm.	Log ₁₀ i.
15	61.3	1.79	48	1.68
20	77.0	1.89	63.6	1.80
25	88.1	1.99	79.6	1.98
30	123	2.09	104	2.02
35	154	2.19	136	2.13
40	189	2.28	168	2.23
45	240	2.40	190	2.29
50	343	2.53	278	2.44
55	395	2.60	—	—
60	—	—	412	2.61
62.5	440	2.76	—	—
65	—	—	526	2.72
67.5	654	2.82	—	—
70	762	2.88	696	2.84
72.5	885	2.95	742	2.87
75	1,020	3.01	872	2.94
77.5	1,140	3.06	946	2.98
80	1,280	3.11	1,145	3.06
81	1,350	3.13	1,250	3.10
82	1,420	3.15	—	—
84	1,540	3.19	1,320	3.12

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TABLE V.

 $(\text{Am}_2\text{O})_{37}\text{MoO}_3$. *Formation Period 1 Day.*

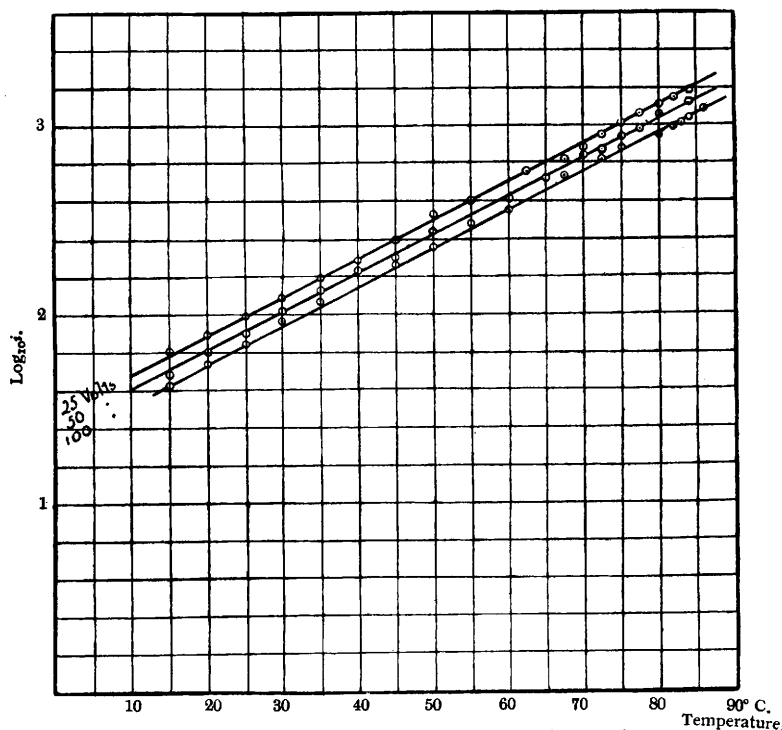
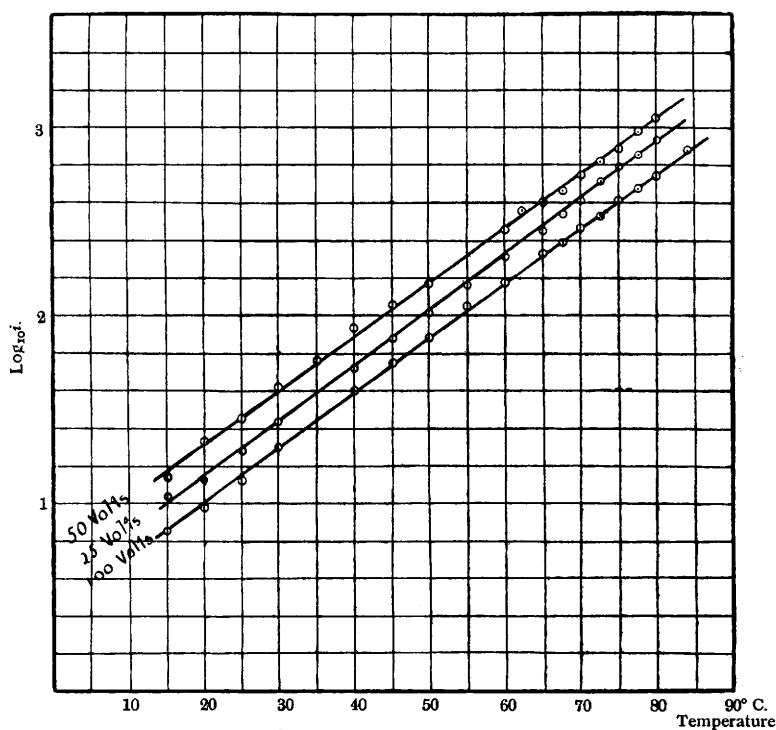
Temp. ° C.	50 Volts.	
	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$	$\text{Log}_{10}i$.
15	13·8	1·14
20	20·2	1·33
25	28·2	1·45
30	42·2	1·62
35	57	1·76
40	84·5	1·93
45	114	2·06
50	149	2·17
55	—	—
60	292	2·46
62·5	362	2·56
65	403	2·60
67·5	455	2·66
70	550	2·74
72·5	660	2·82
75	743	2·88
77·5	950	2·98
80	1,110	3·05

TABLE VI.

 $\text{Am}_2\text{C}_2\text{O}_4$. *Formation Period 1 Day.*

Temp. ° C.	50 Volts.		25 Volts.	
	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$	$\text{Log}_{10}i$.	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$	$\text{Log}_{10}i$.
15	86	1·93	74·2	1·87
20	118	2·07	110	2·04
25	165	2·22	152	2·18
30	233	2·37	211	2·32
35	340	2·53	304	2·48
40	495	2·69	435	2·64
45	710	2·85	—	—
50	947	2·97	826	2·92
55	1,250	3·10	1,120	3·05
60	1,720	3·24	1,490	3·17
62·5	2,160	3·34	1,930	3·29
65	2,340	3·37	2,110	3·32
67·5	3,030	3·48	2,420	3·39
70	3,270	3·56	3,010	3·48
72·5	3,960	3·60	—	—
75	4,900	3·69	4,010	3·60
77·5	5,700	3·76	4,400	3·69
80	—	—	5,000	3·75

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FIG. 5.— Am_2HPO_4 , 1 Day's Formation at various Voltages.FIG. 6.— $(\text{Am}_2\text{O})_{37}(\text{MoO}_3)$, 1 Day's Formation at various Voltages.

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Voltage.	<i>a.</i>
25	·0990
50	·0952
100	·0930

It will be noticed that the line representing the second stage is less steep for 100 volts than it is for 50 or 25, and leaves the line belonging to the first stage more abruptly.

The above facts may be explained in the following manner. A solution of AmHCO_3 at a temperature of 58° (which is near the turning-point above mentioned, 55°) decomposes into carbon dioxide and ammonia, and we may assume therefore that at about this temperature the basic carbonate forming the film on the anode will change its composition and become practically the oxide, so that the first part of the curves refers to a film of the basic

TABLE VII.

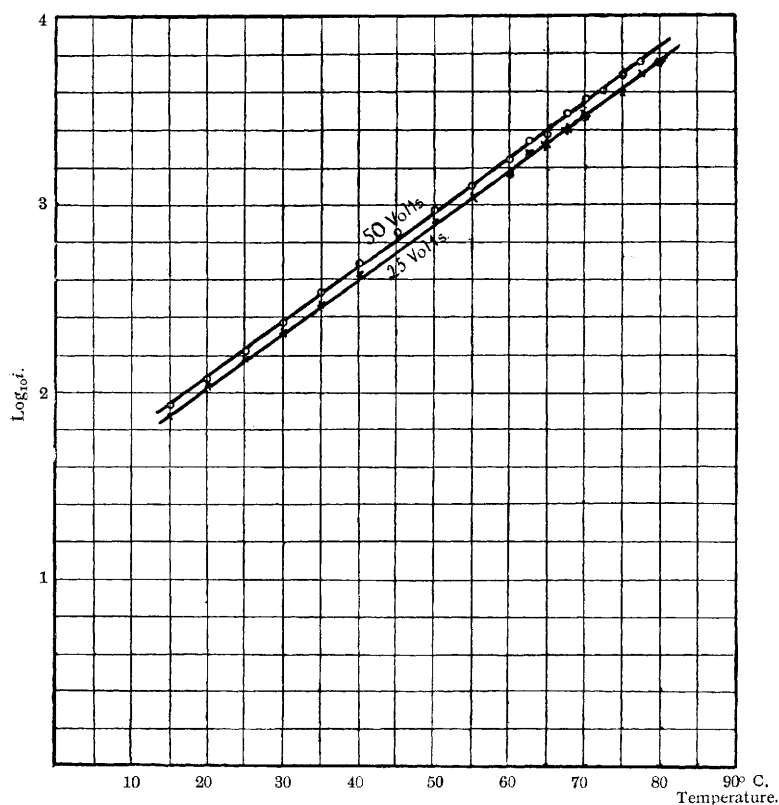
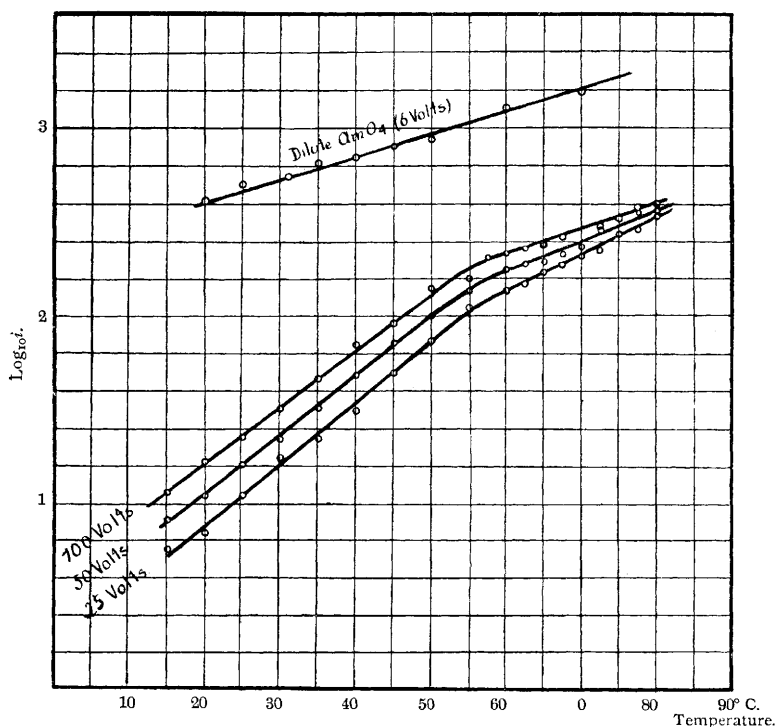
AmHCO_3 , Formation Period 1 Day.

Temp. ° C.	25 Volts.		50 Volts.		100 Volts.	
	Microamps Sq. Cm.	$\text{Log}_{10} i$.	Microamps Sq. Cm.	$\text{Log}_{10} i$.	Microamps Sq. Cm.	$\text{Log}_{10} i$.
15	5·6	·75	8·2	·91	11·4	1·06
20	6·7	·84	10·9	1·04	16·6	1·22
25	11·0	1·04	16·0	1·20	22·2	1·35
30	17·2	1·24	21·9	1·34	31·7	1·50
35	22·0	1·34	31·8	1·50	46	1·66
40	31·6	1·49	48·2	1·68	70	1·84
45	49	1·69	71	1·85	96	1·96
50	72·5	1·86	100	2·00	143	2·15
55	110	2·04	137	2·14	160	2·20
57·5	—	—	—	—	203	2·31
60	135	2·13	179	2·25	212	2·33
62·5	148	2·17	194	2·28	228	2·36
65	169	2·23	197	2·29	237	2·38
67·5	184	2·27	213	2·33	265	2·42
70	207	2·32	235	2·37	—	—
72·5	231	2·35	286	2·46	302	2·48
75	277	2·44	344	2·53	329	2·52
77·5	291	2·46	350	2·55	380	2·58
80	338	2·53	360	2·56	400	2·60

carbonate and the second to one of the oxide. We may imagine the film to be more stable at a low voltage than at a high one, so that the initial line will be steeper at a lower voltage, and further, the final line also to be steeper at a lower voltage.

If now we were to test an anode formed in a solution of ammonia, we should expect the line representing the variation of the logarithm of its leakage current with temperature to be straight throughout its course and

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FIG. 7.— $\text{Am}_2\text{C}_2\text{O}_4$, 1 Day's Formation at various Voltages.FIG. 8.— AmHCO_3 , 1 Day's Formation at various Voltages, and AmOH (dilute) at 6 Volts.

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to be parallel with, or perhaps not quite so steep as, the final part of the 100-volt curve. The upper line in the same figure gives the results of such a test made with dilute AmOH at 6 volts after one day's formation. It will be seen

TABLE VIII.

Dilute AmOH. 1 Day's Formation at 6 Volts.

Temp. ° C.	Microamps. Sq. Cm.	Log ₁₀ i.
20	408	2'61
25	500	2'70
31	550	2'74
35	650	2'81
40	690	2'84
45	805	2'90
55	1,090	3'04
60	1,280	3'11
70	1,560	3'19

TABLE IX.

(Am₂O)₃7(MoO₃). 1 Day. 100 Volts.

Temp. ° C.	Concentration = $\frac{1}{2}$ (Saturation).		Concentration = $\frac{1}{8}$ (Saturation).	
	Microamps. Sq. Cm.	Log ₁₀ i.	Microamps. Sq. Cm.	Log ₁₀ i.
15	11'1	1'05	12'9	1'10
20	14'2	1'16	16'3	1'21
25	20'2	1'30	24'7	1'39
30	29'2	1'47	33'7	1'53
35	42'4	1'63	48	1'68
40	59'2	1'77	69	1'84
45	84'5	1'93	96	1'98
50	117	2'07	137	2'14
55	163	2'22	186	2'27
60	218	2'34	249	2'40
62'5	262	2'42	284	2'45
65	305	2'49	336	2'54
67'5	341	2'53	—	—
70	415	2'62	363	2'56
72'5	470	2'67	—	—
75	530	2'73	690	2'84
80	755	2'88	906	2'96
84	—	—	1,110	3'05

that it has the above-mentioned characteristics, its a being '0335 as against '0395, the value for the upper part of the 100-volt curve.

The experimental results of the AmOH test are given in Table VIII.

4. The Influence of the Concentration of the Electrolyte.

Since the general result of decreasing the concentration of the electrolyte in which an Al anode-film is formed is to increase the leakage current, it

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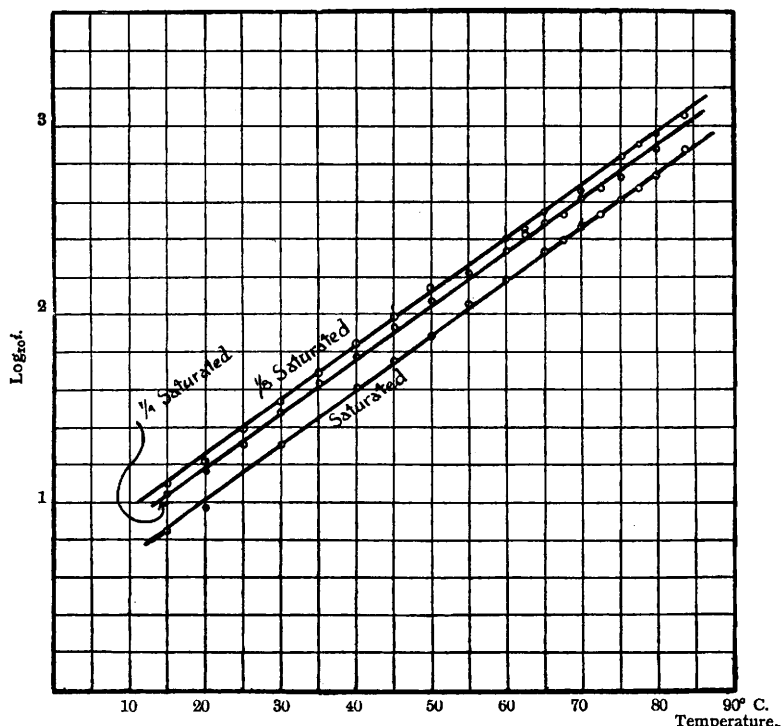


FIG. 9.—Concentrated and dilute $(\text{Am}_2\text{O})_{3.7}(\text{MoO}_3)$ after 1 Day's Formation at 100 Volts.

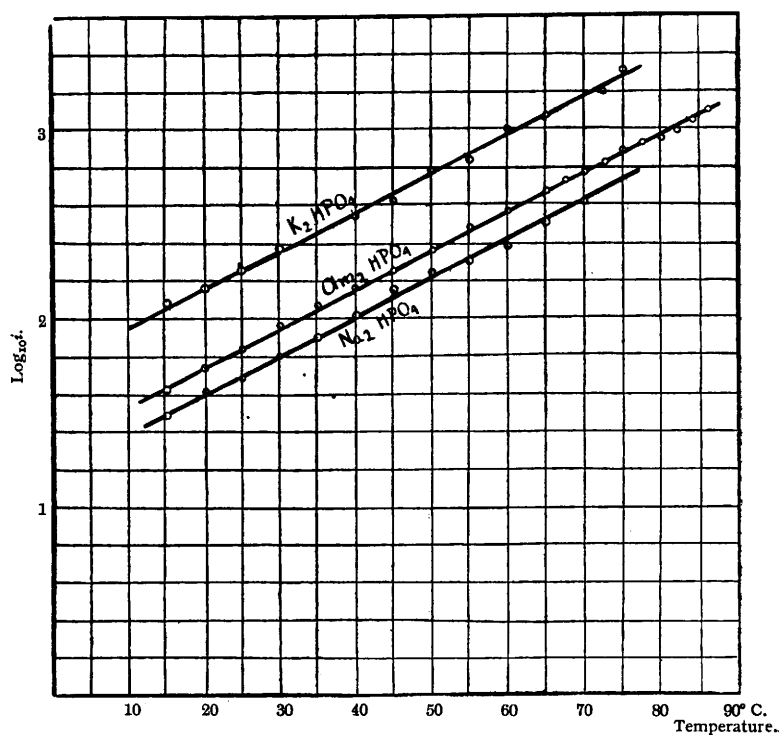


FIG. 10.— Am_2HPO_4 , Na_2HPO_4 , K_2HPO_4 , 1 Day's Formation at 100 Volts.

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TABLE X.
1 Day. Formation Volts 100.

Temp. ° C.	Na ₂ HPO ₄ .		K ₂ HPO ₄ .	
	Microamps Sq. Cm.	Log ₁₀ i.	Microamps Sq. Cm.	Log ₁₀ i.
15	30	1'48	119	2'08
20	41	1'61	146	2'16
25	48	1'68	179	2'25
30	63	1'80	236	2'37
35	79	1'90	—	—
40	104	2'02	345	2'54
45	141	2'15	415	2'62
50	174	2'24	600	2'78
55	200	2'30	695	2'84
60	239	2'38	1,010	3'00
65	334	2'52	1,180	3'07
70	413	2'62	1,470	3'17
72'5	—	—	1,580	3'20
75	—	—	2,060	3'31

TABLE XI.
(Am₂O)₃7(MoO₃). Formation Volts 100. Tested at various Voltages.

Temp. ° C.	90 Volts.		75 Volts.		50 Volts.		25 Volts.	
	Microamps. Sq. Cm.	Log ₁₀ i.	Microamps. Sq. Cm.	Log ₁₀ i.	Microamps. Sq. Cm.	Log ₁₀ i.	Microamps. Sq. Cm.	Log ₁₀ i.
20	4'15	'62	2'10	'33	1'28	'11	'63	1'80
25	5'76	'76	—	—	1'80	'25	'91	1'96
30	8'2	'91	4'2	'62	2'45	'39	1'16	'06
35	10'5	1'02	4'45	'65	3'25	'51	1'43	'16
40	—	—	7'05	'88	4'55	'66	1'89	'28
45	22'3	1'35	9'35	'97	6'3	'80	2'65	'42
50	27'7	1'44	14'8	1'17	8'6	'93	3'38	'53
55	50'1	1'70	18'3	1'26	12'4	1'09	4'45	'65
60	95	1'98	24'5	1'37	14'8	1'17	5'84	'77
62	133	2'12	28'7	1'46	17'0	1'23	7'22	'86
64	182	2'26	33'8 (65°)	1'53	21'5 (65°)	1'33	8'00 (65°)	'90
66	252	2'40	—	—	—	—	—	—
68	275	2'44	43'8 (67'5°)	1'64	23'3 (67'5°)	1'37	9'4 (67'5°)	'97
70	330	2'52	57'2	1'76	29'5	1'47	10'8	1'03
72	392	2'59	116	2'05	—	—	—	—
74	442	2'65	288	2'46	50'5	1'71	14'6	1'16
76	501	2'70	535	2'73	79	1'90	17'5	1'24
78	627	2'80	—	—	112	2'05	24'2	1'38
80	750	2'87	822	2'91	185	2'21	35'5	2'55
81	791	2'90	872	2'94	254	2'40	44'6	1'65
82	—	—	—	—	345	2'54	60	1'78
83	—	—	—	—	477	2'68	83	1'92
84	—	—	—	—	670	2'83	133	2'12
85	—	—	—	—	1,220	3'09	191	2'28
86	—	—	—	—	—	—	890	2'95

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might be supposed that a film formed in a weak solution would not give the same value for a as one formed in a strong solution. However, this is not the case, as Table IX. and Fig. 9 show. Here curves are given for a concentrated solution of $(\text{Am}_2\text{O})_{37}(\text{MoO}_3)$ for one day's formation at 100 volts, and also for very weak solutions of one-quarter and one-eighth of that of a concentrated solution respectively, and again we have a set of parallel straight lines, the values of a being $\cdot 0870$, $\cdot 0872$, and $\cdot 0865$ respectively.

5. *A Comparison of the Behaviour of a Series of Electrolytes having the same Anion.*

The previous work has shown that the only variable so far considered that has any influence on a is the nature of the electrolyte. The question presents itself as to whether the cation has any influence on the value of a . Table X. and Fig. 10 illustrate this point. They give the results for the three phosphates of ammonium, sodium, and potassium. It will be seen that while the initial value of A varies considerably with the nature of the cation, a has the value $\cdot 0612$, $\cdot 0615$, and $\cdot 0610$ respectively for the three phosphates, and is therefore independent of the cation.

6. *The Influence of the Voltage at which the Test is made.*

The final variable whose influence has to be considered is that of the voltage used during the test. Table XI. gives the results for films formed at 100 volts in $(\text{Am}_2\text{O})_{37}(\text{MoO}_3)$ for one day, with the temperature tests made at 90, 75, 50, and 25 volts respectively.

In Fig. 11 we have the usual $\log i$ curves plotted to temperature. It will be seen that each curve is straight for part of its course, but that at a certain point it curves up, crosses the normal curve for a test made at the voltage of formation, and finally tends to become parallel to it. The lower the voltage the more rapidly does it curve up. The straight portions of the lines are not quite parallel to one another; as the voltage decreases the gradient becomes gradually smaller, as the following table shows:—

Voltage of Test.	a .
100	$\cdot 0875$
90	$\cdot 0840$
75	$\cdot 0810$
50	$\cdot 0710$
25	$\cdot 0655$

Another point of interest is that all the curves depart from a straight line at practically the same current density; this is shown by the dotted line, which corresponds to a current density of about 200 microamps per square centimetre.

In Figs. 12 and 13 the variation of the current density with the voltage of the film formed at 100 volts is delineated for different temperatures. In Fig. 12 the results are given for steps of temperature of 10° from 20° to 60° . It will be seen that for most of the range of voltage they are straight, but rapidly shoot up as the voltage of formation is reached, and that as the temperature rises the part of the curve which is straight becomes shorter and shorter. Above 60° the shape of the curves alters (in Fig. 13 they have been

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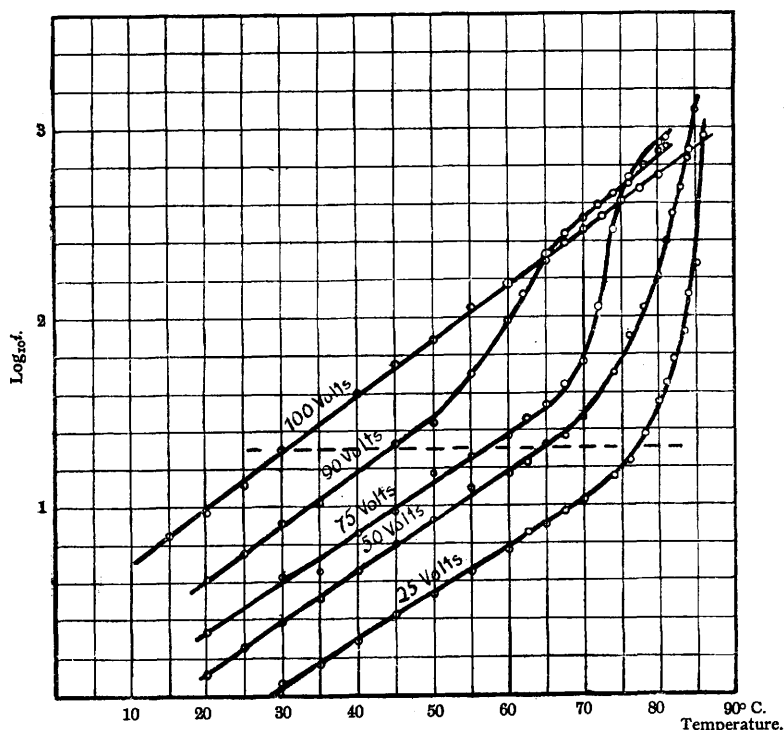


FIG. 11.— $(\text{Am}_2\text{O})_{3/7}(\text{MoO}_3)$ formed at 100 Volts and tested at various Voltages.

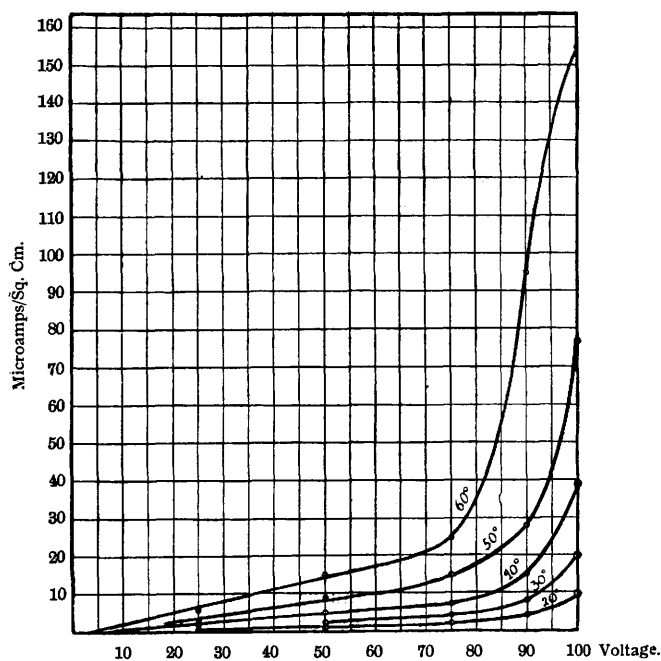


FIG. 12.—Showing the Variation of Current Density with Voltage of an Al Anode-film formed at 100 Volts, for different Temperatures (low).

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TABLE XII.

Cooling-down Experiments. (Am₂O)₃₇(MoO₃). 1 Day's Formation.

Temp. °C.	25 Volts.				50 Volts.			
	Ascending Temp.		Descending Temp.		Ascending Temp.		Descending Temp.	
	Microamps. Sq. Cm.	Log ₁₀ i.	Microamps. Sq. Cm.	Log ₁₀ i.	Microamps. Sq. Cm.	Log ₁₀ i.	Microamps. Sq. Cm.	Log ₁₀ i.
20	13.2	1.12	—	—	20.2	1.33	—	—
25	18.6	1.27	28.2	1.45	28.2	1.45	—	—
30	26.8	1.43	36.4	1.56	42.2	1.62	—	—
35	—	—	49	1.69	57	1.76	94	1.97
40	52	1.72	80	1.90	84.5	1.93	112	2.05
45	76	1.88	114	2.06	114	2.06	162	2.21
50	102	2.01	135	2.12	149	2.17	—	—
55	144	2.16	197	2.27	—	—	302	2.48
60	202	2.31	268	2.43	292	2.46	427	2.63
62.5	—	—	—	—	362	2.56	—	—
65	285	2.45	345	2.54	403	2.60	555	2.74
67.5	348	2.54	—	—	455	2.66	—	—
70	417	2.61	520	2.72	550	2.74	780	2.89
72.5	510	2.71	—	—	660	2.82	—	—
75	615	2.79	675	2.83	745	2.88	1010	3.00
77.5	745	2.87	—	—	950	2.98	—	—
80	850	2.93	—	—	1,110	3.05	—	—

TABLE XIII.

Cooling-down Experiments. Am₂B₄O₇. 1 Day's Formation.

Temp. °C.	25 Volts.				100 Volts.			
	Ascending Temp.		Descending Temp.		Ascending Temp.		Descending Temp.	
	Microamps. Sq. Cm.	Log ₁₀ i.	Microamps. Sq. Cm.	Log ₁₀ i.	Microamps. Sq. Cm.	Log ₁₀ i.	Microamps. Sq. Cm.	Log ₁₀ i.
20	2.4	1.38	—	—	4.3	.63	—	—
25	3.6	1.56	6.9	.84	6.65	.82	2.15	.32
30	5.4	1.73	10.9	1.04	10.8	1.03	—	—
35	—	—	16.7	1.22	21	1.30	48.7	1.69
40	16.8	1.23	31	1.49	30.7	1.49	74	1.87
45	25.5	1.41	51	1.71	50.2	1.70	108	2.03
50	49	1.69	95	1.98	94	1.97	—	—
55	79	1.90	164	2.22	147	2.17	284	2.45
60	154	2.19	224	2.35	233	2.37	468	2.67
62.5	168	2.23	—	—	306	2.49	—	—
65	237	2.37	400	2.60	416	2.62	—	—
67.5	296	2.47	—	—	562	2.75	800	2.90
70	390	2.59	695	2.84	780	2.89	—	—
72.5	502	2.71	—	—	845	2.93	1,120	3.05
75	650	2.81	960	2.98	1,260	3.10	1,340	3.13
77.5	860	2.93	—	—	1,560	3.19	—	—
80	1,140	3.06	—	—	1,910	3.28	—	—
83	—	—	—	—	2,470	3.39	—	—

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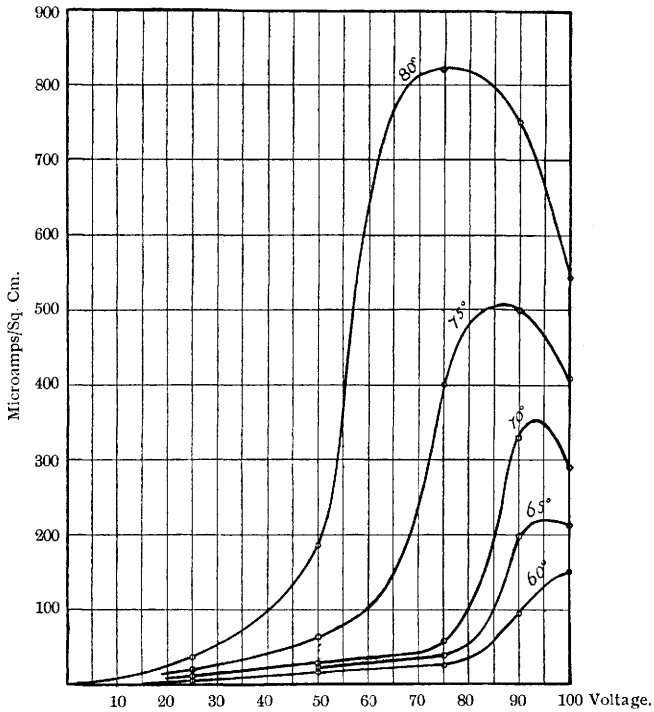


FIG. 13.—Showing the Variation of Current Density with Voltage of an Al Anode-film formed at 100 Volts, for different Temperatures (high).

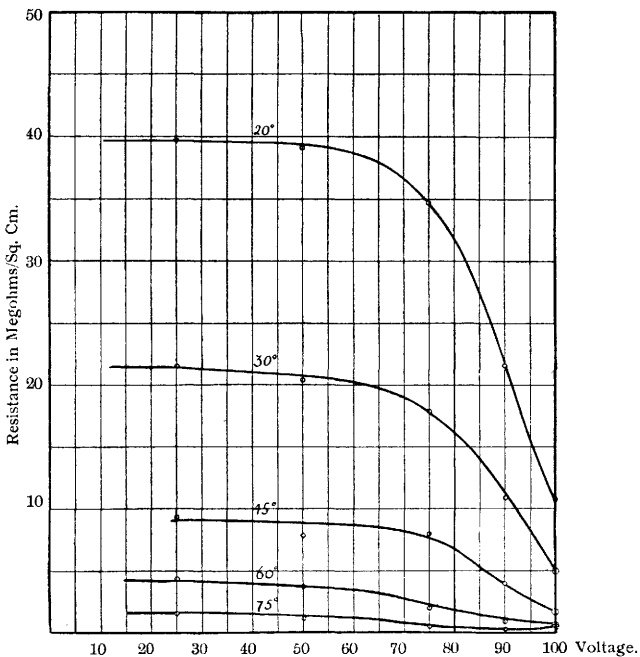


FIG. 14.—Showing the Variation of Resistance with Voltage of an Al Anode-film formed at 100 Volts, for different Temperatures.

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plotted for steps of 5° from 60° to 80°) and each tends to reach a maximum, which maximum becomes more and more pronounced as the temperature rises, and occurs at a lower and lower temperature.

In Fig. 14 the results are depicted in a different manner, the resistance being plotted to voltage for different temperatures. Up to about one-half of the voltage of formation, the resistance is practically constant, but rapidly falls off as the voltage reaches that of formation.

7. The Connection of "*a*" with the Equivalent Weight of the Anion.

Since *a* is a property solely of the anion, the question arises whether there is any numerical relationship existing between them. A brief inspection of Fig. 4 shows that *a* is not related to the valency of the acid radical. If, however, we calculate the quantity given by the sum of the atomic weights of the elements in the anion and divide this by the valency, *i.e.*, the equivalent weight of the anion, it will be found that one is a definite function of the other, as the following table shows:—

Anion.	Equivalent Weight.	<i>a</i> .
$\text{B}_4\text{O}_7''$	78	·1090
HCO_3'	61	·0990
MoO_3'''	48	·0890
$\text{C}_2\text{O}_4^{2-}$	44	·0865
PO_4'''	31	·0612
OH'	17	·0335

a increases with the equivalent weight, and if one is plotted against the other (see Fig. 15) they give a very good curve—a curve which is a straight line initially and then gradually bends over.

In the above table the value taken for the HCO_3 anion is that corresponding to the 25-volt curve, since it has been shown this is a truer figure than that for a higher voltage, because of the influence of the OH anion.

When once this curve has been obtained it furnishes us with a method for the determination of the equivalent weight of the anion in an electrolyte.

8. Cooling-down Curves.

The final question to be considered is whether, after the electrolyte has been carried up to the boiling-point, the conductivity for decreasing temperatures is the same as for increasing temperatures. This point is illustrated by Table XII. and Fig. 16, which give the heating-up and cooling-down curves for $(\text{Am}_2\text{O})_3(\text{MoO}_3)$, for 25 and 50 volts. In each case the cooling-down curve is higher, but eventually as the temperature falls, becomes nearly parallel to the heating-up curve. There is perhaps a tendency for *a* to be slightly less. This becomes more marked in the 100-volt curve for $\text{Am}_2\text{B}_4\text{O}_7$, given in the next figure (see Table XIII. and Fig. 17).

SUMMARY.

1. The law of the variation of the conductivity of an Al anode-film with temperature is given by $i = A\epsilon^{a\theta}$, the curves obtained by plotting $\log. i$ to θ being straight lines over the whole range of temperature from ordinary temperatures to the boiling-point of the electrolyte.

2. The value of the exponent *a* is independent of the voltage of formation, the time of formation, the concentration of the electrolyte, and the cation present in the electrolyte, and depends only on the anion (provided the test

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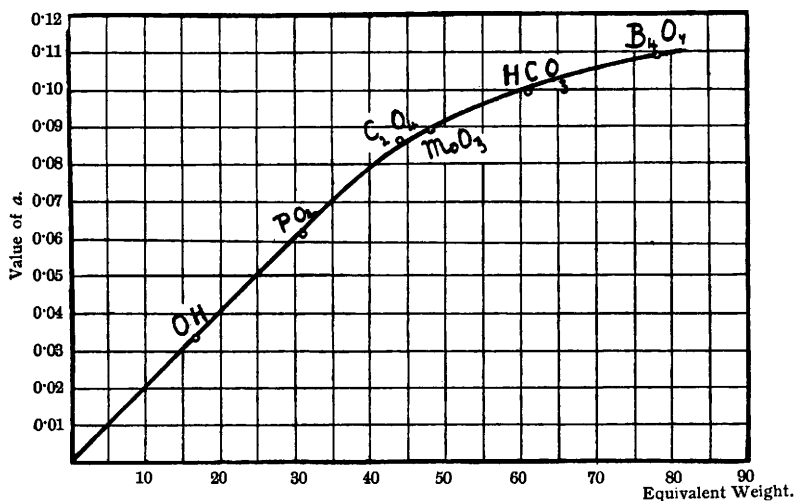


FIG. 15.—Showing the Variation of α with the Equivalent Weight of the Anion present in the Electrolyte.

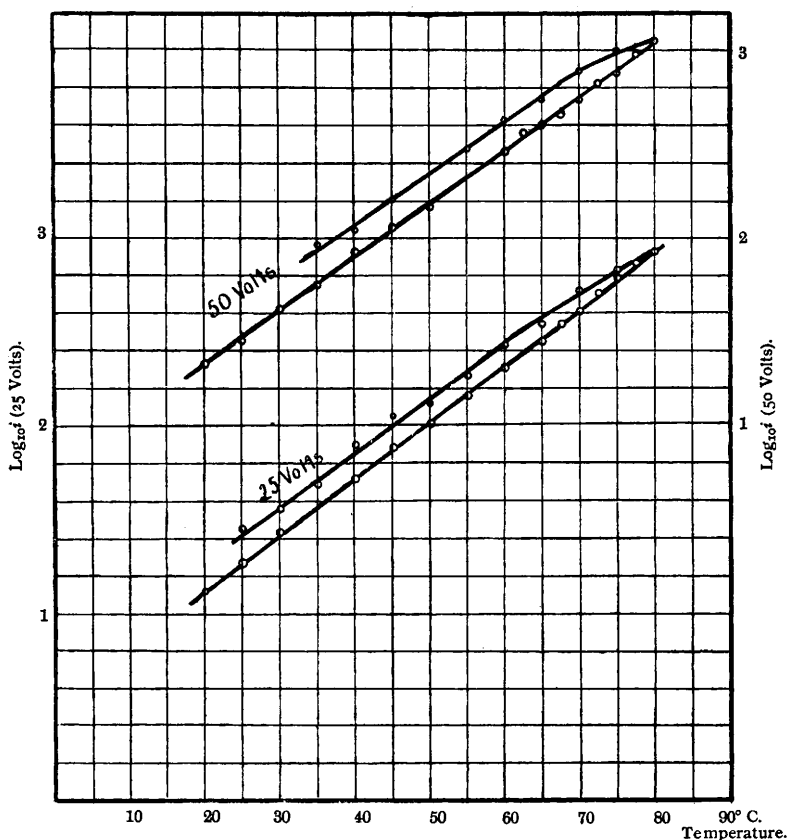


FIG. 16.—Heating-up and Cooling-down Curves for $(Am_2O)_{37}(MoO_3)_3$.
(The lower portion of each curve refers to rising temperatures, the upper to falling temperatures.)

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is made at the voltage of 'formation'), whereas A varies widely with these variables.

3. AmHCO_3 is an exception to the general law. At 55° its a abruptly changes, but this behaviour is explained by the decomposition of the film and by the OH ions playing most part in the conduction.

4. For a given formation voltage a decreases with the voltage of test, but when a certain current density (which is the same for all voltages of test) is reached, the conductivity increases much more rapidly than that given by $Ae^{a\theta}$, in such a fashion that for temperatures above about 60° the current-volt curves have a maximum at a voltage below that of formation.

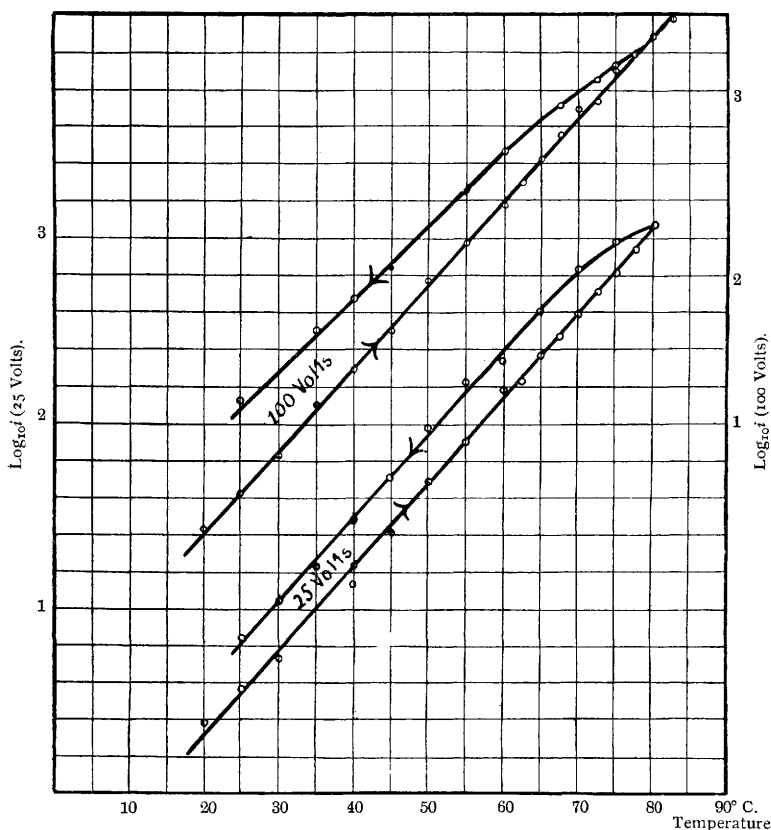


FIG. 17.—Heating-up and Cooling-down Curves for $\text{Am}_2\text{B}_4\text{O}_7$.

5. For voltages up to about one-half of the voltage of formation the resistance of an Al anode-film is practically constant, but rapidly falls off as the voltage reaches that of formation.

6. a is a definite function of the equivalent weight of the anion in solution, and it furnishes a means of determining the latter quantity.

7. A cooling-down curve lies above the heating-up curve, but a ultimately becomes practically the same for both.

The above experiments were carried out in the Laboratories of Applied Electricity, Liverpool University.

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