CALIFORNIA INSTITUTE OF TECHNOLOGY.

SODIUM BY ELECTROLYSIS
THROUGH GLASS

A Thesis
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fulfillment of the requirements of
the degree of

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Department of Physics.

by

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SODIUM BY ELECTROLYSIS
THROUGH GLASS.

ABSTRACT.

For the electrolysis of sodium into glass containers from salts of sodium, I have developed a stable circuit which permits electrolysis to be carried on with currents as large as .3 amperes.

The purity of this sodium has been tested by spectral analysis of the ionized vapor in the bulb. Light from this ionization has been used to excite resonance radiation.

Some unexplained phenomena have been observed in the relation between electrolysis current and filament current. A similar relation has been noted in some photo-cells between voltage and photo-current. Potassium has been electrolyzed through special potash lime glass.

Photo-cells have been produced which show no change in total photo-current with change in temperature from 20° C. to -190° C., and then these cells have been contaminated with vapor. These contaminated surfaces show greater or less sensitivity at low temperature, depending upon the amount of contamination.

The electrolysis into light bulbs has been used as a voltameter and found to agree with themselves to 1 part in 3000.

The agreement between such voltameters and the silver voltameter improves with the care used in preparing the electrolyte for the silver voltameter. With most carefully prepared electrolyte the agreement is to 1 part in 2000, the silver always being heavier.

The silver voltameter when compared with a standard cell seems to run consistently heavy. The introduction of 1% of potassium nitrate does not interfere with the agreement between sodium voltameters.

A sodium cathode sodium voltameter has been developed which has no filament. This voltameter has a volume of about 12 c.c., a current carrying capacity of about .1 amperes, and is accurately reversible. Its resistance at various temperatures has been measured.

A high vacuum pendulum has been developed which has a life to half amplitude of about ten hours.

A complete Bibliography on the conductivity of glass is appended.

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INTRODUCTION.

The following work was the out-growth of a search for a source of electrons at low temperatures to be used in ionization potential work. I have not been primarily interested in the theory of electrical conduction through glass, but have merely used it as a means of obtaining sodium for various experiments. I shall, therefore, quote somewhat from a splendid paper by W. J. Sutton, and A. Silverman, (See Bibliography at end).

I have used this method of producing sodium for photo-electric work, for resonance radiation experiments, and also for the sodium voltameter, as explained in this paper.

HISTORICAL REVIEW.

Glass, which is ordinarily classed as an insulator, was shown by Buff to be a conductor at 100° C., as early as 1854. Warburg, in 1884, using 60 volts and mercury electrodes, passed current through a glass tube, and found the resistance of the glass increased rapidly to one thousand times its original value. He found sodium in the mercury cathode and a white, poorly conducting, layer in the glass at the anode surface.

Using a sodium amalgam anode, the resistance did not change nor the white layer form. Several investigators, including Warburg and Kraus, have shown that only the positive metal ions take part in the electrolysis which obeys Faraday's laws. Heydweiller, Kopferman, Kraus and Darby have electrolyzed glass, using molten salts as anodes. Lithium, Sodium, potassium, copper, zinc, lead, silver and others can be electrically driven into glass, but the introduction of anything but sodium into soda lime glass, results in glass which cracks after, if not before cooling.

Foussereau has shown that glass conducts better when tempered than when it is annealed and porcelain has been reported by Haber and others to act like glass at high temperatures and to obey Faraday's laws. Sutton and Silverman used a Vreeland oscillator and the improved method of Kohlrauch for determining the conductivity of molten glass, while Kraus and Darby have made measurements on the rate of migration of various ions through glass from molten salt electrodes, and J. A. Barth has described the electrolysis of glass into a bulb containing a hot cathode. Much light has been thrown upon the mechanism of this phenomenon by Joffé.

NEW EXPERIMENTS ON ELECTROLYSIS THROUGH GLASS.

E. Warburg electrolytically introduced sodium into Geissler tubes. At the international convention in Heidelberg in 1889 such tubes were shown. He describes a method of introducing sodium electrolytically through the glass in a gas discharge tube, but this method requires the use of a 1000 to 1200 volts direct current and is possible only in tubes containing gas.

With the advent of thermoionic discharge it became possible to adapt the method to the introduction of pure sodium into a very high vacuum at a rate as high as one-fourth gram metallic sodium per hour and without the use of high voltage. The use of the incandescent lamp bulb for this purpose was brought to my attention by Dr. A. W. Hull, who, I believe,was the first to use thermoionic emission to this end and whose suggestions I wish to acknowledge.

The simplest arrangement of this electrolysis is shown in Fig. 1. The most common material used in the manufacture of the vacuum-type incandescent lamp is a soda lime glass in which 80 percent of the sodium ions are mobile. The method is not limited to vacuum lamps, as the author has succeeded in putting as much as 1/2 gram of sodium through the wall of a gas-filled lamp of the kind known as 50 watt mill type. However, most of the gas-filled lamps

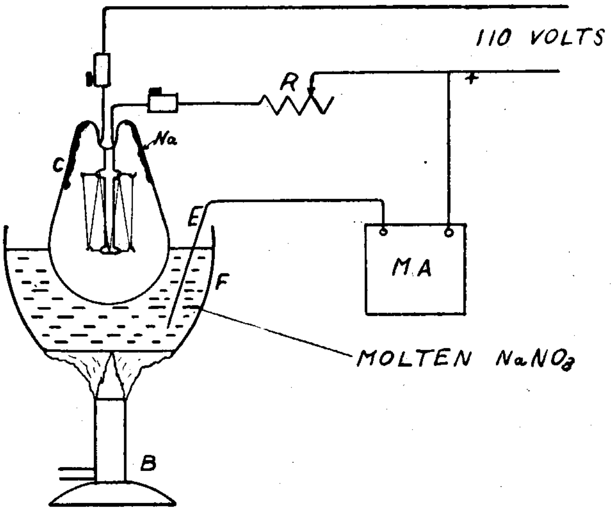


FIG. 1

are made of a glass such as pyrex, for instance, in which the sodium ion is not mobile.

Referring to Fig. 1., C is a common 40 or 60 watt metal-filament lamp from which the base has been removed by heating. The filament is lighted from a 110 volt source through a resistance R. The bulb is partly immersed in a bath of molten sodium nitrate which is kept molten in an iron crucible F by a Bunsen burner B. An electrode E, (a carbon rod or a heavy copper wire is satisfactory) is also introduced into the molten salt and connected to the positive wire of the 110 volt source through a milliameter MA or a lamp.

If now the resistance R be reduced until the filament of C begins to emit electrons, these electrons will be carried to the glass wall opposite the molten salt by the field. These electrons neutralize sodium ions in the glass which thus become atoms. These are evaporated by the heat at the bottom of the bulb, and condense at the top of the bulb where the glass is cooler. Sodium ions from the molten salt replace those of the glass and migrate through it, being in turn neutralized at the inner surface. In this way we are driving sodium electrolytically through the glass wall. NO_3 has been observed coming up from E.

Of course, any source of sodium ions might replace the molten nitrate. Warburg used 1/2 per cent sodium amalgam. However, as the mobility of the ion in the glass increases rapidly with increase in temperature, the nitrate which melts at 312° C, is very convenient. The temperature 312° C is well below the melting point of the glass and yet sufficiently high to allow a large electrolytic current to pass through the glass with a small potential drop in the glass. Alternating current can, of course, be used in place of direct in the arrangement of Fig. 1, for the filament itself acts as a rectifier.

The field in the case of Fig. 1, is due to the potential drop in R and in part of the filament and the objections to be urged against the simple connections of Fig. 1 are:-

(1) One end of the filament carries much more current than the other and becomes overheated, especially if the electrolytic current is as large as 0.1 ampere.

(2) If the entire bulb gets hot and so increases the pressure of sodium vapor, ionization is likely to start between the filament leads, burning them out and spoiling the cell.

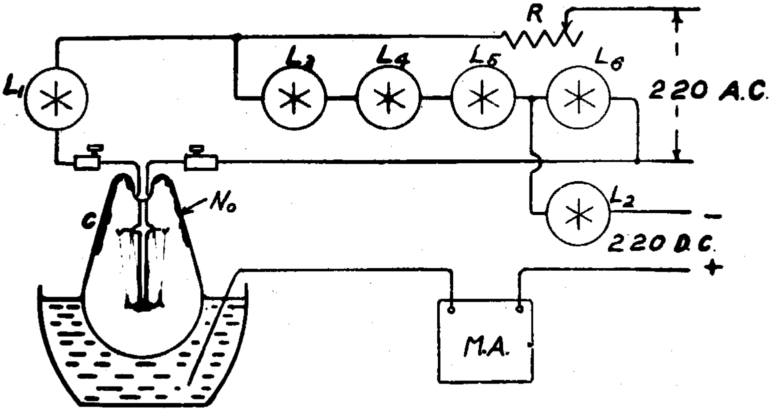


FIG. 2

To overcome these faults, I have used series resistances (lamp bulbs) to limit the ionization currents; also, I have applied the electrolytic field between the midpoint of the filament and the molten salt. This is accomplished by the arrangement shown in Fig. 2. The cell C is connected in series with a similar light bulb L_1 and both filaments are lighted by 220 volts A. C. through the resistance R. The resistance L_1 now prevents too large a current through C, thereby removing the second objection given above. To obtain the midpoint of the filament four light bulbs all alike, L_3, L_4, L_5, and L_6 are connected in series across the terminals of L_1 and C. The connection between L_5 and L_6 then is the potential of the middle of the filament in bulb C, and by applying the source of direct current to this point, local heating of the filament is greatly reduced. Other experimenters have written me about using wire resistances instead of lamp bulbs, but I prefer lamps because they automatically show any external connection between the direct and alternating current sources. A transformer with 220 volts secondary and 55 volt tap is also very satisfactory. L_2 like L_1, is a lamp used as a stabilizing resistance to prevent destructive ionization current between the filament and the glass wall. MA is again a current measuring device.

By the use of the connections of Fig. 2, currents as large as 0.3 amperes can be used, which results in a deposit of 257 milligrams of sodium in an hour, using a 60 watt 110 volt lamp.

Apparently potassium ions will not pass through the glass although one would expect them to replace the sodium easily. I have repeatedly tried using potassium nitrate instead of sodium nitrate around the bulb in order to get pure potassium into the bulb. The electrolytic current, at first comparable to that obtained with sodium nitrate, decreases in only a few minutes or even less, nearly to zero. If the voltage is maintained at a high value, a very small current will continue until the glass fractures. This break always occurs at a number of points in the plane of the interface between the air and molten nitrate, and the glass has the appearance of being etched all over the part in contact with the nitrate and is apparently strained. Thus it flies to pieces when put in a flame.

If the nitrate of lithium, a smaller ion than sodium, is used in place of sodium nitrate, the glass of the bulb in a few minutes closely resembles a white egg shell; it is very weak and will not hold a vacuum.

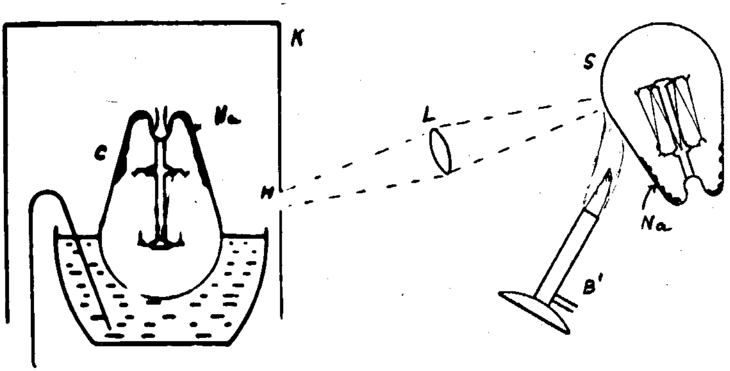


FIG. 3

A word of caution should be given on melting sodium nitrate. Because of its mechanical strength (after being once fused), and its large thermal expansion, a geyser will be formed if it is melted at the bottom first while the surface is encrusted. To avoid this, it is desirable to melt by placing the flame against the side of the crucible. Furthermore, no water should be allowed to drop into the molten salt because steam forms quickly and spatters the nitrate which burns rather badly.

This arrangement of apparatus is also good for a lecture room experiment. Light bulbs are familiar to all. The sodium appears to go through the glass very quickly, a deposit visible to everyone in a large room appearing in a few minutes.

Ionization within the bulb has been mentioned before. It may be increased by raising the temperature of the bulb, which is easily accomplished by putting a metal hood (K of Fig. 3), or an asbestos cone, over the bulb; the connections of Fig. 2, must be used for safety and stability. When the vapor pressure of the sodium is thus raised, the arc will become quite brilliant. The lines are, of course, very narrow on account of the low pressure of the sodium vapor at the highest temperature possible in soda glass.

The narrowness of the lines in this arc make it a useful source, particularly for resonance radiation studies. No reversals have been observed. Striking evidence of the purity of the sodium is obtained from spectroscopic examination of this arc. It shows sodium lines of the principal series and also many pairs of lines of the first and also of the second subordinate series, all very distinctly, and at the same time no trace of any other line even potassium. In all 18 lines can be seen in the visible with a direct vision spectroscope. With ionization strong enough to give such a sodium spectrum as this and no other lines at all, Dr. William R. Smythe, after observing it, tells me this is splendid evidence that potassium is not present as an impurity in quantities larger than one part in 500,000. It is worthy of note that all of the foregoing results were obtained without taking any precautions whatsoever to have pure sodium nitrate. The iron crucible was not cleaned, nor was the copper electrode, and the salt used was only commercially pure.

On account of the fact that the lines which are emitted by the glowing vapor are very narrow and are apparently unreversed, it occurred to Dr. E. H. Kurth that these bulbs might prove to be a particularly efficient and convenient source of radiation for resonance experiments. The arrangement which was employed here recently to demonstrate the resonance of sodium vapor in a large lecture room is shown in Fig. 3. Light coming from a small hole H, in the arc container was focused on a second bulb S, into which sodium had previously been electrolized. When this bulb was warmed by the burner B, the resonance radiation was evident at once as a strongly illuminated column along the path of the incident light.

As has been previously stated, potassium and lithium will not go through soda glass. With a special potash lime glass made by the Corning Glass Works, we did succeed in getting quite a deposit of potassium, perhaps 1/10 gram, and the arc in this gave six potassium lines as well as the D lines of sodium. The sodium may have been in the bulb before the electrolysis, as it was not especially cleaned prior to the electrolysis. Nothing more has been done with the electrolysis of potassium through glass, although it is contemplated to examine its photo-electric current at low temperatures.

If during an electrolysis the filament current is increased, Fig. 2, the bulb will suddenly show strong sodium ionization and the electrolysis current will increase 10 to 50 per cent. Graphically this is shown in Figure 4. The filament current at which this

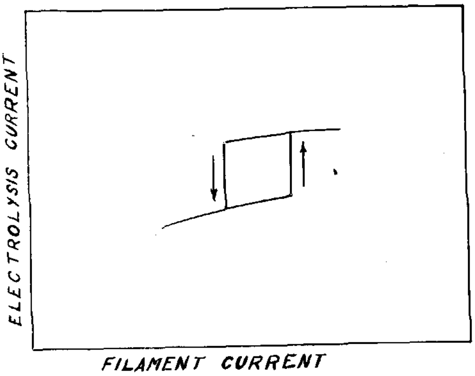
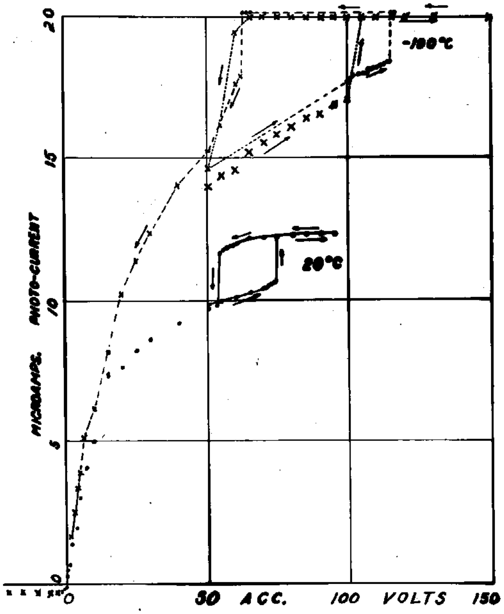


FIG 4



MICROAMPS. PHOTO-CURRENT
0
5
10
15
20
-190°C
20°C
0
50
ACC.
100
VOLTS
150

FIG. 5

occurs decreases if the entire bulb is heated so as to increase the pressure of the sodium vapor.

If the filament current is reduced, the ionization persists to a smaller value of filament current than that at which it started. Similar curves were obtained, Fig. 5, between applied voltage and photo-current, with some photo-cells not having the highest vacuum. The difference in the case of the photo-cells of the critical voltages going up and coming back was in various cases 9,20 and 53 volts. I am not prepared to offer any explanation of these phenomena.

CONSTANCY OF TOTAL PHOTO-CURRENT FROM SODIUM WITH TEMPERATURE CHANGE 20° C. to -190° C.

In order to obtain uncontaminated sodium surfaces, the cells used in this experiment were prepared by driving sodium electrolytically through the walls of a highly evacuated bulb. I have used molten sodium nitrate, which melts at 312° C. This is well below the baking-out temperature which had previously been maintained for more than 24 hours. At the temperature of 312° C, the sodium evaporates and condenses at the top inside of the bulb above the level of the hot surrounding sodium nitrate. However, it can be redistilled into the bottom when it is once inside. The filament when not lighted is used as a collector for the photo-electrons. By keeping it heated during the redistillation no sodium can condense upon it. During the redistillation the pressure of sodium vapor must not become too high else a sodium arc will form and burn out the filament.

It was found that the vacuum inside cells which had been sealed off the pumps was not sufficiently perfect to keep the sodium surface clean, even with the use of charcoal side tubes. The sodium in these sealed off photo-cells was exceedingly beautiful and extremely clear. Moreover, it did not turn the glass brown though redistilled from side to side many times. It also left no trace of residue upon the evaporation of a large drop. For this reason the results reported here were obtained with cells which were attached to the mercury pumps, although results similar to those given here on contaminated surfaces were obtained in cells which had been sealed off.

In the center of Fig. 6, is shown the cell which is connected through two liquid-air traps to two diffusion pumps. Light is incident from above on the sodium surface at the bottom of the bulb. With a constant potential (measured by a Weston model 45 voltameter) on the collector the total photocurrent is measured (by means of a Rawson unipivot milliameter.

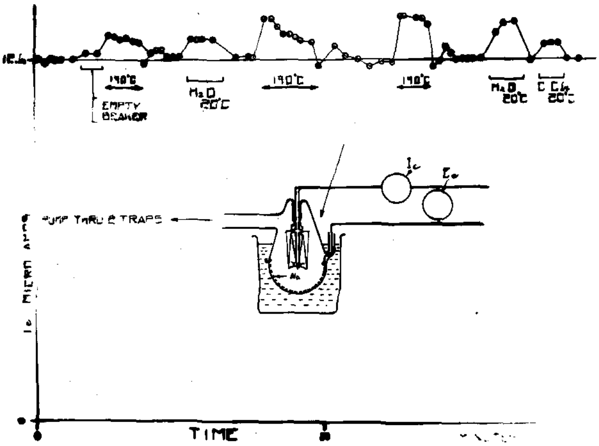

12.6
190°C
EMPTY BEAKER
H₂O 20°C
190°C
190°C
H₂O 20°C
CCl₄ 20°C
PUMP THRU 2 TRAPS
Ic
Ev
Na
Ic MICRO AMPS
TIME

FIG 8

type 501) while the illumination is held constant.

At the top of Fig. 6, have been plotted photo-currents against time. Under the influence of the light the photo-current was constant at 12.6 micro-amperes. But when the empty beaker was put in place about the cell there was a small increase in the current as shown and when liquid air was put in the beaker there was a greater increase. The photo-current decreased as the liquid air evaporated. When the air was removed, the current returned to 12.6, and when water was placed in the beaker, the current increased to the value shown in the second maximum. A full beaker of liquid air gave the third maximum, but the current returned to its original value when the air was removed; when again dipped in air, the fourth prominent maximum was obtained. With water at room temperature the next maximum was found. A beaker of carbon tetra-chloride raised about the cell gave the last maximum. The variation when the liquid air is removed is due probably to fog or mist in the air and on the glass immediately after the removal of the liquid air. The constancy of total current at $12,6 \times 10^{-6}$ ampere from this cell at room temperature over such a long period as that shown on the curve when the cell is subjected to such intense light as required to give this current is, I think, worthy of note. When surrounded by liquid the fluctuations are without any doubt due to scattered light effect of the photo-electric cell.

To test this more thoroughly, blackening the bulb with paint, lamp-black, and other things was tried. Cracked cells and cracked paint were the usual results, but finally a cell with the bottom wrapped in black paper gave the results shown in Fig. 7. The light used in this case was a 250 watt stereopticon lamp. Fig. 7, shows current plotted against time. The cell was at room temperature except for the time embraced by the double arrows. It will be seen from a glance at the points marked A that when the bulb was immersed in liquid air no appreciable change in the value of the photo-current resulted. This seems to show quite conclusively that if there is any temperature effect upon the photo-sensitiveness of sodium between liquid air and room temperature, it must be an extremely small one.

During the time-intervals indicated in Fig. 7, by I and II, two complete photo-current potential curves were taken. These curves are shown in Fig. 8, the dots representing the curve taken at

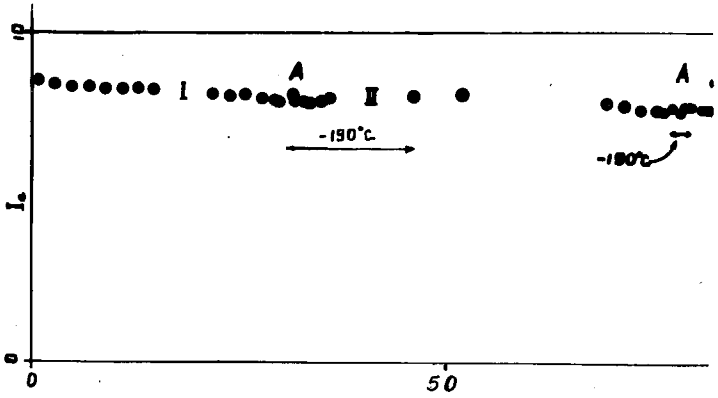


FIG 7

TABLE I.

Voltage	Photo-current Room Temp.	Photo-current at -190 C.
E_c	1_{20}	1 -190
50	8·25	8·20
40	7·80	7.82
30	7·35	7·44
25	7·10	7·26
20	6·80	6·95
15	6·37	6·21
10	5·10	5·20
9	4·70	4·84
8	4·38	4·40
7	3·97	3·99
6	3·52	3·56
5	3·06	3·10
4	2·60	2·62
3	2·07	2·10
2	1·48	
1	·38	.30
0	·20	·28

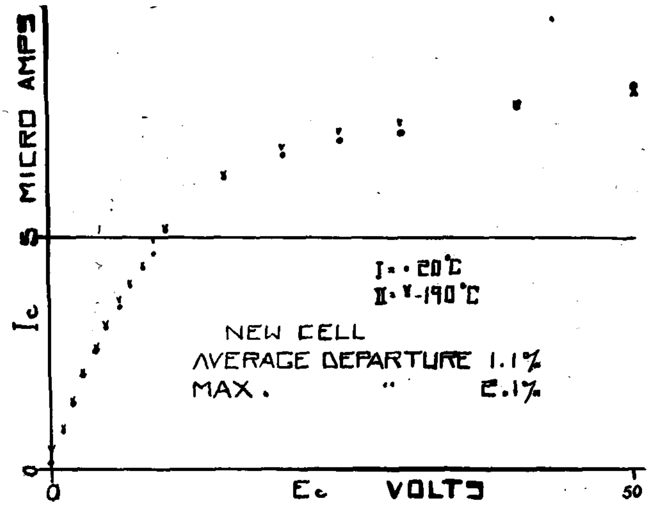

5 MICRO AMPS
I_c
5
0
0
E_c VOLTS
50
I = • 20°C
II = × -190°C
NEW CELL
AVERAGE DEPARTURE 1.1%
MAX. " 2.1%

FIG [illegible]

20° C. and the arrowheads that at -190° C. It will be seen that the two curves are everywhere practically coincident, though there are four points which show a systematic difference all in the same direction. The actual readings in the case of both curves are shown in Table I.

These observations are taken in the same way as those recently published by H. E. Ives, but fail to show any such variations with temperature as he found.

Fig. 9 is a continuation of the photo-current time curve begun in Fig. 7. At the time marked "Air off 2nd trap" the pump was disconnected from the system by a mercury cut-off close to the pump, and at the same time the liquid air was removed from that one of the two liquid-air traps in series which was nearest to the bulb and which had been cooled a considerable time after the first liquid-air trap had been functioning. The object of removing this liquid-air trap was to allow a very minute amount of impurity to flow back into the bulb. The effect of this impurity was observed instantly by an increase in current as shown by the arrow in Fig. 9, above the comment "Air off 2nd trap". A voltage-current curve was taken at III, and then the cell was cooled in

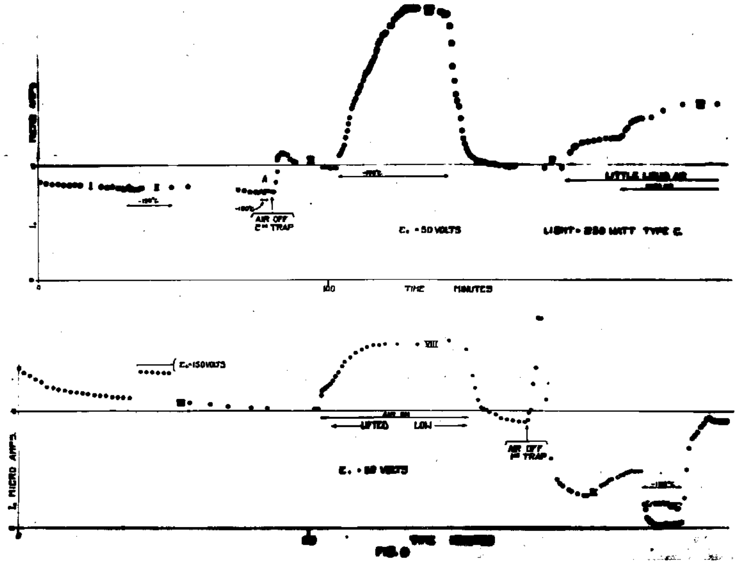

MICRO AMPS
I
II
-100°C
A
-100°C
AIR OFF
2nd TRAP
E₀ = 50 VOLTS
LIGHT = 250 WATT TYPE C
LITTLE LIQUID AIR
0
100
TIME MINUTES
E₀=150 VOLTS
III
VIII
AIR ON
LIFTED
LOW
AIR OFF
1st TRAP
I₀ MICRO AMPS
0

FIG. [illegible]

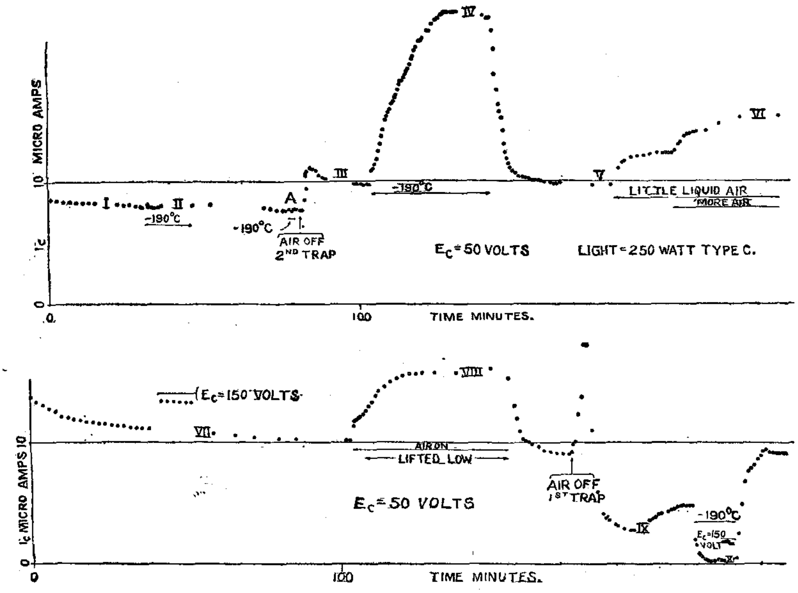

10 MICRO AMPS
ic
0
0
100
TIME MINUTES.
I
II
-190°C
-190°C
A
AIR OFF
2ND TRAP
III
IV
-190°C
V
VI
LITTLE LIQUID AIR
MORE AIR
Ec = 50 VOLTS
LIGHT = 250 WATT TYPE C.
Ec = 150 VOLTS
VII
VIII
AIR ON
LIFTED LOW
AIR OFF
1ST TRAP
IX
-190°C
Ec = 150 VOLT
X
Ec = 50 VOLTS
ic MICRO AMPS 10
0
0
100
TIME MINUTES.

Fig. 9.

liquid air and a large increase in total current occurred; another voltage-current curve was taken at IV. These last two are shown in Fig. 10. Liquid air was then removed and other similar curves were taken at V and VI, and they are plotted in Fig.11. The same current curve, taken the following day, is continued at the bottom of Fig. 9. Voltage-current curves were taken at VII and VIII, the first at room, the latter at liquid-air temperature. These last two curves are not reproduced since they were practically identical with V and VI.

At the point marked "Air off 1st trap", the liquid air was removed from the trap nearest the pump. This was the first trap to be cooled during evacuation and hence contained much more condensed vapor. With illumination and the collector voltage constant, the photo-current at first doubled, then dropped to about one-third its former value, as shown in Fig. 9. When it was believed constant at IX, another voltage-current curve was taken. Next it was cooled in liquid air, and this time a decided drop in the total current occurred. At X a voltage-current curve was again taken (Fig 12). Removal of the liquid air caused an increase in total current.

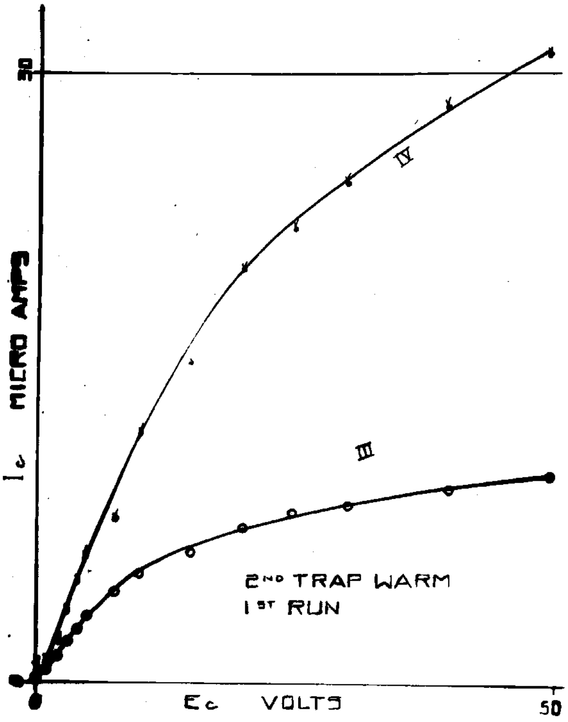


FIG. 10

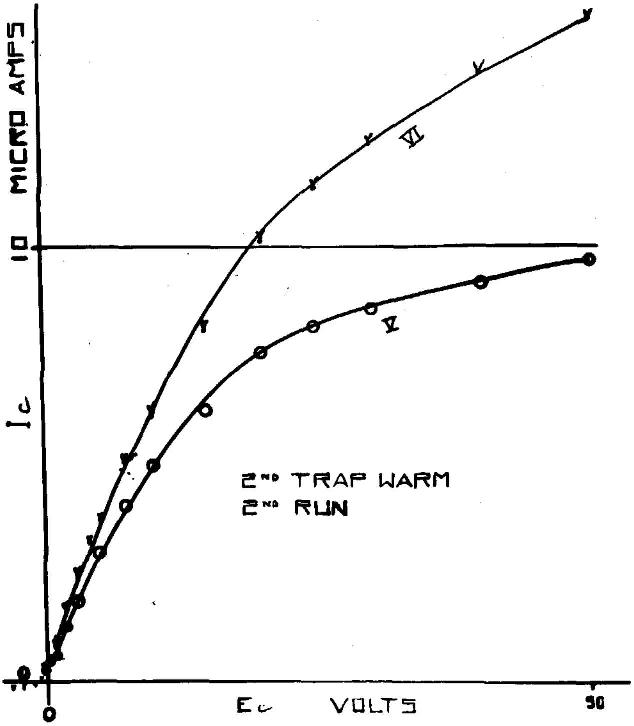


FIG 11

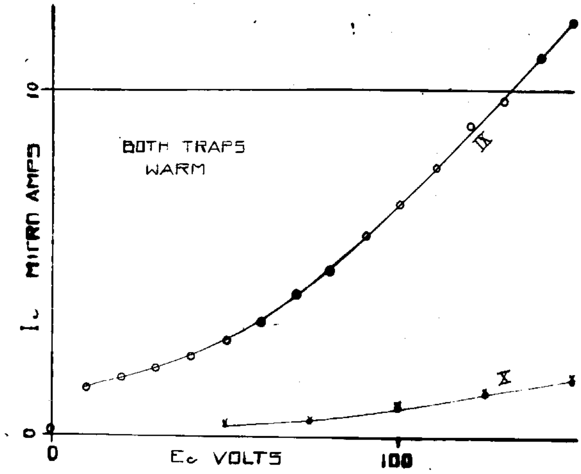


FIG 12

Further experimenting on this cell was prevented by a crack which developed at this point of the bulb.

The question as to whether there may be minute traces of impurities in the sodium within the bulb of the sort not dependent upon residual gases or vapours has no bearing upon the main conclusion which is drawn below. For the sake, however, of obtaining evidence as to the possible existence of impurities coming through or out of the glass the following tests were made:-

1. An effort was made to drive both potassium and lithium through this glass without any success whatever.

2. A bulb of this kind has been used as a sodium voltameter and the correct atomic weight of sodium to one part in 2000 was obtained. This limit of accuracy was set in this experiment simply by the uncertainty in the measurement of the quantity of electricity producing the deposit of sodium.

3. A sodium arc was formed in the bulb, and no trace of lines other than sodium obtained. The last test presumably means a purity of at least one part in 500,000.

Dr. Ives appears to find a temperature effect upon photo-currents from both sodium and potassium between these temperature limits. In the foregoing experiments it appears that when the utmost precautions are taken against contamination no temperature effect on photo emission from sodium is found. By contaminating the surface, however, both of the types of temperature effects which Dr. Ives obtains, namely, an increase in one case and a decrease in another, are found.

It is believed that the above evidence is convincing that: (1) The total photo-current of sodium is constant, within a few per cent at most, over a temperature range 20° C to -190° C., if the surface is sufficiently pure; (2) if the surface is just slightly contaminated, it may be much more sensitive at low temperature than at room temperature; and (3) if slightly more contaminated by some unknown vapour, the surface may be several times less sensitive at liquid air temperature than at room temperature.

That the change of total photo-electric current within the temperature limits noted should be less than 1 per cent for a pure surface is supported by some theoretical work of Dr. J. R. Nielsen in this labratory. This work has been submitted for publication in the Physical Review.

THE LIGHT BULB SODIUM VOLTAMETER.

About the first of October, 1924, it was decided to investigate how closely the electrolysis of sodium through glass follows the Faraday laws of electrolysis.

In the first sodium voltameter experiment, Fig. 2, one hour of electrolysis showed an increase in the weight of a bulb of 55.8 milligrams, while the theoretical gain from the time and current, as measured on a Weston type 280 millameter, was 55.55 milligrams. As no special precautions were taken to clean and dry the glass or to correct for bouyancy, this was considered a good check. A bulb was next cleaned and weighed, using a similar bulb on the other side of the balance to eliminate bouyancy. After being in the molten nitrate for three hours, its weight was found to be unchanged by more than 0.1 milligrams. Hence the glass dissolves little, if any, in the molten bath or cleaning.

I next made a run against a new Weston type 45 millammeter and a good watch, getting a deposit of .1594 grams of sodium against an indicated deposit of .15972 grams from the current and time. This is a check to .2 per cent which is as good as the meter.

An attempt to measure the electrolysis current accurately by a potentiometer failed because the current had small variations of 1 per cent probably due to the ionization before mentioned. Even though we suppress this ionization by keeping the top of the bulb cool and so reduce the pressure of sodium vapor, we still get a slightly varying current. An attempt to use 80 per cent sodium nitrate and 20 per cent of potassium nitrate resulted in a cracked bulb after about one hour.

An insulation transformer was obtained and tested for insulation leakage between secondary and ground. Its leakage current at 200 volts was found to be less than 10^{-6} amperes. The connections of Fig.13 were then used to check two sodium voltameters against each other. In this figure the circles represent light bulbs. The result of this was a gain in weight of

#1= .43297 grams
#2= .43284 "

<u>This is a check of one part in 3000 of one sodium voltameter against another.</u>

For the next experiment two silver voltameters were set up, designed as shown in Fig. 14. The cathodes were platinum cylinders of diameter 2.5 cm. and height 2.5 cm., weighing about 5.7 grams. The anodes were silver cylinders, diameter 6.5 cm., height 4 cm. These were about 1 mm. thick and were covered with silver by electrolysis to increase

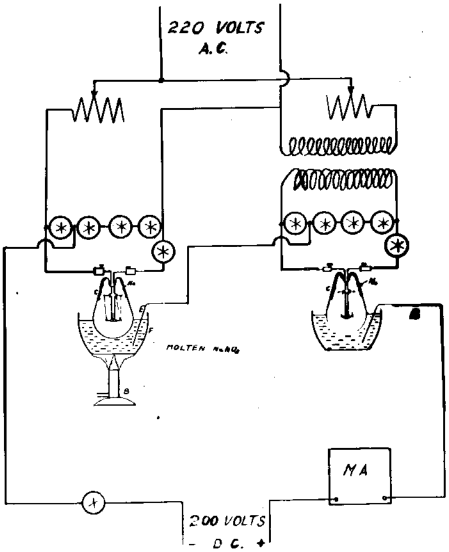


FIG. 13

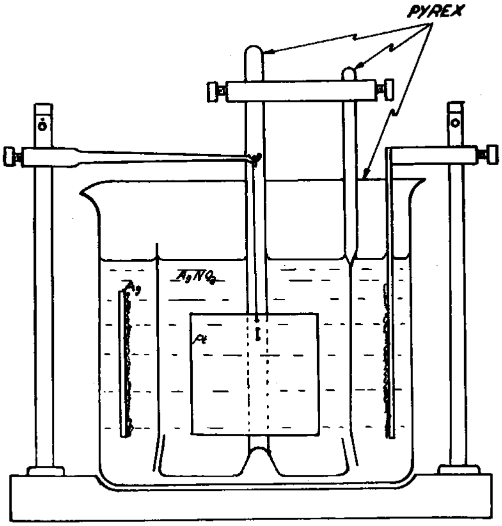


FIG. 14

their weight 50 per cent. The anode and cathode chambers were separated by a ground glass trap (shown closed) of pyrex and the beaker was also pyrex. The silver nitrate was crystallized and fused as described in the Bulletin of the Bureau of Standards, Vol. 13, and was tested for acidity using methyl red, (Ibid, Vol. 9). These two silver voltameters were connected in at B in Fig. 13. The two silver voltameters gave deposits of 1.94404 and 1.94405 grams respectively while the two sodium voltameters increased in weight .41332 and .41363 grams, respectively. This gives a silver equivalent of 1.93865 and 1.94010 grams respectively. This would indicate that the sodium voltameters were running light by 1 part in 400 or 500 and that the sodium voltameters checked each other to 1 part in 1200. However, we had in this run deliberately contaminated one of the nitrate baths by 1 per cent of potassium nitrate.

A Leeds and Northrup potentiometer, a certified standard cell, and a 19 jewel Hamilton watch (calibrated by radio time signals) were used to check the silver voltameters. The agreement between the two silver voltameters was about 1 in 20,000, but the agreement between theoretical and actual was about one part in 865, the silver voltameters being too heavy, which reduces the discrepancy in the preceding paragraph. It is to be noted that the silver voltameter is most apt to run heavy. Slight traces of acid, organic matter, or colloidal silver being sufficient to cause considerable deviation.

Next, a careful examination of the soluibility of the glass in various solutions was made. Five 40 watt lamp bulbs were weighed against a similar bulb and 5 gram weight as tare. The weights were placed on the pan under the bulb to be weighed, hence increase in balance weights means loss of weight to the bulb.

Bulb #2 was treated by being over half submerged in molten sodium nitrate containing 1 percent of potassium nitrate.

Bulb #3 was treated by submersion in distilled water.

Bulb #4 was treated by submersion in cleaning solution (H_2SO_4 and K_2CrO_3)

Bulb #5 was kept in a desiccator.

Bulb #6 was treated by half submersion in molten nitrate.

Bulb #2 was new, while all the others had had sodium electrolyzed into them. The results follow, omitting first three figures:

	#2	#3	#4	#5	#6
	5.76281	4.64902	2.88422	4.89150	3.91260
forty hours treatment	275	903	416		242
four days treatment	280	910	433	133	260
9 days treatment		908	420		255

This would indicate that the glass is soluble to a smaller extent than the accuracy of weighing would disclose. The analysis of standard lime bulb glass used in lamp manufacture as given to me by C. D. Spencer of the glass technology labratory of General Electric Company at Cleveland, was:-

SiO_2	72.75%
NaO	17.28
CaO	5.28
MgO	3.40
Al_2-O_3	1.11
Fe_2O_3	0.18

We may conclude that the light bulb sodium voltameter is precise to 1 part in 1,000, and is a most convenient instrument to set up and use. It will carry a current of .2 to .3 amperes but its resistance is somewhat variable.

THE SODIUM CATHODE SODIUM VOLTAMETER.

Work was now started on the development of a sodium voltameter without a filament, but using in its place a molten metal in contact with the glass. The type of bulb is shown is Fig. 15, The metal is introduced, the bulb is evacuated and sealed off with a lead wire running into the metal cathode in contact with the glass. Various metals were tried, Mercury - which boils making the current unsteady - Lead - which breaks the glass on cooling - 80 solder - which also breaks the glass on cooling - and

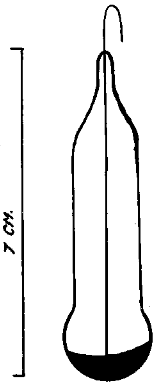


FIG. 15

metallic sodium which has finally been used inside the bulbs with good success.

One of these cells in series with two silver voltameters gave a deposit of 0.10 percent lighter than the equivalent silver deposit when the same electrolyte was used again. While the silver voltameters were consistent to 1 part in 27,000, it will be recalled that they formerly ran about .15 percent heavy against the standard cell which might indicate that the sodium voltameter was about .05 percent heavy. This, however, is about the accuracy of our weighing.

It has been found that these voltameters with metal cathodes can be more conveniently weighed and connected in series. Also the current through them is much steadier and can be measured by a potentiometer.

Because of the difficulty in obtaining sufficiently accurate time, I have developed a high vacuum pendulum, weighing about 40 grams and of 30 cm. length which has a life to half amplitude of about ten hours. When this development has been completed we should have an accurate source of time for an absolute determination of the atomic weight of sodium.

The sodium voltameter, with molten sodium inside, has been run backward. That is, I have electrolyzed the sodium out of the bulb instead of into it. We have run two sodium voltameters in series, one with sodium running into the bulb, the other with sodium running out. The result checked to 1 part in 1,000, which is about the experimental error of this run.

The next investigation was to vary the voltage across and read the current through one of the sodium cathode sodium voltameters like that shown in Fig. 15, at various temperatures. The results are plotted in Fig. 16. These lines might be called voltage current isotherms. From the conditions of the experiment it was difficult to keep the temperature exactly uniform. The variation probably did not exceed 3 degrees, however. I would not care to say whether Ohms law holds rigorously or not, but it is certain that there is an initial potential of 4 to 3 volts, depending upon the temperature, this voltage being due to the action of the cell as a primary voltaic cell. There seems to be a tendency for the current isotherms to bend down at the upper end. This may be due to local heating of the glass by the electrolysis current and its subsequent change of resistance. Derived

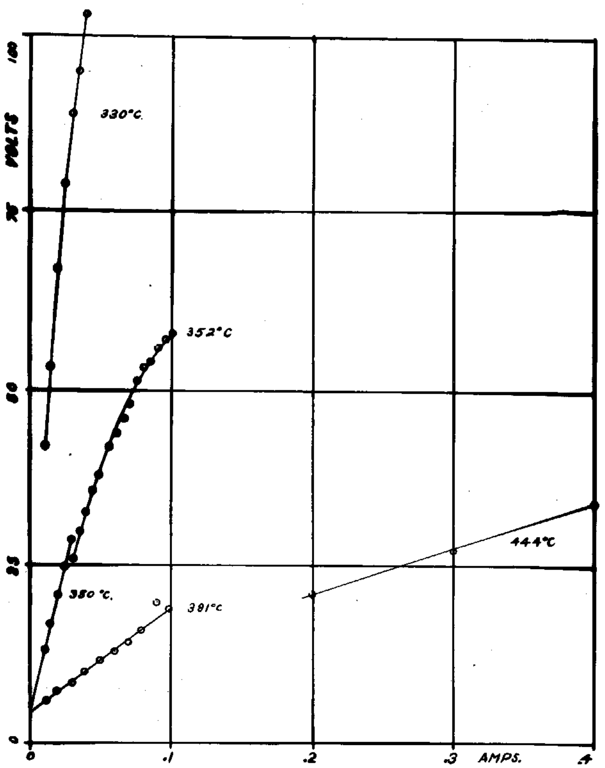


FIG.16

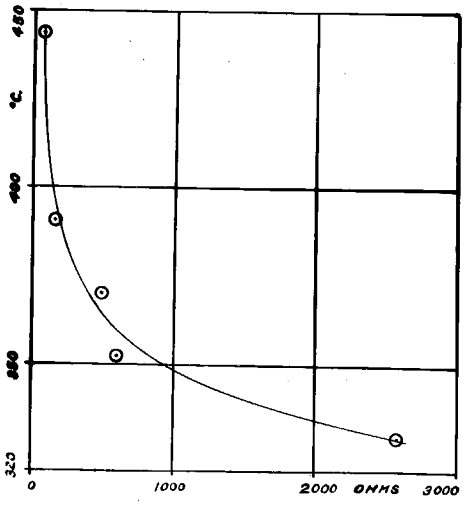


FIG.17

from Fig. 16, is the curve of Fig. 17, which shows, in a general way, the change of resistance with temperature. These measurements were not made precise as the conditions of the experiment would not warrant it.

We now come to the final test of the sodium voltameter. Fresh electrolyte for the silver voltameter shown in Fig. 14, was prepared from chemically pure silver nitrate. This nitrate was recrystallized and fused with all the ritual prescribed by the Bureau of Standards. Here I wish to extend my sincereest thanks to Drs. Raymond and Bates for their assistance in the matter. Conductivity water was prepared and used to dissolve the nitrate, 15 grams nitrate per 100 cc. of water. The prepared nitrate was tested with methyl red and found acid by about one part in two million.

Four sodium voltameters were set up in series with a silver voltameter with the results shown in Table 2. It will be seen that the maximum deviation from the average among the sodium voltameters was one part in 3,000. It will also be seen that the silver voltameter was heavier by 1 part in 2,000. The current for this run was about .04 amperes and the temperature of bath about 330° C. The atomic weights used in the conversion were Hg. 107.880 and Na 22.997.

TABLE 2.

		change of weight grams	equivalent sodium	
	silver voltameter	1.80535	.38485	
1.	sodium voltameter C. P. Sodium nitrate		.38464	average .38466
2.	Sodium voltameter Comm. Sodium nitrate		.38457	
3.	Sodium voltameter C. P. sodium nitrate 1% potassium nitrate		.38469	
4.	sodium voltameter sodium removed from bulb		.38479	

The electrolyte was not disturbed at the end of this run, the platinum cylinders were simply lifted out, washed in conductivity water and dried. The electrodes were next cleaned and returned and a new run started at .1 amperes, temperature about 380 C.

The silver deposits in equivalents of silver were .89210 and .89224 grams, while the sodium voltameters gave deposits of .89181 and .89120, the latter being from the $NaNo_3$ with 1 percent of KNO_3. These last agree to about 1 part in 1,500, while the silver voltameters are now heavier by about 1 part in 1,200 with this twice used electrolyte. The agreement between the silver voltameters in this last case is seen to be about 1 part in 6,000.

While much work remains to be done, I think from this work we may conclude:

1. The sodium voltameter is limited to currents of about 0.1 ampere where metal cathode is used, due to local heating and breaking of glass.

2. The sodium voltameter is known to agree with the silver voltameter to 1 part in 2,000.

3. Purity of electrolyte is of no importance to the sodium voltameter. Two of them in series, one using chemically pure $NaNO_3$, the other using crude commercial salt petre or $NaNO_3$ plus 1 percent of KNO_3 agree to within 1 part in 3,000, with deposits of only .4 grams.

4. No damage can be done to the sodium deposit after it has been electrolyzed through the glass bulb.

5. The small glass bulb into which we introduce the sodium is a very easy thing to clean, dry and weigh, both before and after electrolysis.

6. Large fluctuation and even reversal of the current make no difference to the sodium voltameter.

7. The glass used does not dissolve appreciably in the molten nitrate even after many days.

8. My difficulties with the silver voltameter for the past year have been so large that it seems easier now to make an absolute determination against a standard cell, standard time and potentiometer than to go on with the silver comparison.

9. Any freshman can run the sodium voltameter and the accuracy of his results will depend upon the care he exercises in determining the increase of weight of a small glass bulb.

10. No special equipment, chemicals, or technique are required to set up and operate the sodium voltameter.

11. The sodium voltameter has no specific tendency to run heavy as does the silver voltameter.

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