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A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

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Edwin W. Stevens

October 7, 1944

MONTANA SCHOOL OF MINES
BUTTE, MONTANA

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ABSTRACT

A method to measure hydrogen overvoltage was developed and checked with metals of known overvoltage. Alloys of bismuth and antimony and of bismuth and cadmium were prepared and their overvoltages determined. For alloys of bismuth and antimony it was found that the overvoltage of bismuth was greater than that of antimony, with a uniform decrease in the overvoltage of the alloy as its percentage of antimony increased. For the alloys of cadmium and bismuth it was found that the addition of a small amount of bismuth to cadmium decreased its overvoltage appreciably, while small additions of cadmium to bismuth raised its overvoltage considerably. Between these extremes, overvoltage varied almost linearly with the cadmium content. A relation does exist between the overvoltage of alloys and the constitutional diagram.

INTRODUCTION

Much time and effort have been spent on the study of hydrogen overvoltage, but, as yet, there is no general agreement as to the best methods to be used in measuring overvoltage, the terms used in discussing it, or even the fundamental reasons for the existence of such an effect.

The definition of overvoltage, as accepted throughout this work, is that overvoltage is the difference between the decomposition voltage as actually measured in a given cell and the theoretical decomposition voltage in that cell at the same conditions. Glasstone[1] makes this distinction concerning overvoltage: "The difference between the actual potential at which gas evolution commenced and the thermodynamically reversible value is called the minimum overvoltage." He also states, "The difference between the potential of an electrode at which hydrogen was being evolved by electrolysis at a definite current density (C.D)* and that of a reversible hydrogen electrode in the same solution is called the overvoltage." The definition of minimum overvoltage, as stated by Glasstone, is essentially the same as the definition of overvoltage accepted in this paper, while his definition of overvoltage itself corresponds to polarization voltage, as the term is here used.

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*Current-density, written C.D., is defined as current per unit area of electrode surface; it is generally expressed as amps. or milliamps, per sq. cm., or per sq. dm., or, in commercial work, as amps per sq. ft.

Polarization voltage, as the term is used in this paper, includes all departures of potential of the electrode from the equilibrium potential of that electrode, excluding IR drop, and is a measure of the irreversibility of the electrode process. The term equilibrium potential refers to the theoretical potential requirement, based on the free energy change of the electrode process. The polarization voltage thus includes overvoltage; it is never smaller than overvoltage, but can be larger. Throughout this work, it is considered that overvoltage is the voltage difference between the reversible (theoretical) potential requirement of the electrode process and the experimentally determined decomposition potential, the latter being the minimum potential actually required for continuous electrolysis. A graphical representation of this will be found in Figure 2. The minimum potential required for continuous electrolysis is called decomposition potential.

Creighton[2] states that, "The difference between the actual, observed voltage and the theoretical voltage is termed the polarization voltage," which agrees with the above definitions. However, Carmody and Rohn[3] measured the polarization voltage and called it overvoltage. Ferguson[4], in checking the direct and commutator methods of measuring overvoltages, measured the polarization and gave these results as the hydrogen overvoltage values at different current densities. The authors mentioned above have taken overvoltage and polarization as being the same, as Glasstone does in the second definition quoted above.

In the present research, a careful distinction is made between polarization and overvoltage.

In most publications dealing with overvoltage, the works of Newbery, written three decades ago, are quoted. Ferguson[4] has since concluded that the ordinary commutator method for overvoltages gives doubtful results. Unfortunately, Newbery's work on overvoltage was carried on by the use of this method, so that the data upon which much of the published work on overvoltage is based may be viewed with suspicion.

The method of observing the voltage at which bubbles of hydrogen first evolve at the electrode has been used by many other authors in the measuring of overvoltage. This is also the point at which current begins to flow freely. It, therefore, corresponds to the sudden rise in the current versus potential curve used in the present work to determine the overvoltages of bismuth-cadmium and bismuth-antimony alloys.

Considerable study of hydrogen overvoltage on alloys has been undertaken in recent years, but the results have, in general, been fragmentary and incomplete. Fisher[5] found that overvoltage on Cd-Pb, Cd-Sn, Sb-Zn, Sn-Pb, Sn-Zn, Ag-Cd, and Cu-Sn alloys, was independent of the composition and equal to that of the component with the lower overvoltage. He determined his values by the bubble method. Harkin and Adams[6] found that the overvoltage on monel metal was below that of its components. Onada[7] reported that Ag-Hg had a higher overvoltage than mercury, and that Pb-Hg and Sn-Hg had a lower value than mercury. Raeder and Brun[8] as well as Raeder and Efjiestad[9] determined the current density versus potential curves for Cu-Ni, Ag-Pb, Pb-Sb, Bi-Sn, Pb-Sn, Cu-Sn, Hg-Cd. For the Cu-Ni, they found a gradual change from overvoltage on copper to that on nickel without maxima or minima. They found a sharp maximum overvoltage for Ag-Pb, Pb-Sb, Bi-Sn, Pb-Sn, Cu-Sn, and a very flat minimum overvoltage for Hg-Cd. Thompson[10] studied brass and found overvoltage as a straight line relationship between pure copper and pure zinc except for decided minimum for epsilon-brass. This is the first sharp minimum ever found in alloys.

It seems that much of the confusion in the writings of former workers could have been eliminated if they had all interpreted overvoltage to mean the same thing. The chief difficulty is that one author measured overvoltage as it is defined in this paper, while another measured polarization and called it overvoltage. In the above work, apparently no consideration was given to the alloys in regard to whether they were completely soluble or insoluble in the solid state.

In spite of the confusion apparent in the results quoted above, it seemed possible that the hydrogen overvoltage of a binary alloy could be correlated with the constitutional diagram of its alloy system. Since alloy deposition by an electric current is becoming increasingly important in the field of metallurgy, this seemed a worth-while field for investigation.

THEORY

Although the phenomenon of overvoltage has been carefully studied, there is no agreement as to its cause or the mechanism of the hydrogen evolution in which it is evolved. The high negative potential of an electrode from which hydrogen is being evolved suggests the accumulation on its surface of an electromotively active substance, capable of exerting a back E.M.F. Therefore, it is necessary when studying the theory of overvoltage to account for this accumulation and to indicate the nature of the active material.

When a hydrogen ion is discharged at the cathode, the resulting hydrogen atom may: (a) remain as such, (b) unite with another hydrogen atom to form a molecule, or (c) unite with the electrode material to form a hydride. Regardless of the condition of the hydrogen, it must be removed from the electrode as fast as it is deposited by the current if deposition is to occur. The removal of this gas is possible in the following ways by: (a) gas diffusion into the electrode, (b) diffusion into the electrolyte, (c) chemical action (oxidizing agent present or by stirring to allow oxygen to enter from the air), (d) formation of gas bubbles. Only small residual currents flow through an electrolyte that has no depolarizer before the decomposition voltage is reached or before bubbles evolve. Therefore, the processes (a) and (b) could only account for the removal of small amounts of hydrogen from the cathode. Since there is no oxidizer present and only in special cases is overvoltage measured while the solution is being stirred, removal of the gas by chemical action can usually be ignored. This leaves (d), the formation of gas bubbles, as the important factor in overvoltage. Since the cathode potential does not increase greatly beyond the "break point" in the current-potential curve and since no noticeable accumulation of active material is observed after bubble formation commences, the actual mechanism of formation of gas bubbles is a factor for further consideration. If bubble formation occurs readily, the active material will not accumulate and overvoltage will be low. If, however, the active material does accumulate and bubble formation is slow, then the overvoltage will be high.

Glasstone[1] states: "The pressure of gas which must be attained in the electrode surface before bubbles can be evolved probably depends on the tension at three interfaces--electrode-gas, electrolyte-gas, and electrode-electrolyte; the first two oppose bubble formation, but the third aids the process." A decrease in the electrode-gas and electrolyte-gas tensions should lower the overvoltage; a decrease in the electrode-electrolyte tension should raise the overvoltage. "For a series of metals, the overvoltage varies in a manner parallel with the variation of angle of contact* between hydrogen bubbles and the metal in dilute sulphuric acid; this angle of contact is a function of the three interfacial tensions."[1] The measurement of this angle is successfully accomplished in flotation work.

---

* The angle of contact θ is given by the expression $Q_{1.2} \cos\theta = Q_{1.3} - Q_{2.3}$ where $Q_{1.2}$, $Q_{1.3}$, $Q_{2.3}$ represent electrode-electrolyte, electrode-gas and electrolyte-gas interfacial tensions, respectively.

Therefore, it is probable that overvoltage of hydrogen at a cathode is related to the ease with which gas bubbles are formed and the surface forces. The reduction of the surface forces may be partly responsible for the decrease of overvoltage on roughened electrodes.

If the accumulative active material on the electrode is molecular hydrogen, pressures of 10^{30} atmospheres[1] would be required to account for the high negative potentials of mercury and zinc. Glasstone[1] considers this improbable and, therefore, offers the following alternative theory. In his opinion, evolution of hydrogen at the cathode probable takes place in two stages, such as:

$$(1)\quad H^+ + e \rightarrow H$$

$$(2)\quad 2H \rightarrow H_2$$

$$(3)\quad H_2 \rightleftharpoons 2H^+ + 2e^-$$

Reaction (3) probable occurs in two steps, (1) and (2), and the reaction whose slowness causes overvoltage is (2). In these circumstances, there would be no appreciable evolution of hydrogen at the reversible potential, even if surface forces exerted no opposition.

Any retardation of the discharge of hydrogen ions to molecules would result in polarization. If equation (2) occurs slowly, the atomic hydrogen will accumulate at the cathode and the potential will be more negative than the reversible value because of the change in concentration of the electrolyte around the electrode. At one atmosphere pressure, atomic hydrogen would have a potential of about -1.9 volts in a normal solution of hydrogen ions. Therefore, it is not necessary to postulate high pressures in order to account for overvoltage of the order of one volt. Overvoltages do not exceed a value of 1.3 volts with a partial pressure of atomic hydrogen at the cathode much less than one atmosphere, according to Knobel, Caplan, and Eisman[12]. (Creighton[2] reported the overvoltage of gold at current densities of 1000 amperes per sq. cm. to be 1.63 volts. This, however, is apparently polarization voltage rather than overvoltage.)

If this concept of overvoltage is accepted, it is reasonable and helpful to assume that different metals have different catalytic influences on the reaction of equation No. 2. Metals with low overvoltage are, then, those which are the best catalysts, and those having high overvoltages are the poorest. Since a catalyst must effect both direct and reverse reactions to the same extent, metals of low overvoltage should catalyse the reverse reaction of equation No. 2. It is interesting to note in this connection that platinum and other low overvoltage metals are the best catalysts for hydrogenation purposes, in which the formation of atomic hydrogen is perhaps an intermediate stage[13]. "Hydrogen at ordinary temperatures is rather an inert substance, but in the presence of palladium or platinum black, it readily reduces a large number of substances. Furthermore, in every known case where hydrogen is produced by a reaction, the reaction is catalyzed by these metals."

To regard overvoltage as due to the accumulation of atomic hydrogen at the cathode is not unreasonable. The catalytic effect of the metal in the production of molecular from atomic hydrogen and the surface forces preventing bubble formation will control the amount of atomic hydrogen that accumulates. It is possible that equations (1) and (2) on Page 8 are catalyzed in a specific way, but it is easier to believe that in every case the metal catalyzes only the slow reaction, equation (2), and that this is also the explanation of the electrolytic reaction that we are considering. "Metals like mercury and lead on which the overvoltage is highest, that is, which are the poorest catalyzers of electrolytic reaction, have little influence on any of the reactions mentioned above."[2]

Another theory accepted by many authors is that the electrode absorbs electrified gas which leaves the surface supersaturated with non-electrified gas under high pressure. Likewise, cathodic overvoltage may be due to high single potential of metallic hydrides formed under similar conditions. These hydrides, as solid solutions, would generate back electromotive forces and would give high hydrogen overvoltages. The above theory is supported by the fact that when an antimony cathode is used in acid solutions, the hydrogen liberated contains stibine[2]; and when a carbon cathode is used, the hydrogen contains hydrocarbons. Considerable quantities of copper hydride sometimes form on the surface of copper cathodes.[2] If no hydride is formed, such as in the case of platinized platinum, the metal will act as a reversible electrode and give an overvoltage of zero. The above theory was presented by Newbery, but is not very widely accepted today.

A fairly recent theory has been presented by Eyring, Glasstone and Laidler[14]. This hypothesis is based on the theory of absolute reaction rates. The authors suggest that in an aqueous solution, a layer of water molecules becomes attached to the electrode and a corresponding adjacent layer is associated with the solvent. It is believed that the transfer of a proton from a molecule of water attached to the solvent to one on the electrode surface is a slow process, and, therefore, the cause of overvoltage. This theory is quite new and, as yet, has no general acceptance.

All of the theories mentioned above have been criticized. This, again, is probably due in part to the different interpretations many workers have given overvoltage. Chiefly, however, it indicates that the fundamental reasons for the phenomenon of overvoltage are not yet well understood.

THE CHOICE OF ALLOYS

The bismuth-antimony alloy series was chosen for investigation here because it is a good example of an alloy system showing complete solid solubility. Also, the melting points of antimony, 630 degrees Centigrade, and of bismuth, 271 degrees Centigrade, are sufficiently low for convenience in preparing alloys of these metals with the facilities available. Since both of these metals are in the same group in the periodic table, this also allowed determination of whether or not their overvoltages are the same, as some authors have stated to be generally true of any pair of metals in the same period[11].

The alloys of bismuth-cadmium were chosen for the second investigation because these metals are almost completely insoluble in the solid state, and it was desired to compare the curve of overvoltage versus percent composition for a completely soluble binary series with that of a series having complete insolubility in the solid state. Cadmium also has a low melting point, 321 degrees Centigrade; consequently, no difficulty would be anticipated in making up the alloys from the temperature required to melt the metals.

METHOD OF MAKING ALLOYS

Alloys of the following compositions were used in overvoltage determinations:

Bismuth-Antimony Alloy

Bi.%	100	90	80	70	60	50	40	30	20	10	0
Sb.%	0	10	20	30	40	50	60	70	80	90	100

Bismuth-Cadmium Alloy

Bi.%	100	90	80	70	60	50	40	30	20	15	10	5	0
Cd.%	0	10	20	30	40	50	60	70	80	85	90	95	100

Commercially pure metals were used in all cases. Each alloy composition was made up in the amount of 50 grams, the necessary amount of each of the pure metals being weighed on an analytical balance. Thus, to make an alloy such as 90 per cent bismuth, 10 per cent antimony, 45 grams of bismuth were carefully weighed and placed in a small fire clay crucible. Then 5 grams of antimony were weighed and added to it, and a charcoal cover was sprinkled on.

The fire clay crucibles containing this charge were placed in a gas-fired muffle furnace, one at a time. A careful watch was kept of each crucible, and when the alloy became liquid, it was thoroughly stirred with a carbon stirring rod. The crucible was withdrawn and its alloy charge cast into a small rectangular mold. These castings were allowed to cool and then placed in a paper bag with the percentage composition of the alloy plainly written on the bag to avoid possible mixups.

The mold used for casting cathodes was made of steel, rectangular in shape, and horizontal in position. Each ingot was about four inches long, one-half inch wide, and three-sixteenths inch thick. For use as electrodes, these ingots were polished on one side, finishing with a #0 polishing paper.

The final step in the preparation of the electrodes was to coat the back and sides with "Picein 105."* The polished surface was then again cleaned on the #0 paper; the electrodes, at this point, were ready for use. Approximately 2½ square inches of the electrode surface was left exposed. (The "Picein 105" was used so that a certain definite area of the cathode would be exposed in the electrolyte. This made it possible to arrange the cathode in such a manner that the exposed surface was facing the anode, thereby eliminating the difference in overvoltage found between the side of the cathode facing the anode and the one farthest away from the anode.)

In the melting of these metals, although a careful watch was kept to minimize volatilization, it was noticed that some small amounts of the metals did volatilize from the crucible. Thus, any alloy may be slightly richer in one or the other of the components than the nominal composition indicates. This discrepancy was not checked by

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* "Picein 105"

A cement developed for the purpose of rendering apparatus used in chemical and physical laboratories gas tight and water tight. It can also be used for an insulating purpose. Melting point is 221 degrees F.

Prepared by
New York Hamburgor Gummi-Waaren Compagnie, Hamburg, Germany.
Sole Distributing Agents for U. S. A. and Canada: Schrader & Ehlers, 239 Fourth Avenue, New York, N. Y.

chemical analysis, and, therefore, will probably lead to a slight error in the overvoltages herein presented. The error will not exceed 0.005 volts in any case.

All alloys were used in the cast conditions; no attempt was made to control the grain size or structure of the ingot. The metal was poured into an ingot mold and allowed to remain in the mold until it had solidified, at which time it was removed and allowed to cool to room temperature. Substantially similar structures would be expected in all alloys of a given series so prepared. However, the size of the grains in the alloys may have some small effect on the accuracy of the overvoltage results presented in this paper.

Diagrams

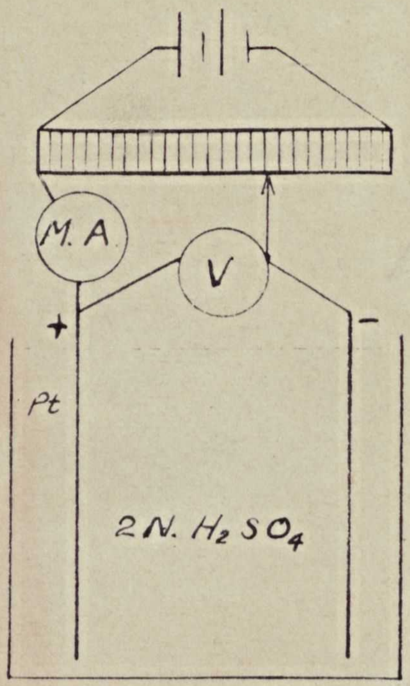


Fig. 1

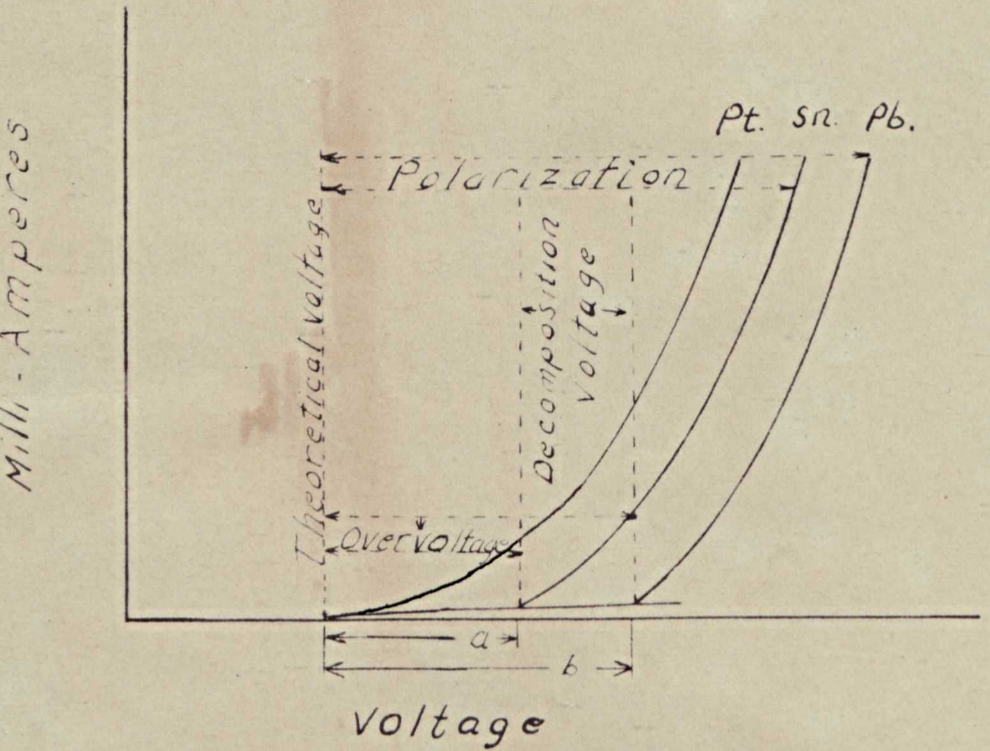


Fig. 2

METHOD USED IN MEASURING OVERVOLTAGE

<u>APPARATUS</u> (refer to diagrams, Figure 1.)

M.A.	Milliammeter (Model 1) Weston direct current milliammeter. Built by Western Electrical Instrument Co., Newark, New Jersey, U. S. A.
V.	Voltmeter Weston Voltmeter, Model 280. Res. 300 ohm. Built by Western Electrical Instrument Co., Newark, New Jersey, U. S. A.
R.	Resistance (slide wire) 920 ohms. 0.6 amps. Beck Brothers, Philadelphia, Pennsylvania
E.	Batteries (3V.) Glass-cased lead storage cells.
Pt.	Platinum Electrodes
+	Anode
-	Cathode

Electrolyte 2n H_2SO_4 in all cases

PRINCIPLE

The method used was first to determine the milliampere-voltage curve, using platinum electrodes. This was done by taking a series of simultaneous milliammeter and voltmeter readings at different settings on the variable resistance. In this way, a curve of voltage versus current, in milliamperes, is determined for platinum in 2n H_2SO_4 solution. The point at which the curve breaks and starts to rapidly ascend is the decomposition voltage as shown in Figure 2. The determination of this point was made by lining as many experimental points as possible in the early part of the curve along a straight edge and drawing a straight line through them. This line was extended beyond the curve, as shown in the following graphs, and was helpful in determining the exact point where the curve started to break upward. The above method proved quite simple and was an easy method of locating the point at which decomposition voltage occurred.

Since platinum has no hydrogen overvoltage, it can then be used as a reference electrode by substituting various metals for the platinum cathode, deriving similar curves for these metals as shown in Figure 2, and so determining the actual decomposition voltage of water in each case. (The actual curves for metals shown in Figure 2 will be found on Page 25 of the graphs.) The difference between the decomposition voltage so determined and the decomposition voltage when platinum is used, as determined from these curves, is the overvoltage on the metal in question. The decomposition voltage for platinum was found to be 1.67 volts. For each metal and alloy substituted for the platinum cathode, a decomposition voltage was determined from the graphs on the following pages. From this decomposition voltage, the value, 1.67 volts, was subtracted; the difference is the hydrogen overvoltage for that particular metal. For example, (a) on Figure 2 would be the overvoltage of tin, and (b) the overvoltage of lead.

Equipment required for application of this method was first set up using a Weston milliammeter, Model 280. The scale on this instrument was so high that in the low range of milliammeter readings used, high accuracy was found to be impossible. This difficulty was overcome when the Weston direct current milliammeter, Model 1, was used.

Some trouble arose in the early part of the experimental work, due to improper wiring. The first setup was made with the milliammeter and variable resistance electrically in series with the cell. Under these conditions, first readings were taken using 1.5 volts applied E.M.F. and a low ohmic resistance. Resistance was diminished as readings were taken, until, in order to get above the break in the curve, it was necessary to increase the applied E.M.F. to 3 volts. Then, when the slide wire was adjusted to give the previous milliammeter reading, the voltmeter reading was not the same as had been previously read with the lower external E.M.F. Investigation showed that this was due to the comparatively low resistance of the voltmeter used. With the parallel circuit, shown in Figure 1, this difficulty was eliminated.

In order to check this method of measuring overvoltage against the results of previous investigators, several pure metals, whose overvoltages are known, were used as cathodes in preliminary runs. The results obtained from these metals are shown on Page 1 of the graphs. The overvoltages determined are shown in comparison with those given in Glasstone[1] for the same metals on Page 23 of this paper.

Due to the source of error illustrated by the calculations on Page 22, the experimental values for overvoltages, on Page 23, are slightly lower than the true values. The reason for this is that the milliammeter reading was made with the voltmeter circuit open, then the voltmeter reading was made by closing the switch on the voltmeter circuit. This reading was assumed to be the true voltage at the time that the current was read. However, with readings taken in this manner, the conductance of the voltmeter was not taken into consideration. This resulted in a voltage reading lower than the true value, as is shown by the calculations on Page 22. If a potentiometer were substituted for the voltmeter in Figure 2, this error would be eliminated. However, the overvoltages on Page 23 agreed quite closely with those of roughened electrodes of the same metals, which Glasstone[1] admitted were probably lower than the values for an average electrode; and, since this error should have been quite consistent throughout, its effect on overvoltage values is neglected.

Other methods used to measure overvoltage and polarization are:

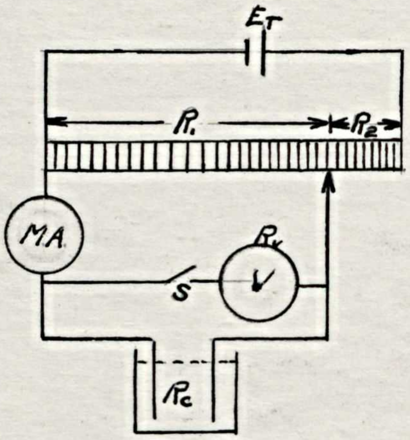
The "direct" method of measuring overvoltage consists of measuring the electrode potential while the current is flowing by pressing the end of a capillary tube against the electrode in question. This method is objected to since the tube interrupts the flow of the atoms and diverts them from the end of the capillary tube where the overvoltage is being measured. There is also ohmic resistance between the end of the capillary tube and the electrode if the tube is not tightly pressed against the electrode.

The commutator method, which was used by Newbery, was shown by Ferguson[4] to give erroneous results. The objection to this method of measuring overvoltage is that the current is shut off momentarily (for about 0.01 sec.) while the potential of the electrode is determined. This period during which the current is shut off will allow the potential to drop, thus giving results which are too low.

The method of measuring overvoltage whereby the bubbles are observed as they are discharged from the cathode was also considered. This method is slow and required very careful adjustment in order to arrive at the particular voltage where only one bubble is evolved every two minutes.

Of the three methods just described, the bubble method is the least objectionable. In using the current potential curve method for determining the decomposition voltage, the bubble method was useful in determining the approximate potential at which the curve began to rise. However, for simplicity, and at least indicative results, the determination of overvoltage from the graph of voltage versus current, with the desired metal as cathode, was here primarily relied upon.

SOURCE OF ERROR IN METHOD OF MEASURING OVERVOLTAGE



E_t = Total voltage = 3 V.

R_1 = Resistance in parallel portion of coil = 600 ohms (assumed)

R_2 = Resist. in series portion of coil

R_t = Total resist. of coil = 920 ohms.

R_c = Resist. in cell = 75 ohms (assumed)

R_v = Resist. of voltmeter = 300 ohms.

R_p = Resist. of the parallel circuit

E_p = Voltage across the parallel circuit

E_{r_2} = Voltage across R_2

With switch (S) open

$R_2 = 920-600 = 320$ ohms.

$$\frac{1}{R_p} = \frac{1}{R_1} + \frac{1}{R_c} = \frac{1}{600} + \frac{1}{75} = \frac{9}{600}$$

$$R_p = \frac{600}{9} = 66.67 \text{ ohms}$$

$$\frac{E_p}{E_{r_2}} = \frac{E_p}{3-E_p} = \frac{R_p}{R_2} \quad \text{therefore} \quad \frac{E_p}{3-E_p} = \frac{66.67}{320} \quad \text{and}$$

$$320E_p = 200.01-66.67E_p \quad \text{then} \quad E_p = \frac{200.01}{386.67} = 0.517 \text{ Volts.}$$

Therefore, 0.517 V. equals actual voltage across cell when current is read.

With switch closed:

$$\frac{1}{R_p} = \frac{1}{600} + \frac{1}{300} + \frac{1}{75} = \frac{11}{600} \quad \text{then} \quad R_p = \frac{600}{11} = 54.54 \text{ ohms.}$$

$$\frac{E_p}{E_{r_2}} = \frac{E_p}{3-E_p} = \frac{54.54}{320} \quad \text{then} \quad E_p = \frac{163.62}{374.54} = 0.437 \text{ V.}$$

then, 0.437 V. apparent voltage reading, as actually taken. 0.517 - 0.437 0.080 volts. Therefore, 0.080 V. is the difference between the true voltage and the voltage as read. While an appreciable error, this should be a quite consistent one, and, therefore, should approximately be cancelled when voltage readings for platinum are subtracted from voltage readings for the base metals in determining overvoltages.

RESULTS OBTAINED
(Data & Curves, pp. 24-31)

Overvoltage of pure metals in 2n H_2SO_4 solution: polished electrodes
(area of anode exposed to electrolyte was 8 sq. cm.)
(area of cathode exposed to electrolyte was 4 sq. cm.)

Metal	Observed Overvoltages	Minimum Overvoltages (Glasstone)
Pt.	0.00 (assumed P)	0.000
Sn.	0.23	0.19
Ni.	0.14	0.137
Pb.	0.40	0.40
Cu.	0.19	0.19

ANTIMONY BISMUTH ALLOY

Overvoltages of alloys in 2n H_2SO_4 solution: polished electrodes

Alloy % Sb.	% Bi.	Overvoltage Observed
0	100	0.40
10	90	0.38
20	80	0.36
30	70	0.34
40	60	0.32
50	50	0.30
60	40	0.28
70	30	0.26
80	20	0.24
90	10	0.22
100	0	0.20

CADMIUM BISMUTH ALLOY

Overvoltages of alloys in 2n H_2SO_4 solution: polished electrodes

Alloy % Cd.	%Bi.	Overvoltage Observed
0	100	0.40
10	90	0.46
20	80	0.50
30	70	0.51
40	60	0.52
50	50	0.53
60	40	0.54
70	30	0.55
80	20	0.56
85	15	0.57
90	10	0.58
95	5	0.59
100	0	0.72

DATA

COMMERCIALLY PURE METAL CATHODES USED IN CHECKING METHOD OF MEASURING OVERVOLTAGE.

Pt.

M.A.	V.
0.0	0.60
1.0	0.66
1.1	0.95
1.2	1.05
1.3	1.12
1.4	1.15
1.5	1.20
1.9	1.30
2.1	1.40
2.5	1.50
2.9	1.61
3.0	1.66
3.2	1.71
3.4	1.72
4.2	1.80
4.6	1.87
5.6	1.94
7.2	1.99
10.8	2.05

Sn.

M.A.	V.
0.0	0.80
2.0	1.00
2.3	1.10
2.7	1.20
3.0	1.30
3.3	1.40
3.6	1.50
3.9	1.60
4.3	1.70
4.6	1.80
4.9	1.85
5.0	1.90
5.2	1.95
5.9	2.00
6.2	2.10
6.5	2.20
7.3	2.30
8.3	2.40
10.2	2.50
14.7	2.60
25.5	2.70

Ni.

M.A.	V.
0.0	0.50
2.0	0.84
2.5	1.00
3.0	1.10
3.2	1.20
3.5	1.30
4.0	1.40
4.3	1.50
4.9	1.60
5.0	1.65
5.2	1.70
5.3	1.75
5.8	1.80
6.0	1.85
6.2	1.90
6.8	1.95
7.0	2.00
7.8	2.05
8.2	2.10
9.5	2.15
11.1	2.20
19.2	2.30

Pb.

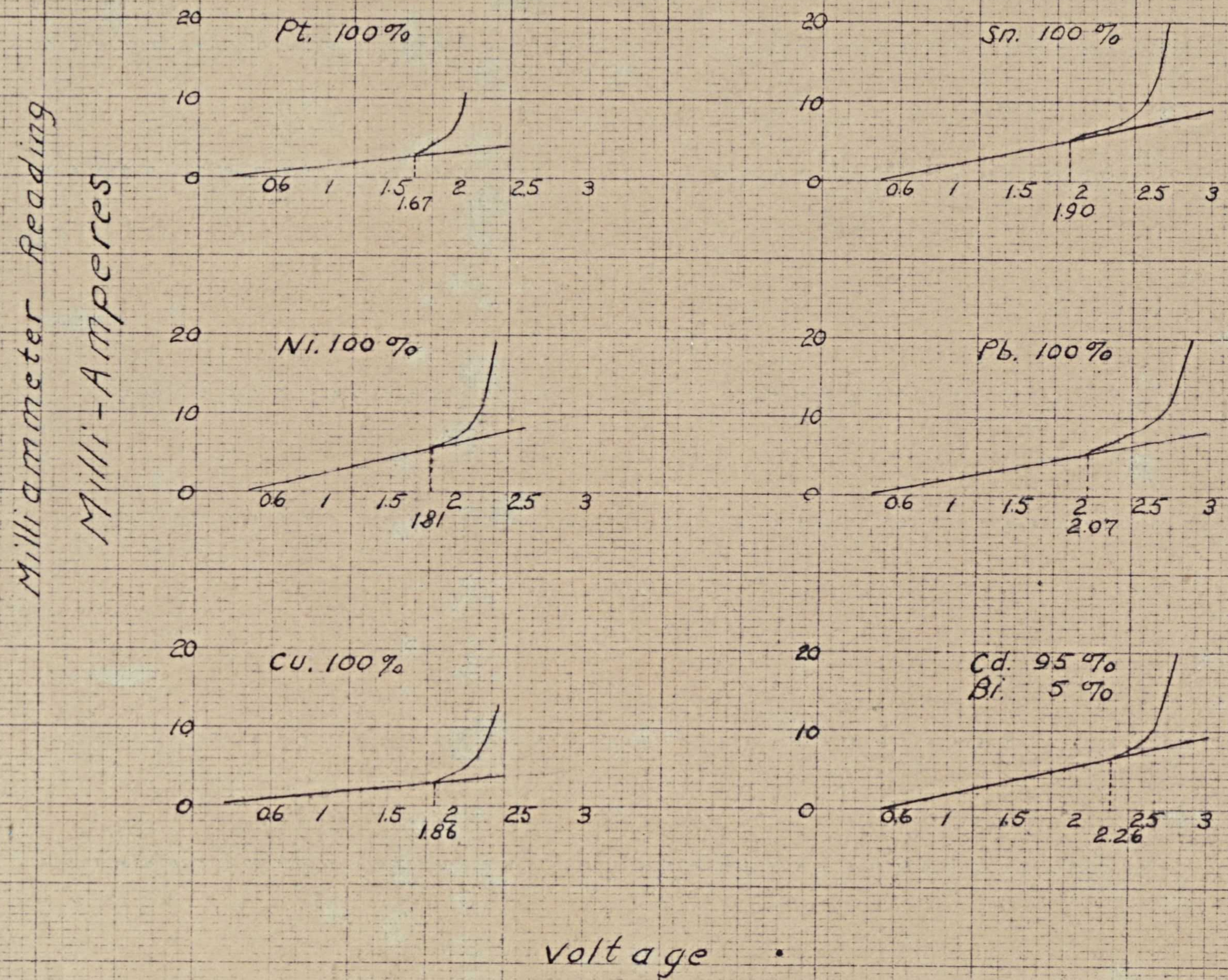
M.A.	V.
2.5	1.10
3.0	1.20
3.1	1.30
3.2	1.40
3.5	1.50
4.0	1.60
4.1	1.70
4.4	1.80
4.9	1.90
5.0	1.95
5.1	2.00
5.5	2.05
6.0	2.10
6.9	2.20
7.2	2.30
8.0	2.40
8.9	2.50
10.0	2.60
11.9	2.70

Cu.

M.A.	V.
0.0	0.44
1.0	0.62
1.2	0.80
1.25	1.04
1.4	1.10
1.7	1.20
1.9	1.30
2.0	1.50
2.1	1.60
2.5	1.70
2.9	1.80
3.2	1.90
4.0	2.00
5.0	2.10
7.4	2.20
12.8	2.30
40.0	2.40

Bi. 5% Cd. 95%

M.A.	V.
0.0	0.50
2.0	1.23
3.0	1.30
3.5	1.45
4.0	1.60
4.5	1.80
5.0	1.90
5.5	2.05
6.0	2.15
6.5	2.25
7.0	2.32
7.5	2.39
8.0	2.44
8.5	2.48
9.0	2.51
9.5	2.55
10.0	2.58
20.0	2.76


Milliammeter Reading
Milli-Amperes
Pt. 100%
20
10
0
0.6
1
1.5
1.67
2
2.5
3
Sn. 100%
20
10
0
0.6
1
1.5
2
1.90
2.5
3
Ni. 100%
20
10
0
0.6
1
1.5
181
2
2.5
3
Pb. 100%
20
10
0
0.6
1
1.5
2
2.07
2.5
3
Cu. 100%
20
10
0
0.6
1
1.5
1.86
2
2.5
3
Cd. 95%
Bi. 5%
20
10
0
0.6
1
1.5
2
2.26
2.5
3
Voltage

DATA

CADMIUM BISMUTH ALLOY

100% Bi. 0% Cd.

M.A.	V.
0.0	0.05
2.5	1.10
3.0	1.45
4.0	1.60
5.0	1.90
5.0	1.95
5.0	2.00
5.2	2.05
6.0	2.10
7.0	2.30
8.0	2.45
9.0	2.52
15.0	2.70
25.0	2.80

90% Bi. 10% Cd.

M.A.	V.
0.0	0.50
2.5	1.25
3.0	1.35
3.5	1.45
4.0	1.60
4.5	1.75
5.0	1.90
5.5	2.05
6.0	2.15
6.5	2.25
7.0	2.30
7.5	2.35
8.0	2.40
8.5	2.45
9.0	2.50
9.5	2.52
11.0	2.57
12.0	2.61
20.0	2.74

80% Bi. 20% Cd.

M.A.	V.
0.0	0.50
2.0	1.20
2.5	1.25
3.0	1.30
3.5	1.45
4.0	1.55
4.5	1.62
5.0	1.90
5.5	2.04
6.0	2.15
6.5	2.21
7.0	2.27
7.5	2.32
8.0	2.35
8.5	2.38
9.0	2.41
9.5	2.45
10.0	2.47
20.0	2.65

70% Bi. 30% Cd.

M.A.	V.
0.0	0.50
2.0	1.20
2.5	.
3.0	1.25
3.5	1.45
4.0	1.55
4.5	1.62
5.0	1.82
5.5	2.02
6.0	2.10
6.5	2.22
7.0	2.28
7.5	2.32
8.0	2.35
8.5	2.40
9.0	2.45
9.5	2.48
10.0	2.50
20.0	2.05

60% Bi. 40% Cd.

M.A.	V.
0.0	0.50
2.5	1.25
3.0	1.35
3.5	1.45
4.0	1.55
4.5	1.75
5.0	1.85
5.5	2.02
6.0	2.14
6.5	2.24
7.0	2.30
7.5	2.35
8.0	2.40
8.5	2.45
9.0	2.50
9.5	2.53
10.0	2.54
20.0	2.72

50% Bi. 50% Cd.

M.A.	V.
0.0	0.50
2.5	1.22
3.0	1.30
3.5	1.46
4.0	1.57
4.5	1.76
5.0	1.86
5.5	2.04
6.0	2.12
6.5	2.22
7.0	2.30
7.5	2.35
8.0	2.40
8.5	2.45
9.0	2.49
9.5	2.51
10.0	2.54
15.0	2.66
30.0	2.80

DATA

CADMIUM BISMUTH ALLOY

40% Bi. 60% Cd.

M.A.	V.
0.0	0.50
2.5	1.25
3.0	1.26
3.5	1.44
4.0	1.55
4.5	1.80
5.0	1.96
5.5	2.09
6.0	2.15
6.5	2.25
7.0	2.35
7.5	2.40
8.0	2.45
8.5	2.50
9.0	2.55
9.5	2.60
10.0	2.62
12.0	2.69
15.0	2.75
30.0	2.88

30%Bi. 70% Cd.

M.A.	V.
0.0	0.50
2.0	1.20
2.5	1.24
3.0	1.30
8.5	1.48
4.0	1.57
4.5	1.76
5.0	1.90
5.5	2.06
6.0	2.15
6.5	2.25
7.0	2.32
8.0	2.40
9.0	2.50
10.0	2.54
15.0	2.65
30.0	2.80

20% Bi. 80% Cd.

M.A.	V.
0.0	0.50
2.5	1.25
3.0	1.30
3.5	1.45
4.0	1.60
4.5	1.75
5.0	1.90
5.5	2.07
6.0	2.19
6.5	2.25
7.0	2.32
7.5	2.40
8.0	2.45
8.5	2.47
9.0	2.50
9.5	2.53
10.0	2.56
20.0	2.75

15% Bi. 85% Cd.

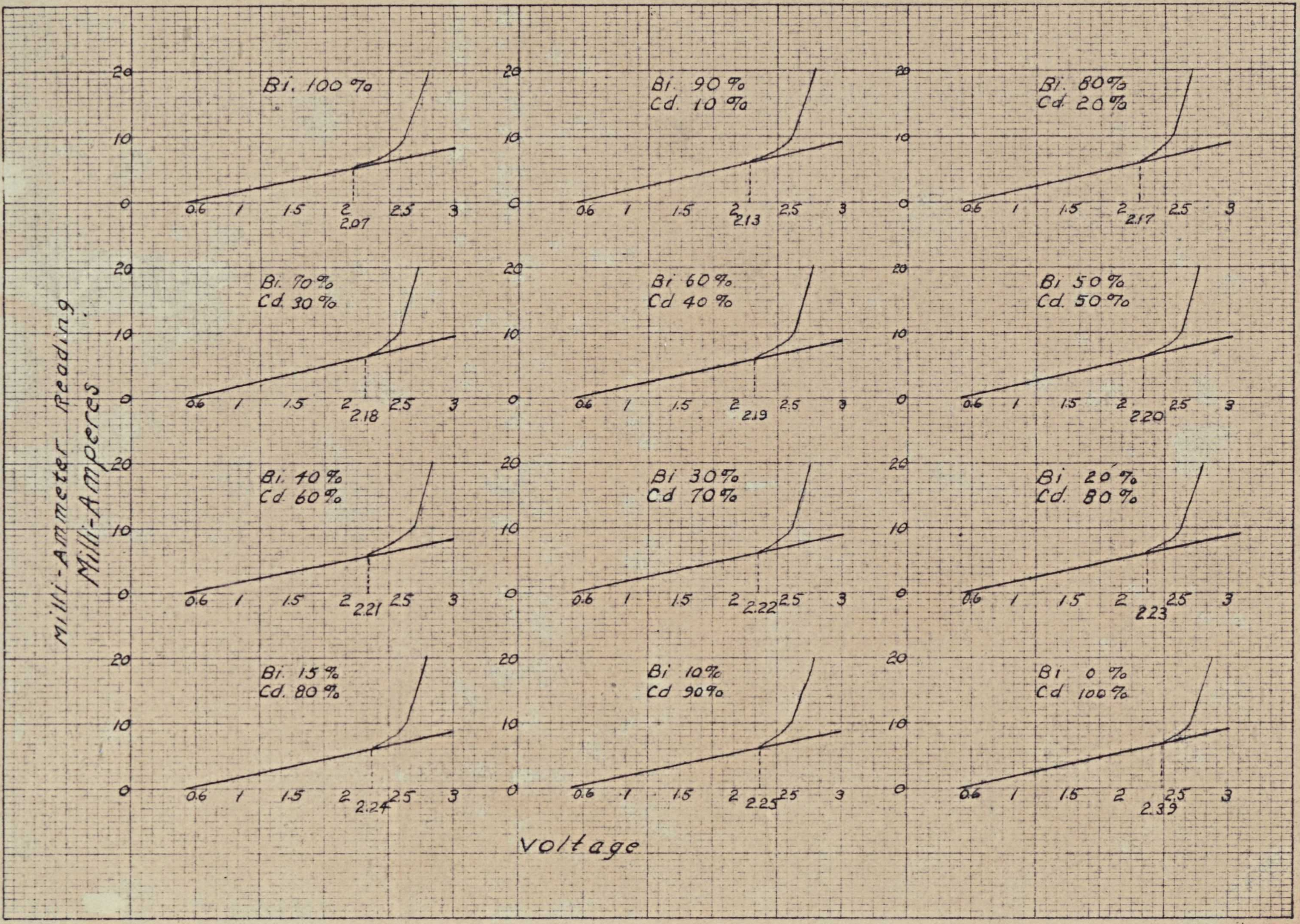
M.A.	V.
0.0	0.50
2.0	1.20
2.5	1.25
3.0	1.35
3.5	1.55
4.0	1.66
4.5	1.87
5.0	1.97
5.5	2.13
6.0	2.20
6.5	2.30
7.0	2.35
7.5	2.40
8.0	2.45
8.5	2.48
9.0	2.51
9.5	2.54
10.0	2.56
20.0	2.74

10% Bi. 90% Cd.

M.A.	V.
0.0	0.50
2.0	1.20
2.5	.
3.0	1.30
3.5	1.45
4.0	1.55
4.5	1.75
5.0	1.95
5.5	2.06
6.0	2.16
6.5	2.25
7.0	2.30
7.5	2.35
8.0	2.40
8.5	2.45
9.0	2.47
9.5	2.50
10.0	2.54
20.0	2.74

0% Bi. 100% Cd.

M.A.	V.
0.0	0.50
2.2	1.24
3.0	1.30
3.5	1.55
4.0	1.65
4.5	1.80
5.0	1.95
5.5	2.10
6.0	2.20
6.5	2.30
7.0	2.40
7.5	2.45
8.0	2.50
8.5	2.55
9.0	2.60
9.5	2.62
10.0	2.65
20.0	2.85


Milli-Ammeter Reading
Milli-Amperes
Voltage
Bi. 100 %
2.07
Bi. 90 %
Cd. 10 %
2.13
Bi. 80%
Cd 20%
2.17
Bi. 70%
Cd. 30%
2.18
Bi 60%
Cd 40%
2.19
Bi 50%
Cd. 50%
2.20
Bi. 40%
Cd. 60%
2.21
Bi 30%
Cd 70%
2.22
Bi 20%
Cd. 80%
2.23
Bi. 15%
Cd. 80%
2.24
Bi 10%
Cd 90%
2.25
Bi 0 %
Cd 100%
2.39
0
10
20
0.6
1
1.5
2
2.5
3

DATA

ANTIMONY BISMUTH ALLOY

100% Bi. 0% Sb.

M.A.	V.
2.5	1.15
3.0	1.35
3.5	1.45
4.0	1.55
4.5	1.70
5.0	1.82
5.5	1.96
6.0	2.05
6.5	2.15
7.0	2.20
7.5	2.30
8.0	2.36
8.5	2.40
9.0	2.45
10.0	2.50
30.0	2.75

10% Sb. 90% Bi.

M.A.	V.
2.5	1.10
3.0	1.20
3.5	1.40
4.0	1.55
4.5	1.70
5.0	1.80
5.5	1.95
6.0	2.05
6.5	2.15
7.0	2.25
7.5	2.30
8.0	2.35
8.5	2.40
9.0	2.45
10.0	2.50
30.0	2.75

20% Sb. 80% Bi.

M.A.	V.
2.5	1.10
3.0	1.25
3.5	1.45
4.0	1.55
4.5	1.70
5.0	1.85
5.5	2.00
6.0	2.10
6.5	2.20
7.0	2.28
7.5	2.35
8.0	2.40
8.5	2.45
9.0	2.48
10.0	2.52
30.0	2.75

30% Sb. 70% Bi.

M.A.	V.
2.5	1.10
3.0	1.22
3.5	1.45
4.0	1.56
4.5	1.75
5.0	1.90
5.5	2.00
6.0	2.10
6.5	2.20
7.0	2.25
7.5	2.35
8.0	2.40
8.5	2.45
9.0	2.50
10.0	2.52
30.0	2.75

40% Sb. 60% Bi.

M.A.	V.
2.5	1.05
3.0	1.25
3.5	1.45
4.0	1.62
4.5	1.75
5.0	1.88
5.5	2.00
6.0	2.10
6.5	2.20
7.0	2.30
7.5	2.35
8.0	2.40
8.5	2.45
9.0	2.49
10.0	2.51
30.0	2.75

50% Sb. 50% Bi.

M.A.	V.
2.5	1.05
3.0	1.25
3.5	1.46
4.0	1.58
4.5	1.75
5.0	1.89
5.5	2.01
6.0	2.08
6.5	2.20
7.0	2.25
7.5	2.30
8.0	2.35
8.5	2.40
9.0	2.45
10.0	2.50
30.0	2.72

DATA

ANTIMONY BISMUTH ALLOY

(cont'd)

60% Sb. 40% Bi.

M.A.	V.
2.5	1.06
3.0	1.30
3.5	1.40
4.0	1.55
4.5	1.75
5.0	1.87
5.5	2.00
6.0	2.05
6.5	2.15
7.0	2.25
7.5	2.30
8.0	2.35
8.5	2.40
9.0	2.45
10.0	2.50
30.0	2.74

70% Sb. 30% Bi.

M.A.	V.
2.5	1.05
3.0	1.25
3.5	1.46
4.0	1.55
4.5	1.75
5.0	1.90
5.5	2.04
6.0	2.12
6.5	2.20
7.0	2.26
7.5	2.30
8.0	2.36
8.5	2.40
9.0	2.45
10.0	2.50
30.0	2.72

80% Sb. 20% Bi.

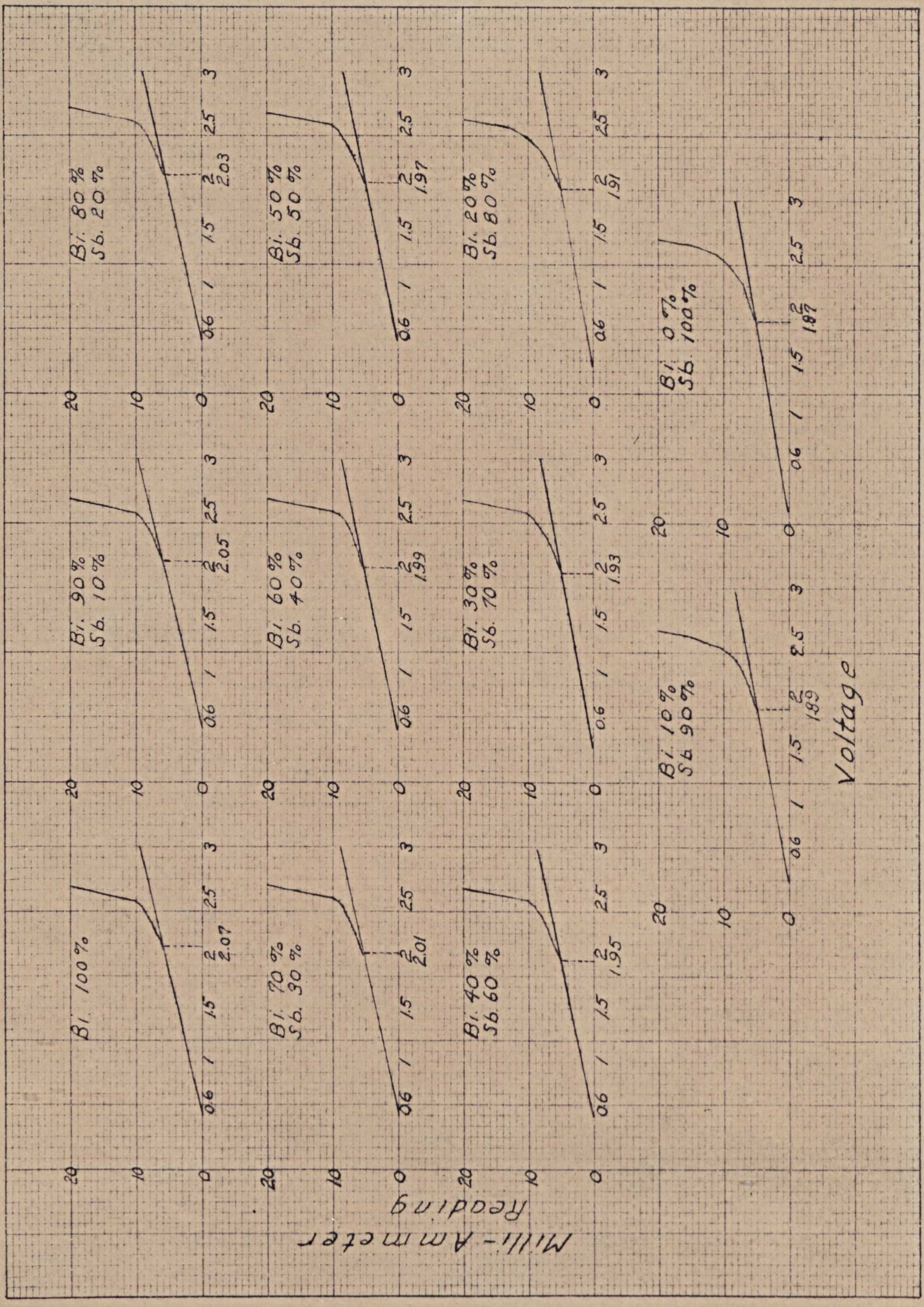
M.A.	V.
3.0	1.08
3.5	1.40
4.0	1.55
4.5	1.75
5.0	1.85
5.5	2.00
6.0	2.05
6.5	2.10
7.0	2.15
7.5	2.20
8.0	2.25
8.5	2.30
10.0	2.40
15.0	2.50
30.0	2.62

90% Sb. 10% Bi.

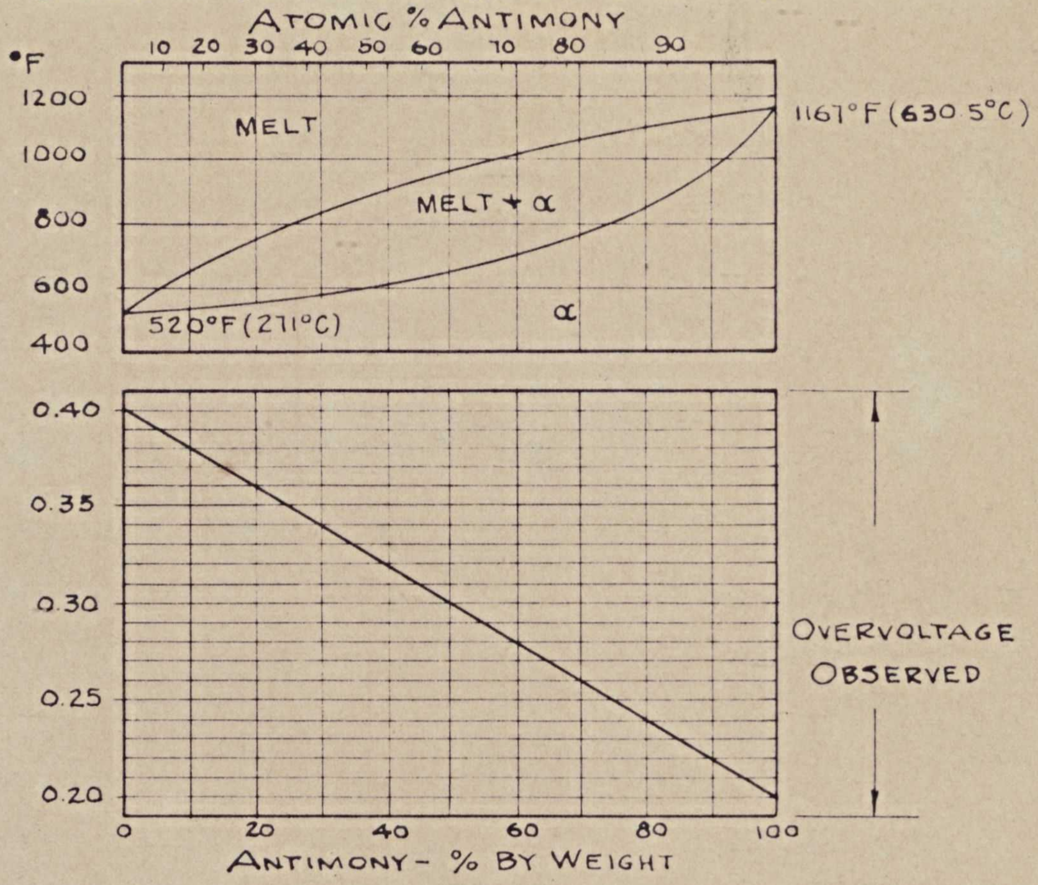
M.A.	V.
3.0	1.10
3.5	1.40
4.0	1.55
4.5	1.70
5.0	1.84
5.5	1.96
6.0	2.10
6.5	2.18
7.0	2.24
7.5	2.28
8.0	2.33
8.5	2.36
9.0	2.40
10.0	2.44
15.0	2.55
30.0	2.68

100% Sb. 0% Bi.

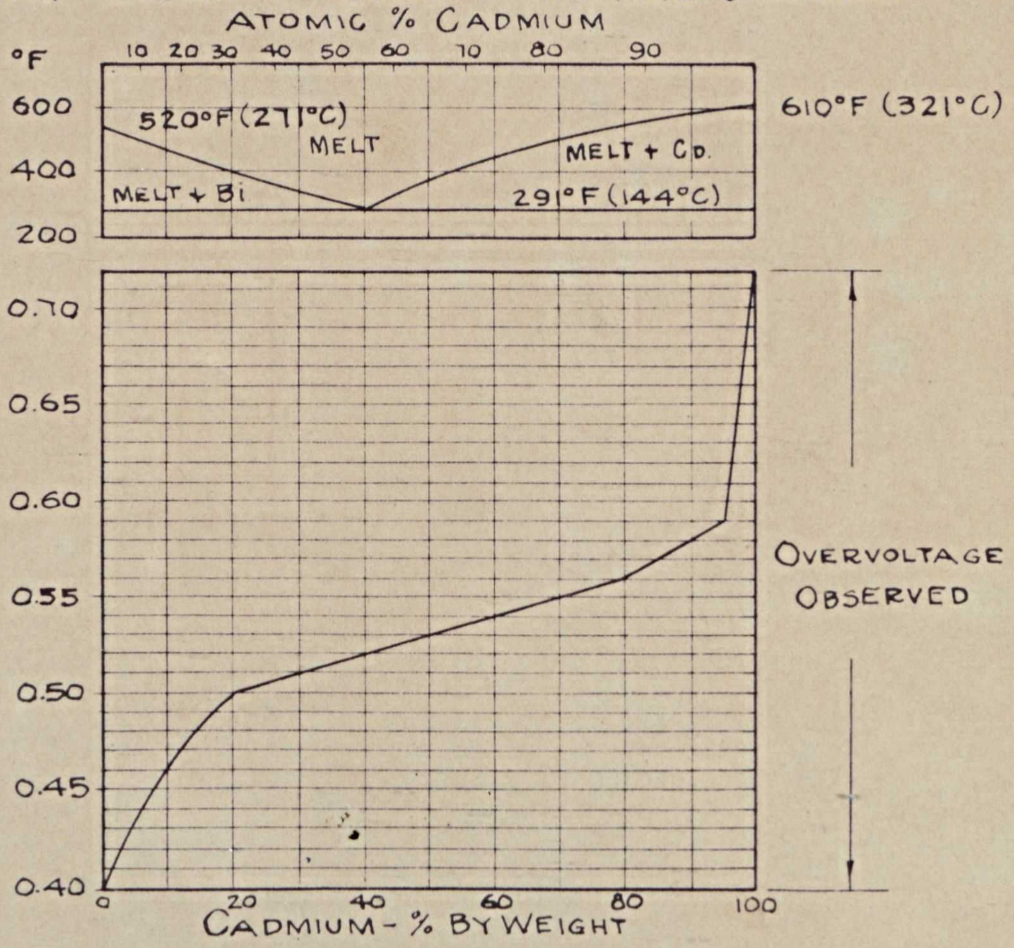
M.A.	V.
3.0	1.02
3.5	1.34
4.0	1.54
4.5	1.70
5.0	1.83
5.5	1.96
6.0	2.03
6.5	2.10
7.0	2.22
8.0	2.30
9.0	2.40
10.0	2.45
11.0	2.50
15.0	2.60
30.0	2.70


Milli-Ammeter Reading
Voltage
0
10
20
0.6
1
1.5
2
2.5
3
Bi. 100 %
2.07
Bi. 90 % Sb. 10 %
2.05
Bi. 80 % Sb. 20 %
2.03
Bi. 70 % Sb. 30 %
2.01
Bi. 60 % Sb. 40 %
1.99
Bi. 50 % Sb. 50 %
1.97
Bi. 40 % Sb. 60 %
1.95
Bi. 30 % Sb. 70 %
1.93
Bi. 20 % Sb. 80 %
1.91
Bi. 10 % Sb. 90 %
1.89
Bi. 0 % Sb. 100 %
1.87

BISMUTH - ANTIMONY CONSTITUTIONAL DIAGRAM



BISMUTH - CADMIUM CONSTITUTIONAL DIAGRAM



SUMMARY OF RESULTS

The results presented are mainly first determinations. However, check determinations were run on most of the bismuth-cadmium alloys and on the pure metals. For the pure metals, checks were obtained without difficulty; for the cadmium-bismuth alloys, re-runs were made until consistent results were obtained, and only data so checked is here presented.

Conclusions

From the data presented on the preceding pages, it was found that in at least two cases metals in the same group in the periodic table did not have the same overvoltage. Lead and tin, which are metals in group four, showed overvoltages of 0.40 and 0.23 volts respectively. The other discrepancy occurred in group five, between antimony and bismuth; bismuth had an overvoltage of 0.40, and antimony, 0.20 volts. It cannot be accepted then, as some authors have stated, that metals in the same period have the same overvoltage.

In the antimony-bismuth series, it was found that the overvoltage was highest on the pure metal having the lower melting point. This agrees with Mott[15], who states that metals of low melting points have high overvoltages, and, conversely, those of high melting points have low overvoltages. However, in the case of cadmium and bismuth, the reverse was true. Cadmium, with a melting point of 321 degrees Centigrade, has a hydrogen overvoltage of 0.72 volts, while bismuth, having a melting point of 271 degrees

Centigrade, has an overvoltage of 0.40 volts. Apparently, then, no correlation of overvoltage with melting point can be accepted.

In the case of alloys of bismuth and antimony, it was found that the overvoltage decreased uniformly as the percentage of antimony increased. Figure 3 on Page 29 gives the constitutional diagram for the binary system of antimony-bismuth. Below this diagram, the observed overvoltages are plotted against the percent composition of the alloy. These results are what one would expect in a system that is reciprocally soluble in all proportions. Apparently, there is a definite relationship between the constitutional diagram and the overvoltage. If the overvoltages of the pure metals are known, it may be possible to predict the overvoltage of any alloy in this type of a system. It cannot be accepted, then, that the overvoltage of an alloy will be the same as that of the metal of highest percentage in that alloy.

In the case of cadmium-bismuth alloys, a small amount of bismuth decreases the overvoltage of cadmium considerably. With the addition of more bismuth, the overvoltage continues to decrease more slowly but quite uniformly until about 80 per cent bismuth and 20 per cent cadmium is reached, at which point it drops quite rapidly to the value obtained for bismuth. Figure 4 on Page 29 gives the constitutional diagram for the binary system of bismuth and cadmium. Below this diagram, the observed overvoltages are plotted against the percent composition of the alloys. This constitutional diagram is typical of alloys whose components are insoluble in one another in the solid state.

Near the cadmium rich end, the alloys were made up of 5 per cent difference in composition instead of the customary 10 per cent used throughout this work. This showed some interesting results; and, if time had permitted, alloys of even smaller percentage would have been made in order to determine just where the uniform portion of the curve commenced and the point where the rapid rise occurred. This point lies between an alloy containing 5 per cent bismuth, 95 per cent cadmium, and pure cadmium. This same line of reasoning should be carried out on the bismuth rich end of this system. Apparently, the constitutional diagram is not complete. From the overvoltage curve, it appears that there may be two solid solutions in this constitutional diagram, which would make the bismuth-cadmium constitutional diagram one of two metals that are partially soluble in one another in the solid state. Here, again, there perhaps is a definite relation between the constitutional diagram and the overvoltages of the alloys of that system, with the changes in slope of the overvoltage versus composition curve corresponding to solubility limits. This, however, is speculation.

SUGGESTIONS FOR FURTHER INVESTIGATIONS

Further investigations should be made with alloy systems having the same types of constitutional diagrams as those presented in this paper, and also with alloys of much more complicated constitutional diagrams. Enough work along this line might eventually lead to some valid generalizations regarding the relationship of alloy overvoltages to alloy structure.

An interesting investigation would be to measure the overvoltage of a metal on which the grain size has been determined; then, by proper heat treatment, change the grain size and again measure the overvoltage.

With electrodes made in the same manner as those prepared for this work, the difference between the overvoltage when the prepared surface is facing the anode and when this same surface is not facing the anode could be determined.

Temperature variations of the electrolyte may throw some light on the theory of overvoltage, since it is thought that an increase in temperature will increase the rate at which the slow reaction occurs, thus giving lower overvoltages.

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