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ELECTROLYTIC RECTIFIERS

by

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ELECTROLYTIC RECTIFIERS.

More than a half-century ago, Wheatstone, in experimenting with the electro-chemical behavior of certain elements, laid the foundation for the modern chemical rectifier. In the year 1855, he found that aluminum as anode in certain electrolytes, offered great resistance to the passage of the electric current, while as kathode, offered very little. This experiment was repeated two years later by Buff. He thought he observed that when the aluminum was used as the anode, that a dark skin formed upon its surface. This was verified by Beetz in 1877. Tait, in 1869, observed a high counter E. M. F. Overbeck and Streintz considering the film as a non-conductor, separating two conductors, the electrolyte and plates, saw in the arrangement a typical condenser. This application was studied and developed until within the last few years, but has not yet been brought to the point of utility.

The use of the aluminum cell as a rectifier was conceived by two men, each working independently of the other; Pollak in 1897, and Graetz about seven years earlier. This discovery was received with considerable enthusiasm over the whole world. Immediately great possibilities were prophesied, and men in Germany, France, and later in the United States, set to work to see if these predictions could be fulfilled. The fact that alternating,currents lent themselves so readily to transmission, made a good form of rectifier a very valuable asset, especially where direct currents were desirable. So from the year 1897 up to 1904 or 1905, there was considerable literature published on the rectifier. Within the last four or five years, an occasional ar-

ticle appears. The falling off was probably due to the discovery of the arc rectifier with its higher efficiency and simplicity.

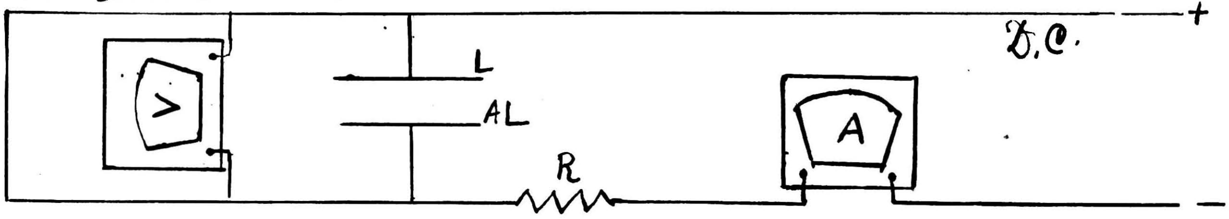
The electrolytic rectifier seemed to reach the zenith of its popularity about the years 1902-1904. Wilson, in 1898, had worked out its efficiency. Nordon, in addition to studying its efficiency, investigated the chemical composition of the film finding the hydroxide and sulphate of aluminum. Various theories were offered at the time, and are still being offered for the apparent stoppage of the current when aluminum is the anode. Norden's theory, later upheld by Burgess and Hambeuchen of Wisconsin University, was that it was simply an ohmic resistance. Wilson had observed the resistance of the cell to be something like ten thousand ohms. Guthe, Taylor and Inglis, and Cook each offered different theories. Cook's is the most important. He held the resistance to be due to a counter electro-motive force set up by the highly charged anions collecting about the anode, and not being allowed to discharge on account of the nonconductivity of the film. In addition to working on the theory of the film, these men were varying the electrolyte, the voltage, current strength, etc., working out the efficiency to find out whether it was of practical value. In 1904, a Paris firm placed a rectifier on the market. Rather meager information is to be had concerning its success, but from that available, it did not appear to come up to expectations.

Several American firms at the present time have rectifiers for sale, the most promising being that of the Central Scientific Co. This piece of apparatus in its present form has been on sale four or five years, but its fullest capabil-

ities had not been worked out; so it was to determine as far as possible the efficiency, the practicability, the usefulness of this article, that the present work was undertaken.

Before setting up the rectifier proper, it was decided to work with a single aluminum lead cell in order to become better acquainted with the possibilities of the simpler type first. This consisted of aluminum and lead plates 6'' x 3'', dipping in com'l sodium bicarbonate. Both A.C. and D.C. 110-volt circuits were available.

The first observations were taken with the direct current, aluminum being made the cathode. A volt meter was attached across the terminals of the cell, while an ammeter and resistance were placed in series.



This was designed to verify the statement that very little obstruction was offered to passage of current when the aluminum plate was made cathode.

Readings.	Volts.	Amp.	Tem. of Electrolyte
1.	2.75	.22	26.2° C
2.	2.75	.22	26.2° C

The second reading was taken several minutes after the first. Then the resistance R was decreased and another set of readings taken.

Readings.	Volts.	Amp.	Temperature.
1.	3.3	.53	26.3° C
2.	3.3	.53	
3.	3.3	.53	
4.	3.4	.53	

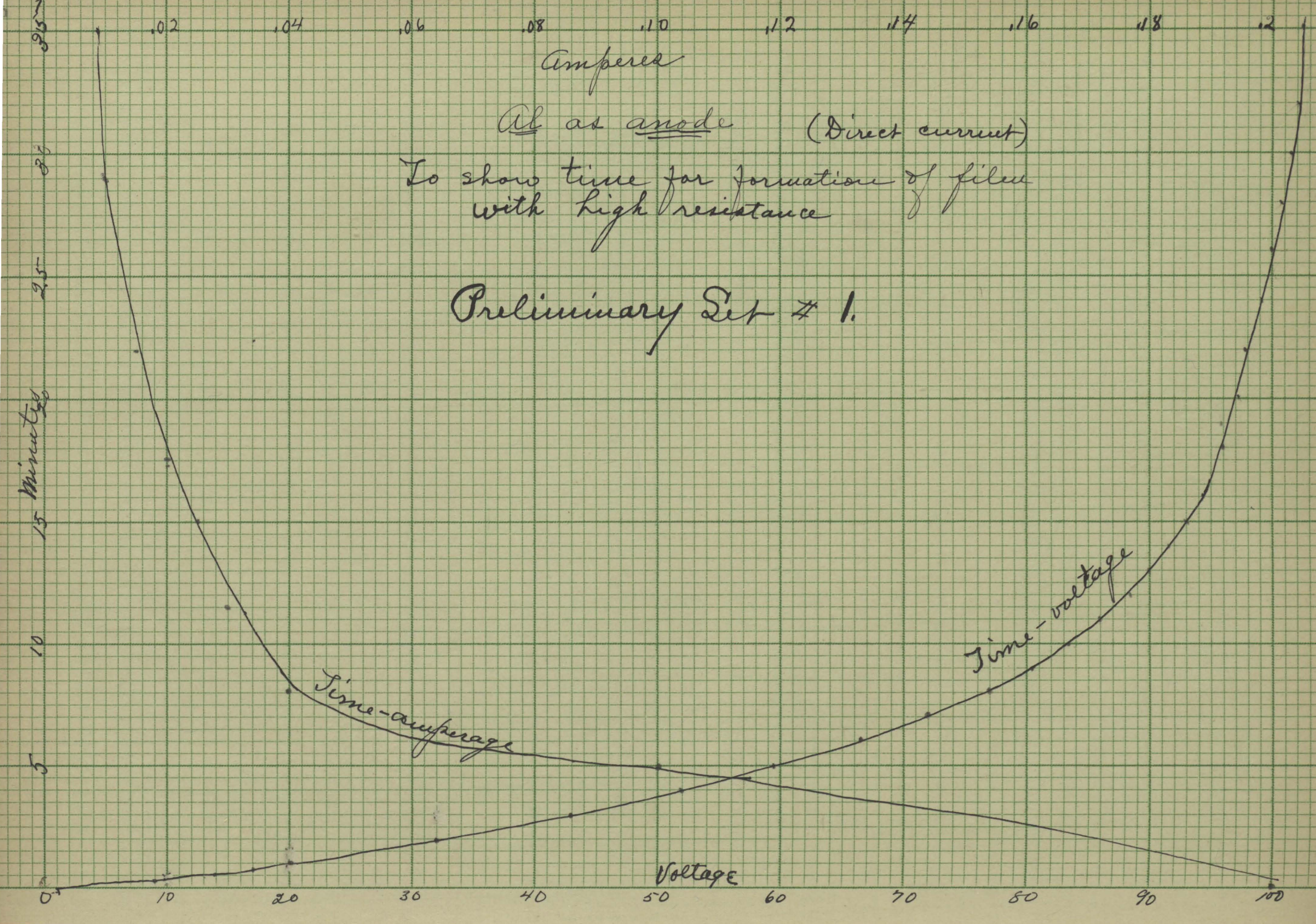
At this point, the current was shut off, and the cell was tested for storage effects; the voltage at first was 1.5, but fell in twenty minutes to .6 and at the end of $1\frac{3}{4}$ hours, regis-

tered .1. The effect was so small that it was considered negligible. The above set of observations was then continued, the resistance, R. being gradually decreased-the time taken was a little less than two hours. Only one reading for a given resistance is given-the readings being practically the same.

Volts	Amp.	Temp.
3.75	1.2	27.2 C
4.4	2.17	27.9
5.3	3.35	28
6.25	5.1	28.1
7.8	6.	28.2
8.5	7.	31.8
9.	7.9	32.7

The low fall of potential and large current capacity show what the literature of the subject mentioned; viz, that the cell offers very little resistance to the passage of the current with aluminum as cathode.

The aluminum was then made the anode and the D.C. 110-volt current was sent through the cell with about six hundred ohms in series. A D.C. volt-meter and ammeter were used just as before. The object was to determine the rate at which the so called "film" would form. When the circuit was first closed, the volt-meter read practically zero; the current strength, about .15 amperes. At the end of the first, second, third, and fourth minutes, the voltages were respectively twenty, thirty-two, forth-three, fifty-two; at the end of ten minutes eighty-three and five tenths; fifteen minutes, 93; twenty minutes, 97.3; thirty-five minutes, 102.5; meanwhile, the current strength had dropped to .01 amperes. See curve for Preliminary Set #1. The film being "formed", the current was shut off and the plates allowed to stand in solution over night to determine the dissolving effect on the film by the electrolyte. When the circuit was closed, the next morning,



Al as anode (Direct current)

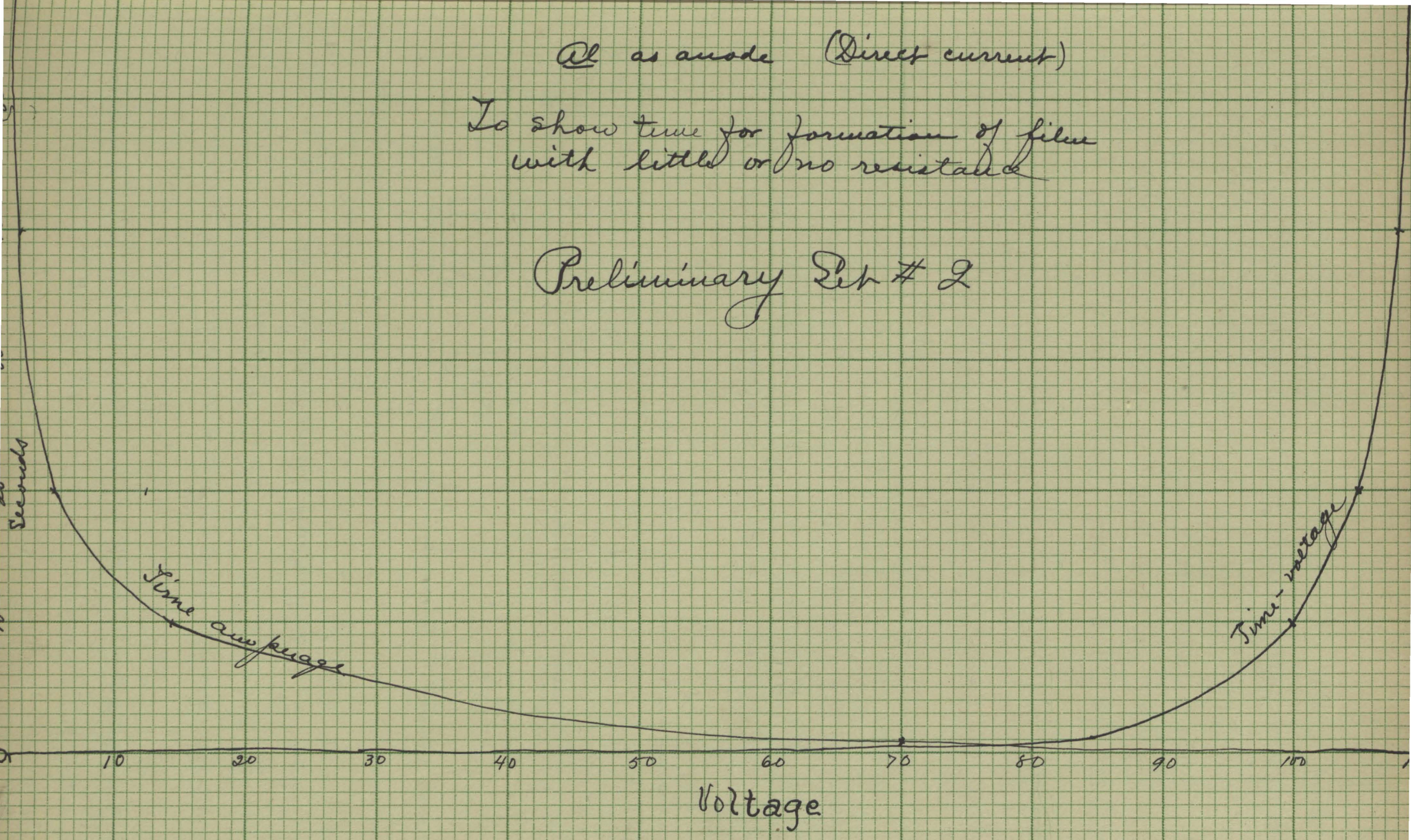
To show time for formation of film with high resistance

Preliminary Set # 1.

after an interval of fourteen hours, the voltage rose almost instantaneously to 80, then more slowly to its maximum value of 102½. By cutting out resistance, it rose to 108; the current fell from .05 to .01 amperes, the time consumed being about ten minutes. This would indicate that there was a slight weakening of the film by the solution. This was borne out by experience with the rectifier. If the rectifier has been standing, the value of the rectified current on closing circuit gradually increases for a few minutes, showing that there had been a deterioration of the film and as its valve-action became more efficient, the value of the rectified current increased. It is to be noted that when the six hundred ohms resistance was cut out, the voltage arose from 102.5 to 108. This gives us by the fall of potential method a resistance of about 10500 ohms for the resistance of the cell. This was checked up by The Wheatstone Bridge method. The first value obtained was something over 11000 ohms, but as I tried to get more accurate values, the resistance was found to be changing and in a short time had fallen to 7000 ohms. The value of the resistance found at first was practically that found by Wilson; while its changing values confirms the statement made above regarding the weak~~in~~ening of the film on open-circuit- this being practically an open circuit so far as the aluminum cell was concerned.

The "forming" of the film was then tried with low resistance in series-probably ten ohms. This was with the D.C. as before. The following results were obtained with a cell provided with a new aluminum plate:-

Time	Volts	Amperes
3-32-0	80	9.5
3-32-15	100	1.
3-33-45	109	.01



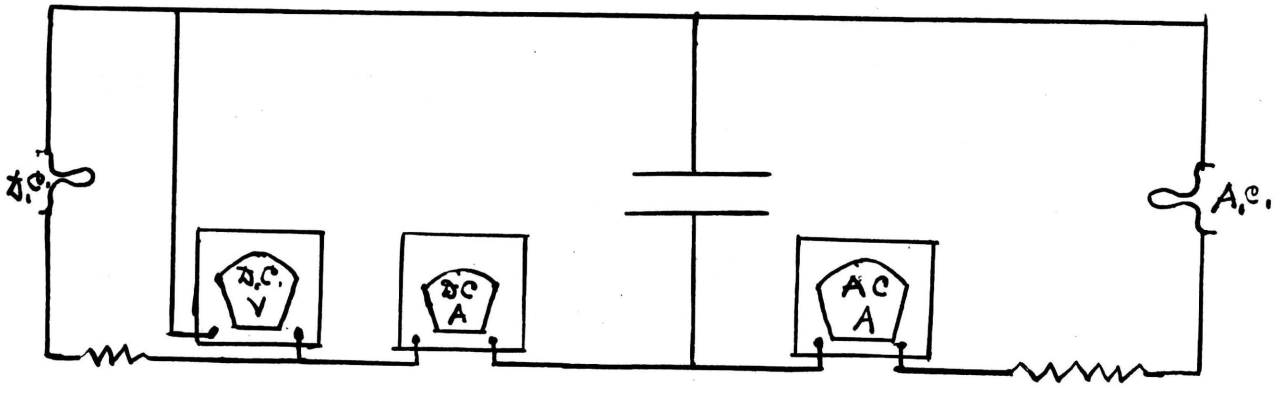
Al as anode (Direct current)

To show time for formation of film with little or no resistance

Preliminary Set # 2

When the current was turned on the voltage rose in two or three seconds to 80-the index moving so rapidly made it impossible to take any readings under 80. In three-fourths of a minute, the film was fully formed, as against thirty-five minutes, with resistance of six hundred ohms mentioned above. It would seem then that under a strong current the formation of the film is almost instantaneous. See curve for Preliminary Set #2..

The inefficiency of rectifiers had been attributed largely to leakageon increase of temperature. That is to say, as the temperature increased, the anodic resistance of the aluminum decreased, allowing current to break through and destroy the valve-effect.. As this was the main problem to be solved, it was thought best to investigate it with the simple cell first. The apparatus was arranged as shown in figure:-



The alternating current was thrown on and temperature allowed to rise, readings being taken every minute. Then with a hand on each switch as A.C. was thrown off, D.C. was thrown on and readings taken as quickly as possible. It was thought that the D.C. readings would indicate the leakage.

On the following pages will be found readings for "Leakage Set # 1. It is the only one that will be given, and may be

taken as a type.

Leakage Set # 1.

Problem:- To note whether increase of temperature produced by A.C. was accompanied by increase of leakage.

	Volts	Amp.	Temp.	Time
A.C.	40	7.8	32	9:04
D.C.	100	.05	33	9:05
	105	.03	-	9:06
A.C.	40.5	7.8	34	9:07
D.C.	105	.04	35	9:08
	105	.03	35.5	9:09
A.C.	38.5	8	40.2	9:11
D.C.	104	.04	41	9:12
	105	.03	-	9:13
A.C.	38	8	43	9:14
	37	8.05	45	9:16
D.C.	104	.05	47	9:17
	104	.04	-	9:18
A.C.	34	8.05	50	9:20
	30	8.2	53	9:21
D.C.	--	.15	55	9:22
	--	.12	54.5	9:23
A.C.	30	8.2	55	9:24½
	31	8.1	59	9:25
D.C.	96	.22	60.5	9:26
	97	.15	--	9:27
A.C.	35	7.9	--	9:28
	33.5	7.9	61.5	9:29
	34	7.9	64	9:30
D.C.	89	.25	67.5	9:32
	91	.22	67.5	9:33
A.C.	34	7.95	68	9:34
	33	8.	69.5	9:35
D.C.	78.5	.4	73	9:37
	83.5	.31	72	9:38
A.C.	33	8.1	-	9:39
	30	8.3	75	9:40
D.C.	74	.54	75	9:41
	81	.34	74.5	---
A.C.	20	9.2	77.5	9:44
	15	9.8	79.5	9:44½

D.C.	-	1.	80	9:45
	84	.3	77.5	9:46
A.C.	14	9.8	80	9:47
	14	9.8	81	9:48
D.C.	-	1.	82.8	9:49
	81	.33	82.5	--
A.C.	13	9.8	83	9:51
	13	9.9	84.5	9:52
D.C.	40	1.2	85.7	9:53
	70	.45	85.	9:53½
	80	.35	84.3	9:54
A.C.	12.5	10	86.2	9:56
D.C.	40	1.3	87.5	9:57
	64	.55	86.5	9:57½
	76	.4	---	9:58
	87	.25	83.5	9:59
	90	.21	82.5	10:00

The above shows that as temperature increases, the leakage with D.C. increases, being .05 amp. at temperature of 32°C and 1.3 amp.at 87.5° C. But it evidently does not represent the entire leakage, for as the D.C. is turned on, the leakage current gradually diminishes. At the end of a minute the current is not more than one-third its value when the first reading is taken. The first reading itself is only an approximation. The readings are taken while the needle is moving. The instant that the D.C. is turned on the"reforming" of the aluminum plate begins; even before the needle reaches its maximum position. And the leakage is being cut down so rapidly, that the needle after reading its maximum position, swings toward its zero position, at first almost as rapidly as it did in the opposite direction. Referring again to formation of film on new cell it was seen that with a current of 8 or 10 amp., the film formed in a very short time; 70-80 volts back pressure in less than a second. So from these facts we learn that the increased temperature

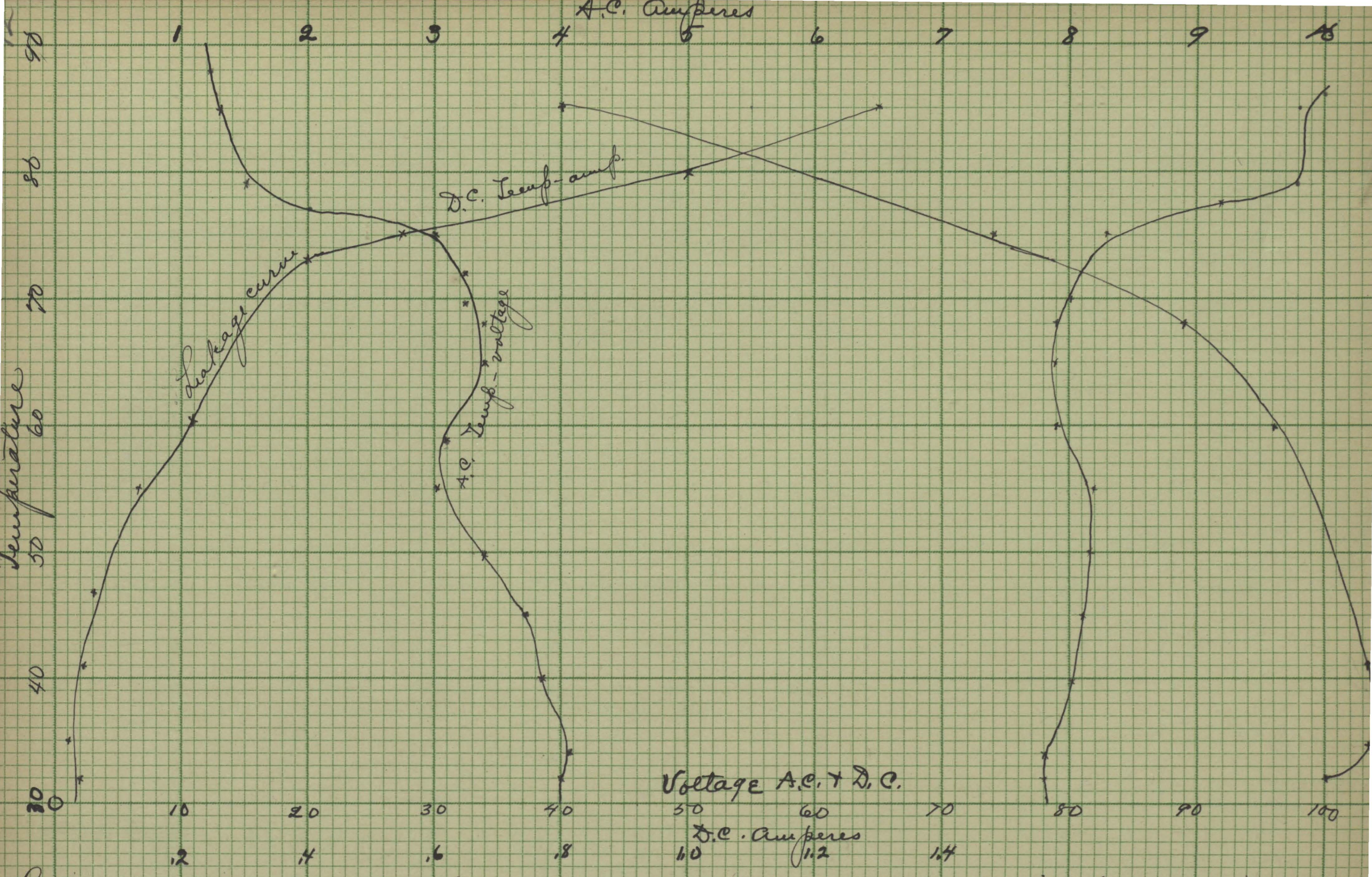
means increased leakage; but just what its actual value is, can not be determined by this method. In the literature of the subject it was suggested that with the A.C. one alternation would tend to puncture the film, that is, when A.C. is cathode; but the other,-aluminum as anode- would tend to reform it.

This was shown in my first work with the cell, but I did not call attention to it. The aluminum was made anode and "formed". Several observations were then taken with aluminum as kathode. But when I returned to the use of aluminum as anode, its value action was entirely gone and had to be "reformed".

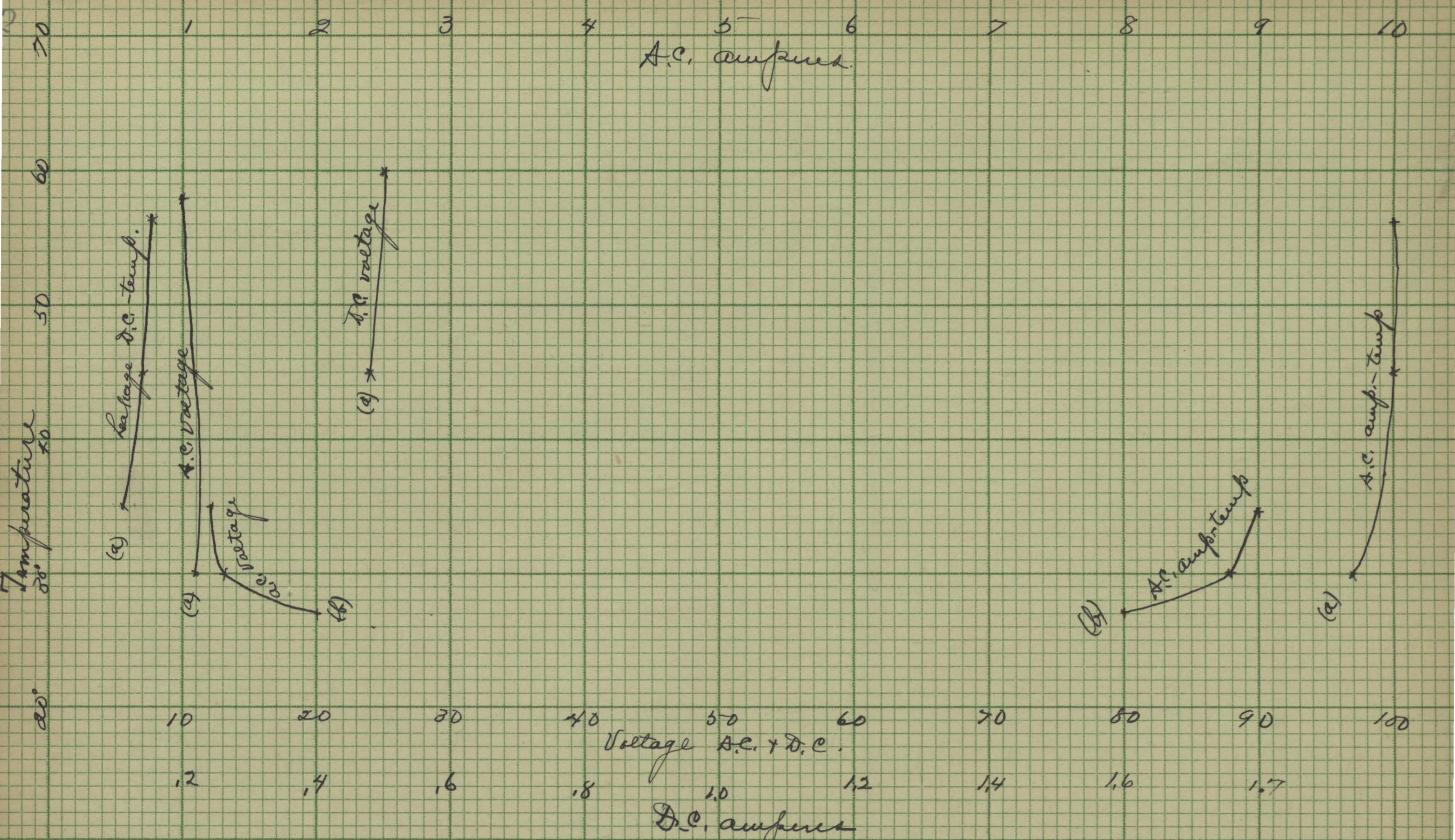
With a constant temperature, the constructive work of one alternation just about balances destructive work of the other. But with the increase of temperature, the destructive agencies gain the ascendency.

It was noticed also during this set of observations, that after the temperature reached 50 or 60 °, sparking was considerable, especially at edges of plate and surface of electrolyte. The electrolytic action on the aluminum plate was greater with increased temperature. The surface had become eaten full of little holes, indicating that the action of the electrolyte was greater at certain points on surface than at others. A heavy white flaky precipitate was formed which settled to the bottom of the jar. This was tested and found to be al-hydroxide.

When the temperature reached 87.5° C as shown above, it was not deemed wise to allow it to run any higher, so was allowed to cool under D. C. The leakage grew less with fall of temperature as was expected until 70° C was reached. At this point the leakage began to increase and at 51° C was as high as at 80° C. The plates being examined were found to be covered with a heavy coating of crystallized salts,



Leakage Set #1. Curve to show leakage with rise of temperature High resistance in D.C.
Al plate 3" x 3" Electrolyte – com'l sod. bicarbonate.



Leakage Set #9

Curves to show leakage

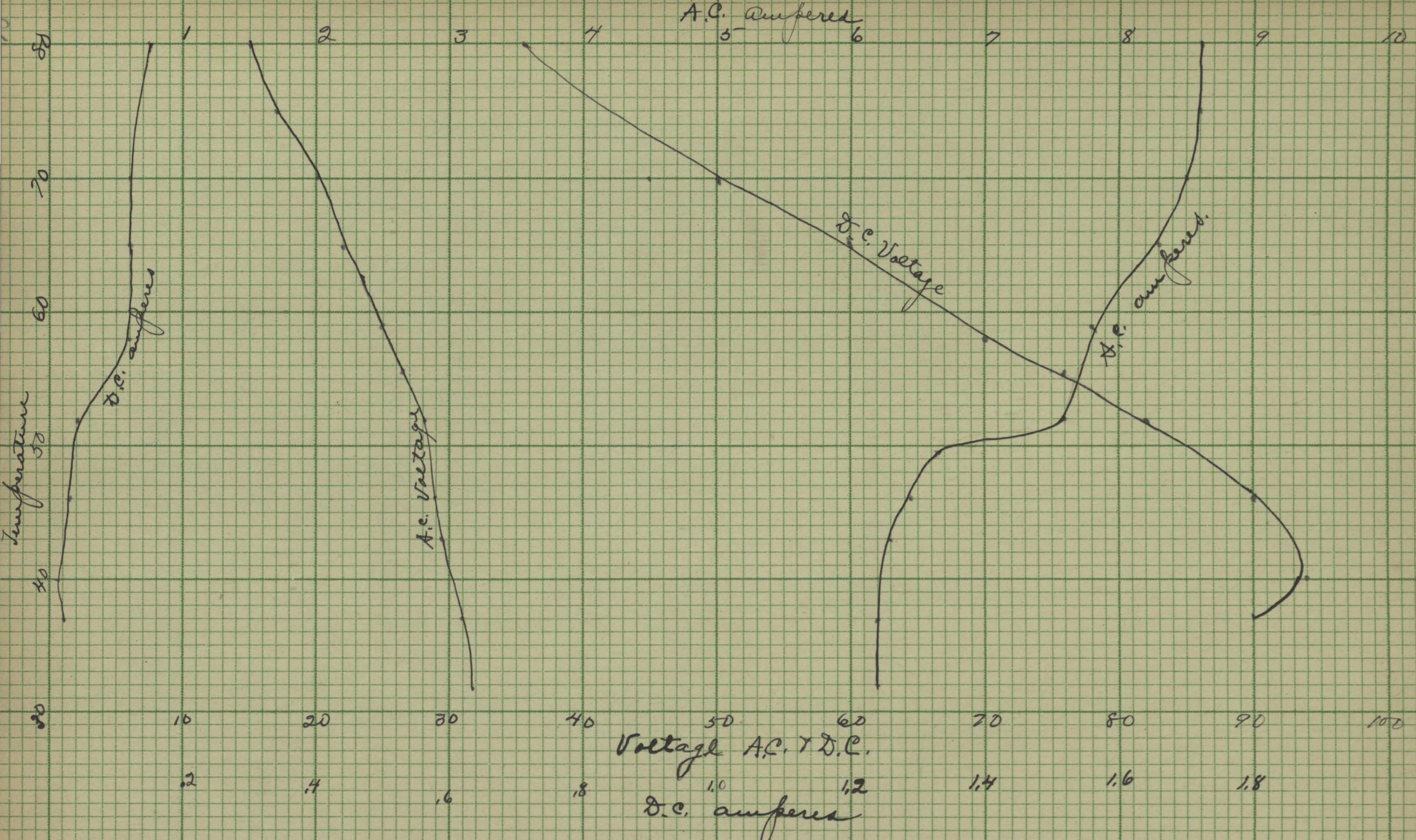
Al plate 7" × 3"

High resistance in D.C. →

Electrolyte – Com'l ammon. phos.

formed no doubt by cooling of electrolyte. When this was removed and plates again tested, the leakage fell to .018 amp. at 34° C. This phenomenon will be referred to later. The results of observations in Set 1 are shown in curves for Leakage Set #1. The D.C. amp. curve is designated as the leakage curve. It is noticed that it is beginning to increase rapidly about 50°C, and from 70°C to 85° C quite rapidly. The D. C. voltage curve shows the same fact probably just as conclusively. When the film begins to weaken, the anodic resistance falls and is manifested by a fall in potential across the cell. Likewise both A.C. curves demonstrate the fact of leakage. With the decreased valve action, the value of the A.C. is increased, while the corresponding voltage is decreased.

The electrolyte was now made Commercial Ammonium Phosphate $(NH_4)_2HPO_4$ and a new aluminum anode was used. The results of observation are shown in curves for Leakage Set #2. It can be seen at a glance that the valve action is almost nothing. The curves marked "a" represent the first result obtained. The A.C. and D.C. voltages were 10 and 25 respectively as compared with 40 and 100 in preceding set. At first it was thought that perhaps the film did not form so readily with this electrolyte. The plates were accordingly removed and "formed" in sodium bicarbonate solution,- the phosphate solution being allowed to cool. The plates were then put back into the cooled phosphate solution, and the curves "b" were the result. But while the first values promised slightly better results the "b" curves almost immediately merge into the "a" curves showing that the commercial ammonium phosphate solution could not maintain a film that would give any appreciable valve effect.



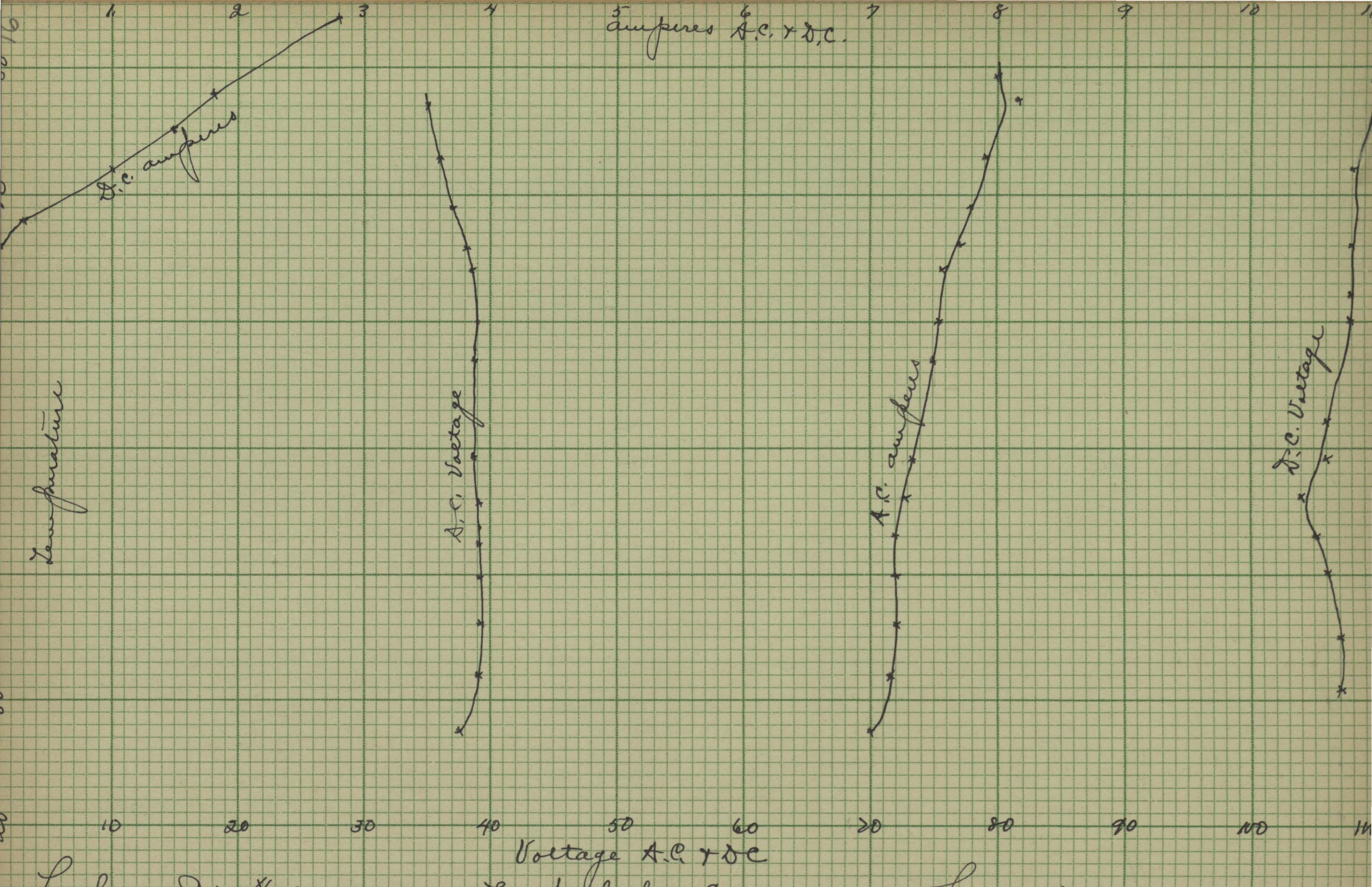
Leakage Set #9.

Curves to show leakage

Al plate 3" x 3"

High resistance in D.C.

Electrolyte C.P. Am Phosphate



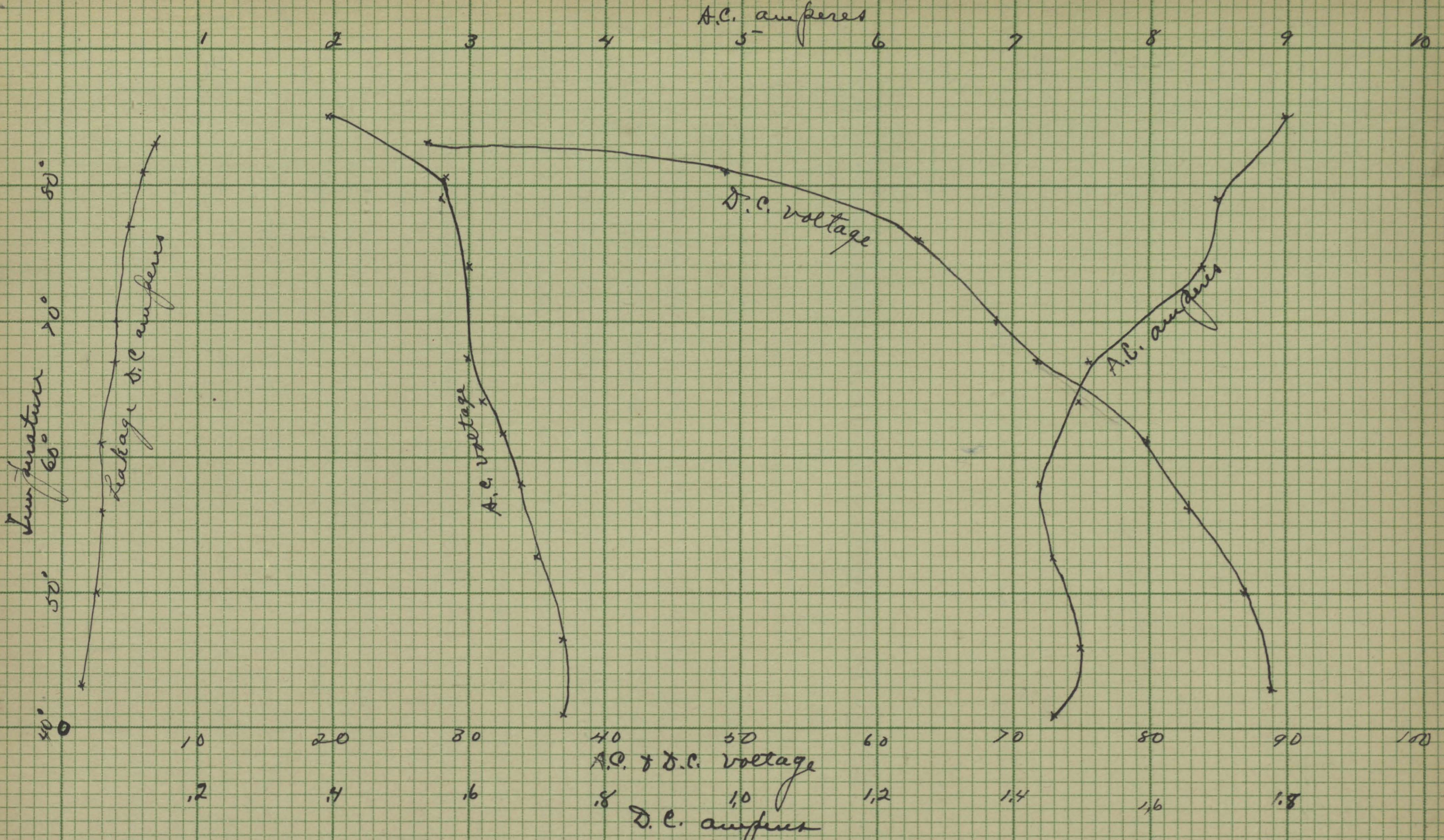
Leakage-Set #4

Temp-leakage Curves

Al plate 3" by "

Low resistance in D.C.

Electrolyte - C.P. sod bi carbonate



Leakage Set #5

Leakage curves

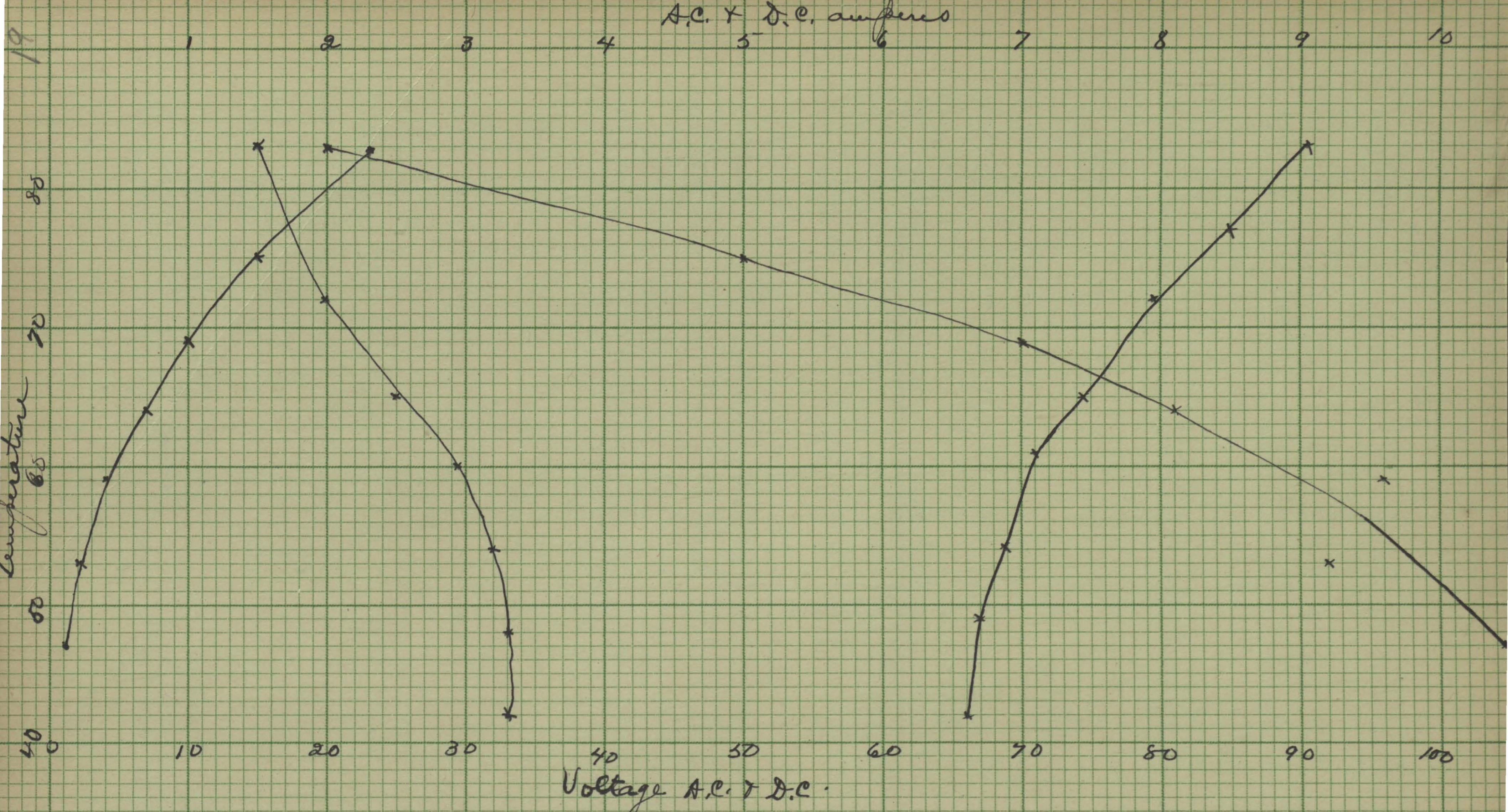
Al-plate 3" × 3"

High resistance in D.C.

Electrolyte C.P. Sod. bicarbonate

In Leakage Set # 3, C.P. Ammonium phosphate, and a new aluminum anode were used, the results are shown in curves for that set. Compared with the curves for Leakage Set # 2, the values are much better. In the region of 45° C the film begins to weaken and in 10 ° more has almost given away. With the sodium bicarbonate solution this point was not reached until the temperature was about 75° C. This weakening of the film was noticed in another way which is not shown by the curves. It was noticed in set #1, that just as soon as the D.C. was turned on the film was strengthened as evidenced by decrease in leakage and rise in voltage. In this set, the same thing was observed up to 45° C. Above this temperature the longer the D.C. ran, the lower became the voltage across the cell. The film would then reform with the A.C; but again weaken under the D.C. For example, at temperature of 65° C, the D.C. voltage fell in two minutes from 60 to 2. I have not been able to offer any explanation of this peculiar behavior in phosphate solution. The breaking down of the film may in some way be connected with the decomposition of the electrolyte, as a strong odor of ammonia was given off at the higher temperature.

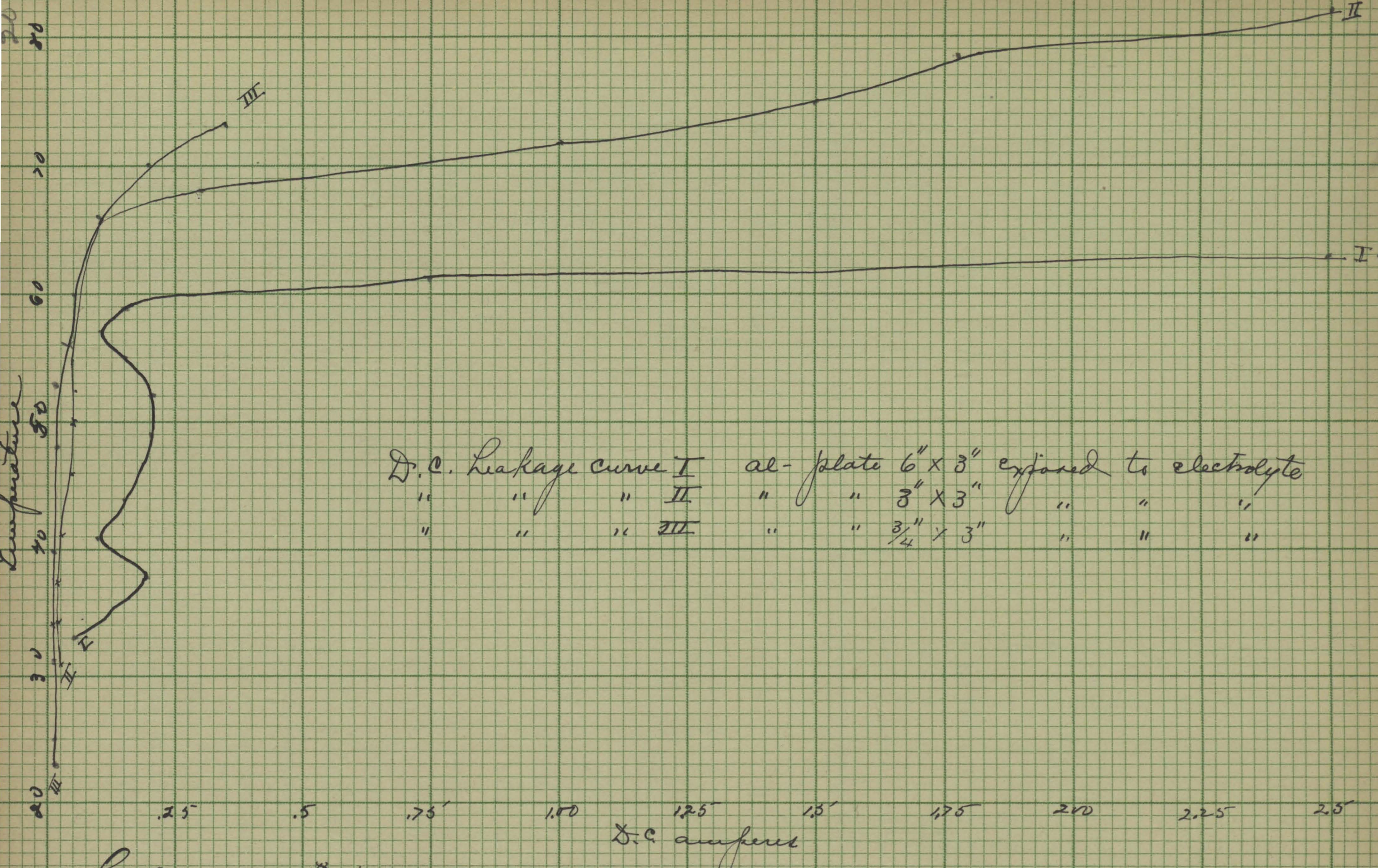
In Leakage Sets #4 and # 5, C.P. sodium bi-carbonate is used- the difference being that low resistance in D.C. is used in #4, high in #5. If we take #1 and #5, we can compare curves made by commercial and C.P. salt. The curves are practically the same, if the scale is taken into consideration- the breaks in the curves appearing at about the same temperature. Comparing # 4 and # 5, we see curves that appear quite different but the differences can be accounted for, by change of resistance in D.C. With high resistance-400 or 500 ohms, the D.C.



Temp- Leakage curves
al-plate 3" x 3"

Lower resistance in D.C.
Electrolyte - C.P. am. phosphate

Leakage Set #6

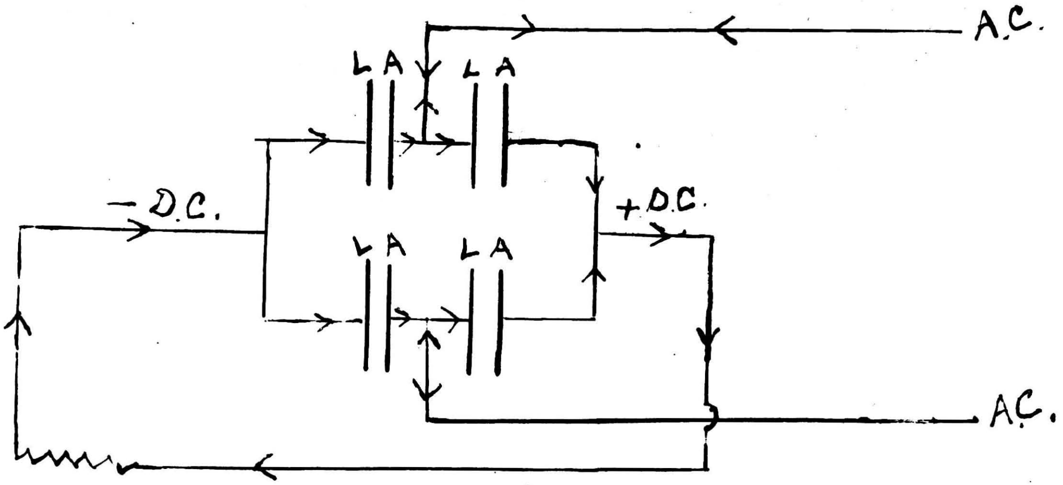


Leakage Sets #8, #9, & #10

voltage falls off pretty gradually after temperature of 45° C. is reached. In #4, since the only resistance in the circuit is that of the cell, the D.C. voltage will remain practically constant. Also under the higher pressure, the leakage is practically nothing until the break comes, then increases rapidly. Leakage set #6 shows practically the same facts when compared with #3 in reference to ammonium phosphate, with the exception that the resistance outside the cell could not be made zero on account of the entire breaking down of the film when D.C. was turned on. The voltage curve therefore in #6 falls.

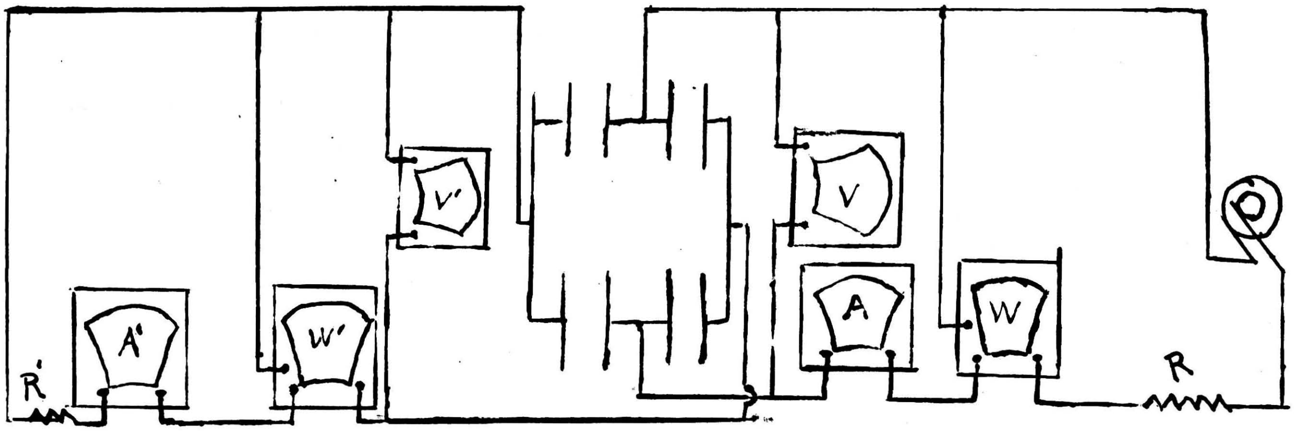
Leakage sets #8, #9, and #10 show effect of different sized plates. The results here seem to bear out the literature of the subject; viz., that there was less leakage in greater current intensity. The larger plates not only show greater leakage at the ordinary temperature but completely break down at a much lower temperature than do the smaller ones.

With the information thus gained by this preliminary work it was thought possible to take up the work of testing the rectifier proper. The rectifier, as before mentioned, is that sold by the Central Scientific Co., and is of the Graetz type-essentially four simple lead aluminum cells so arranged as to rectify both alternations of the current as shown in figure:-



Four cells are arranged as above. The A.C. flows in on either side. But since the current can go only from lead to aluminum, both alternations are directed toward the point marked + D.C. From this it flows around as a pulsating direct current to -D.C. From this point one pulsation passes through a cell and out A.C. on one side; the other pulsation through the other cell and out the other side.

For taking observations the rectifier with other apparatus was arranged as shown below:-

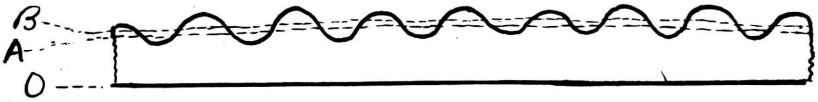


V, A, W, and R are respectively Voltmeter, Ammeter. Wattmeter, and variable resistance on A. C. side, while V', A', W.' and R' are the corresponding instruments on D.C.

side. For reading each of the quantities, current strength-both A.C. and D.C., and power, there were two or three instruments, and that one was used whose scale would best accommodate the values to be taken. A thermometer was kept in the electrolyte, and readings taken. Eight different readings were taken as nearly simultaneously as possible-six on the instruments and the temperature, and the time. It took from 30 to 45 seconds to read and record all the values. The readings were taken in groups of four or five, and usually at intervals of five minutes. Each group represented readings with same resistance in circuit. After changing resistance an interval of ten minutes was usually allowed for readjustment of conditions, before taking next group of readings.

Recorded in the tables of observations in addition to points mentioned above, are computed values of D.C. Power, power efficiency, current efficiency and voltage efficiency. The computed values of the D.C. power were taken as products of observed D.C. Voltage and amperage, and this value was used in computing power efficiency rather than the observed value. On this point, there was considerable difference of opinion. Sebor and Simek (Zeit Elect Chemie, May 1907), say that since the rectified current is a pulsating one and practically amounts to a sine curve, that in figuring the power each factor should be multiplied by $\frac{\pi}{2\sqrt{2}}$ or 1.12, or the product by the square of 1.12 (1.233-+). In my observations if the computed value of D.C. power obtained from product of D.C. amperes and volts be multiplied by the factor 1.23, the observed value of the power given by D.C. Watts, is almost exactly obtained. But the trouble in the above lies in the assumption that the rectified current, practically

is a sine curve. Paul McGahan (Elect Journal '09) goes quite deeply into the subject of meters for rectified circuits. By means of the oscillograph he obtains the curve for the mercury arc rectifier. This is shown in figure:-



It appears as the resultant of a direct current and a smaller alternating current. O represents the zero value, A the average value of the current given by meters in which torque varies as 1st power and B the square root of the mean square, in which the torque varies as the square of the current. The first would represent the electrolytic or chemical effect; the second, the beating effect. He goes on to say that power could not be taken as product of square root of the mean square of current and square rootof the mean square of voltage except in pure sine waves in phase.

While nothing is known of the curve made by the chemical rectifier, it doubtless is less that of a pure sine curve than the curve of the mercury arc rectifier. And since the rectified current may be considered the resultant of a direct current and a smaller alternating current, the observed D.C.Watts would include the effect of both- the Wattmeter being a type suitable for either A.C. or D.C. This value of the power would represent the heating effect. This is confirmed by the fact mentioned above: viz., that the computed value of D.C. Watts multiplied by the constant 1.234 gives practically the D.C. Watts observed on meter. But outside of producing heat, the alternating current effect mentioned above would be of little use. The direct current effect only being useful in most cases. Therefore, since

it is the chemical and not the heating effect which is desired, the power efficiency is taken as relation of observed A.C. Watts and computed D.C. Watts. The current efficiency represents the relation of the observed values of the current; and voltage efficiency the relation between observed values of A.C. and D.C. voltage.

The plan to be followed in taking the observation on efficiency was to start with a small value of the current and take readings as the temperature of the electrolyte rose. Then increase the current after the electrolyte cooled and try again as the temperature rose, and so on, getting sets of observations with increasing current strength as nearly over the same temperature ranges as possible. It was thought that possibly the efficiency was a function of the current strength.

Efficiency Sets 1 and II were more in the nature of tryouts. Efficiency Set #3 is shown with tabulated readings. In this set, the value of D.C. is gradually increased from three to four amperes. The voltage efficiency remains fairly constant while in the main ampere-efficiency and power-efficiency fall with increase of temperature. Efficiency Set #4 is shown with readings. Conditions are the same except electrolyte is cool and is intended as a continuation of #3. The efficiency results are best seen from the curves for Efficiency Set #4. It is noted that up to 35°C, the efficiencies are fairly constant. At that point, the ampere-efficiency slightly rises and both the voltage and power efficiencies fall. Efficiency Set #5 begins just where #4 left off, with the exception that the electrolyte is cool, and a cooling apparatus has been added. The latter consisted of glass tubes bent into spirals. One of these was placed around each aluminum cylinder and cool water from the tap was allowed to flow through. The results

Efficiency Set #3.

Typical Central Scientific Cell. **Lead plates 6" x 3"**

Plates 6 inches in Electrolyte--com'l sod bicorb.

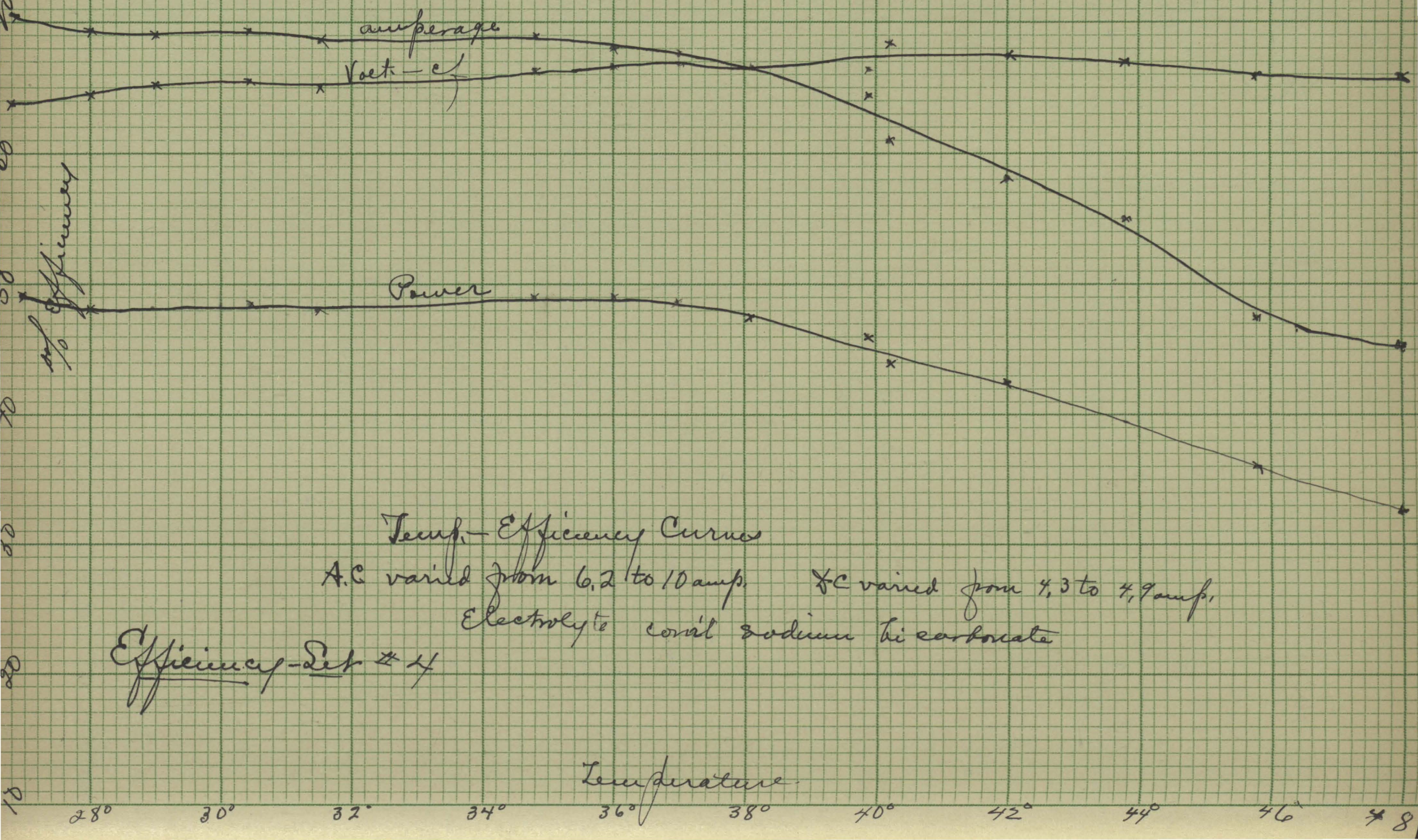
A C.					D C.						
						(obs)	(cal)				
Volts	Amp.	Watts.	Time	Volts	Amp.	W	W	V-ef	A-ef	P-ef	Temp.
54	4.6	240	2:45	34	3.15	140	107	63	68.5	44.5	30.5
54	4.62	247	2:50	34	3.14	140	107	63	68	43.3	31.1
54	4.62	250	2:55	34	3.15	140	107	63	68	42.8	31.8
54.1	4.64	250	3:00	34	3.15	140	107	63	67.5	42.8	32.5
53.5	4.56	245	3:05	33.7	3.1	135	105	63	68	42.8	33
56	4.92	265	3:15	35.6	3.28	150	117	63.6	66	44.1	33.6
56.3	4.95	265	3:20	36	3.33	150	120	63.9	67.2	45.3	34.4
57.8	5.14	270	3:25	37	3.4	160	126	64	66.1	46.6	35
58	5.22	273	3:30	37	3.4	160	126	63.8	65.1	46.1	35.7
57.5	5.2	273	3.35	37	3.38	160	125	63.9	65	45.8	36.4
62.5	5.8	344	3:40	40	3.75	192	150	64	64.7	43.6	37.2
62.3	5.83	345	3:45	40	3.73	180	149	64.2	64	43.2	38
62.3	5.91	347	3:50	40	3.72	188	149	64.2	63	43	38.9
61	5.8	330	3:55	38.8	3.36	170	138	63.6	61.4	42	39.7
60	5.85	328	4:00	38.5	3.54	170	136	64.2	60.5	41.2	40.4
66.2	6.65	405	4:05	43.9	4.07	222	179	63.3	61.1	44.2	41.3
66.3	6 87	420	4:10	43	3.97	210	171	64.8	57.8	40.7	42.2
65	6.95	415	4:15	42	3.9	204	163	64.6	56.1	39.5	43.6
64.5	7.05	420	4:20	42	3.88	200	162	65.1	55	30.6	44.8

……

Efficiency Set #4.

Conditions similar to those in Set # 3.

72	6.2	405	11:00	46	4.38	255	200	63.9	70.6	49.4	27.2
72.7	6.26	423	11:05	47	4.35	250	204	64.7	69.5	48'6	28.1
71.4	6.2	408	11:10	46.3	4.27	240	197	64.8	69	48.3	29.3
71	6.24	415	11:15	46.5	4.32	247	201	65.5	69.2	48.4	30.5
70.7	6.22	408	11:20	46	4.26	240	196	65.1	68.5	48	31.5
77.8	7	508	11:35	51.8	4.82	305	250	66.6	68.9	49.2	34.8
76.5	6.96.	495	11:40	51	4.75	292	242	66.6	68.3	48.9	46.1
77.	7.1	508	11:45	51.5	4.8	300	247	66.9	67.6	48.6	37
76	7.04	500	11:50	50.5	4.6	290	237	66.5	66.7	47.4	38.1
75.8	7.15	510	11:55	50.3	4.68	287	235	66.4	64.5	46.1	39.5
84.6	8.4	678	12:10	58	5.12	376	297	68.6	61	43.8	40.2
85.8	8.84	695	12:15	57.8	5.1	365	295	67.4	57.7	42.4	42
83.5	9	700	12:20	55.8	4.95	343	276	66.8	55	39.4	43.8
81.3	9.78	710	12:25	53.7	4.74	310	255	66.1	48.5	36	45.8
77.5	10	710	12:30	51	4.55	283	230	65.8	45.5	32.4	48.



Temp.– Efficiency Curves

A.C varied from 6.2 to 10 amp. D.C varied from 4.3 to 4.9 amp.

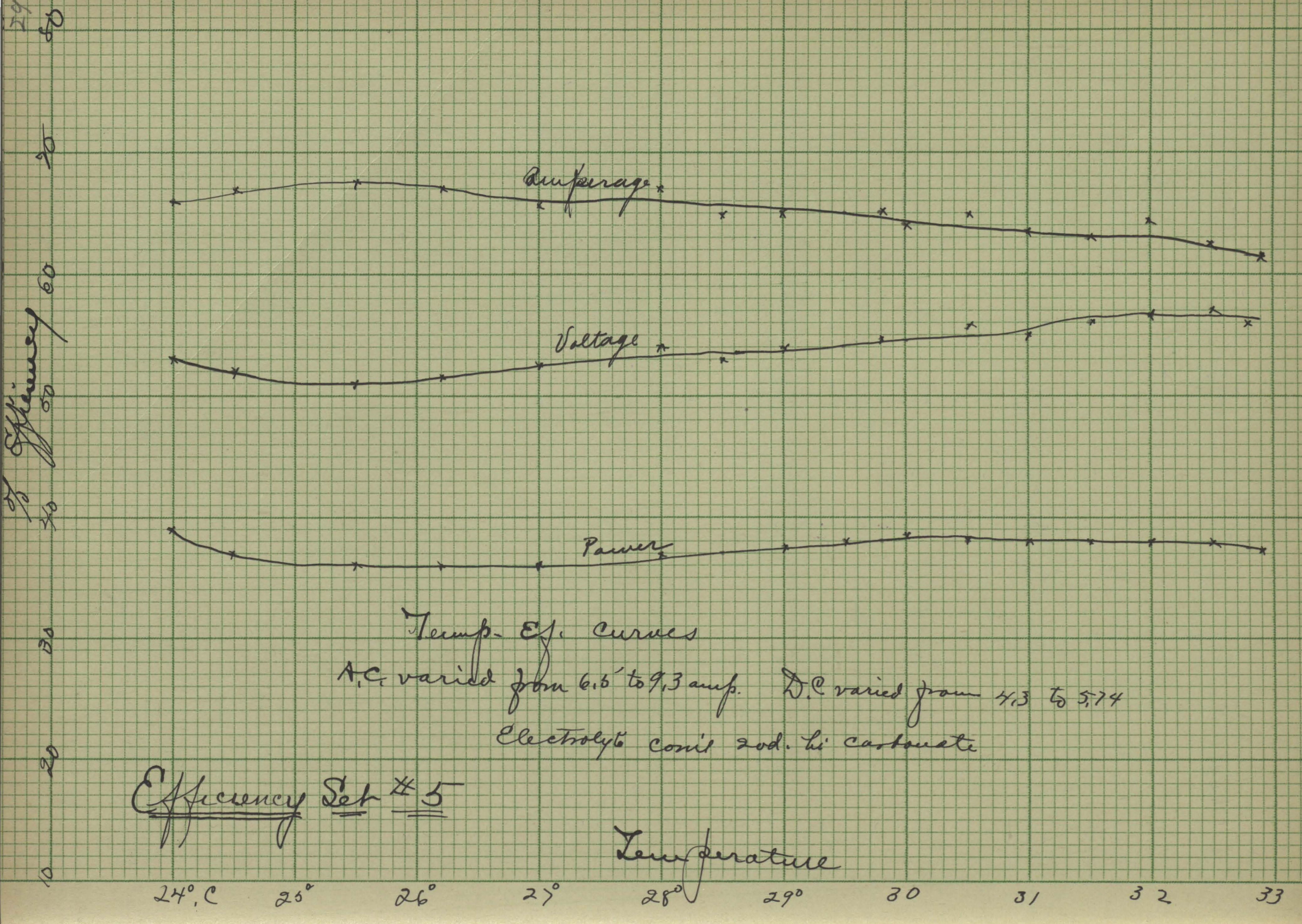
Electrolyte const. sodium bicarbonate

Efficiency – Set # 4

Efficiency Set #5.

Conditions same as in #4 except cooling device has been added.

A C				D C							
Volts	Amp.	Watts.	Time	Volts	Amp.	W.	W.	V-ef	A-ef	P-ef	Temp.
88.8	6.5	520	10:00	47.5	4.3	278	204	53.5	66.1	39.2	24
88	6.25	525	10:05	46.4	4.17	250	194	53	66.7	37	24.5
88.2	6.1	510	10:00	45	4.06	243	183	51	66.6	36	25.4
90	6.28	540	10:15	46.5	4.18	260	194	51.7	66.6	36	26.2
90.6	6.5	560	10:20	47.5	4.25	270	202	52.4	65.4	36	27
92.3	7.23	663	10:30	50	4.88	330	244	54.2	67.5	36.8	28
94.3	7.5	668	10:35	50	4.9	332	245	53	65.3	36.7	28.5
95	7.6	682	10:40	51.6	5	348	258	54.3	65.8	37.8	29
94.8	7.63	682	10:45	51.6	5	345	258	54.5	65.8	37.8	29.4
93.3	7.6	665	10:50	51	4.98	340	253	54.7	65.5	38	29.8
95.8	8.1	717	11:00	53.4	5.18	366	277	55.7	64	38.6	30
96	8	725	11:05	53.4	5.18	365	277	55.6	64.7	38.2	30.5
96	8	725	11:10	53.6	5.2	370	279	55.6	65	38.5	30.6
95.6	8.05	630	11:15	53.8	5.2	370	280	56.3	64.6	38.4	30.7
95.6	8.15	730	11:20	53.4	5.18	367	277	55.8	63.6	38	31.
104.4	9.05	880	11:30	58.8	5.7	448	335	56.3	63	38.1	31.3
104	9.05	890	11:35	59	5.74	455	339	56.8	63.4	38.1	31.6
106	9.3	930	11:40	60	5.82	465	349	56.6	64.4	37.5	32.
104	9.2	900	11:45	59.2	5.74	455	340	56.9	62.4	37.8	32.5
102.5	9.3	900	11:50	59	5.7	447	336	57.6	61.3	37.3	32.8

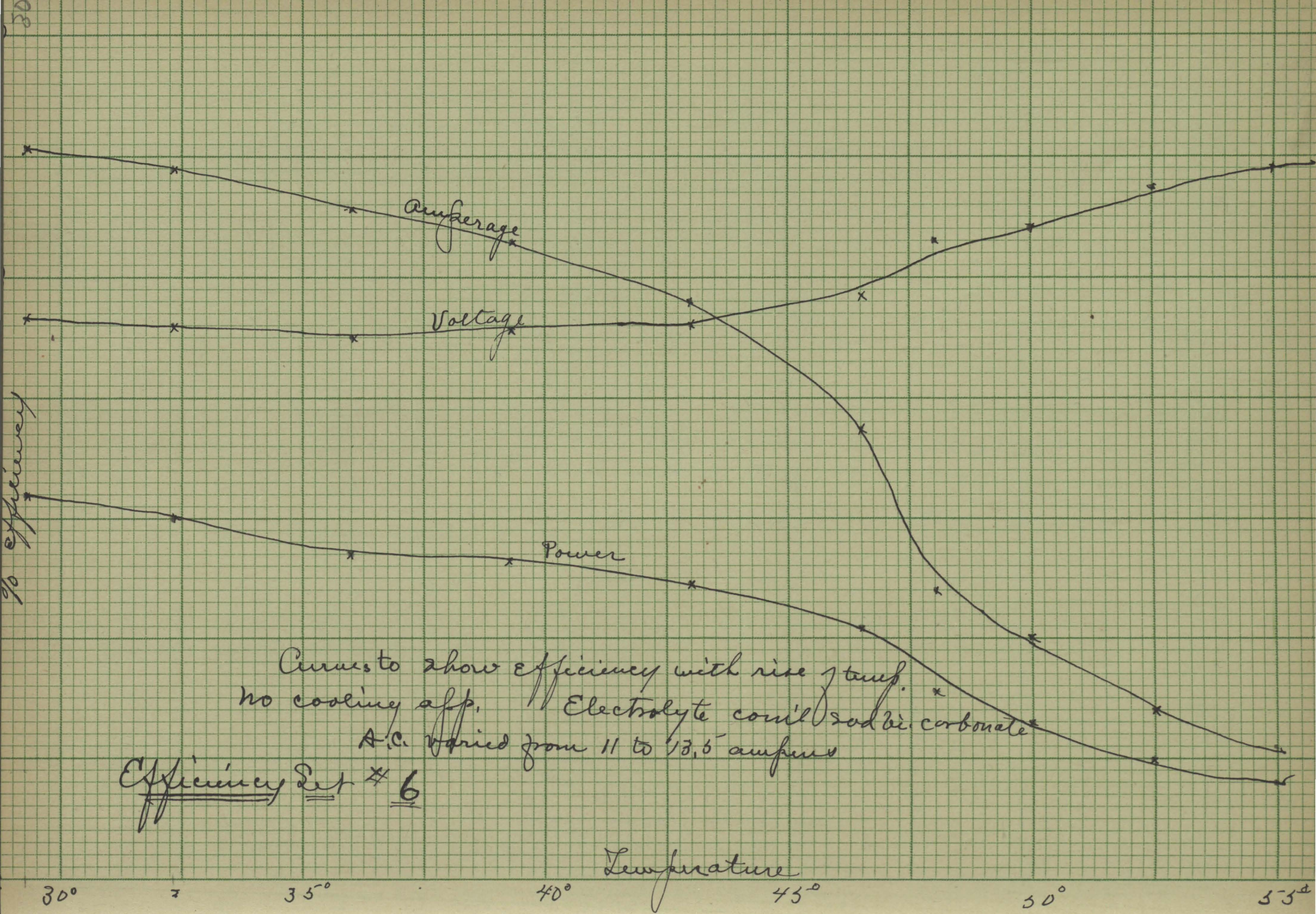


Temp- Ef. curves

A.C. varied from 6.5 to 9.3 amp. D.C. varied from 4.3 to 5.74

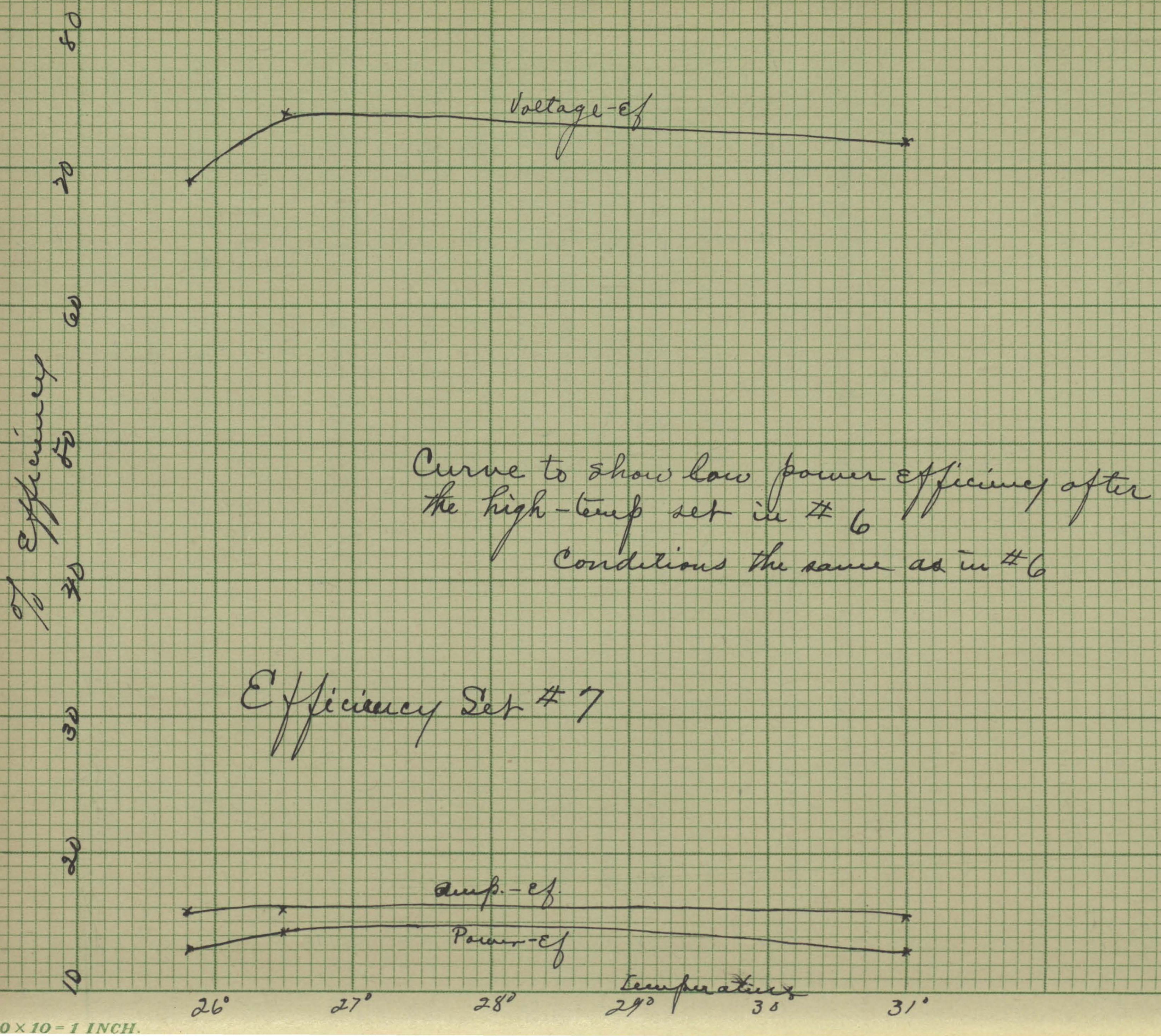
Electrolyte consis sod. bi carbonate

Efficiency Set # 5



Curves to show Efficiency with rise of temp.
no cooling app. Electrolyte com'l sod bi. carbonate
A.C. varied from 11 to 13,5 amperes

Efficiency Set # 6



Efficiency Set #7

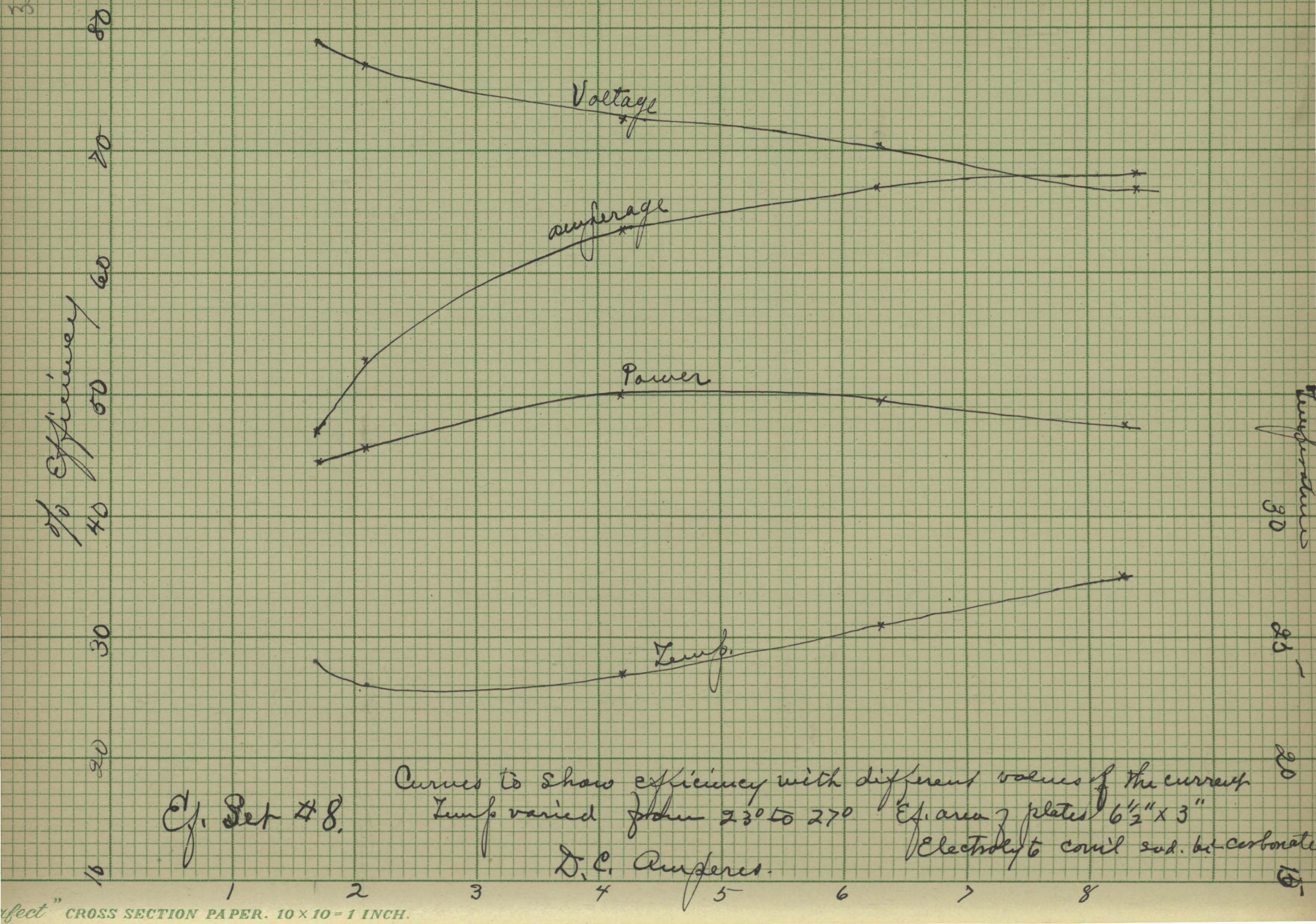
Curve to show low power efficiency after
the high-temp set in #6
Conditions the same as in #6

of #5 are platted and tabulated. In an hour and fifty minutes, the temperature arose about 9 degrees, while in the preceding run without cooling apparatus, during one hour and thirty minutes the temperature rose twenty-one degrees.

Comparing the curves for #4 and #5, it is seen that the curves in each set bear about the same relation to each other, except that the power efficiency and voltage efficiency are much lower in #5. This was probably due to the temperature rising to a high point in #4.

At this point it was decided to remove the cooling apparatus and make a high temperature, high-current run. The results are best studied from curves for #6. Using a current on A.C. side from 11 to 13.5 amperes, the temperature rose rapidly and in fifty minutes had reached 58° C. The apparatus was just in the condition at the beginning of #6 as at close of #5. The curves in #6 will be seen to start approximately where they stopped in #5. They run along almost as in preceding runs until the temperature of 40° to 45° is reached. Here the current efficiency falls very low taking with it the power efficiency. On the other hand the voltage efficiency at this point rises slightly.

Efficiency set #7 was begun the next morning without any change in conditions except that the electrolyte was at a temperature of 22.8° C. Several readings were taken and the values were practically the same as at the close of #6. Up to this time I had been inclined to think that the low efficiency at the end of a high temperature run would return to normal conditions with the return to normal temperature. But in the last few runs each succeeding set of curves began just where the preceding set stopped notwithstanding the fact that each new set was begun with a cool



Ef. Set #8.

Curves to show efficiency with different values of the current
Temp varied from 23° to 27° Ef. area of plates 6½" x 3"
Electrolyte comm'l sod. bi-carbonate

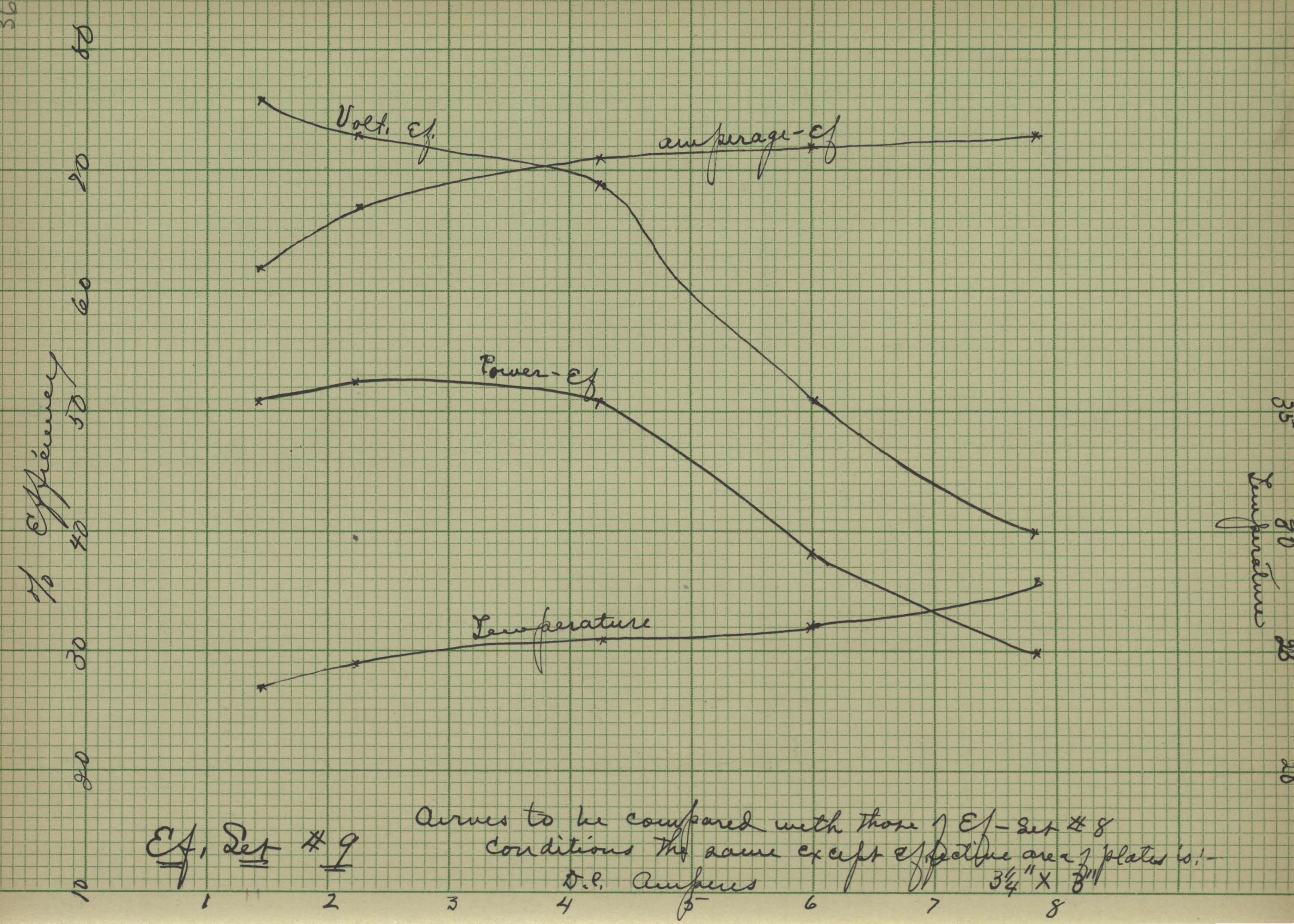
Efficiency Set #8 (plates 6½'' x 3'')

To test efficiency with currents of 1, 2, 4, 6, and 8 amperes in D.C. No resistance in A.C.. Begin with load in D.C. and lessen gradually. Al.electrodes clean.

A C			D.C.								
Volts	Amp.	Watts.	Time	Volts	Amp.	W.	W.	V-ef	A-ef	P-ef	Temp.
107	3.35	300	10:05	84.8	1.47	148	124	78.8	43.9	41.2	25
106	3.15	270	10:10	82.6	1.44	140	120	78	45.7	44.3	24.5
105	3.05	270	10:15	83	1.44	142	120	78.7	47.	44.4	24.4
105	2.95	260	10:20	82.5	1.43	140	118	78.6	48.5	45.4	23.6
105	2.92	260	10:25	83	1.45	145	120	79.	49.6	46.1	22.9
107	4	400	10:35	81.5	2.05	208	167	76	51.	42	23.3
107	3.95	375	10:40	82	2.08	208	171	76.6	52.6	45.6	23.2
107	3.8	360	10:45	82	2.08	208	171	77	54.7	47.5	23.2
106	3.8	355	10:50	81	2.05	203	166	76.2	54	47.7	23.2
108	3.8	360	10:55	81.7	2.07	207	169	76.5	54.5	46'9	23.
106	6.65	645	11:05	76.7	4.2	410	322	72.2	63.2	50	23.2
106	6.6	640	11:10	76.5	4.2	407	321	72.5	63.6	50	23.5
106	6.5	640	11:15	76.8	4.22	415	324	72.5	65	50.8	23.6
105	6.6	643	11:20	76.8	4.31	412	323	72.9	63.8	50.2	24
108	6.8	670	11:25	78.3	4.28	423	335	72.7	63	50	24.3
106	9.3	950	11:40	74.7	6.3	605	471	70.2	67.7	49.5	24.2
105	9.3	940	11:45	73.8	6.23	595	459	70.3	67	48.8	24.8
106	9.35	940	11:50	74.2	6.26	595	464	70.3	67	48.8	25.7
106	9.43	955	11:55	74.8	6.3	600	471	70.6	66.8	49.4	26.5
104	9.37	930	12:00	73.2	6.19	585	471	70.5	66.	50	26.5
98	11.78	1115	1:55	66.4	8.12	705	539	67.6	69.	48.2	26.3
98	11.83	1125	2:00	66.3	8.17	705	542	67.3	69	48.2	27.3
99	12.1	1150	2:05	67.	8.22	722	550	67.4	68	47.8	27.9
103	12.7	1255	2:10	69.6	8.51	775	592	67.4	67	47.2	28.7
103	12.75	1265	2:15	69.8	8.55	780	597	67.6	67	47.2	30.2

electrolyte. This led me to believe that the high temperature had produced a permanent low efficiency condition in some way connected with plates or electrolyte. The plates were lifted up out of the solution and there was revealed without a doubt the secret of the whole difficulty. The aluminum electrodes were encrusted with a coating of crystallized salts almost an eighth of an inch in thickness. They were removed, washed and sand papered. The surface of the aluminum electrodes presented a sieve like appearance indicating that at certain points the aluminum had been acted upon with great chemical activity. Then the electrodes, now thoroughly clean, were tried as shown in Efficiency Set #8. The efficiencies were again good.

In Set #8, readings were taken for values of the D.C. current from 1½ or 2 amperes up to 8 amperes. To the three efficiency curves, is now added the temperature curve, all being plotted against the current (D.C.) With the electrodes in good condition, the cooling apparatus added, the best values thus far obtained are shown in this set. The power efficiency approaches again and really surpasses the value obtained in #4,-for the first time reaching 50%. The voltage efficiency and ampere efficiency, of necessity to produce the high power efficiency, are both high. The temperature curve shows that for low values of the current, the electrolyte was actually lowered in temperature for a time, and at no time rose higher than 27° C. The values for #8 are tabulated. It is noticed that five readings of each value of the current were taken and the average of these plotted. Two values of the temperature were given for each reading. In arranging the cooling apparatus, it was found best to put a Y-tube in the main tube leading from the tap



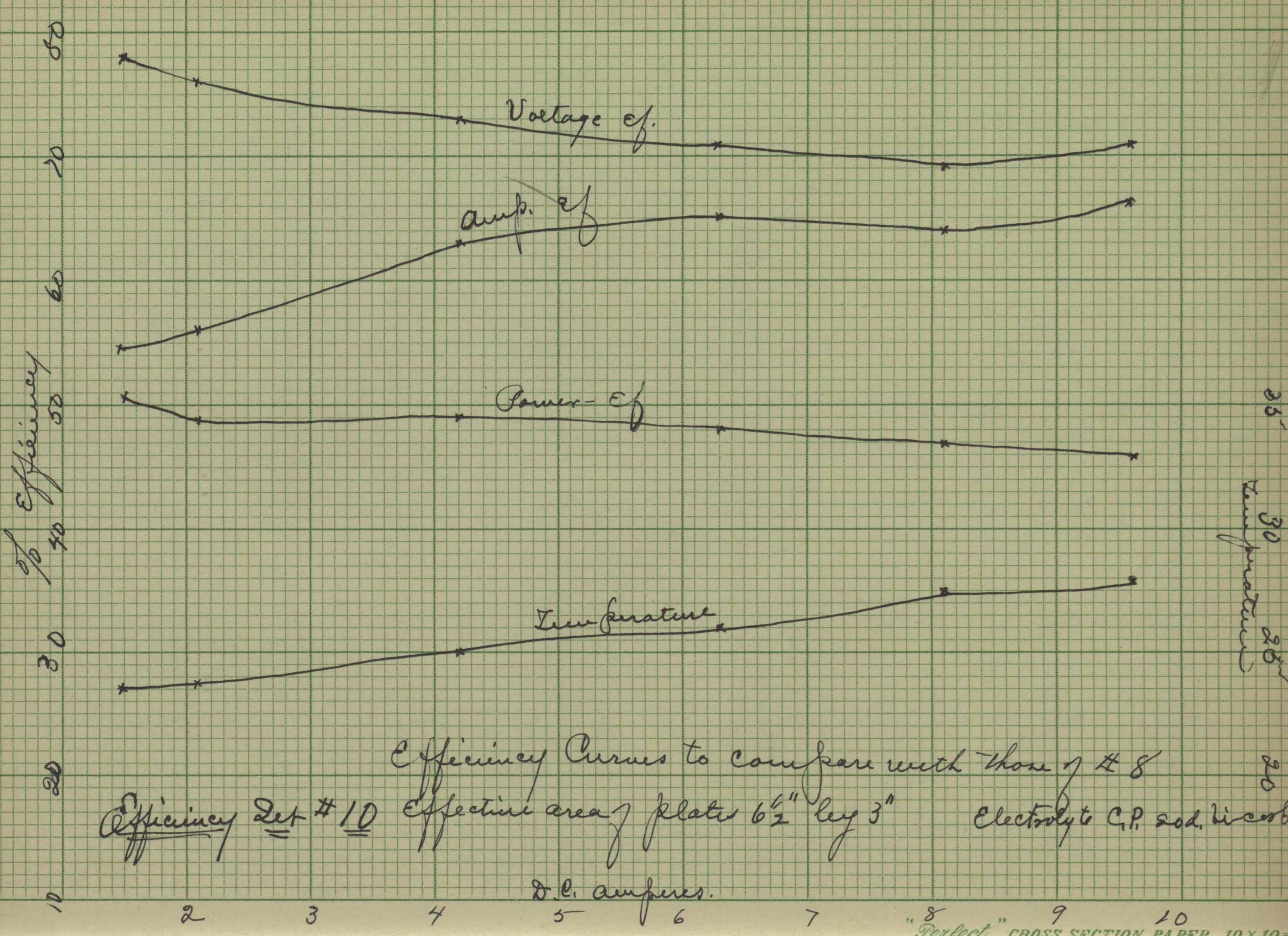
Ef, Set #9

Curves to be compared with those of Ef-Set #8
conditions the same except effective area of plates is:- 3¼" X 8"

and thus send cold water through each half of the rectifier at the same time. The two cells through which the water first passed were at slightly lower temperature than those from which it left the rectifier. The cooling effect of each branch remained the same so it was necessary to read only the two temperatures, that of one of the cells where the water entered the rectifier, and that of one of the cells where it left the rectifier. These temperatures with the stronger values of current sometimes varied 1½ °.

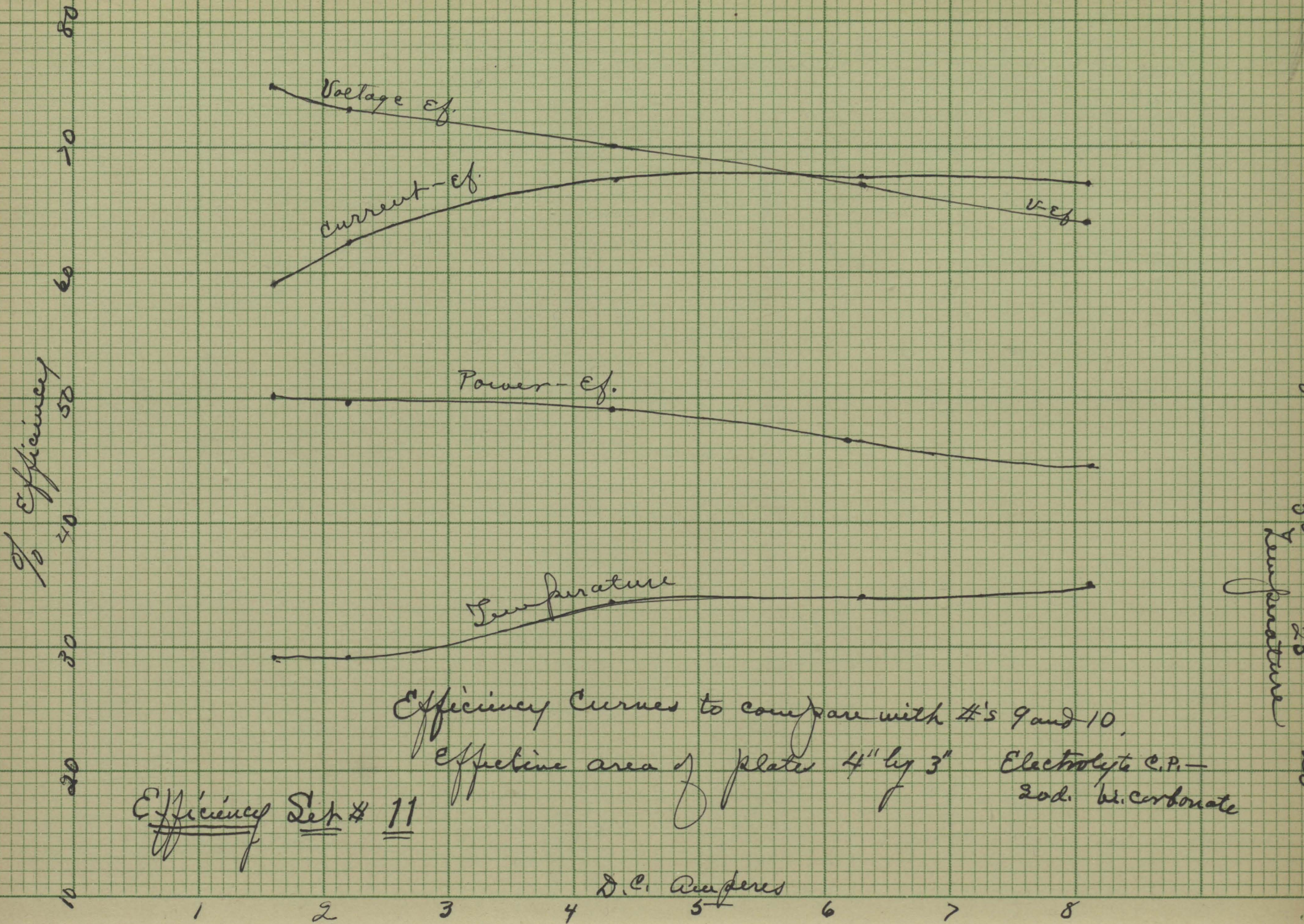
From these observations, the effect of high temperature of electrolyte is clearly seen,- that of the encrustation or coating of the aluminum electrodes. With this coating on, Efficiency Set #7 shows the power efficiency to be from 13 to 15%, with it off, #8 shows 50%. The coating partly forms during a high temperature run and partly afterwards during the cooling. The temperature is highest at the aluminum electrode. Here evaporation takes place rapidly, and the coating of aluminum hydroxide and bicarbonate of soda begins to form there. Then as cooling takes place, the electrolyte concentrated on account of more salt going into solution with high temperature, and on account of evaporation, deposits its crystals, adding to these already formed on the aluminum electrode. During this cooling process, a slight amount is deposited on the lead, but the most is left on the aluminum. With those crystals there, the valve-effect is practically nothing, the anodic high resistance film is displaced by a low resistance one of salts.

The next set #9 was made with the same conditions as #8 except that the plates dip just one half as far into the electrolyte. Comparing the curves with those of #8, it is seen that in the first part of the set, there is a higher



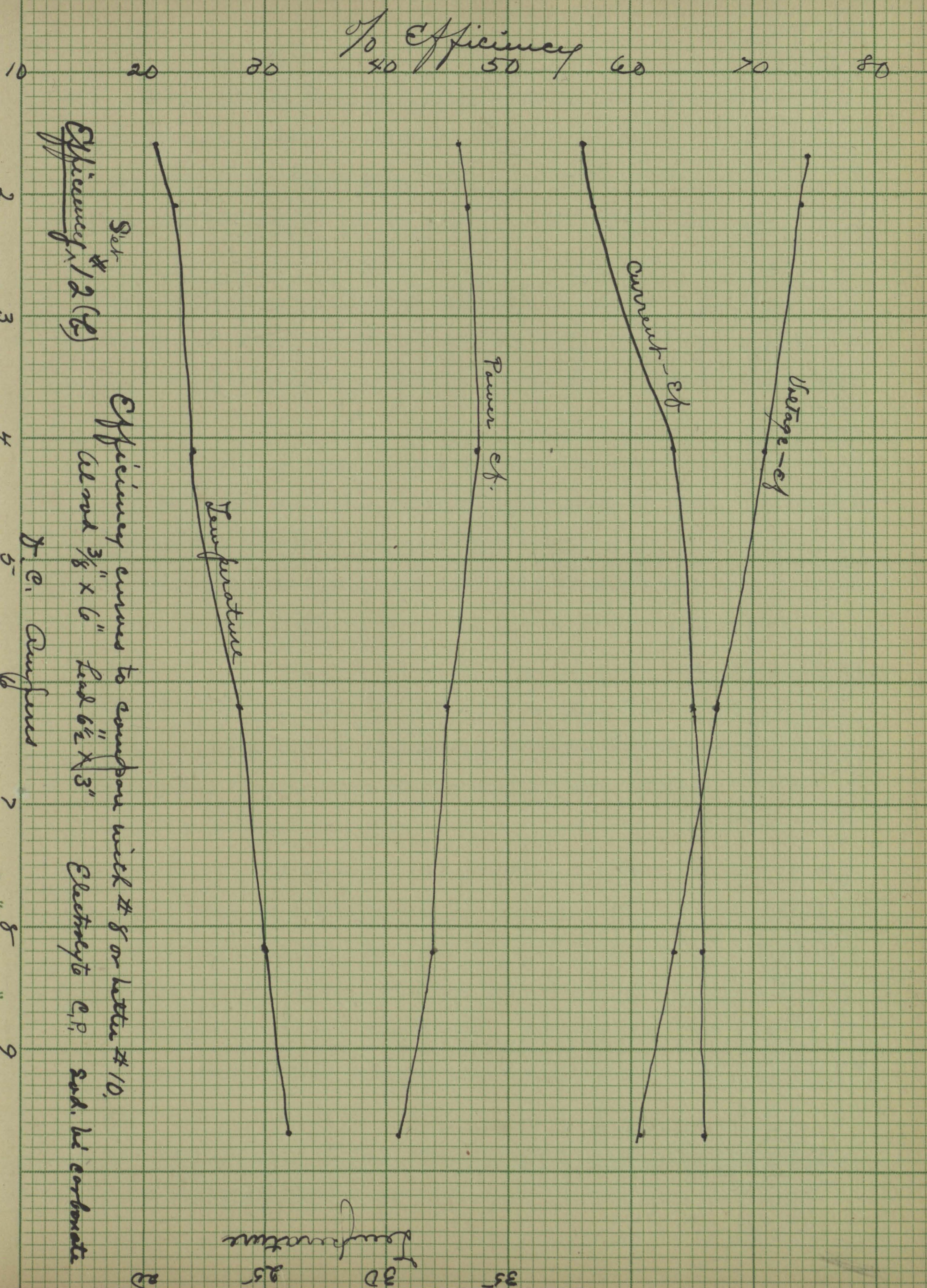
Efficiency Curves to compare with those of # 8

Efficiency Set # 10 Effective area of plate 6½" by 3" Electrolyte C.P. sod. bicarb



Efficiency Curves to compare with #'s 9 and 10.
Effective area of plates 4" by 3" Electrolyte C.P.—
Sod. bi.carbonate

Efficiency Set # 11



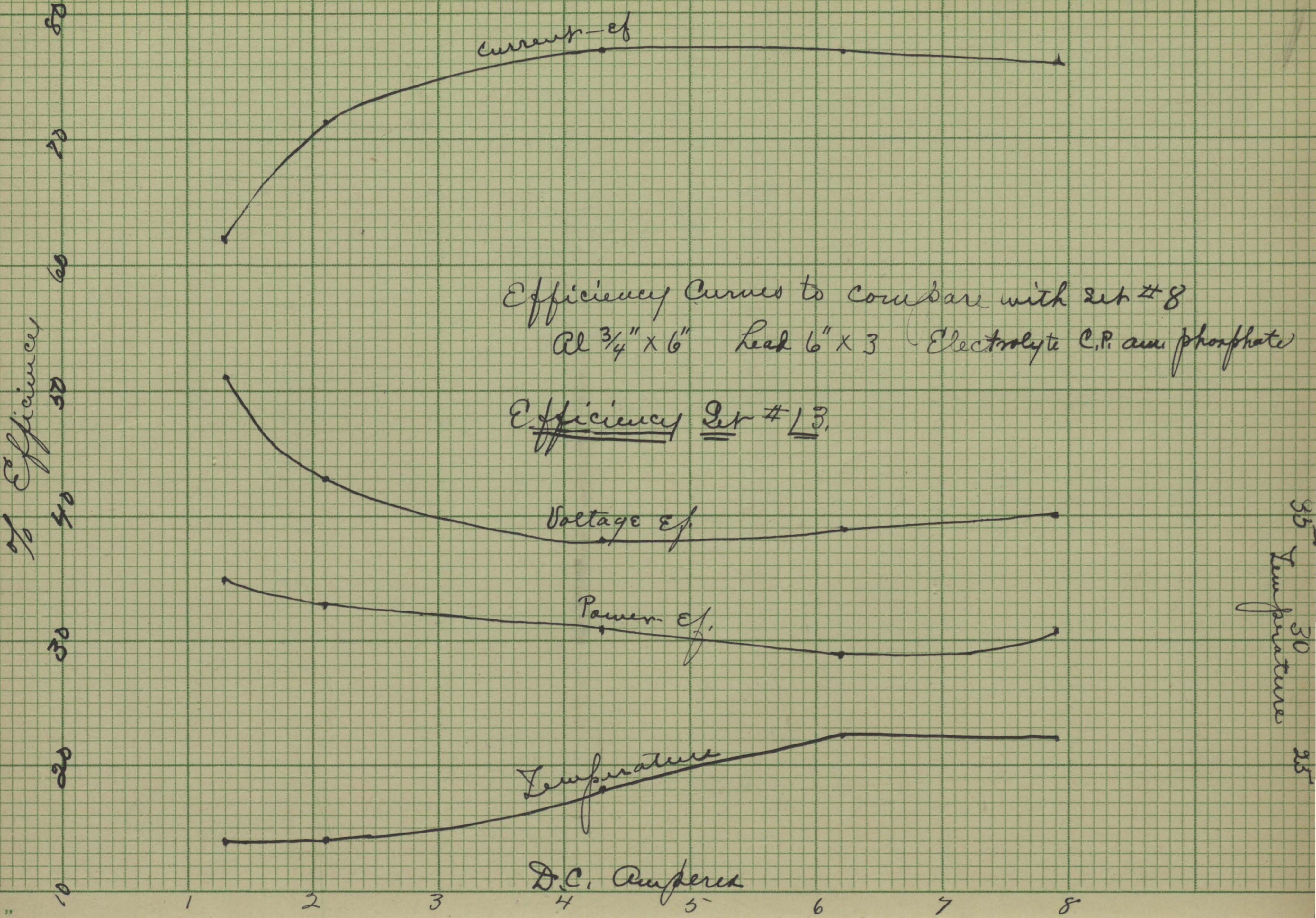
Efficiency of Set #12 (b)

Efficiency curves to compare with #8 or better #10.
Cel rod 3/8" × 6" Lead 6½" × 3" Electrolyte C.P. Sod. bi carbonate

ampere efficiency and hence higher power efficiency (52%). The set was begun one evening and completed the next morning, and the sudden fall of voltage efficiency, carrying down with it the power efficiency, was due no doubt to the plates standing in solution over night. It will be noticed in the curves from #8 on, in which the efficiency and temperature are plotted against the current, that the voltage efficiency falls with increase of current. This was called attention to by Charters who explained it by saying that with increased current was developed an increased counter E.M.F.

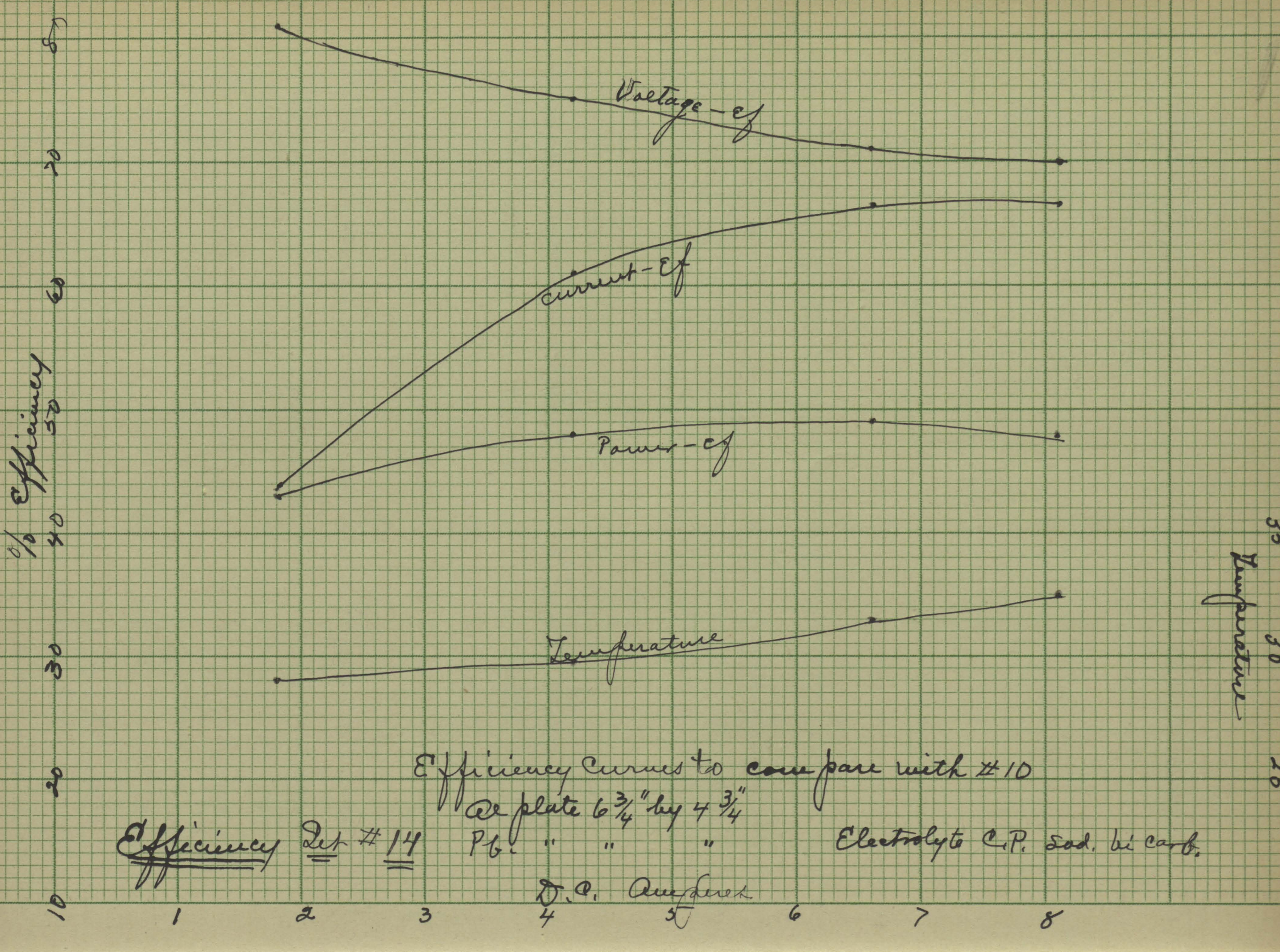
Efficiency sets #10 and #11 duplicate conditions in #8 and #9 except that C.P. Sodium bicarbonate is used. By comparing the curves it is seen that there is little to choose between the commercial and C.P. salt as was noted in the preliminary runs. With respect to the depth the plates are immersed, whether six inches or half of that, the observations do not show any definite difference, except possibly a more rapid falling off in voltage efficiency, as the current is increased, in the case of the smaller area exposed. This will be referred to again.

Efficiency Sets #12 (a) and #12 (b), were similar to #10 except that an aluminum rod $\frac{3}{8}$'' in diameter was substituted for the typical $\frac{3}{4}$'' rod. #12 (a) gave slightly better results in the beginning, but with the action on the rod there came a falling off of the efficiency. #12 (b) was then taken as the more typical run and this is plotted. When compared with #10, the only difference in conditions being the size of aluminum rod, it is seen that the voltage efficiency falls more rapidly with the smaller rod. This is what we should have expected. Since the voltage efficiency falls with in-



Efficiency Curves to compare with Set #8
Al 3/4" × 6" Lead 6" × 3 Electrolyte C.P. am. phosphate

Efficiency Set #13.



Efficiency Curves to compare with #10
Al plate 6 3/4" by 4 3/4"

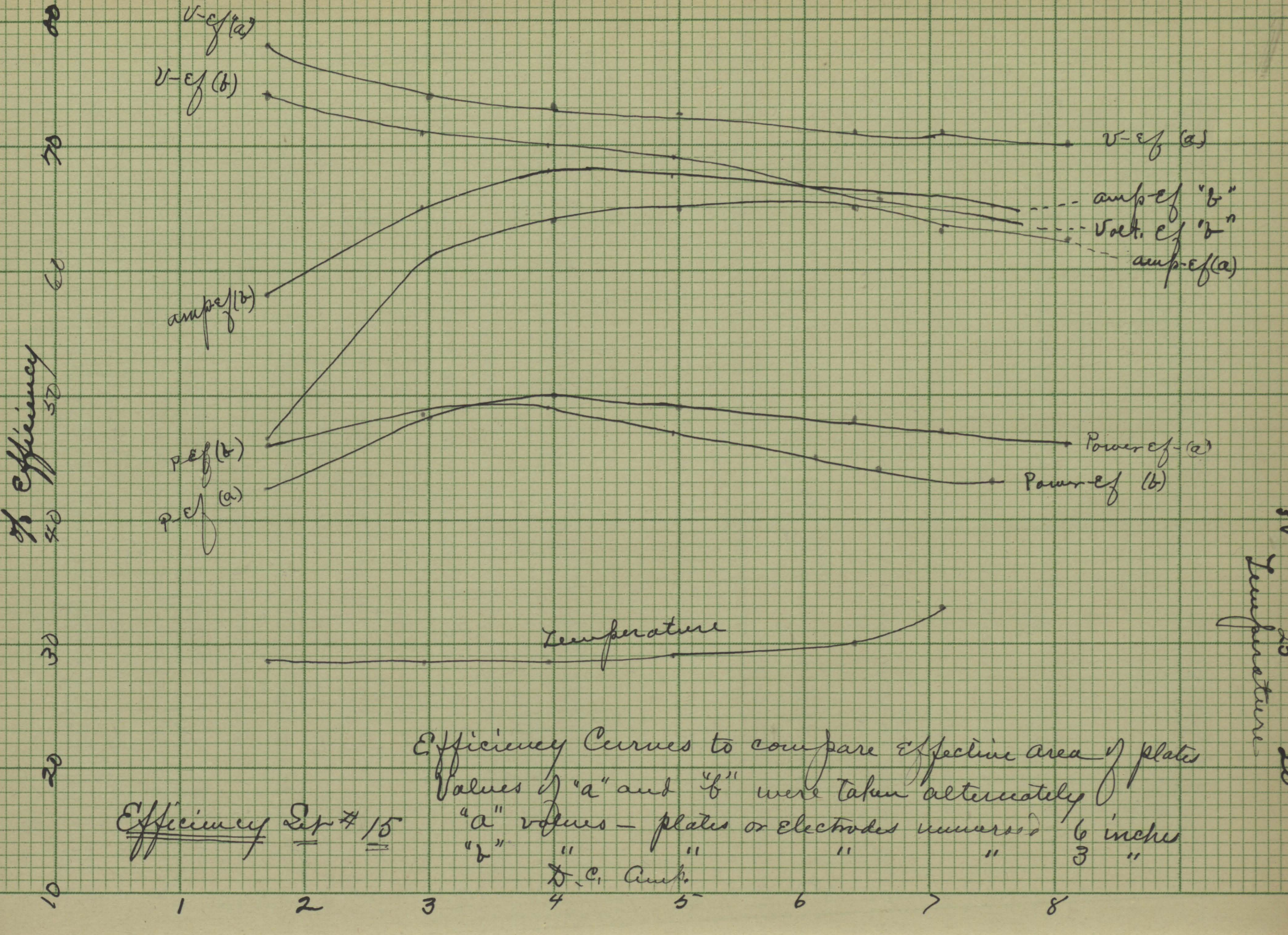
Efficiency Test # 14 Pb. " " " Electrolyte C.P. Sod. bi carb.

crease of current, it should fall with a decrease in the size of the aluminum rod, as this increases the current intensity. This partly explains also, the voltage fall with the plates part way but of solution in #9 and #11.

Efficiency set #13 with C. P. ammonium phosphate confirms what was stated in the preliminary experiments. The low voltage would make it too inefficient. By referring to the curves for #13, it is seen that the power efficiency is little above 30%. This is due to the low voltage efficiency, of course, The current efficiency, however, reaches almost 80%, but it is of little avail in raising ppwer since the voltage factor is many times that of the current factor.

An improvised rectifier was constructed to admit using large plates of both lead and aluminum. The results are given in curves for efficiency run #14. With the decreased current intensity, is associated the higher voltage efficiency, and good power efficiency. The power efficiency shows no marked advantage, however, over that given by the typical cell. The efficiency might have been a little better if the temperature could have been kept down. In this cell there was no cooling apparatus, and although the jars were large and held considerable electrolyte, the temperature rose six or seven degrees higher than with the typical cell and cooling apparatus.

The problem of determining what effect the area of plate exposed to electrolyte makes on efficiency. begun in #9 and, with the exception of #13, continued in each successive set in some form, was tried out in #15 in a slightly different way. Heretofore, however, favorable things might appear, it was almost impossible to make two successive runs under exactly the same conditions. In this run, two sets of readings were taken (a) and (b), the "a" readings with the plates immersed



Efficiency Exp # 15

Efficiency Curves to compare Effective area of plates
Values of "a" and "b" were taken alternately
"a" values – plates or electrodes immersed 6 inches
"b" " " " " 3 "

six inches; the "b" readings just half that amount. These were taken as nearly the same time as possible. The "a" readings would be taken, and then the plates lifted up and "b" readings taken as quickly as they could be read. The plates were then lowered, and after an interval the readings were again taken. The results are shown in curves for Efficiency Set # 15. While the results are practically what were pointed out in preceding runs, it is felt that they are more conclusive in this run. The possibility of any other condition entering has been entirely eliminated. The best results are given with the larger area, or lower current intensity. This is due, of course, to the higher voltage efficiency as has been mentioned before, notwithstanding the "b" readings had the higher current efficiency.

The rectifier was then tried out in a practical way. A current of one ampere under pressure of eleven volts was sent through a solution of copper sulphate for one hour. Below are given the results;-

1st weight of cathode	27.730	grams
2nd " " "	28.905	
copper deposited	1.175	grams
One ampere in one hour deposits	1.174	"
Error	.001	

This shows the measurement of the chemical effect of the rectified current reasonably accurate to one part in a thousand. The rectifier was then tried for arc light in stereopticon. Since the resistance of the arc varied, the following observations are the nearest approximations:-

A.C.			D.C.		
Volts	Amperes	Time	Volts	Amp.	Temp.
109	10-11	10:30	74	7-8	22
109	11-12	10:45	75	8	24.5
109	11-12	11:00	78	65-8	25.5
109	12-13	11:15	78	7-8	26.5
109	12	11:30	78.5	7	27.1

The observations were made for an hour, during which the

temperature rose about 5° C. The light was good in the opinion of those called in to witness the test. However, the noise made by the reversals of an alternating current which we had hoped to eliminate in our rectified current, was not gotten rid of entirely. The pulsations of the rectified current still produced considerable noise.

The rectifier was used also for charging storage batteries and gave excellent results. In fact, I have used the rectified current in my laboratory for four years, to run D.C. motors, induction coils, to charge storage batteries, and to do anything for which a direct current is necessary.

Conclusion.

1. Coating of electrodes due to rise of temperature or other conditions is almost fatal to high efficiency. Therefore cooling device must be added if high amperage is used.

2. Rectifier should be kept in good condition by:

(a) Sand papering al-electrodes at intervals.

(b) Lifting electrodes out of solution and rinsing with distilled water after a run.

(c) Leaving no excess salt in jars to be dissolved with a rise of temperature, and adding distilled water to take place of water evaporated.

3. As the current passing through the rectifier is increased, the current efficiency is increased. the voltage-effect and power-effect, decreased.

4. Increasing the effective area of the plates or electrodes decreases the current-efficiency, but increases the voltage and power -efficiency.

5. Ammonium-phosphate (C.P.) gives only a 30% power-effect

6. There is no choice between com'l and C.P. sodium bicar-

bonate; have used the same solution for three years.

8. Rectified currents give good results in electroplating, charging storage batteries, running motors, etc..

9. The rectifier put out by the C. S. Co., on the whole, has given good results and for laboratories not provided with D.C. should be of considerable value.

Bibliography

Theory of Electrolytic Rectifier

K. Nordon-Elect. World and Eng. '01

Wilson--Electrical Review 1898

Electrolytic Rectifier

Burgess and Hambuechen, Trans. Amer. Chem. Soc. '02.

Theory of Electrolytic Rectifier

Cook, Phys. Rev. '04

Aluminum Rectifier

Charters, Journal Phys. Chem. '05

Efficiency of Nordon Valve

Partridge Electrical Times '03

Grouping of Electrolytic Rectifier

Siemen Bros. & Co., Eng. '08

Electrification of Alt. Currents

Sebor & Simek Zeit. Elect. Chemie '07

Meters on Rectified Circuits

Paul McGahan, Elect. Journal '09

Elect. Rectifiers for Amateurs

Fred E. Word, Scientific Amer. '08'

Meters on Rectified Circuits

Yasudivo Sakai, Elect. Journal, '10.