

LVIII.—*Overpotential at Antimony Cathodes and Electrolytic Stibine Formation.*

By HENRY J. S. SAND, JULIUS GRANT, and WILLIAM VERNON LLOYD.

As is well known, two methods yielding different results are in common use for the measurement of electrolytic polarisation, *viz.*, the "direct" and the "commutator" method. In the former, the *P.D.* between the working electrode and the liquid in immediate contact with it is measured *during* the passage of the current and compared with that found in the absence of current; in the latter, the same *P.D.* is measured as soon as possible *after* interrupting the current. The attitude taken up by one of us (H. J. S. S.) to results obtained by the former method has been that only that portion of the measured *P.D.* should be considered to be a polarisation which is definitely proved to be so by the latter method. To indicate this attitude, the term *transfer-resistance* introduced by Gore (*Proc. Roy. Soc.*, 1885, **38**, 209; also numerous papers in *Phil. Mag.*) was revived in 1909 by Sand and Black (*Z. physikal. Chem.*, 1910, **70**, 496). This term has since been extensively used by Newbery (*Trans. Faraday Soc.*, 1919, **15**, 126) and others. The term may appear to imply definitely the irreversible character of the phenomenon measured, and, in so far as its unknown character was primarily to be indicated, it is now recognised that the term *transfer-impedance* would better comprise both reversible and irreversible effects. Both the direct and the commutator method have been extensively criticised without finality having been reached; but it is remarkable that very little attention has been hitherto directed to the entirely different character of the results obtained by the two methods. Whilst the direct method appears to lead to the conclusion that polarisation increases indefinitely with *C.D.*, the commutator method always yields results which point definitely to the existence of a maximum of polarisation. Experiments are now recorded which were carried out to determine whether there is any indication in the current density-polarisation (overvoltage) curves, determined by the direct method, of the polarisation-maxima shown by the commutator method.

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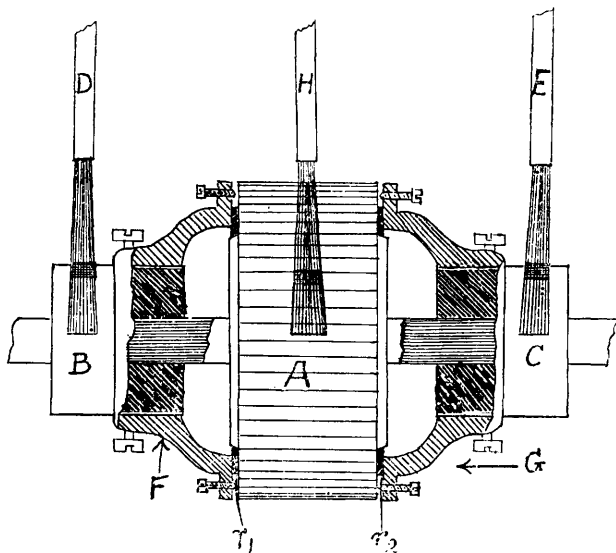
An antimony electrode was used as in previous work (Sand, Weeks, and Worrell, J., 1923, **123**, 456; Sand and Weeks, J., 1924, **125**, 160). An advantage of this metal is that it allows the phenomenon of polarisation to be studied in conjunction with that of hydride formation. The experiments reported by Sand, Weeks, and Worrell (*loc. cit.*) were repeated. We very much regret that we have been unable to confirm the numerous and detailed reports of his experiments supplied by Mr. Worrell, even when working with the same materials and apparatus. We are unable to account for these reports and wish to sever all association with them. The reports furnished by Mr. Weeks we have confirmed in general outline, but not in detail. The experimental arrangements used have been in part further developed for the purposes of the present investigation. The electrolytes employed were: (1) Solutions of various acids in varying concentrations; (2) solutions of acids containing salts; and (3) solutions of alkaline substances.

The main points studied have been (1) the dependence of polarisation on the time which has elapsed since the breaking of the current; (2) the relation between the overvoltage-current density curves for a given solution and electrode, determined on the one hand by the direct and on the other by the commutator method; (3) the relation between the values obtained and the composition of the solution, including hydrogen-ion concentration; and (4) the dependence of hydride formation on the conditions of the experiment. The first point has been studied for other electrodes by a number of workers (Glasstone, J., 1923, **123**, 2926; 1924, **125**, 250, 2646; 1925, **127**, 1824; *Trans. Faraday Soc.*, 1924, **19**, 808; Knobel, *J. Amer. Chem. Soc.*, 1924, **46**, 2613; Newbery, J., 1924, **125**, 511; *Proc. Roy. Soc.*, 1925, *A*, **107**, 486; 1926, *A*, **111**, 182). Whereas Glasstone and Knobel employed mechanical commutators, Newbery used the cathode-ray oscillograph. The method employed in the present investigation belongs to the class employed by the first-named authors, but the apparatus allows readings to be made after very much shorter time-intervals than have been hitherto attempted.

Figs. 1a and 1b illustrate the principle of the commutator employed. In the design and construction of this instrument we have had the assistance of Messrs. F. S. M. and J. F. Wright, of Messrs. F. Cox, Ltd., which we gratefully acknowledge. The apparatus consists essentially of a 64-segment dynamo commutator of commercial construction, A, which was mounted on the same spindle with two insulated slip-rings, B and C, the latter being in communication

through the wire brushes, D and E, with the source of current and the potentiometer, respectively. To each slip-ring was screwed a cup-shaped casting, F and G, each of which was supplied with 64 screw-holes and screws that were placed opposite the 64 segments of the commutator. It was thus possible to bring any one segment into electrical communication with either or both of the slip-rings. These castings were spaced relatively to the central commutator by means of the rubber rings, r_1 and r_2 . The commutator brush, H, was connected to the working electrode, and it was thus possible to connect the latter during time-intervals equal to

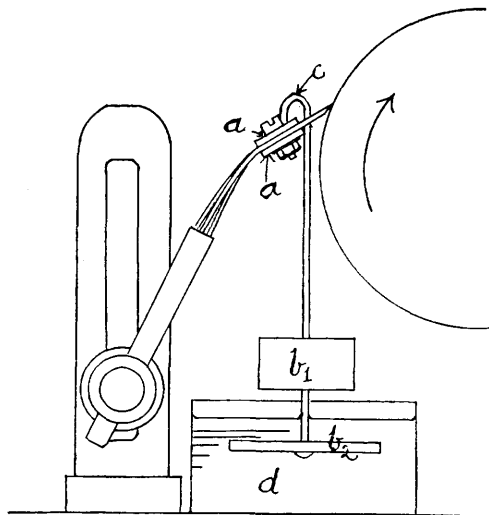
FIG. 1a.



that of $1/64$ of a revolution to either the source of current or the potentiometer. Thus, if 32 successive segments were connected to the current slip-ring B, 32 being left unconnected to B; if, further, these latter were connected individually in successive experiments to the potentiometer slip-ring C; and if the number of revolutions of the commutator was r per min., the current would pass through the cathode during $32/64r$ min. and would be off for an equal time, during which the average cathode potential could be measured in intervals of $1/64r$ min. An ordinary bearing was at first employed but, later, ball-bearings were fitted. The spindle of the commutator was driven by means of a pulley and belt from an electric motor, and the drive was sufficiently powerful to allow a speed counter to be pushed against the spindle without slowing it

down appreciably. The speed at which the instrument was run in many of the experiments recorded was 4200 revs. per min.

The main difficulty encountered was due to electrical leakage. General electric leakage from outside was obviated by placing the apparatus on insulating material which lay on earthed metal plates. To prevent leakage across the segments, which was apt to occur owing to metal or other dust, it was necessary to brush out the apparatus. For this purpose, all parts of the commutator were accessible after the screws locking the castings F and G had been loosened and the latter had been pushed back. An ordinary brass wire brush, as indicated in Fig. 1*a*, was at first employed; later, however, it was replaced by a copper brush the construction of which is explained in Fig. 1*b*. This consisted of 13 copper wires, of about 16 wire-gauge, which were soldered into a brass holder and spread out into a flat band by clamping them between the two plates *a, a*. The wires were cut off obliquely in the manner shown, so as to form a contact along a straight line on the commutator

FIG. 1*b*.

surface. In order to prevent the brush from vibrating unduly, it was weighted by means of the weights b_1 , b_2 amounting altogether to about 150 g. These were hung from *a, a* by means of the hook *c*, and their motion was damped by placing b_2 in oil contained in the dash pot *d*. The mica insulation between successive segments of the commutator was cut away at the top for a distance of about 1 mm. in order to obtain a sharper break. A difficulty met with when a large number of successive segments was connected simultaneously to the same slip-ring was due to the fact that tightening up one screw tended to loosen its neighbours. To obviate this, only one or two screws were employed to make the connexion to the slip-ring, and the successive segments were put into communication with each other by means of pieces of tin foil that were held down by a rubber band slipped over the commutator.

The efficiency of the instrument is of the same order as that of the cathode-ray oscillograph. Thus, large numbers of experiments were carried out in which the average potential was measured during 2.2×10^{-4} sec. after the breaking of the current, which is approximately the instantaneous potential after 1.1×10^{-4} sec. The smallest times after the breaking of the current recorded by Glasstone are 20×10^{-4} sec., and the corresponding shortest time shown by Knobel in his curves is 5×10^{-4} sec.

Currents were measured in all experiments by moving-coil ammeters suitably shunted. Where intermittent current is employed, such instruments do not register the instantaneous value of the current, but act with sufficient accuracy as coulombmeters (J., 1923, 123, 2896). It must therefore be understood that all current densities are stated in millicoulombs/sec./sq. cm., even where for brevity the term "milliamperes" is employed. Where measurements by the direct method were made in alternation with those by the commutator method, the former were carried out by introducing a short-circuit between the current slip-ring brush and the commutator brush without altering any other connexion.

The electrolytic apparatus was approximately the same as that hitherto used, but was adapted to the measurement of the cathode potential by the direct method. As in previous work, the electrolyte in the hydrogen-electrode chamber was the same as that around the cathode. Hydrogen was kept bubbling continuously through it, and, except in some of the experiments on yields of stibine, was afterwards led past the exposed surface of the cathode. The method of measuring the yield of stibine was generally the same as that previously employed, *i.e.*, the hydrogen issuing from the cathode chamber was passed through a solution of silver nitrate and the increase of weight determined. The method might perhaps be criticised on the ground that hydrogen, even when purified carefully, is found always to precipitate small amounts of silver from silver nitrate solutions, the increase of weight thus produced being equal to that of the hydrogen absorbed. This increase was, however, negligible in all cases. Thus, in an experiment in which 1000 c.c. of dried hydrogen were bubbled slowly through the silver nitrate absorption bulbs, the total increase in these *plus* the calcium chloride tubes was found to be less than 2 mg., corresponding to a calculated volume error in the ratio of stibine to hydrogen of only about 3 parts in 10,000 parts. In many of the experiments, yields of stibine were determined by passing the issuing gas through a heated quartz tube of about 3 mm. bore and estimating the increase of weight. In no case

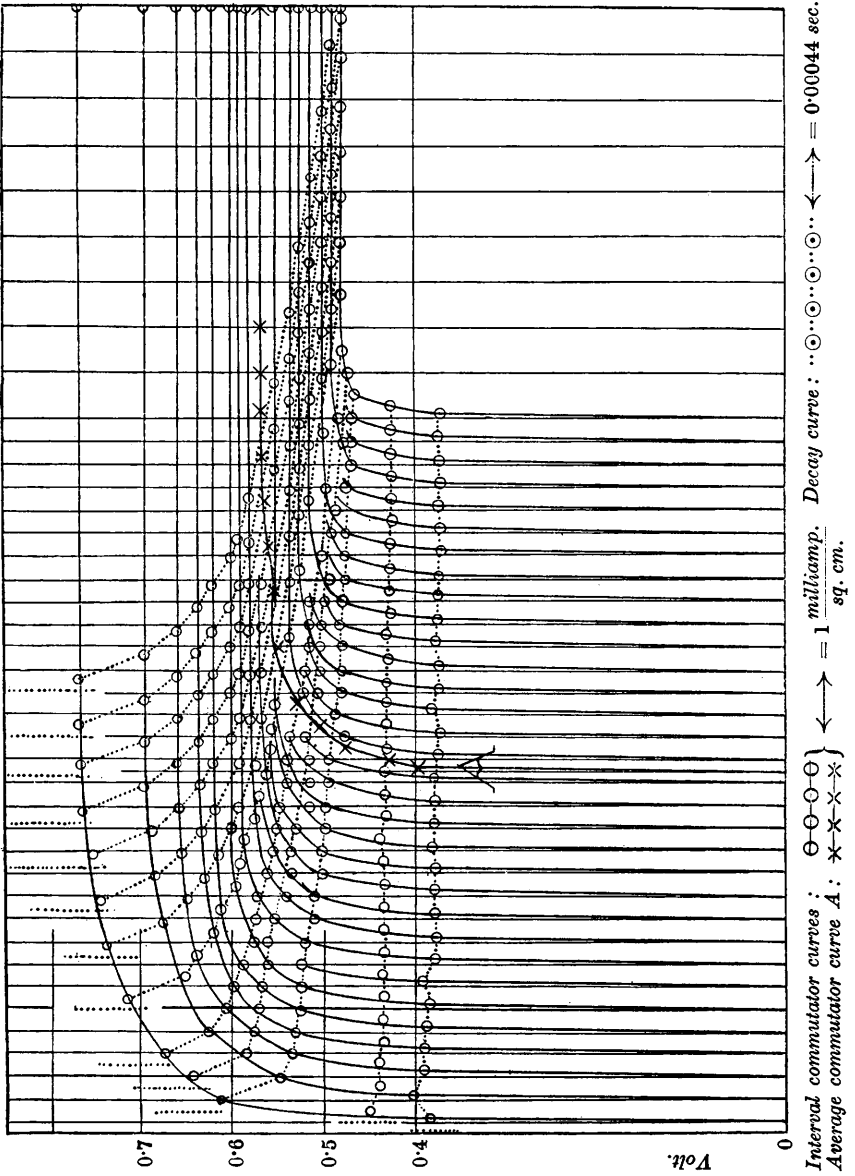
was a perceptible difference obtained between such experiments and those in which silver nitrate solution was employed.

Results in Acid Solution. (Experiments by W. V. LLOYD.)

Solutions of Acids in the Absence of Salts.—Experiments were first carried out on the reproducibility of results. Most of these were performed with one of the commutators used in former work. Hydrogen was bubbled past the electrode, as previously explained. With a definite commutator speed at a given temperature, closely reproducible results were obtained. In a series of experiments it requires about 10 minutes to polarise the antimony cathode to its maximum, a *C.D.* slightly over the critical value being used. After this, results are reproducible, under carefully controlled conditions, to within a few millivolts. The material of the electrodes was purchased at various times and was the purest obtainable. Some of the antimony bars were obtained as such; others were cast from powder. A series of experiments showed that, when the antimony was suspended from platinum wires, or when platinum was wound round it, the same values of overvoltage were ultimately obtained, but these took longer to establish themselves. The antimony appeared to be very little attacked in these experiments and the surface was only very slightly dulled. The electrodes were polished by means of fine emery paper before the experiments.

A large number of readings were taken with the commutator shown in Fig. 1*a*, to determine the relation between polarisation and time for various intervals after interrupting the current, and with various *C.D.*'s. A complete study of polarisation was made in the case of *N.*-, *4N.*-, and *16N.*-sulphuric acid. Thirty-two segments of the commutator were connected to the current slip-ring, and the potentiometer slip-ring was successively connected to each of the other thirty-two. The speed of the commutator was 4200 revs. per min.; the readings on the potentiometer thus represent average polarisations during 2.2×10^{-4} sec. and the current was alternately on and off during $1/140$ sec. The results of the study of *N.*-sulphuric acid have been graphically represented in Fig. 2 in such a manner as to give (1) for each segment a curve representing the relation between overvoltage and *C.D.*, and (2) for each *C.D.* a curve indicating the relation between overvoltage and time since the breaking of the current. To make this possible, all voltages are plotted as ordinates on the same scale and have the same zero. Current densities are plotted as abscissæ, likewise all on the same scale, but they start from different zeros for each segment. These zeros have been made recognisable for each current density-overvoltage curve by arbitrarily extrapolating it

FIG. 2.



backwards to zero overvoltage for zero *C.D.* The current density zeros for successive segments have been placed at an equal distance from each other, and since the time interval between the polarisations on such segments was 2.2×10^{-4} sec., this time interval is

also represented by the distance chosen. Points corresponding to overvoltages measured on successive segments for the same *C.D.*'s have therefore been connected by dotted curves which may be termed decay curves, and represent the rate of decay of overvoltage with time. The zero line of the abscissæ of each dotted curve has also been dotted in as a vertical line. The current density–overvoltage curve, corresponding to the combined effect of 30 segments simultaneously connected to the potentiometer, has been drawn for purposes of comparison half-way between the curves belonging to the two middle segments and is indicated by A. The following new facts emerge. (1) For each individual segment the polarisation rises to a maximum which it maintains constant in every case for *C.D.*'s between about 8 and 100 milliamps./sq. cm. In the case of the segments furthest removed from the break of the current, the maximum is attained at a *C.D.* below 2 milliamps./sq. cm. At *C.D.*'s above 100 milliamps./sq. cm. there is a slight decrease in polarisation, which may probably be explained by local heating. (2) The sharpest drop in polarisation occurs between the first and second segments. It is therefore unsatisfactory to extrapolate to zero time from values obtained on later segments, as advocated by Glasstone (*loc. cit.*). The first reading employed by this investigator in his studies of overvoltage of other metals corresponds approximately to the fourth point of the dotted decay curves shown in our diagram. It will be apparent from the first three additional points given here, that in the absence of an agreed equation, extrapolation leads to quite uncertain results. We therefore suggest that polarisation is best expressed by stating not only its value but also the time-interval during which it is measured. In many cases it might be sufficient to state the mean time between the beginning and end of the measurement. (3) The curves show that, when overvoltage on antimony electrodes in *N/1*-sulphuric acid does not exceed about 0.45 volt, it maintains itself sensibly constant over the whole range examined of 1/140 sec.

For the further study of polarisation, overvoltages obtained by the direct and by the commutator methods in the same solutions were compared. A thorough study was made of solutions of sulphuric acid in strengths varying from 16*N* to *N/160*; of hydrochloric acid (4*N* to *N/16*); of phosphoric acid (8*N* to *N/16*); and of *N/1*-oxalic acid. Some of the numbers obtained for *N/1*-sulphuric acid are recorded in Table I, those for the other electrolytes being similar in general character. The commutator overvoltages were obtained by means of the Whetham commutator employed in previous investigations and are average polarisations during the first 0.0059 sec. after breaking the current. Measurements by the

TABLE I.

(N-H₂SO₄.)

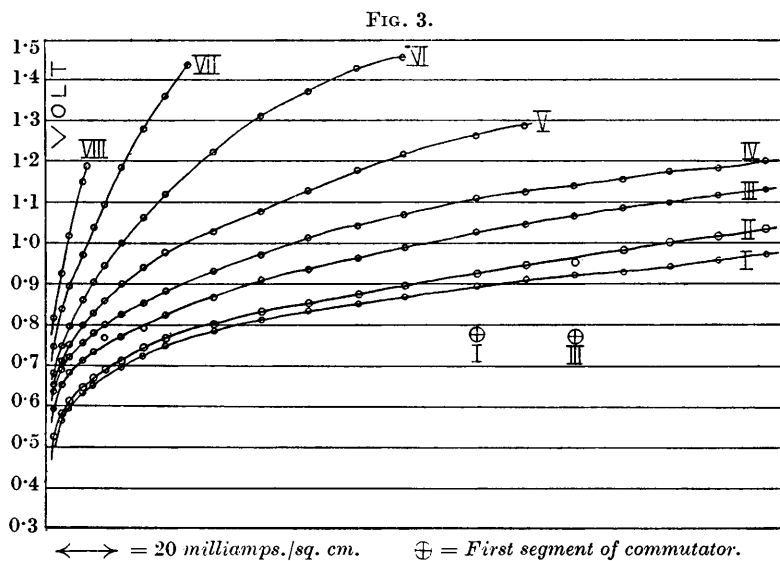
	0.06	0.18	0.31	0.50	0.63
Milliamps./cm. ²	0.06	0.18	0.31	0.50	0.63
Millivolts (Comm.)...	322	383	415	447	467
„ (Dir.)	331	398	428	459	477
Milliamps./cm. ²	0.75	0.87	0.98	3.0	4.9
Millivolts (Comm.)...	483	496	509	557	559
„ (Dir.)	492	507	520	618	658
Milliamps./cm. ²	6.9	8.8	11.7	17.7	21.6
Millivolts (Comm.)...	559	559	559	559	559
„ (Dir.)	685	704	725	755	770
Milliamps./cm. ²	25.5	29.5	43.7	70.0	87.5
Millivolts (Comm.)...	558	558	556	554	554
„ (Dir.)	784	796	840	903	935
Milliamps./cm. ²	105	122	140	166	184
Millivolts (Comm.)...	552	552	552	550	548
„ (Dir.)	964	988	1014	1049	1075
Milliamps./cm. ²	201	219	236	262	
Millivolts (Comm.)...	548	546	546	546	
„ (Dir.)	1092	1106	1119	1138	

direct method were made alternately with those by the commutator method for each *C.D.* It will be seen that for low polarisations up to and slightly beyond 0.45 volt, the value previously mentioned, overvoltages measured by the direct and by the commutator method are sensibly identical, when expressed in coulombs/sec./sq. cm.

The further study of the results is best made in conjunction with Fig. 3 in which current density-overvoltage curves, obtained by the direct method, are plotted for solutions of sulphuric acid of various strengths. It will be seen that at high *C.D.*'s increases in direct overvoltages become nearly proportional to increases in *C.D.* For very high *C.D.*'s, however, such as those for which the commutator overvoltages begin to show a decrease, there is a falling off from the linear relation. The simplest way to explain this phenomenon is to assume that at high *C.D.*'s an almost constant transfer- (or surface) resistance establishes itself, which, however, shows a tendency to decrease with increase of the *C.D.* to extremely high values. The overvoltage measured should then be equal to the sum of a true polarisation ω , plus a term $i\kappa$, where ω is a value approaching the commutator overvoltage extrapolated to zero time-interval, i is the current density, and κ is the transfer-resistance per unit surface. Commutator overvoltages, determined by measurement on the first segment of the interval commutator, are shown separately on the diagram for 16*N.* and *N.* acid. It can be seen that in the case of the strong solutions of sulphuric acid the commutator overvoltage thus determined is almost identical with the voltage indicated by the ordinate corresponding to zero current density on the asymptote found by the direct method. In

the case of the other solutions shown, there is an approximation to a like result. Phosphoric acid solutions gave results similar to those found with sulphuric acid. In hydrochloric and oxalic acid solutions, the differences between the commutator- and the extrapolated direct-method overvoltages were considerably greater than with sulphuric and phosphoric acids.

Relation between Overvoltages and the Composition of the Solution.—To investigate this, overvoltages were determined for a large number of electrolytes by means of the Whetham commutator giving average polarisations corresponding to an interval of 0.0059



I, 16N-H₂SO₄. II, 8N-H₂SO₄. III, N-H₂SO₄. IV, N/4-H₂SO₄.
 V, N/16-H₂SO₄. VI, N/32-H₂SO₄. VII, N/64-H₂SO₄. VIII, N/160-H₂SO₄.

sec. after breaking the current. The maximum values (critical overvoltages) for some of the sulphuric acid solutions examined are assembled in Table II.

TABLE II.
 (Sulphuric acid solutions.)

Conc.	16N.	8N.	4N.	2N.	N.	N/4.	N/16.	N/32.	N/64.
Volts	0.522	0.524	0.537	0.547	0.559	0.557	0.560	0.576	0.587

It will be seen that the variation of overvoltage with concentration of the sulphuric acid is only slight, but there is a distinct rise with decrease of concentration throughout. Part of this may possibly be due to concentration polarisation set up by local dilution of

the electrolyte, particularly in the case of the very dilute electrolytes. The values given were obtained with stirring by means of a rapid current of hydrogen. The overvoltages obtained in other acid electrolytes are very close to those quoted. Thus, overvoltages in phosphoric acid are almost identical with those found for sulphuric acid of the same p_H , whereas overvoltages in hydrochloric and oxalic acids are about 2 centivolts higher. The overvoltage found for tartaric acid was distinctly abnormal. It first assumed a value about 5 centivolts below that of other acids, and after the cathode had been in the electrolyte for about 45 minutes a further decrease of 7 centivolts was observed. It was also noted that during electrolysis for a few minutes the cathode assumed a dark colour. Further, when the cathode was left standing in fresh tartaric acid solution over-night, a small amount of antimony went into solution. The abnormal behaviour of tartaric acid with regard to overvoltage should be considered in conjunction with the abnormally high yield of stibine obtained in this electrolyte (*vide infra*). The results obtained are in general agreement with those found by Glasstone for lead and mercury cathodes (J., 1924, 125, 2414, 2416).

Acid Solutions containing Alkali Salts.—Solutions of the following acids containing also their sodium salts were studied: Sulphuric, hydrochloric, phosphoric, and acetic. The original object of the experiments was to trace a connexion between the p_H value of the solution and the maximum (characteristic) overvoltage observed. For this purpose solutions of the pure acid were usually employed initially, and to these, successive quantities of sodium hydroxide solution were added. No simple results were obtained, however. The principal conclusions drawn were the following. (1) When the concentration of the alkali salt and the *C.D.* are not very high, overvoltage values are obtained which are either identical with, or only slightly higher than, those of pure acids having the same p_H value, and the appearance of the cathode is similar to what it would have been in the solution of the pure acid. Thus a *N*-solution of sulphuric acid gave a p_H voltage of 0.273 and an overvoltage of 0.538, whereas a similar solution which was also *N*/2 with respect to sodium sulphate gave a p_H voltage of 0.269, and an overvoltage of 0.559. On the other hand, when the quantity of acid was small relatively to that of the alkali, wholly different results were obtained. A very much higher *C.D.* and a longer time were required to establish the maximum overvoltage and the results were not so definite. The electrode appeared to be covered with a black deposit after an experiment, such as is met with when alkaline electrolytes are used. The final results were entirely different from those obtained

with pure acid solutions of the same p_H . Thus a solution which was N with regard to sodium sulphate and approximately $N/25$ with regard to sulphuric acid required a $C.D.$ of about 80 milliamps./sq. cm. to establish the maximum overvoltage of 1.245 volt. A solution containing only acid and having the same p_H voltage of 0.374 would have shown an overvoltage smaller by about 0.67 volt. Similarly, a solution which was approximately N with regard to phosphate and to which enough sodium hydroxide was added to give it a p_H voltage of 0.355 had not attained a constant overvoltage even for a $C.D.$ of 140 milliamps./sq. cm. The overvoltage then was 0.85 volt as compared with 0.57 volt for a sulphuric acid solution of similar p_H value. Results of this kind were obtained whether the porous diaphragm or the bottle apparatus was used. They point to considerable concentration changes in the boundary layer at the electrode.

Yields of Stibine.—A lengthy series of experiments on yields of stibine in acid solution showed that stibine is formed only with great difficulty and in small yield. A scarcely perceptible unsteadiness in overvoltage is the only indication of the evolution of the gas. Experiments were carried out in which antimony cathodes were employed in solutions of sulphuric, hydrochloric, and tartaric acids. Further, both antimony and lead cathodes were used in solutions of the same acids to which antimonious or antimonie compounds had been added. Direct, intermittent, and alternating currents were used. The last named consisted of alternating pulses of direct current obtained by means of a rotating commutator from a continuous current supply, the strength of the pulses in either direction being capable of independent adjustment and measurement (J., 1926, 2971). The following is a brief survey of the results obtained, none of which confirmed those reported by Worrell (*loc. cit.*). No stibine was formed in N -sulphuric or hydrochloric acid with continuous current with $C.D.$'s up to about 100 milliamps./sq. cm. At a $C.D.$ of 112 milliamps./sq. cm. an unweighable trace of the gas was detected. Smooth electrodes and electrodes roughened by previous electrolysis, both in acid alone and in acid containing antimony sulphate, were tried. The highest yield obtained in sulphuric acid solution was 0.25% with 16*N*-acid and continuous current of 1600 milliamps./sq. cm. density. In hydrochloric acid, similar figures were obtained. When alternating current was employed in 4*N*-hydrochloric acid, a $C.D.$ of 30 millicoulombs/sec./sq. cm. when the working electrode was the cathode, and of 12 when it was the anode, sufficed to produce a yield of 0.3%. The yields obtained by continuous-current electrolysis of tartar emetic in tartaric acid solution were higher than

those in other electrolytes. The electrode here becomes covered with a voluminous, black, spongy deposit. The highest yield obtained hitherto is 2.34%. This was found when a solution of *N*-tartaric acid was electrolysed with an alternating current of 7.8 milliamps./sq. cm. while the working electrode was the cathode, and of 2.9 while it was the anode. In general, it may be said that high *C.D.*'s are necessary for stibine formation. A limit is, however, soon reached in practice owing to heating of the electrolyte. Special experiments showed that when a hot electrolyte was used initially, no stibine was obtained in any circumstances. With both sulphuric and hydrochloric acids, a high concentration favours the formation of stibine, and results were given by very much lower *C.D.*'s with alternating than with direct current.

Results obtained in Alkaline Solution. (Experiments by J. GRANT.)

In the experiments in alkaline solution, hydrogen was always bubbled through the liquid. It was found particularly necessary to do this when the direct method was employed in order to remove small bubbles from the mouth of the glass capillary leading to the hydrogen electrode. Considerably more time elapsed in these experiments before readings became constant than in those in acid solution. It varied in different cases from 5 to about 30 minutes, but the final results were repeatable. Overvoltages in the following solutions were studied: 8*N*-, *N*-, and *N*/10-Sodium hydroxide; *N*-sodium carbonate and -sodium hydrogen carbonate; half-saturated baryta, calcium hydroxide, and disodium hydrogen phosphate; *N*-ammonium hydroxide and -ammonium carbonate; approximately *N*/45- and *N*/19-tetramethylammonium hydroxide; *N*/37-tetraethylammonium hydroxide; and *N*-sodium sulphate. The temperature was in all cases about 20°.

Table III gives overvoltages determined both by the direct and by the commutator method in solutions of *N*-sodium hydroxide and half-saturated baryta. These results may be taken as representative of those obtained in other solutions. Current densities are recorded in the first line in milliamps./sq. cm. under the heading *C.D.* (see p. 382). The overvoltages are assembled in the other lines, and are stated in millivolts. They are classified according to the solution and type of measurement—direct or commutator—as NaOH, *d*; NaOH, *c*; etc. The commutator employed for the latter gave average polarisations during the first 0.0137 sec. after breaking the current in the case of baryta, and in the case of the sodium hydroxide both 0.008 and 0.005 sec. were used without alteration of the results. It will be seen that, as in acid solution, the results obtained in a given electrolyte by the direct and com-

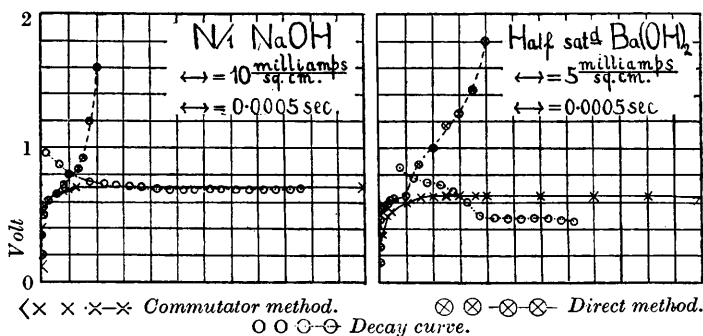
mutator methods do not differ much for a given *C.D.* as long as this is small. The large divergences only occur at higher *C.D.*'s.

TABLE III.

<i>C.D.</i>	0.2	0.3	0.5	0.7	1.5	5.0	10.0	12.5	15	20	40	170
NaOH, <i>c</i>	390	420	455	525	550	635	690	710	715	715	715	715
NaOH, <i>d</i>	200	355	500	530	585	655	800	840	920	1600	—	—
Ba(OH) ₂ , <i>c</i>	115	190	325	350	495	595	635	635	635	635	635	635
Ba(OH) ₂ , <i>d</i>	135	255	455	535	590	640	995	1160	1250	1800	—	—

The decay of polarisation was also determined by means of the new commutator, the interval during which a measurement was made being 1/4000 sec. In Table IV, the mean times, *t*, of these intervals and the polarisations ω are given for *N*-sodium hydroxide and half-saturated baryta for *C.D.*'s well above the critical values. The results for other solutions are similar in nature.

FIG. 4.



<i>t</i> (10 ⁻⁴ sec.).		1.25	3.75	6.25	8.75	11.25	13.75	16.25	18.75
ω	NaOH	945	870	795	750	745	730	720	715
(Millivolts)	Ba(OH) ₂	—	845	780	755	740	675	600	500
<i>t</i> (10 ⁻⁴ sec.).		21.25	23.75	26.25	28.75	31.25	33.75	36.25	38.75
ω	NaOH	700	695	690	690	690	690	690	695
(Millivolts)	Ba(OH) ₂	480	470	475	480	475	470	450	—

The numbers recorded in Tables III and IV are plotted in Fig. 4. The full lines refer to results obtained by the commutator method, the broken lines to those found by the direct method; the abscissæ are current densities and the ordinates overvoltages. It will be seen (1) that, as is known, the commutator overvoltage in every case reaches a constant maximum; and (2) that at voltages not far removed from these maxima, the overvoltage-current density curve determined by the direct method shows a distinct inflexion or bend, which appears to indicate the setting in of some constant-voltage

process absorbing considerable current and possibly of a chemical nature. The results of Table IV have been plotted into the diagram as dotted lines, and may be termed decay curves of polarisation; the abscissæ of these are times on the scale shown. It will be seen that the curves descend from a high polarisation value to one that remains nearly constant for a comparatively long time, and is not far removed from that indicated by the full curves. This again points to a large reserve of polarisation at certain voltages and indicates a chemical rather than a physical explanation. It may be connected with the formation of sodium alloys on the surface of the cathode.

Table V gives a summary of overpotentials found in alkaline solution. The overvoltages given under the heading ω_c in the second line were determined by means of one of the commutators; they are in most cases polarisations during the first 1/200 sec. after interrupting the current, some of them being averages of a number of determinations. On the line marked ω_d are assembled values of overvoltage which have been determined from the current density-overvoltage curves given by the direct method. These values are taken from the curves at positions as close as possible to where the inflexion occurs. The electrolytes are given in the order of decreasing p_H . It will be seen that, although there is a general increase of overvoltage with decreasing p_H , a number of the electrolytes examined fall out of line. There is thus no question of an accurate agreement with the relation previously proposed (J., 1924, 125, 162), viz., $\omega + 2h = c$, where ω is the overvoltage, h the *P.D.* between a standard electrode and the hydrogen electrode in the solution examined, and c a constant. The possibility cannot, however, be dismissed that we are dealing with a relation of the form proposed which is vitiated by secondary interfering influences. The matter is being further investigated also with electrodes other than antimony. Except in the case of sodium hydroxide solutions, there is no indication of any direct relation between sodium-ion concentration and overvoltage as was suggested by Herasymenko (*Rec. trav. chim.*, 1925, 44, 503).

TABLE V.

	8N-	N-	Ba(OH) ₂	N/10-	N-	Ca(OH) ₂
Solution.	NaOH.	NaOH.	(half-sat.).	NaOH.	NH ₄ OH.	(half-sat.).
ω_c (volt)	0.64	0.72	0.60	0.73	0.50	0.46
ω_d (volt)		0.70	0.65			0.90
	N-	N/37-	N/90-	Na ₂ HPO ₄	N-	N-
Solution.	Na ₂ CO ₃ .	NEt ₄ OH.	NMe ₄ OH.	(half-sat.).	NaHCO ₃ .	Na ₂ SO ₄ .
ω_c (volt)	0.74	0.87	0.93	1.22	0.94	1.24
ω_d (volt)		0.95		1.20		1.27

Experiments on the Evolution of Stibine by Electrolysis in Sodium Hydroxide Solution.—Reference has already been made to the fact that in alkaline solution the antimony cathode becomes blackened during electrolysis. Some antimony is always found dissolved in the solution after the experiments. The black deposit is loose and may be rubbed off with a finger. It appears to have little effect on overvoltage results. It is different in character from deposits obtained under similar conditions on metals such as cadmium which form insoluble hydroxides in alkaline solution. As the *C.D.* is increased a precipitate begins to deposit in the electrolyte. The supposition previously made, that it is formed from stibine which is primarily evolved, has been proved correct as will be shown below. The precipitate appears to have all the properties of metallic antimony. Experiments were also carried out in which hydrogen containing stibine was generated from hydrochloric acid containing tartar emetic by means of zinc and then passed through 8*N*-sodium hydroxide. A precipitate forms very slowly and again appears to have all the properties of finely-divided metallic antimony. We can in no wise confirm the statement made by Weeks and Druce (*Rec. trav. chim.*, 1925, **44**, 971) that either of these precipitates has the properties ascribed by these authors to their hydride (J., 1925, **127**, 1069). The total quantity of antimony present in solution and as metal appears to increase continuously with *C.D.* for a given amount of current. Experiments were carried out, in the manner recorded previously, in which the hydrogen generated electrolytically on the antimony cathode was collected after drying and passing through absorption apparatus for stibine. Only at very high *C.D.*'s was blackening in the latter noted. In 8*N*-sodium hydroxide, the maximum yield of stibine gas amounted to 0.18% by volume for a *C.D.* of 150 milliamps./sq. cm. (intermittent). Experiments were also performed in which the amounts of antimony precipitated as metal by intermittent current of various densities, and also the amounts which had dissolved, were determined, the electrolyte being *N*- or 8*N*-sodium hydroxide. From these experiments, yields of stibine were calculated on the assumption that all the antimony found owed its presence to the primary production of this gas. The yields thus found varied between 0.32 and 1.71% by volume for *C.D.*'s varying between 15 and 150 milliamps./sq. cm. The lowest *C.D.* at which the antimony precipitated as metal was weighable was 35 milliamps./sq. cm. for *N*-, and 50 for 8*N*-sodium hydroxide. After metallic antimony has begun to form, the amount going into solution does not increase appreciably with increasing *C.D.* The experience gained from these experiments suggested the possibility that if

hydrogen were blown rapidly past the working electrode it might carry the stibine with it before the latter had time to decompose. To test this, a small cone-shaped electrode was used, which pointed downwards towards the flared exit of a tube from which purified hydrogen was rapidly blown. The amount of hydrogen generated electrolytically was calculated from the current strength and time. The exposed area of the cathode varied in different experiments from 2 to 3.5 sq. cm. The results fully justified expectations, and prove that the antimony found distributed in the electrolyte has been formed from stibine primarily produced. The yields obtained in this way in *N*-sodium hydroxide are recorded in Table VI. It will be seen that the highest yield of stibine obtained as such amounted to 2%. It is noteworthy that with the very high *C.D.*'s the antimony cathode showed progressively less of the black deposit. The heating which occurs with high *C.D.* sets a limit to the yields. The experiments are being continued.

TABLE VI.

Type of current.	Millicoulombs per sq. cm.	Yield %.		
		As SbH ₃ .	Sb in pot.	Total.
Continuous	150	0.22	0.05	0.27
	250	0.21	0.26	0.47
	500	0.13	0.24	0.37
	1000	0.47	0.56	1.03
	2500	2.03	0.42	2.45
Intermittent	20	0.12	—	0.12
	50	0.32	0.22	0.54
	200	1.10	0.56	1.66
	370	1.50	2.00	3.50

Summary of Results and Conclusions.

1. In all cases examined, the current density—overvoltage curves obtained by the direct method bear a relation to those found under corresponding conditions by the commutator method.

2. It has been shown that in acid solution small polarisations maintain their value practically constant for periods up to 1/140 sec. At higher *C.D.*'s the polarisations fall off rapidly with time, but in all cases the polarisation measured during a given time-interval after the breaking of the current assumes a maximum value independent of the polarising current. Even when the interval during which the measurement is made is only 1/5000 sec. after the breaking of the current, such a maximum is obtained, and there is thus a discontinuity between it and the polarisation value shown by the direct method, the latter increasing indefinitely with *C.D.* This is in agreement with results obtained by means of the cathode-ray oscillograph by Newbery (*loc. cit.*) for other cathodes, but not with

the views propounded by Knobel (*loc. cit.*) on what appears to the authors to be insufficient experimental evidence.

3. In the best-conducting solutions, the increase of overvoltage found by the direct method becomes almost proportional to increase of *C.D.* for high values of the latter. This may be taken as evidence that overpotential measured by the direct method at high *C.D.*'s consists of the sum of a true polarisation, which is almost independent of the *C.D.*, and a term which results from passing the current through a more or less constant resistance at the surface of the electrode.

4. Replacing Gore's term "transfer-resistance" by the term "transfer-impedance," to describe effects of which the irreversibility or otherwise has not been established experimentally, our results may be described by saying that, in some of the cases examined, transfer-impedance has been proved to be irreversible after $1/5000$ sec.

5. The time-polarisation curve shows considerable change in direction on extrapolating it backwards to zero time, and we therefore recommend that the polarisation measured and the time-interval of its measurement should be stated, rather than that attempts should be made to extrapolate to zero time from a small number of measurements as advocated by Glasstone (*loc. cit.*). We have confirmed in a number of cases that the values obtained sufficiently closely represent the average polarisation during the time of measurement and that they are not greatly affected by slight variations of the latter.

6. Overpotentials found in acid solution increase slightly with dilution. The effect is, however, smaller than corresponds to the relation $\omega - h = c$, in which the symbols have the significance attached to them above (p. 392). Experiments by Herasymenko (*loc. cit.*), for which the above relation holds, are therefore of a different character from ours.

7. Solutions containing relatively large amounts of alkali salts require high *C.D.*'s to establish constant overvoltages by the commutator method, and the results are similar in character to those obtained in alkaline solution. Here, doubtless, local changes of composition are operative. Where our results for antimony cathodes cover ground already explored for lead and mercury by Glasstone (*loc. cit.*), they are in general agreement with his.

8. No results of a general nature could be obtained connecting the production of stibine in acid solution with overpotential. The yields were small and appeared to depend largely on the solubility of the cathode in the electrolyte, and on extremely high values of *C.D.*

9. In alkaline solution, the overvoltage-current density curves obtained by the direct method show an arrest or inflexion which usually takes place at a voltage not far removed from the maximum given by the commutator method. The decay curves representing the overvoltage at successive short intervals after breaking the current also give indications of this same value, for they sink to, and become constant for a considerable time at, a potential not far removed from it.

10. The relation $\omega + 2h = c$, previously proposed by Sand and Weeks, could not be confirmed with any degree of accuracy, but the results suggest the probability that a relation of the kind may exist which is vitiated by secondary interfering influences.

11. The formation of stibine appears to proceed somewhat more readily in alkaline than in acid solution, and the conditions favourable to it are similar in the two cases. To obtain appreciable yields of the gas, however, it is necessary to blow a rapid current of hydrogen past the electrode, in order to carry away the nascent gas before it has been decomposed by the alkaline solution. The decomposition product formed, when this is not done, has the properties of metallic antimony.

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