OVERVOLTAGE.

BY

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OVERVOLTAGE.

Overvoltage of hydrogen, as considered by Caspari,[1] is the difference in potential between a Platinised Platinum electrode saturated with hydrogen gas and the electrode in question, while hydrogen is being liberated upon it by electrolysis. His data was obtained by the use of the apparatus in Fig.1. E. is a battery, used as a source of current for generating hydrogen and oxygen on the electrodes A. and B.. The electrodes A, B, and C, are connected by 1mm. tubing and the electrolyte, when not otherwise stated, is normal sulfuric acid. C. is a Platinised Platinum electrode, partially immersed in the electrolyte and kept saturated with hydrogen gas at atmospheric pressure, and serves as a standard electrode. B. is another Platinised Platinum electrode and serves as anode, while A is the electrode to be studied. D. is a burette like tube connected to the apparatus by means of a rubber tube, and is used for filling and emptying the apparatus. By means of the bridge G. the current is regulated so that bubbles of gas just begin to appear on the electrode A. When this occurs the potential between A. and C, is measured by means

[1] Zeit. Phys, Chem. 30, 89.

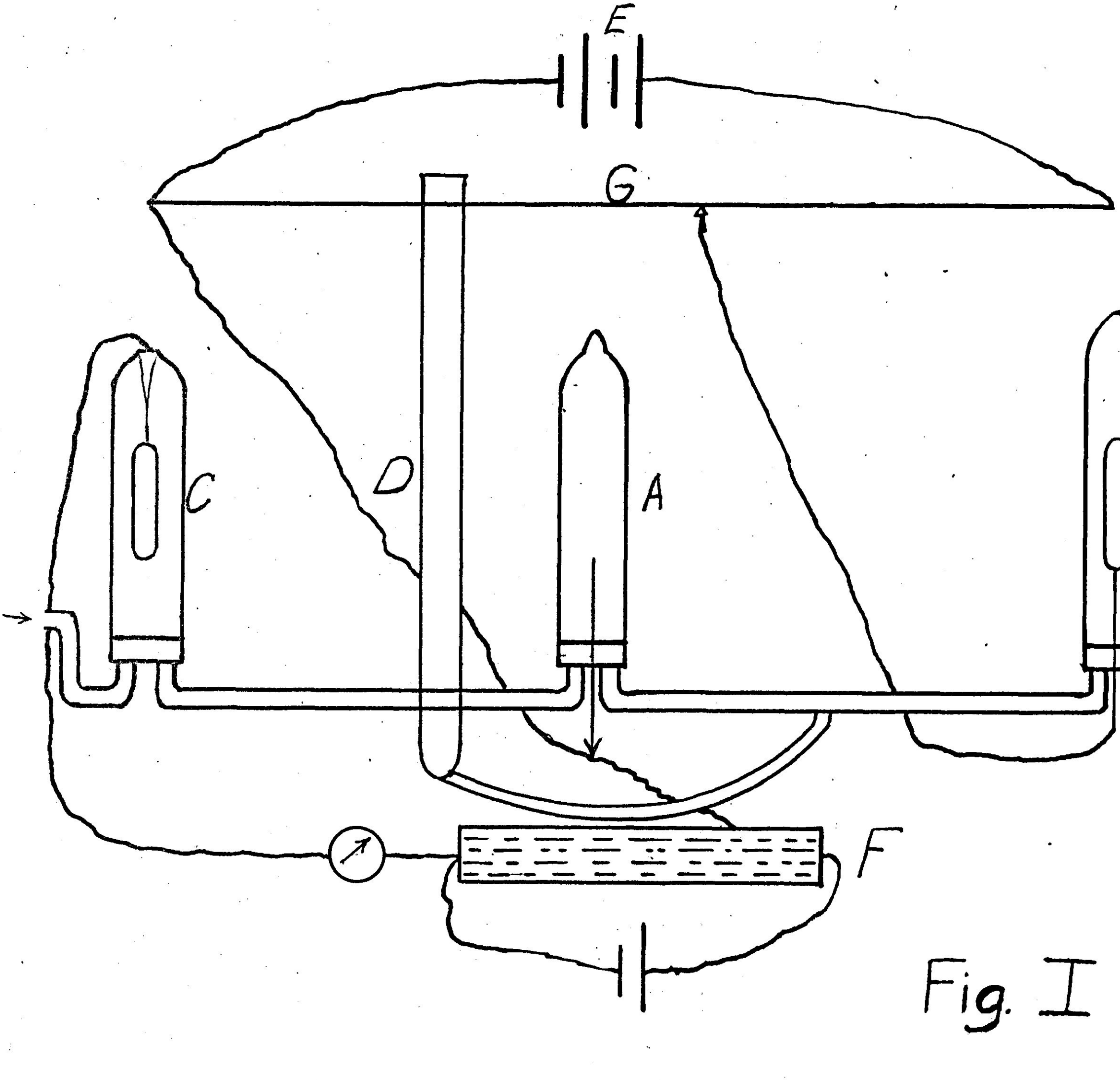


Fig. I

of the potentiometer F. Caspari noted that in order to obtain concordant results, the gas must be evolved on A. until the the electrode is well saturated, before the voltage is read. Also that the readings must be taken on raising and not on lowering the current from the battery E.,which generates the gases on the electrodes. The results obtained by Caspari are given in Table 1.

LeBlanc [2] considers over-voltage as the excess back electromotive force generated at an electrode, over that of a Platinised Platinum electrode. This is also the view held by Newberry [3] who obtained some data similiar to that of Caspari, but who used a commutator which closed and opened the circuit 2500 times per minute. He thus obtained the voltage of the cell after the charging circuit was broken. Bennette and Johnson also have this view in mind in their theory advanced to explain overvoltage[4].

Amony the most important theories advanced to explain overvoltage are probably those of Moller Nernst, Tafel and Bennette and Johnson.

Moller[5] says that before any bubbles of gas can come off from an electrode there must be a layer of gas over the electrode of a certain thickness.

2.Text book. 3, Jr. Chem.Soc. Vol. 105-106

4, Jr. Phys. Chem. Vol.20, 303-321. Zeit.Phy.Chem. 65,228.

For hydrogen he has estimated this layer to be about 10^{-7}cm. in thickness. The overvoltage is a measure of the energy necessary to maintain this layer of gas of a difinite thickness on the electrode.

Foerster[6] is of the opinion that there is an intermediate compound formed on the electrode. This intermediate compound produces a high resistance and hence a high overvoltage. For Anodic overvoltage oxides of the type NiO_2, PtO_x and PdO_y would be the intermediate compounds formed. In the case the oxides are stable the overvoltage is high and when they are unstable the overvoltage is low. In the case of hydrogen overvoltage a complex hydride would be the intermediate product formed.

Nernst and Tafel have similiar views. Nernst believes that before the gas can be liberated the ions must be driven into the electrode and that energy is needed to drive them in. Metals which have no tendency to occlude gases require more energy to force the ions in and hence they have a high overvoltage. This idea of the ions penetrating the electrodes is strengthened by the work of Newberry, who made some Microphotographs of metal

[6] Zeit Phys. Chem. 69. P. 270.

plates of copper, Zinc and Platinum both before and after being run as cathode in electrolysis, with a current density of one ampere per sq. cm. These show extremely minute pittings in the metal. Some of these, when examined under a microscope with oblique illumination, show a peculiar crater-like form, suggesting that the metal had been blow out by an internal explosion. These pittings are very likely caused by the escape of the gaseous hydrogen formed in the electrode by the union of the un-ionised atoms of hydrogen. The Platinum and Palladium electrodes used in this work darkened somewhat, so it is very likely that this pitting was the cause.

Tafel thinks that the gas which accumulates on the electrode is the cause of the back electromotive force. He however, goes further in the case of hydrogen and assumes that there is an intermediate stage between the ionic hydrogen and the hydrogen gas. This intermediate product forms gaseous hydrogen more or less readily, depending on the catalytic effect of the material of the electrode.

If the electrode material is a poor catalyzer, the rate of transformation is slow and consequently its concentration high, and therefore a high overvoltage would result. If the metal were a good catalyzer, just the opposite would be the result.

Newberry[7] attributes overvoltage to three factors,

1, Supersaturation of the metal surface with non-electrified gas under very high pressure, due to the permeability of the metal to the ionised gas, but non- permeability to the molecular gas..

2, Deficiency or excess of non-hydrated ions in the immediate neighborhood of the electrodes.

3, Inductive action of the escaping ionised gas on the electrodes.

According to Bennette and Johnson[8] overvoltage is the excess back electromotive force of the system during electrolysis over the reversible electromotive force of the system, consisting of the final products and is due to the accumulation, during such electrolysis of unstable intermediate products above equilibrium concentration. These intermediate products are assumed to be the substances in the monatomic state, H_1 O_1 etc, for gases and M_1 for metals.

7, Jr. Chem. Soc. Vol.105 P.242-243.

Their reasoning is based on the irreversibility of chemical equations that take place in more than one step, and the high activity of the intermediate products. Hydrogen, in going from the ionic state to the molecular state gives nascent hydrogen, as an intermediate product. Nascent hydrogen is much more active than either ionic hydrogen or molecular hydrogen, as it will bring about reductions which neither of the other varieties will, as for example, the reduction of zinc oxide and cadmium sulfate at ordinary temperatures.

When molecular hydrogen dissolves in water the concentration of the monatomic hydrogen must come from zero up to equilibrium concentration and can go no further, as there is no energy supplied from without. In the reverse direction hydrogen ion goes to monatomic hydrogen and then to molecular hydrogen. The same equilibrium concentration must be reached here as before, and the molecular hydrogen is formed only after this concentration has been reached. In this latter case the concentration of monatomic hydrogen will depend on the conditions of electrolysis, and the kind of electrodes, etc. and

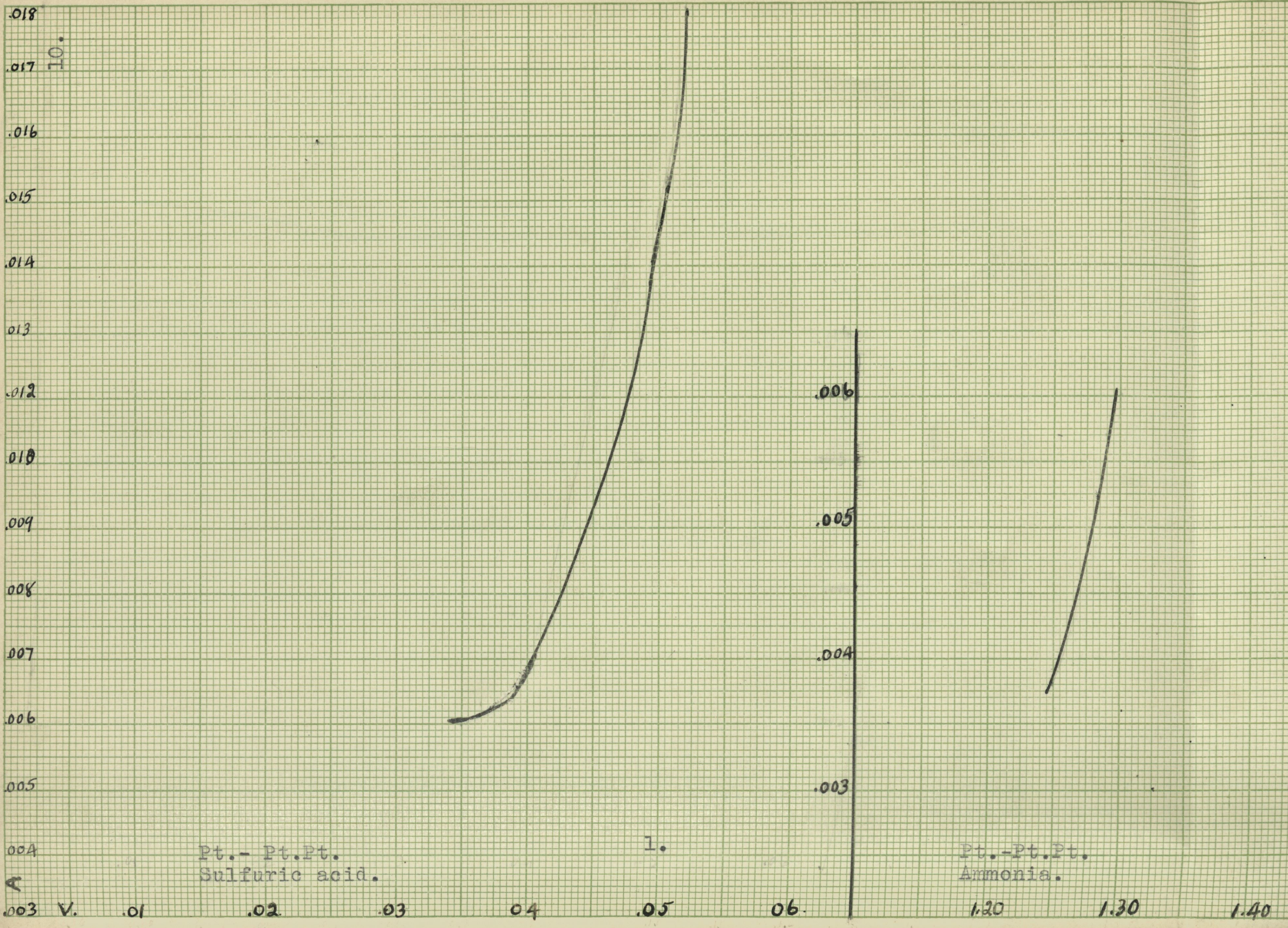
8, Jr. Phy. Chem. Vol.20. P. 521.

the difference between this value and the equilibrium concentration is a measure of the irreversibility of the reaction. This excess of monatomic hydrogen over the equilibrium value, is looked upon by Bennette and Johnson as the cause of overvoltage.

The object of this research was to obtain some overvoltage values for different metals in liquid ammonia. Considerable trouble with the electrodes was encountered on the start, so some data using sulfuric acid as the electrolyte was taken, to serve as a check on the method outlined to be used. However, in this case concordant results could not be obtained until after the sulfuric acid had been electrolised for some time. The acid used, was very likely lead chamber acid and contained a trace of lead, which had to be removed otherwise it was deposited on the electrode thus giving an alloyed electrode, and hence concordant results could not be obtained. After this difficulty had been overcome the overvoltage for bright Platinum and bright Palladium against Platinised Platinum ,given in the tables that follow were obatined. This data is for room temperature when not otherwise noted in the tables.

It will be noted from the curves on Plate 1. that both in aqueous sulfuric acid and in liquid ammonia solution, the overvoltage increases as the current density increases, and that the increase is about of the same order. Newberry[9] found that the overvoltage of hydrogen on Platinum increased with an increase of current density up to 300 milli-amperes per sq. cm. With higher current density the overvoltage decreased, falling to -.03 volts at 2000 milli-amperes per sq. cm. Bennette and Johnson explain this in the following manner, "The decrease of overvoltage at high current density is to be explained in part by the rise in temperature which we have seen lowers the overvoltage, but largely on account of the fact that the concentration of H_1 and O_1 becomes so great that they are forced to break down as soon as formed, namely at the surface of the electrode. The highest current density used, it may be seen is 200 amperes per sq. decimeter, which means that the electrodes will all but be covered by a film of gas. In such concentrations it may be seen that the

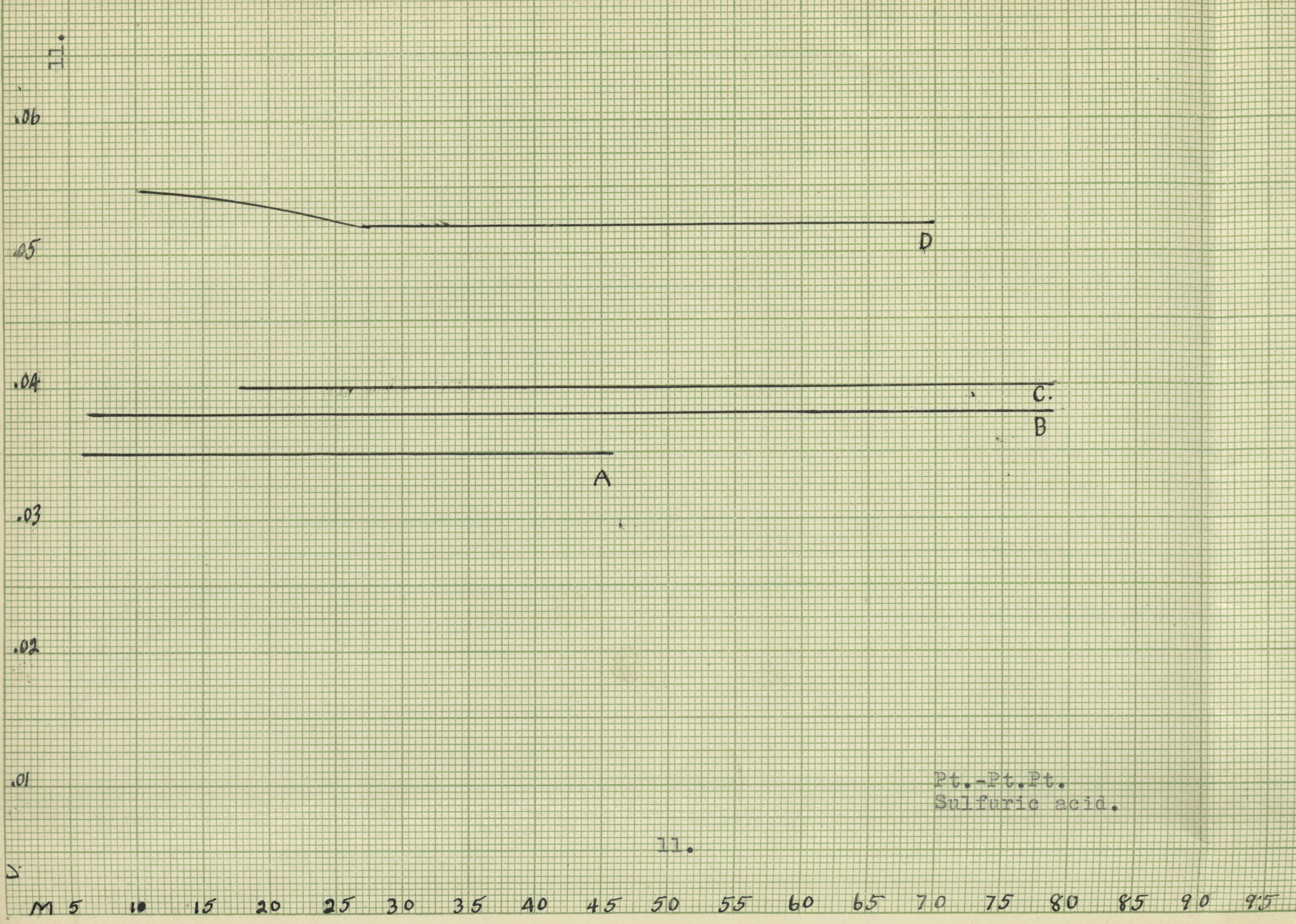
[9] Jr. Chem. Soc. Vol.105-106.



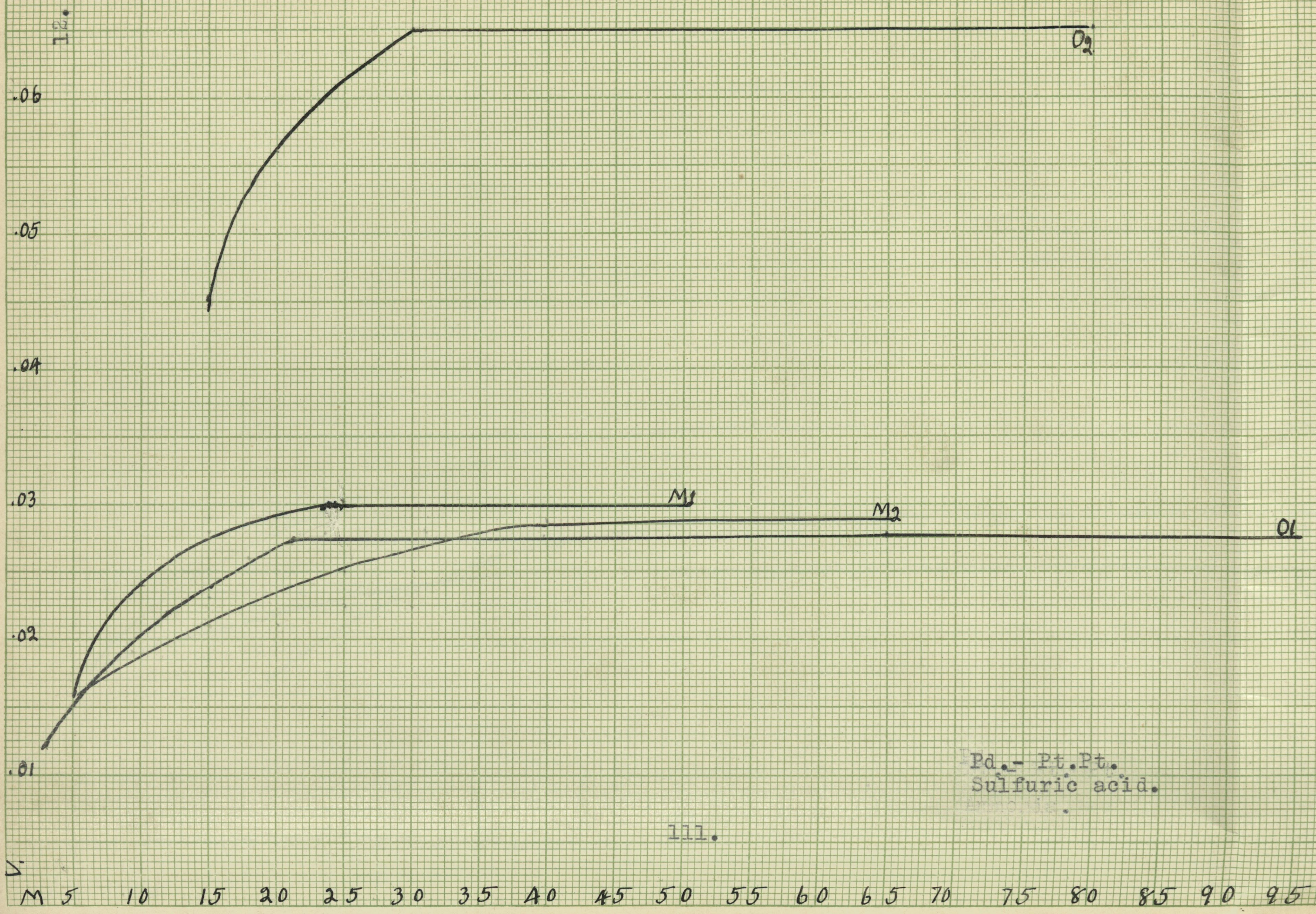
1.

Pt.- Pt.Pt.
Sulfuric acid.

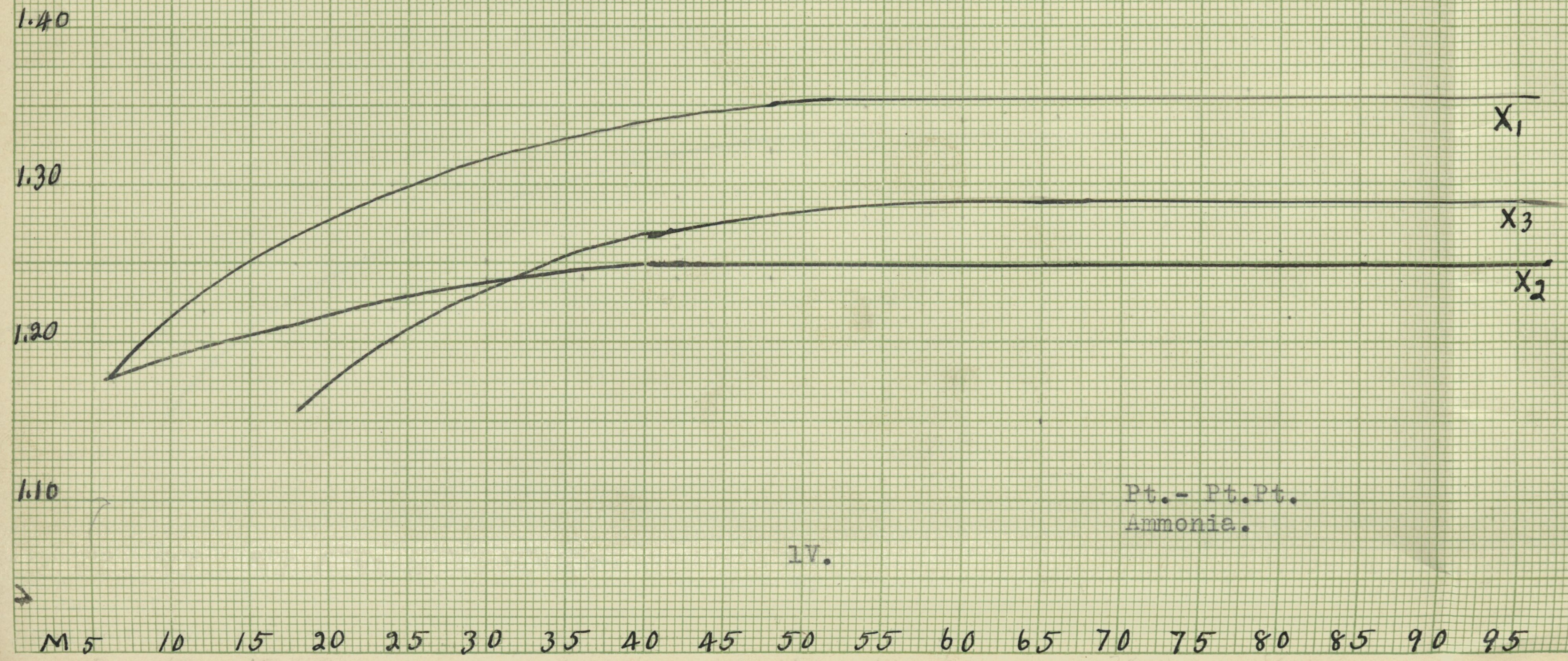
Pt.-Pt.Pt.
Ammonia.



Pt.-Pt.Pt.
Sulfuric acid.

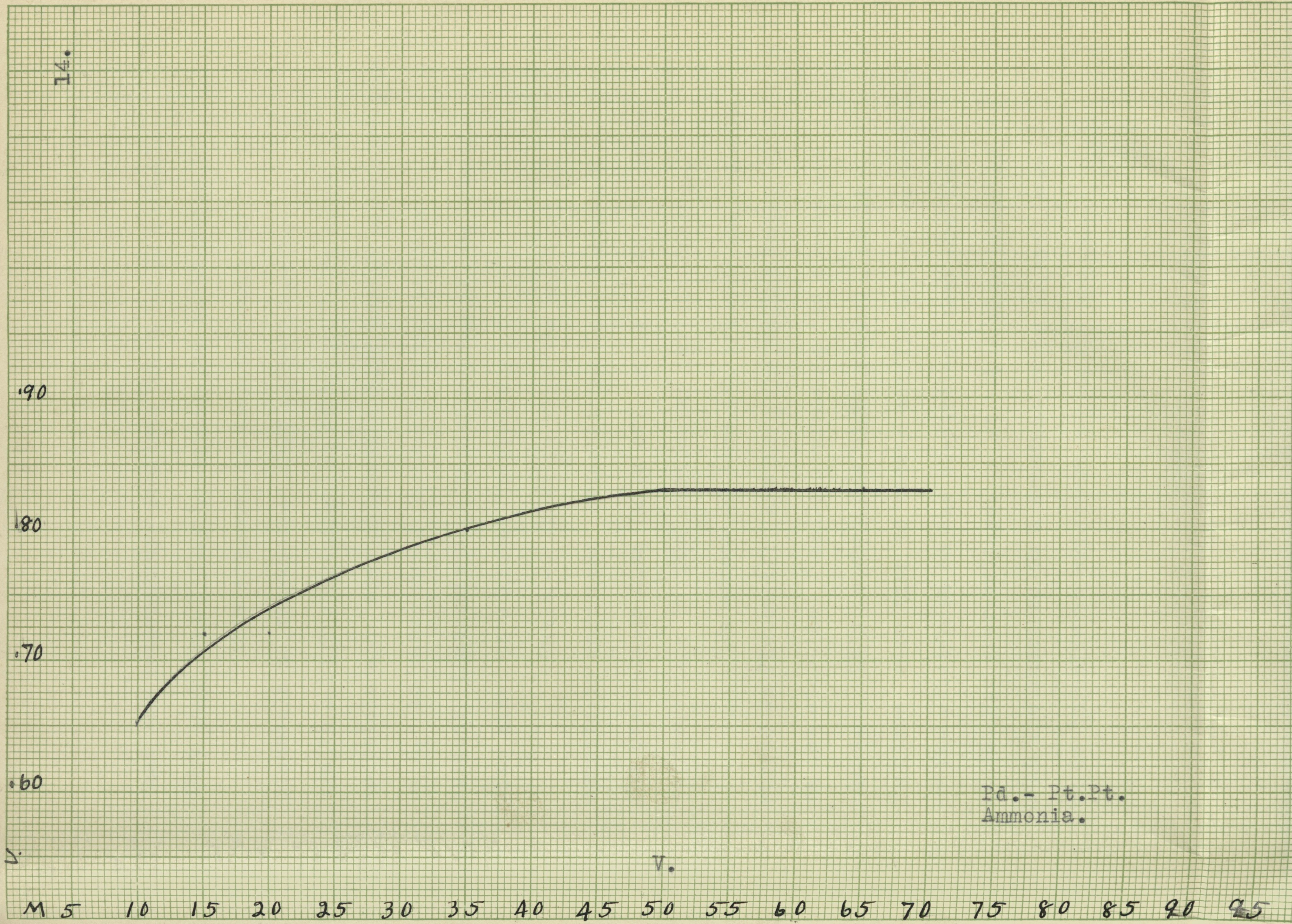


Pd.- Pt.Pt.
Sulfuric acid.



Pt.- Pt.Pt.
Ammonia.

1V.


.90
.80
.70
.60
V.
V.
M 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95
Pd.- Pt.Pt.
Ammonia.

that the intermediate products would be so unstable that they would form molecular gas immediately."

This explanation does not seem very plausible as theyassume that overvoltage is due to a high concentration of H_1. In order to obtain and also maintain a high enough concentration of H_1 to cause rapid decomposition, it seems evident that this high concentration of H_1 would give rise to a higher overvoltage.

Table D. shows us that if the current density is decreased after it has been increased the overvoltage also falls off rapidly to the value corresponding to that particular current density.

The effect of time is brought out by the curves on Plates 111, and 1V., the values being low on the start and finally increasing to a constant value. This is what one might expect, as it requires some time to obtain equilibrium concentrations of the substances on the electrodes, that are the causes for over-voltage. It will also be noted that the increase to a constant value is much more rapid in sulfuric acid than in liquid ammonia.

Palladium rrquires a longer time to reach a constant valuen eve, in acid solution. This may be attributed to the fact that the Platinum electrodes were very thin, thus requiring a short time for the substances on the electrode , to come into equilibrium with it, while the Palladium was much thicker and hence required a longer time.

The effect of temperature on overvoltage with Palladium and Platinised Platinum electrodes is illustrated by the curves O_1 and O_2. It will be noted that the increase of temperature from that of the room, to that of boiling water, was followed by an increase in the overvoltage from .03 to .06 volts. This seems to be contradictory to the results shown by Bennette and Johnson, of Pring and Curzon, in which the overvoltage using a copper cathode, fell from .35 to .25 volts on a rise of the temperature from 11.5° to 60° . From the results obtained with Palladium and Platinised Platinum electrodes, it seems evident that overvoltage cannot be due to the difficulty of hydrogen leaving the electrode, as at the higher temperature it would be easier for the hydrogen to leave, since it would be aided by the high vapor of the solution.

If we were to accept the view of Bennette and Johnson the increase in overvoltage with rise in temperature would seem to imply a lower rate of transformation of H_1 to H_2 at high temperature than at low. Since with rising temperature the rate of reaction is almost invariably increased it would seem that these experiments are in better accord with the theory of Nernst than that of Bennette and Johnson.

It will be noted that the overvoltage of hydrogen on Platinum and Palladium in liquid ammonia is much larger and that the temperature is -33 ° . However, this is at the boiling point of liquid ammonia, and therefore the high vapor pressure of the ammonia, as above, would aid the hydrogen in escaping from the electrode, thus again eliminating the view, that the overvoltage is due to the difficulty of the hydrogen leaving the electrode. For this reason the high overvoltage must be attributed to another cause which is probably as stated later.

The relation between the overvoltage on Platinum and Palladium in sulfuric acid and in liquid ammonia is also brought out.

While the overvoltage values for Palladium and Platinum in liquid ammonia are much larger than the corresponding values in sulfuric acid, yet the ratio between Palladium and Platinum in acid and Palladium and Platinum in liquid ammonia are practically the same, being .70 in acid and .65 in liquid ammonia. Just why the values in liquid ammonia are so much higher is hard to say. If we believe, as Nernst, that the ions penetrate the electrode , which requires energy, we would very likely conclude that , since the ammonium ion from the ammonium nitrate in the liquid ammonia, is so much larger than the hydrogen ion from the acid, it requires more energy to drive it into the electrode. and hence a high overvoltage results. The values given for Palladium cannot be entirely relied upon as the electrodes were giving trouble at the time and they were not at exactly zero potential at the start. However, these values are very close and a very good comparison of Platinum and Palladium can be gotten.

A sketch of the apparatus for carrying out the work is shown in Fig.11. A. is a large Dewar tube containing liquid ammonia for surrounding B. to keep the temperature constant and to prevent rapid evaporation. B.is a tubular flask five cm. in diameter and thirty six cm. long. It is fitted with a large rubber

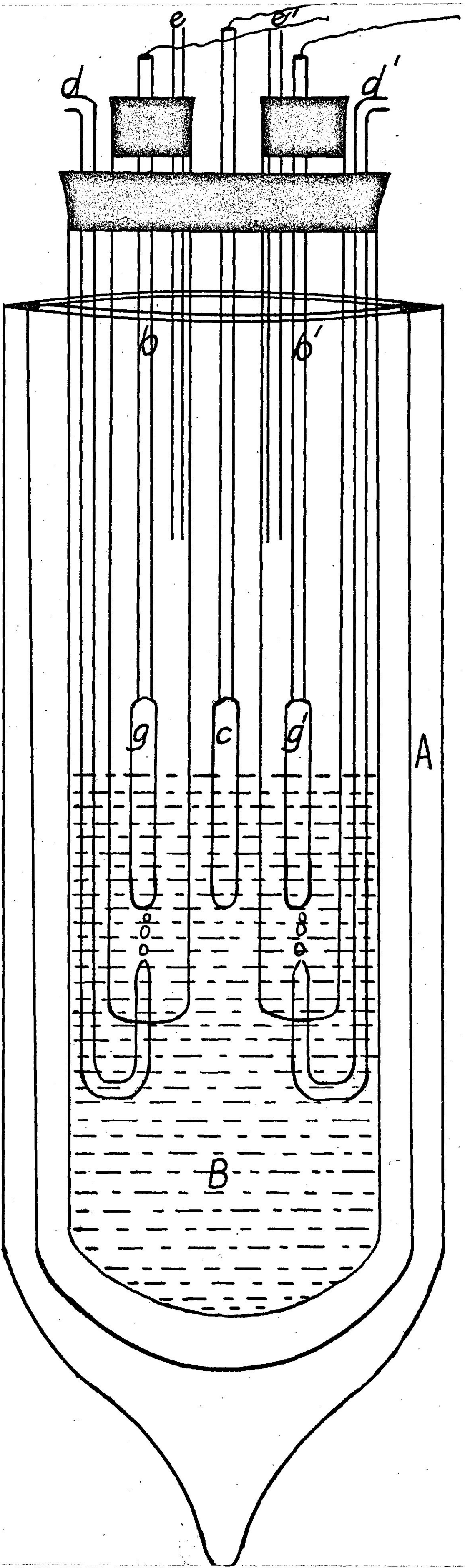


Fig. II.

stopper. Thru two small holes are fitted the tubes b and b'. These are one centimeter in diameter and thirty centimeters long. The lower ends are drawn down to one mm. openings. Into these openings are inserted the drawn down ends of the tubes d and d', thru which the hydrogen gas enters the cell. Into the top of the tubes b and b' are fitted two holed stoppers. Thru one of these holes in the stoppers are fitted the stems of the electrodes g and g' and thru the other the exit tubes e and e', the ends of which extend below the surface of some oil in a flask. c, is an electrode similiar to g and is used as anode to the electrode to be studied.

Pieces of insulated wire lead from the electrodes g and g' and c, from c to the source of current, g to the potentiometer, and g' to a commutator which was connected to the source of current and also to the potentiometer. By means of the commutator , current for half a revolution , went thru c and g generating hydrogen on g and for the other half revolution connection was made thru the potentiometer between the standard electrode g and the electrode g' and thus the potential between the standard electrode g ,which is saturasted with hydrogen gas and the unknown electrode g' is measured. The current used for generating the hydrogen on the electrode g' was regulated by the use of a lamp board and the amount of current going thru the solution measured by means of an ammeter place in the circuit.

The electrodes used were made in the following manner, A piece of four mm. tubing six cm. long was sealed on one end and blown out to uniform size. The other end was drawn down to about one mm. in diameter and sealed on to a piece of one mm. tubing thirty cm. long. A small piece of Platinum wire ,fused on to a long piece of insulated copper wire , was sealed thru the bulb of this electrode, a small amount of lead glass being used to make sure there would be no leak. The bulb of the electrode was then given several coats of "Platin Glanz" , each coat being burned in thoroughly before another was added. By this method a bright Platinum electrode was obtained. However, before using it was first cleaned thoroughly by soaking in chromic acid, after which it was run as anode to remove any metals that might happen to be present as impurities. To make Platinised Platinum electrodes two electrodes prepared and cleaned as above, were placed in an acid solution of Platinic chloride and run alternately as anode and cathode for one minute intervals until a black velvety coat of Platinum black was secured on the electrodes. In case only one electrode is desired to be plated, it is run as cathode, a small Platinum wire being used as anode. The source of current used was two Edison cells. The current should be regulated so that there is a moderate evolution of bubbles on the electrode. If a strong current isused the Platinum black does not adhere well to the electrode and precipitates from the solution.

In carrying out the experiment enough sulfuric acid or ammonia solution ,as the case may be, was placed in A, so that the electrodes were half immersed in the liquid. The hydrogen generator was then started, electrolytic hydrogen being used. The hydrogen, when ammonia solution was used, was dried by passing thru sulfuric acid and then thru shaving of metallic sodium. The gas entered the cell thru the tubes d and d' and bubbled up around the electrodes g and g', g being the standard electrode and g' the one to be studied. The excess of hydrogen passed out thru the exit tubes e and e', escaping finally into the air. The gas was passed over the electrodes for several hours to make sure that they were thoroughly saturated before any readings were taken. The potential between the two electrodes g and g' on the start should be zero and in all cases hydrogen was passed over until there was zero potential between them, before the experiment was begun. The motor which gave about twenty five hundred revolutions per minute and to which the commutator was attached, was then started, the current thru the solution turned on and regulated to the desired current density, so that a moderate evolution of hydrogen resulted on the electrode. Readings were taken at regular intervals as is shown on the data sheets that follow.

DATA

by

CASPARI.

Metal.	Cathode excess.	Anode excess.
Pt. (Platinised)	.005	.36
Au.	.02	.56
Fe.(in NaOH.)	.08	--
Pt. (Polished)	.09	.59
Ag.	.15	--
Ni.	.21	--
Cu.	.23	--
Pd.	.46	.36
Cd.	.48	--
Sn.	.53	--
Pb.	.64	--
Zn.(in acid with Zn.)	.70	--
Hg.	.78	--
Cu. (amalgamated)	.51	--
Pb. "	.54	--
Cd. "	.68	--

Table 1.

DATA.

Bright Platinum against Platinised Platinum.

Electrolyte, 10% solution of Sulfuric acid.

Table A.

.006 amps per sq. cm.

.037	3	min.
.035	6	"
.035	9	"
.035	12	"
.036	15	"
.036	18	"
.038	21	"
.035	24	"
.036	27	"
.035	30	"
.034	33	"
.036	36	"
.035	39	"
.035	42	"
.035	45	"

Table B.

.0063 amps per sq. cm.

.037	3	min.
.038	6	"
.038	9	"
.038	12	"
.038	15	"
.038	18	"
.038	21	"
.038	24	"
.039	27	"
.039	30	"
.036	33	"
.038	36	"
.037	39	"
.037	42	"
.038	45	"
.038	48	"
.037	51	"
.037	54	"
.038	66	"
.038	91	"
.038	116	"

DATA.

Bright Platinum against Platinised Platinum.

Electrolyte, 10 % solution of Sulfuric acid.

Table C.

.0068 amps per sq. cm.

.040	18 min.
.040	22 "
.040	25 "
.040	28 "
.040	31 "
.040	34 "
.040	37 "
.040	41 "
.040	44 "
.040	47 "
.040	50 "
.041	53 "
.040	56 "
.039	59 "
.040	62 "
.040	65 "
.039	68 "
.039	71 "
.039	74 "
.039	106 "

Table D.

.0183 amps per sq. cm.

.051	3 min.
.052	6 "
.055	9 "
.055	12 "
.056	15 "
.054	18 "
.053	21 "
.054	24 "
.052	27 "
.051	30 "
.052	33 "
.052	36 "
.052	39 "
.052	42 "
.052	45 "
.051	65 "

Amps reduce to .0068

.040	121 min.
.040	140 "

DATA.

Bright Palladium against Platinised Platinum.

Electrolyte, 10% solution of Sulfuric acid.

Table M_1

.0067 amps per sq. cm.

.016	5	min.
.024	10	"
.028	15	"
.029	20	"
.030	25	"
.030	30	"
.030	35	"
.030	40	"
.030	45	"
.030	50	"

Table M_2

.0067 amps per sq. cm.

.016	5	min.
.019	10	"
.021	15	"
.021	20	"
.025	25	"
.025	30	"
.027	35	"
.029	40	"
.029	45	"
.027	50	"
.029	55	"
.029	60	"
.029	65	"

DATA.

Bright Palladium against Platinised Platinum.

Electrolyte, 10% solution of Sulfuric acid.

Table O_1

.0065 amps per sq. cm.

.012	3 min.
.015	6 "
.019	9 "
.022	12 "
.023	15 "
.026	18 "
.027	21 "
.028	24 "
.028	27 "
.026	30 "
.028	33 "
.028	36 "
.028	39 "
.029	42 "
.029	57 "
.028	725 "
.028	87 "
.028	102 "
.028	117 "
.028	132 "

Table O_2

.0065 amps per sq. cm.

.025	15 min.
.029	30 "
.030	45 "
.030	60 "

In boiling water.

.045	75 min.
.056	80 "
.071	85 "
.065	90 "
.064	95 "
.064	100 "
.064	110 "
.065	115 "
.065	120 "
.065	125 "
.065	130 "

DATA.

Bright Platinum against Platinised Platinum.

Electrolyte, Ammonium nitrate in liquid ammonia.

Table X_1

.006 amps per sq. cm.

1.180	6	min.
1.222	12	"
1.249	18	"
1.300	21	"
1.250	30	"
1.260	36	"
1.287	42	"
1.321	48	"
1.351	54	"
1.340	60	"
1.332	66	"
1.330	72	"
1.360	78	"
1.360	84	"
1.360	90	"

Table X_2

.0038 amps per sq. cm.

1.176	6	min.
1.200	12	"
1.213	18	"
1.220	24	"
1.246	30	"
1.245	36	"
1.242	42	"
1.240	48	"
1.252	54	"
1.251	60	"
1.251	66	"
1.251	72	"
1.251	78	"
1.251	84	"
1.250	90	"
1.256	96	"
1.250	102	"
1.250	108	"
1.250	114	"
1.250	120	"
1.250	126	"

DATA.

Bright Platinum against Platinised Platinum.

Electrolyte, Ammonium nitrate in liquid ammonia.

Table X_3

.0057 amps. per sq. cm.

1.162	18 min.
1.199	24 "
1.240	30 "
1.246	36 "
1.260	42 "
1.285	48 "
1.284	54 "
1.278	60 "
1.286	66 "
1.291	72 "
1.290	78 "
1.289	84 "
1.290	90 "
1.290	96 "

Palladium against Platinised Platinum.

.005 amps per sq.cm.

.650	10 min.
.722	15 "
.722	20 "
.800	35 "
.834	50 "
.834	65 "

SUMMARY.

Overvoltage values for hydrogen on Platinum and Palladium in aqueous sulfuric acid and in a liquid ammonia solution of ammonium nitrate, have been obtained with the following results.

Overvoltage, after a certain time, approaches a constant value.

The time required to obtain constant values for overvoltage in sulfuric acid is shorter for Platinum than for Palladium

The time required to obtain constant values for Palladium and Platinum is much longer in liquid ammonia than in sulfuric acid.

Overvoltage on Palladium increases with increase of temperature.

Overvoltage increases with the increase of current density, both in liquid ammonia and slufuric acid.

Overvoltage values are higher in liquid ammonia than in sulfuric acid

The ratio of the overvoltage values of Palladium and Platinum in sulfuric acid and Palladium and Platinum in liquid ammonia are practically the same.

The data obtained seems to be in accord with Nernst's theory of overvoltage.