METHOD OF DETERMINING THE COMPOSITION OF GASES REACTING IN A FLOW SYSTEM

by

Stanislas Hempel
Docteur ès Sciences

Poland

Thesis for Degree of Doctor of Philosophy

September, 1946. University of Edinburgh

ACKNOWLEDGMENTS

The author is indebted to Dr.Mowbray Ritchie for his criticism and advice in the execution of this work; he express also his thanks to Mr.R.Klapiński for his help in the preparation of apparatus and in the carrying out of some of the measurements.

The author writes to thank Professor James Kendall for the facilities which he has kindly provided.

CONTENTS

PART I

INTRODUCTION

As far as gas mixtures are concerned, whose reactions are accompanied by a change in volume, the determination of composition and rates of reaction has previously been carried out largely by static methods i.e. by measuring the changes of pressure occurring at definite time intervals under constant volume conditions. To obtain satisfactory rate measurements in relatively rapid reactions, investigations have usually been undertaken at reduced pressures.

Very accurate measurements of this kind by Bodenstein/9-11/ have resulted in the determination of the velocity coefficients of the following reactions:

$$2NO + O_2 = N_2O_4$$

$$2NO_2 = 2NO + O_2$$

The velocity coefficientsthus obtained can be applied only approximately to the measurements of gas reactions taking place in flow systemsat constant pressure; conversely the determination of velocity coefficientsby such flow rate measurements is a matter of some complexity and difficulty./17/.

The work to be here describedrepresents an attempt to determine the composition of gases reacting in a flow system at atmospheric pressure, the reaction investigated being the oxidation of nitric oxide. The method suggested is based essentially on the measurements of volume variations of the reacting gases at different time intervals. This was achieved by measure of a flowmeter acting at the exit from the reaction chamber. When the gas passing the flowmeter dœsnot change in composition during the flow, the volume of gas passing may be easily determined on the basis of previous calibration, but when the composition of the gas alters in density during the flow, this simple method will not suffice. In the method here adopted the flowmeter was calibrated against the flow of equal masses of various gases of definite density, as will be shown. The graphical relationship so obtained may then be used to determine the density and hence the composition of the gases issuing from the reaction vessel.

The changes in flow rate in the reaction were measured on a differential manometer by means of a cathetometer /estimated accuracy 0·01 mm./. With flows applied in the present measurements, 1 mm. of pressure difference corresponded to 2·3°/o of the volume of gases flowing past; hence 0·1 mm. corresponded to 0·23°/o, which is a sufficient accuracy.

The measurements were carried out under atmospheric pressure, the gases escaping into the open. Such a method involves many difficulties. Maintaining a constant gas flow in the present instance of approx. 300 c.c./min., necessitates many manipulations, often difficult to carry out. However, the gas flow was kept constant with an error normally less than 0·5°/o, provided the constant pressure and temperature were suitably maintained in the NO and O_2 containers.

From the experimental data of the flow volumes the contents of NO, O_2, N_2O_4 and NO_2, respectively, in the issuing flow gases were computed for various reaction periods and for different temperatures. Unlike the static method, the method suggested enables one to measure the reaction rate, at very small time intervals /fractions of a second/ after the reacting gases have been mixed with one another.

Such a method is obviously of advantage when reactions under consideration involve the possibility of an induction period or similar initiating phenomena.

PART II

APPARATUS FOR MEASURING THE CONTRACTION OF GASES DURING THE FLOW.

The apparatus which was finally adopted, after many trials and alterations, for the measurement of rates of oxidation of nitric oxide, consisted of four parts /Fig. 1/.

A. apparatus enabling nitric oxide to be delivered to the reaction chamber at a constant flow rate, constant temperature and constant pressure,

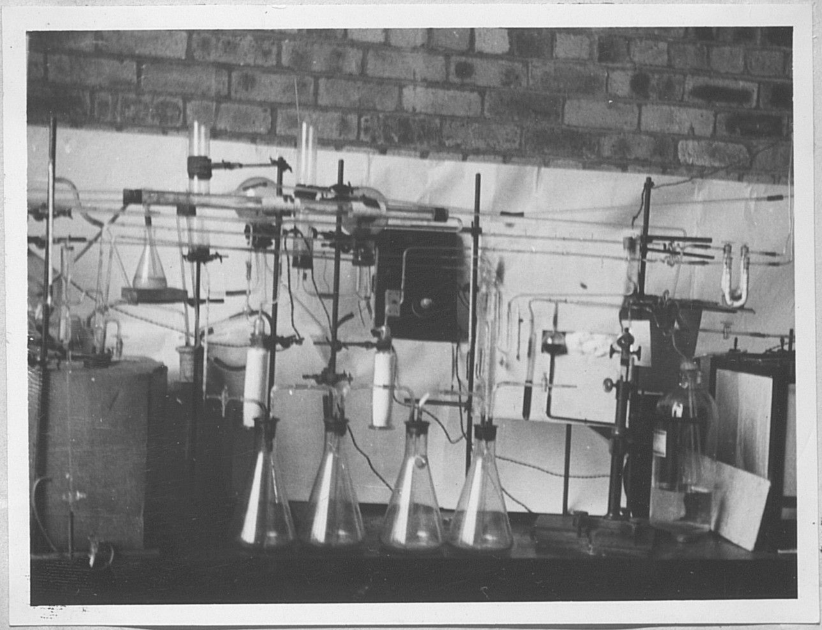
B. nitric oxide producing unit,

C. apparatus in which the reaction takes place, and apparatus for measuring the contraction of the reacting gases,

D. apparatus for oxygen, not shown in the drawing, but similar to that under A.

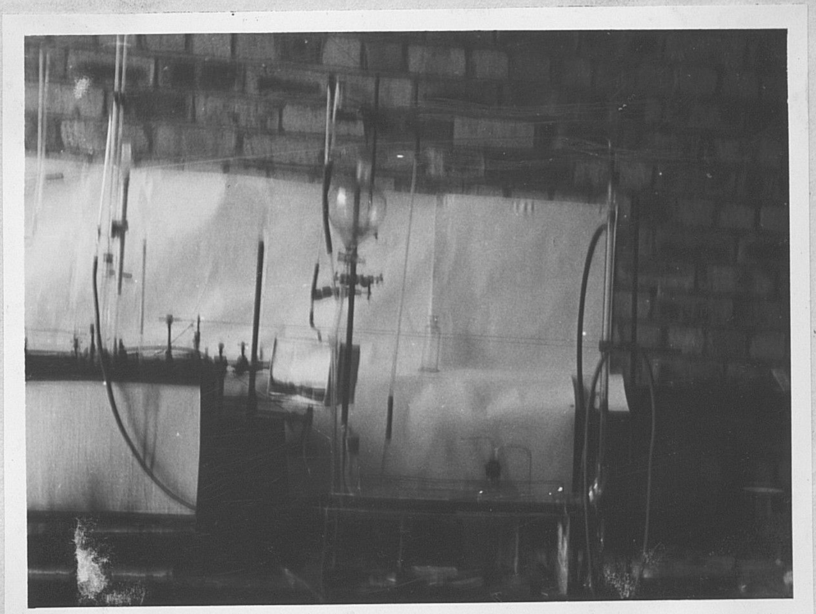
A.

This apparatus consists of a glass vessel /11/ and an arrangement whereby water was delivered into the vessel at a definite flow rate and at room temperature, for the purpose of maintaining an uninterrupted delivery into the reaction chamber of dry gas at a definite temperature and pressure. The vessel /11/ was provided with a tube and stop-cock /12/ for filling with gas, a water manometer, a thermometer, a tube connecting the vessel with the reaction chamber; gas drying vessels with calcium chloride /17/ and phosphorus pentoxide /18/, respectively; and an outlet with stop-cock /8/ for dis-



Vessel of gas and arrangement for gas flow regulation charging water during filling with gas, and for passing water into the vessel when gas is delivered from the vessel. In order to maintain the constant flow rate and constant temperature of displacing water, the respective apparatus consists of: a water tap /1/; a flask /1a/ for heating water; two vessels /2/ and /3/ for maintaining the constant water level; a bottle /4/ in which the water ultimately assumes the temperature of the surrounding air; an outlet /5/ fitted with a nozzle /6/, the level of which can be altered arbitrarily, thus changing the flow rate; a tube /7/ delivering water from nozzle /6/ through /8/ to bottle /11/. The rate of flow of water through nozzle /6/ was controlled by adjusting the nozzle at a corresponding level with regard to the level in vessel /2/ and /3/, and by measuring in a volumetric flask /10/ the quantity of water delivered during a definite time from the stop-cock /9/. In order to obviate the effect of the variable kinetic energy of water falling from the nozzle /6/, a constant high water level is maintained in tube /7/ by means of an automatic device not shown in the drawing. By the above means the gas flow rate of 205·5 c.c.NO/min. within the limits of error of 0·3°/o could be maintained for several hours.

Two identical sets of such apparatus, viz. for nitric oxide, and for oxygen, respectively, were employed.



Apparatus for nitric oxide continuous production

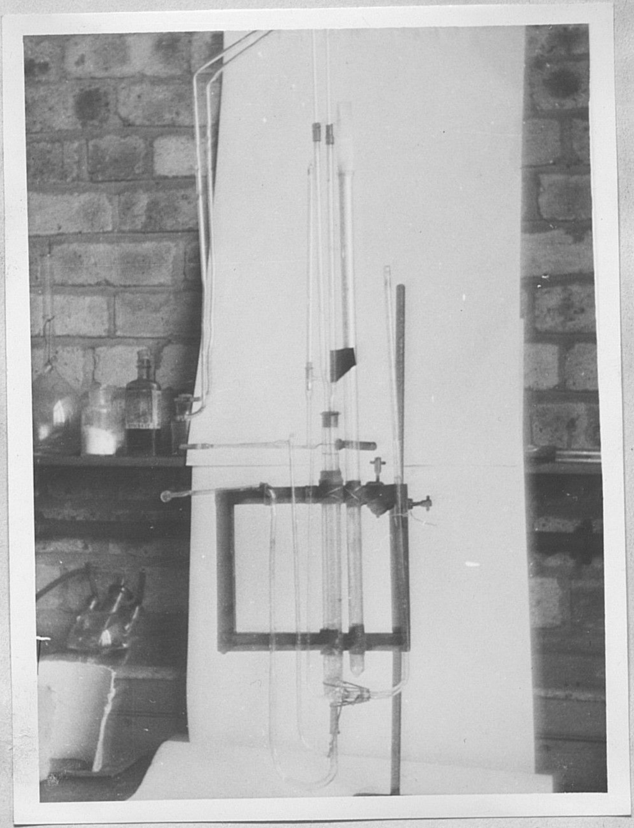
B.

The apparatus for the continuous production of NO consisted of a horizontal Pyrex glass tube /13/ heated by means of a tubular burner. A cooled aqueous ferrous sulfate solution mixed with sulfuric and nitric acid is delivered from vessel /14/ at one end of the tube; at the other end the resultant liquid is discharged at the bottom, while gaseous NO was liberated from water in the vertical condenser /15/. The nitric oxide thus obtained, when analysed in a Hempel burette by means of potassium permanganate, was found to contain more than 99°/o NO, the balance being assumed to be nitrogen.

The oxygen was taken from a cylinder and analysed with an Orsat apparatus.

C.

The apparatus in which the oxidation of NO to NO_2 took place consisted of the reaction chamber /19/ placed in a constant temperature water bath /29/, provided with an electric heater /22/, a mercury-in-glass thermoregulator /23/, a motor driven stirrer /28/, and a thermometer (26) by which the temperature was recorded to the nearest 0·01° C. A gas heated Pyrex coil preheater (21) served for delivering water having the bath temperature into the



Reaction chamber

inner cylinder of the reaction chamber. The reaction chamber was connected to a differential manometer /24/, the reading of which was determined by means of a cathetometer /25/ with an estimated error of 0·01 mm. The differential manometer was filled with alpha-bromonaphthalene, this liquid not being appreciably attacked by NO_2. The manometer /25/ gave the static pressure inside the reaction chamber.

The Variable-Volume Reaction Chamber. /Fig. 2/

The oxidation took place in the space /1/ formed by a glass cylinder /2/ of 23 mm. bore, with a semi--spherical bottom, and by an inner cylinder /3/ closely fitting into the outer cylinder. The position of the inner cylinder defines the size of the reaction chamber. A piece of rubber tubing /4/ prevented the entrance of air.

The reacting gases NO and O_2 reach the reaction chamber through tubes /5/ and /6/ respectively, these tubes having a common outlet at their bottom parts. When passing through the tubes, the gases are heated with water circulating through the interior cylinder from and to the constant temperature bath. The water inlet is at /7/, near the thermometer for determining the temperature of the water. The pointer /8/ is arranged on one of the tubes for the purpose of indicating the chamber space on the scale /9/.

The gas exit in the bottom portion of the outer cylinder is fitted with a small nozzle /10/ which increases the pressure of the gases in the chamber. After passing that nozzle, the gas escapes freely into the air through the tube /11/. The pressures inside the chamber and beyond the nozzle are transmitted to the differential manometer through tubes /12/ and /13/, respectively. The mean temperature in the lowermost part of the chamber is read on a long thermometer, the mercury bulb of which is arranged inside the chamber. Both the thermometer and the nozzle are connected to the chamber by greased ground joints.

PART III

THE PRINCIPLE OF MEASURING THE VOLUMES OF FLOWING GASES WHOSE DENSITIES VARY DURING THE FLOW; THE CALIBRATION OF THE NOZZLE. /DIAGR. 1 AND TABL. 1/.

It was found experimentally that a straight line is obtained if at a given temperature volumes corresponding to equal masses of various gases of different densities /e.g. CO_2, Cl_2, air, N_2/ passing through the chamber, were plotted against the respective rises in pressures on either side of the nozzle. When dealing with the same gases at another temperature, another straight line is obtained.

Chlorine and air were used for the purpose of calibrating the nozzle, since the values between their densities comprise the densities of the mixtures of gases NO, O_2, N_2, NO_2 and N_2O_4, at any degree of dissociation of N_2O_4. At a given temperature and pressure, volumes of Cl_2 and air have been used, corresponding to a mass of 0·4 g. per minute. The same mass was always used when measuring the oxidation of NO, i.e. the sum of masses of NO and N_2 led through the apparatus during one minute was always equal to 0·4 g. The measurements of the pressure difference $p_1 - p_2 = h$ in the reaction chamber, obtained for Cl_2 and air gave the data of <u>h</u> for different temperatures, as shown in diagram D1.

From diagram 1 one obtains diagram 2 in which the abscissae represent the pressure <u>h</u> in millimeters read on the differential manometer, while the ordinates represent the flow rates expressed in c.c./min. at N.T.P. The mass of the gases being always equal to 0·4 g., it

Table 1.

Calibration with air.							
N.	gasvessel		t° of bath	chamber		h m.m bromn.	h x 5
	t°.	p m.m.		t°.	p.		
1	16.5°	114	29.8°	29.8	51.	52.43	262
2	16.5	114	35.8	35.8	52.7	53.80	269
3	16.5	117	40.1	39.6	53.4	54.76	274
4	16.6	120	45.8	45.2	54.2	55.73	278
5	16.5	114	51	50.5	55.3	56.77	284
6	16.6	115	56.1	55.5	56.3	57.76	289
7	16.8	116	60.8	60.4	56.8	58.65	293
8	16.8	115	66.1	66.7	58.1	59.68	298
9	16.8	115	70.3	69.7	59.2	60.68	303
Calibration with chlorine							
10	16.8	41	32	33.3	19.7	20.65	103.
11	16.8	41	41.4	41.8	19.8	21.05	105
12	17.4	44	52.1	52.7	20.0	21.62	108
13	17.4	38	60.9	60.7	20.8	22.46	112
14	17.4	38	70.	69.3	21.8	23.14	116

p = pressure indicated by manometer 11 a (Fig 1) has been found that the flow rate for air was 309·5 c.c./min., and for chlorine 124·5 c.c./min. /N.T.P./. Next, the h points for temperature of 30°, 35°, 40° ... are transferred from diagram 1 to diagram 2. Thus we obtain in diagram 2 a series of straight lines corresponding to temperatures 30°, 35°, 40° ... plotted on axes of h and of flow rates of the gases expressed in c.c./min. at N.T.P.

The diagram 2 enables one to read in c.c./min. the N.T.P. volume of a gas flowing at different temperatures.

The measurements of the rate of the oxidation of NO were carried out with a mixture containing 189·1 c.c. NO, 99·1 c.c. O_2 and 4·5 c.c. N_2 N.T.P. per minute, the total mass being 0·4 g.

The readings of h for various chamber volumes and various temperatures enable one to read directly in diagram 2 the flow rate in c.c./min. at N.T.P. on the corresponding straight line.

Results.

The measurements of differential pressures in reactions with flowing gases which escape freely into the surrounding air involve many difficulties caused by sudden changes in the atmospheric pressure. Consequently, the measurements have been carried out as far as possible under conditions of steady barometer pressure.

After filling the gas containers with NO and O_2, the gases were analysed for NO, O_2 and N_2. Assuming that the pressure in the containers was a known and constant one e.g. 100 mm. water head, the flow rates of the gases were calculated so as to maintain the stoichiometric relation NO : $O_2 = 2 : 1$, and to have the sum total of the gaseous masses equal to 0·4 g./min. The results obtained were: volume of NO - 189·1 c.c./min., O_2 - 99·1 c.c./min., N_2 - 4·5 c.c./min. N.T.P., hence NO : $O_2 = 1·91 : 1$.

After the constant temperature of the bath had been reached and the required water-flow into the gas containers adjusted, the stop-cock /9/ was closed and the stop-cock /8/ opened. Water flowed into the bottle and displaced the volumes of gas equal to the volumes of added water. This refers alike to NO and O_2. Each gas then entered the reaction chamber, in which the gases mixed and reacted with each other.

The measurements always began with the smallest chamber volume, i.e. position 1 corresponding to the volume of 5·7 c.c. The thermometer /20/ showed the rise in temperature, while the differential manometer /24/ indicated the difference of pressures on either side of the nozzle. As soon as the cathetometer readings of the pressure were constant and the temperature in the chamber did not rise any more, readings were taken as already shown in Table 2. Thus, measurements were carried out for sixteen positions of the adjustable tube, corresponding to sixteen different volumes. As shown in Table 2, the variations of temperature in the gas bottles did not exceed 0·5° which is equivalent to 0·3°/o of the volume.

The variation of pressure within the bottle /11/ did not exceed 36 mm. H_2O which is responsible for the maximum variation of another 0·3°/c of the volume of gases in flow.

Table 2.

N position of the cham.	NO vessel			O$_2$ vessel			t° in reac. chamber	t° of the bath	t° of water for cham.	$p_1-p_2=h$ mm α-bromn.	Volume of gas cm³/min. N.T.P.	Volume of gas cm³/min. t° u. pr. of the cham.	Surface in mm.² section of cham.	Average flow of gas cm³/m. N.T.P.	Time of stay of gas in ch. sec.
	t° gas.	pres.	t° of water	t° gas	pres.	t° of water									
0	17.3	105	16.4								292.7				
1	17.3	105	16.4	17.2	102	15.2	69.4	35.6	35	43.53	225.	281	7445	298	1.147
2	17.2	110	16.8	17.5	115	15.6	61.8	35.6		34.42	183	223.5	6263	257	1.363
3	17.7	88	16.9	17.7	93	15.6	50.6			29.23	163	192.4	5079	203.5	1.68
4	17.7	82	16.9	17.7	94	15.8	44.3			26.48	152	176.	4592	183.7	1.861
5	17.7	79	17.	17.7	81	16.0	41.7	35.6	35	25.38	147.5	169.5	4307	172.2	1.985
6	17.9	110	17.4	18.0	115	16.1	40.0			24.63	144	164.5	4187	168.	2.035
7													4093	163.8	2.09
8	17.9	110	17.4	17.9	116	16.7	39.2	35.6	35	23.93	140.5	160	4044	162.	2.11
9													3975	159.2	2.15
10	18.	99	17.6	17.8	117	16.3	38.1			23.33	137.5	155	3925	157.2	2.175
11													3900	156.	2.195
12	18.	99	17.6	17.8	118	16.4	37.6	35.6	35	23.0	136.	154.6	3874	155.2	2.27
13													3850	154	2.22
14	18	99	17.7	17.8	110	16.3	37.5			22.7	134.5	152.5	3825	153.2	2.23
15													3812	152.5	2.245
16	18	99	17.7	17.9	110	16.5	37.5	36.	35	22.52	133.	151.5	3800	152.	2.25

PART IV

INTERPRETATION OF MEASUREMENTS.

The measurements made are condensed in Table 2. They refer to sixteen volumes of the reaction chamber, the first of which was 5·7 c.c.

The pressure difference /$p_1 - p_2 = h$/ read on the differential manometer at the temperature of the reaction chamber as given by thermometer /14/ have been referred to Diagr. 3 thus giving the corresponding gas flow rates in c.c./min. at N.T.P.

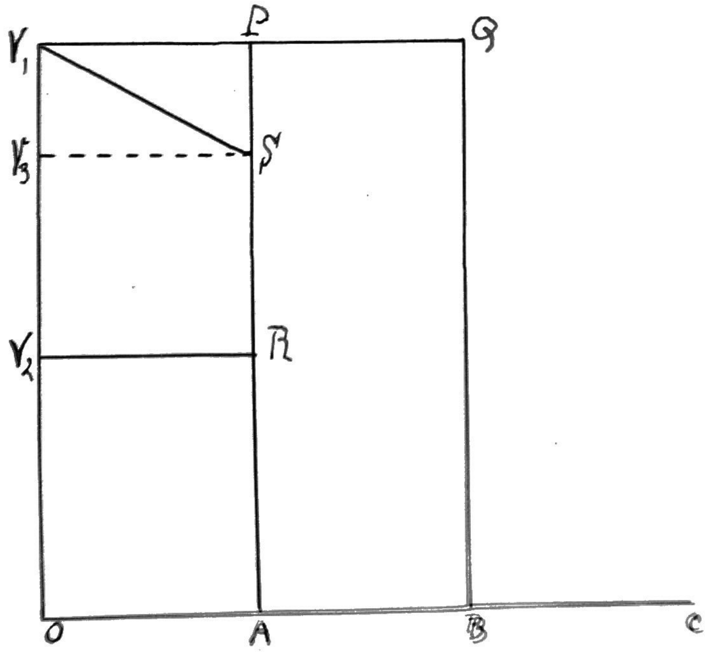
For the first position of the chamber, $h = 43·53$ mm. of alpha-bromonaphthalene head; the thermometer reading being 69·4°, we obtain from diagram 3 the flow rate of 225 c.c./min. /N.T.P./, or 282 c.c./min. for the chamber temperature and pressure observed. Similar calculations have been made for obtaining the flow rate values for each of the sixteen positions of the chamber. These values were expressed in c.c./min. N.T.P. /V_{NTP}/ and in c.c./min. at actual pressure and temperature conditions within the chamber /$V_{t.ch.}$/ and are shown in diagram 3 plotted against the chamber position.

PART V

CALCULATION OF THE TIME OF REACTION IN THE REACTION CHAMBER.

If at constant pressure a volume V_g of a gas of fixed composition e.g. N_2, O_2, ON passes each minute through a vessel of volume V, the "time of stay" in the vessel will be V/V_g min. If, however, the gas in question is a reacting mixture such that a decrease in volume occurs, as in the oxidation of nitric oxide, the average time of stay will be increased: if the reduction in volume is linear with respect to time, then the time of stay will be increased proportionally.

This may be illustrated graphically as follows. If the volume of gas passing per minute is plotted as ordinates against the volume of the reaction vessel as abscissae, then for a vessel volume OA and a flow rate of uniform gas OV_1, the time of stay in the vessel will be proportional to the area $OAPV_1$. For a vessel volume OB /= 2OA/



the time of stay will be double and will be proportional to $OBQV_1$, and so on. For a gas volume V_2 /$= \frac{1}{2} V_1$/ in a vessel volume A, the time of stay will be doubled in relation to the time of stay for gas volume V_1 in vessel volume A; the multiplying factor will be the ratio of the areas $OAPV_1/OARV_2$.

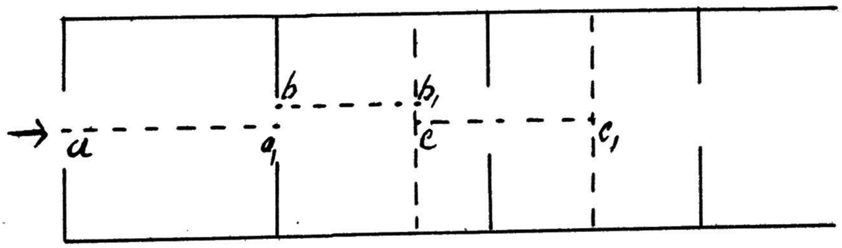
When therefore the gas volume passing per minute decreases linearly due to reaction from V_1 at O to V_3 at A, the multiplying factor will be $OAPV_1/OASV_3$. For the general case, let the area $OASV_3$ be A. When vessel volume is V and gas volume passing is v at V = 0, the proportionality factor is $\frac{V + v}{A}$ and the average time of stay in the vessel will be $\frac{V + v}{A} \cdot \frac{V}{v} = \frac{V^2}{A}$.

As shown in Diagram 3, the relation between vessel volume and gas volume passing is not linear and an integrated area A is therefore required. For the present purposes the area A was determined graphically. It will be noted that, in Diagram 3 the value v approaches a constant at high values of V, this indicating no reaction; apparently for such conditions oxidation was practically complete.

In Diagram 3 the chamber volumes are plotted on the abscissae at intervals of 25 mm. The volume curve is not a straight but a concave line. Thus the area A of the first chamber volume has an area of 7445 sq.mm.; hence the mean gas flow rate is $\frac{7445}{25} = 298$ c.c./min. =

= 4·97 c.c./sec. Consequently, the time during which gas remains in the chamber of volume 5·77 c.c. is 5·7/4·97 = 1·147 sec. Thus one obtains a series of values expressing the time during which gas remains in the subsequent sections of the chamber, respectively, each section having the same volume of 5·7 c.c. These are given in the last column of Table 2.

Let us now consider the behaviour of gas molecules within the chamber, during the steady contraction caused by the reaction itself. When entering the chamber at its position 1, the gas remains in the chamber for 1·147 sec. This means that a molecule *a* which entered the chamber at the moment t_1 will reach the exit nozzle at such a moment t_2 that $t_2 - t_1 = 1·147$ sec.



Let us consider the next position of the chamber, viz. that with double the primary volume. A molecule which passes through b at the moment t_1, will be observed near b_1 at the moment t_2, and $aa_1 > bb_1$.

At the third position of the chamber the place of a molecule at moment t_1 and t_2 will be c and c_1, respectively, and $bb_1 > cc_1$. The distances aa_1, bb_1, cc_1, ... are then proportional to the contraction of the flowing gases at points a, b, c, ..., respectively. The time, however, necessary for a molecule to pass from a to b, from b to c etc. is always the same, viz. 1·147 sec. The positions a, b, c, ... corresponding to time periods of 1·147 sec. have been called here "contraction segments".

In order to obtain the values of flow gas rate per minute at these "contraction segments" corresponding to time periods of 1·147 sec., the abscissae axis has been divided into lengths of 17 mm. each = 1·147 sec. /Diagr. 4/, this being shown by vertical /red/ lines. Next, the times of passage of the gases through the several sections of the chamber as calculated above have been plotted on the same axis, using the same scale of 17 mm.= =1·147 sec., against the volume of gas passing/min. /N.T.P./ Table 2. Through points thus obtained, vertical /black/ lines have been drawn, on which the value of the corresponding gas flow rate per minute /N.T.P./ have been measured. The curve obtained enables one to determine the flow volumes on the "contraction segments" lines. Thus, we obtain flow rates at the contraction points.

The decreasing gas flow volumes at the contraction points correspond to volume changes in the primary gas volume which entered the first chamber section. Thus, we obtain a picture of the contraction, as it were, of a definite portion of the gas, subjected to the reaction of oxidation.

The same Diagr. 4 contains curves representing the chamber temperatures and the dissociation percentage of N_2O_4 at those temperatures.

When measuring the reaction velocity by a static method, one has to measure the decrease of pressure at a constant volume, whereas with the above flow method one has to determine the contraction of gases at a constant pressure. However, the measurements are complicated by the process of dissociation of N_2O_4 occurring within the chamber at the various temperatures. This is discussed in the next section.

PART VI

THE CALCULATION OF THE COMPOSITION OF THE GAS FROM THE CONTRACTION VALUES AT THE CONTRACTION SEGMENTS.

The volumes of gas obtained correspond to different "contraction segments", and express the contraction of the gases due to the gaseous reaction at different temperatures. The values of the gas chamber temperatures, when plotted against the "chamber segments", give a curve which determines the temperatures at "contraction segments", as before /see Table 3 columns 1 and 2/.

The same method has been applied for dissociation percentage of N_2O_4 at different temperatures. The values of the dissociation were taken from Neumann, x/

The first "contraction segment" is identical with the first "chamber segment". Within this common segment the mean chamber temperature was 69·4° C., and the dissociation 65°/o. It should be noted that the dissociation process is a very rapid one, as assumed by Bodenstein, hence it will be considered as occuring instantaneously.

PART VII

COMPOSITION OF GAS OF THE FIRST CONTRACTION SEGMENT.

As an example of computation of the composition of the gas mixture at any "contraction segment", we may consider the following taken from Table 3. Position 1: temperature = 69·4°. Dissociation of N_2O_4 = 65°/o. Initial volume of gas = 292·7 c.c./min. N.T.P. NO = 189·1 c.c., O_2 = 99·1 c.c., N_2 = 4·5 c.c. Volume at position 1 = = 225·0 c.c. Contraction = 292·7 - 225 = 67·7 c.c.

When nitric oxide reacts with oxygen to form N_2O_4, 200 c.c. NO react with 100 c.c. O_2 to give 100 c.c. N_2O_4; if no dissociation of N_2O_4 into NO_2 took place, the contraction would be 300 - 100 = 200 c.c. At the temperature concerned, however, N_2O_4 is 65°/o dissociated; i.e. in the N_2O_4 equilibrium mixture itself 100 c.c. N_2O_4 are replaced by 35 c.c. N_2O_4 and 130 c.c. NO_2, an expansion of 165 - 100 = 65 c.c. Overall, therefore, the contraction of 200 - 65 = 135 c.c. will be observed, and we can say that an observed contraction of 135 c.c. corresponds to the conversion of 200 c.c. NO and 100 c.c. O_2 to 35 c.c. N_2O_4 and 130 c.c. NO_2 at the temperature concerned.

An actual contraction of 67·7 c.c. was observed; then by proportion, 100·3 c.c. NO reacted with 50·1 c.c. O_2 to give 17·5 c.c. N_2O_4 and 65·2 c.c. NO_2, with a residue of NO = 189·1 - 100·3 = 87·8 c.c., O_2 = 99·1 - 50·1 = = 49·0, N_2 = 4·5 Table 4.

The above method of calculation has been used for computing the composition of the resultant gases for twenty-six contraction points. At the point 26, i.e. after the time of 1·147 × 26 = 29·8 sec., there remained 4·63 c.c. NO /N.T.P./ /Table 3/, i.e. 2·45°/o of the initial NO volume. Thus, the nitric oxide has been used to the extent of 97·55°/o, yielding 50·38 c.c. NO_2 and 66·76 c.c. N_2O_4 /N.T.P./.

The decrease of NO during the reaction is shown in Diagram 4, where the volume in c.c. /N.T.P./ is referred to the 26 points on the abscissae axis, expressing the intervals of 1·147 sec. each.

Table 3.

N cotract segment 1	t° in the chamb. 2	o/o of Dissoc. 3	V/m. N.T.P 4	V in t° and pr. of cham. 5	NO cm^3/min N.T.P. 6	NO/2 cm^3/m. N.T.P. 7	NO/2 cm^3/m N.T.P. from straight line 8	O_2 cm^3/m N.T.P. 9	O_2 cm^3/m. N.T.P. fr. straight line 10	N_2 cm^3/m N.T.P. 11	NO_2 cm^3/m N.T.P. 12	N_2O_4 cm^3/m N.T.P. 13
0			292.7		189.1	94.55		99.1		4.5		
1	69.4	65	225.	281	88.1	44.05		48.9	48.95	4.5	65.2	17.6
2	63.8	55.6	185.	230.5	40.	20.		24.5	24.55		82.8	33.2
3	54.5	46.2	170	205	29.5	14.75		19.3	19.35	"	73.8	42.9
4	48.7	39.6	160	188.5	23.6	11.8		16.4	16.35	"	65.6	49.9
5	44.9	35.5	153	176.	19.2	9.6		14.1	14.15	"	60.4	54.8
6	42.9	33.2	149	173.5	16.6	8.3		12.8	14.85	"	57.6	57.5
7	41.7	31.8	147.2	170.	16.1	8.05	8.05	12.6	12.60	"	55	59.
8	40.7	30.7	145.5	167.	15.2	7.6	7.63	12.1	12.12	"	53.4	60.3
9	39.8	29.8	144.	164.5	14.56	7.28	7.21	11.57	11.76	"	52.	61.33
10	39.8	29.6	143	163.	13.39	6.7	6.79	11.2	11.34	"	52.02	61.89
11	39.55	29.3	142	162.	12.5	6.25	6.37	10.8	10.93	"	51.8	62.4
12	39.25	29.1	141	160.8	11.57	5.78	5.96	10.34	10.49	"	51.66	62.94
13	39.15	28.9	140.2	159.5	10.84	5.42	5.54	9.97	10.09	"	51.52	63.37
14	39.8	28.7	139.5	158.5	10.23	5.12	5.12	9.66	9.67	"	51.34	63.77
15	38.65	28.5	138.5	157	9.27	4.64	4.70	9.18	9.25	"	51.26	64.29
16	38.4	28.5	137.7	156.	8.55	4.27	4.28	8.77	8.83	"	51.10	64.78
17	38.2	28.1	137.7	155.5	7.95	3.98	4.10	8.52	8.53	"	50.9	63.13
18	38.	28.0	137.	155.	7.82	3.91	4.02	8.57	8.57	"	50.7	65.18
19	37.7	27.8	136.5	154.6	7.68	3.84	3.85	8.39	8.40	"	50.44	65.49
20	37.6	27.6	136.	154.3	7.31	3.65	3.67	8.20	8.22	"	50.18	65.81
21	37.5	27.4	135.5	154.	6.9	3.45	3.49	8.02	8.04	"	48.92	66.12
22	37.5	"	135.2	153.5	6.5	3.25	3.31	7.8	7.86	"		
23	"	"	135.	153.	6.4	3.2	3.13	7.7	7.68	"	50.	66.4
24	"	"	134	152.7	5.9	2.95	2.96	7.40	7.51	"		
25	"	"	134.	152.4	5.44	2.72	2.78	7.15	7.33	"	50.32	66.67
26	"	"	133.5	152.	4.63	2.36	2.6	6.84	7.15	"	50.38	66.76

PART VIII

DISCUSSION.

As shown in Diagr. 4 the curve obtained by plotting the flow rate of NO against time shows a sharp decrease in the initial stage, this being succeeded by an apparently straight line portion beginning at point 6. This break at position 6 may be due to accentuation of experimental error. To determine the order of the reaction, the ordinary termolecular reaction velocity equation was then applied; this is not strictly justifiable in the present circumstances, because the temperature is not constant for all NO concentrations /see temperature curve Diagr. 4/. The temperature coefficient for this reaction is however small.[9, 10, 11/]

In the reaction

$$2\ NO + O_2 = N_2O_4,$$

when 2 b is the initial concentration of NO, and a is the initial concentration of O_2,

$$\frac{dx}{dt} = k \ . \ 4/b - x/^2/a - x/,$$

when x is the number of O_2 molecules used in time t. Integration of this gives the ordinary termolecular velocity - coefficient

$$k = \frac{1}{t/b - a/^2} \cdot \left\{ \frac{/b - a/x}{a/a - x/} + \ln \frac{b/a - x/}{a/b - x/} \right\}.$$

For comparison with the results of other workers, flow rates were converted into concentration of grammo-lecules per c.c., the unit of time being the second. Thus at time t = 0, the total flow rate was 189+99·1+4·5 =

= 292·7 c.c. per minute, of which the flow rate for NO was 189·1 c.c. per minute. Since the total pressure was atmospheric the partial pressure of O_2 was 99·1/292·7 and of NO 189·1/292·7.

Now 1 grammolecule at N.T.P. occupies 22,410 c.c.; therefore in 1 c.c. the number of grammolecules of

$$O_2 = \frac{99{\cdot}1}{292{\cdot}7 \times 22{,}410} = a,$$

$$NO = \frac{189{\cdot}1}{292{\cdot}7 \times 22{,}410} = 2\,b,$$

$$b = \frac{94{\cdot}55}{292{\cdot}7 \times 22{,}410}.$$

At position 5 /Table 3/

$t = 5 \times 1{\cdot}147$ sec. $= 5{\cdot}735$ sec. $= 5{\cdot}74$ sec.

$NO = 19{\cdot}2$ c.c./min.

$O_2 = 14{\cdot}1$ "

$N_2 = 4{\cdot}5$ "

$NO_2 = 60{\cdot}4$ "

$N_2O_4 = 54{\cdot}8$ "

Total flow 153·0 c.c./min.

$$a = \frac{99{\cdot}1}{292{\cdot}7 \times 22{,}410} = \frac{0{\cdot}339}{22{,}410}$$

$$b = \frac{94{\cdot}55}{292{\cdot}7 \quad 22{,}410} = \frac{0{\cdot}323}{22{,}410}$$

$$/b - a/ = \frac{-0{\cdot}016}{22{,}410}$$

$$x = \frac{0\cdot339}{22,410} - \frac{14\cdot1}{153 \times 22,410} = \frac{0\cdot247}{22,410}$$

$$a - x = \frac{0\cdot092}{22,410}$$

$$b - x = \frac{0\cdot076}{22,410}$$

$$\frac{1}{t/b - a/^2} = \frac{/22,410/^2}{5\cdot74/1\cdot6 \times 10^{-2}/^2} = 3\cdot42 \times 10^{11}$$

$$\frac{/b - a/x}{a/a - x/} = \frac{1\cdot6 \times 10^{-2} \times 2\cdot47 \times 10^{-1}}{3\cdot39 \times 10^{-1} \times 9\cdot2 \times 10^{-2}} = -0\cdot1266$$

$$\ln \frac{b/a - x/}{a/b - x/} = 2\cdot303 \log_{10} \frac{3\cdot23 \times 10^{-1} \times 9\cdot2 \times 10^{-2}}{3\cdot39 \times 10^{-1} \times 7\cdot6 \times 10^{-2}} = 0\cdot142$$

$$3\cdot42 \times 10^{11}\left\{0\cdot142 - 0\cdot1266\right\} = 5\cdot12 \times 10^{9}$$

The results of such calculation as applied to other contraction segments are shown in Table 4, column 4, and are to be compared with those of Bodenstein, given in column 3 for the same units and for the corresponding temperatures. It is to be observed that the coefficients are of the same order of magnitude, particularly for the segments 3, 4 and 5, and to this extent it may be claimed that the present methods of experiment and calculation are so far justified. In the initial stages, however, the present values are decidedly low and in the later times intervals a gradual decrease is to observed, contrary to the recognised rise in velocity coefficient as the temperature falls. This latter is probably due to the non-applicability of the termolecular formula to the present conditions; because of the changing temperature the same constant values of a and b cannot strictly be taken to refer to the entire series.

Accordingly the calculation was carried out over various ranges of segments e.g. positions 19-22, as follows:

$$a = \frac{8{\cdot}4}{136{\cdot}5 \times 22,410} = 0{\cdot}0616; \quad b = \frac{3{\cdot}84}{136{\cdot}5 \times 22,410} = 0{\cdot}0282;$$

$$b - a = \frac{0{\cdot}0334}{22,410} = 0{\cdot}0334;$$

$$x = \frac{0{\cdot}0035}{22,410}; \quad /a - x/ = \frac{0{\cdot}058}{22,410}; \quad b - x = \frac{0{\cdot}0248}{22,410};$$

$$\frac{1}{t/b - a/^2} = \frac{/22,410/^2}{3{\cdot}45/3{\cdot}34 \times 10^{-2}/2} = 6{\cdot}47 \times 10^{11}$$

$$\frac{/b - a/x}{a/a - x/} = \frac{3{\cdot}34 \times 10^{-2} \times 3{\cdot}45 \times 10^{-3}}{6.15 \times 10^{-2} \times 5{\cdot}81 \times 10^{-2}} = 0{\cdot}03215$$

$$\ln \frac{b/a - x/}{a/b - x/} = 2{\cdot}303 \log_{10} \frac{2{\cdot}82 \times 10^{-2} \times 5{\cdot}81 \times 10^{-2}}{6{\cdot}16 \times 10^{-2} \times 2{\cdot}475 \times 10^{-2}} = 0{\cdot}0723$$

$$k = 6{\cdot}47 \times 10^{11} \left\{ 0{\cdot}0723 - 0{\cdot}03215 \right\} = 6{\cdot}05 \times 10^{9}$$

The coefficients so calculated are indicated in column 5 of Table 4. The values are somewhat erratic, probably because the reaction runs very rapidly in the initial segments and experimental error in the slow later stages has a correspondingly large effect; it will noted in this connection that even at position 1, 1·157 seconds after mixing, the NO flow rate has failen from 189 to 88.

The coefficients in the initial stages as shown in

Table 4.

N cont. segm 1	t° in react chamb 2	Bodenstein cc^2. mol^{-2} sec^{-1} k x 10^{-9} 3	Flow Method cc^2 mol^{-2} sec^{-1} k x 10^{-9} calc. from beginning 4	Flow Method cc^2 m^{-2} sec^{-1} k x 10^{-9} calc. between points 5
1	69.4	5.1	0.2	
2	63.8	5.4	2.2	
3	54.5	6.3	6.7	5.2
4	48.7	6.7	5.05	
5	44.9	6.8	5.9	3.9
6	42.9	6.8	5.3	
7	41.7	6.8	4.3	
8	40.7	6.85	4.4	1.8 3.4
9	39.8	6.85	3.88	
10	39.8			3.74
11	39.5			4.33 5.14
12	39.3			
13	39.2			
14	39.0			5.7
15	38.7		3.5	
16	38.4			
17	38.2	6.9		
18	38.0			3.6
19	37.7			
20	37.6			6.0 5.2 5.03
21	37.5		2.23	
22	37.5			
23	37.5			5.6
24	37.5			
25	37.5			
26	37.5			

column 4 shows a rapid rise, but again it is difficult to interpret this as a real effect dependent on the kinetics of the reaction. It is true that Bodenstein's results show a similar phenomenon, and later work/C.Furman, J.Phys.Chem. 1944, 18, 386; Stoddart, J.C.S., 1939, 5/ has been directed to the question as to whether the termolecular reaction is to be more correctly regarded as a stage process, showing only in the initial stages, in which the formation of N_2O_2 is an essential preliminary. Uncertainty regarding the rate of proper mixing in the rapid reaction of the present experiments renders difficult the interpretation of the present rise in coefficient values.

From the experimental point of view, it would seem that the temperature conditions met with in the present research require further consideration. The present results are dependent mainly on the measurement and interpretation of $\underline{h}$, the pressure difference recorded on the manometer measuring the gas exit rate from the reaction chamber. The use of α- bromonaphthalene in this connection appeared free from objection, a conclusion also reached by Bodenstein. The calculation of the gas composition from the value of $\underline{h}$ depends on the temperature of the issuing gas, the equilibrium dissociation of N_2O_4, being also involved. Any error in temperature measurement has here a considerable effect. The thermometer which here has been taken to give the required temperature, while adjacent to the manometer nozzle system, will not give the exact temperature in the early stages where small reaction vessel volumes are concerned with a relatively large temperature gradient between entrance and exit. It would therefore appear that in this connection it would be advisable to have the thermometer as close as possible to the exit from the vessel. At the same time the temperatures recorded in the later stages of the reaction are sensibly the same and little error arises in this way; the segment to segment calculation of velocity coefficient should be in this respect more accurate.

In conclusion it may be claimed that the method here devised is, from comparison of the Bodenstein coefficients, essentially correct. Modifications are however necessary, not only with regard to the temperature factor above but also with further examination of the purity and conditions of entry of the reacting gases; a reaction which takes place less rapidly would also be of advantage.

BIBLIOGRAPHY

1. Ruschig, Ztschr.angew.Chemie, 1904,17,1777; 1905,18,121.
2. Schmidt & Böcker, Ber., 1906,39,1368.
3. Leblanc, Ztschr.Electroch., 1906,12,541.
4. Lunge, Ztschr.ang.Chem., 1906,19,807.
5. Lunge & Berl, Ztschr.ang.Chem., 1907,20,1717.
6. Klinger, Ztschr.ang.Chem., 1914, 27,7.
7. Ramsay, Chem.Soc.Trans., 1890,57,590.
8. Dixon & Peterskin, Chem.Soc.Trans., 1890,75,629.
9. Bodenstein, Chem.Zentr., 1918,11,333.
10. " Ztschr.f.Electro.Ch., 1918,N13/14, 183-220.
11. " Ztschr.f.Phys.Ch., 1922,68; 100,85; 100,78.
12. Burdick, J. of A.Ch.S., 1922,244.
13. Foerster & Blich, Ztschr.ang.Ch., 1910,22,2017.
14. Wegscheider, Ztschr.phys.Chem., 1900, 35,577.
15. H.M.Well, Absorption of nitrous gases, 1923.
16. A.Neuman, A.Spl., 6, 203 /1868/ and Ullmann Enzyklopödie du techn.Chemie, vol. 11, 40.

Previous chemical papers published by the author.

F.Kehrman & S.Hempel, Über die Konstitution der Chlor-toluchinon-oxime von Oliveri u. Fortorici dargestellt aus o-Kresol und m-Kresol, Ber.,1916,49,1211.

F.Kehrman & S.Hempel, Mitteilung über die Farbe der Azokörper und ihrer Salze, Ber., 1917,50,856.

St.Hempel, Action auxochromique du groupe amino dans les colorants azoiques.
These de Docteur ès Science, Genève 1917.

Diagram 1.

D1.

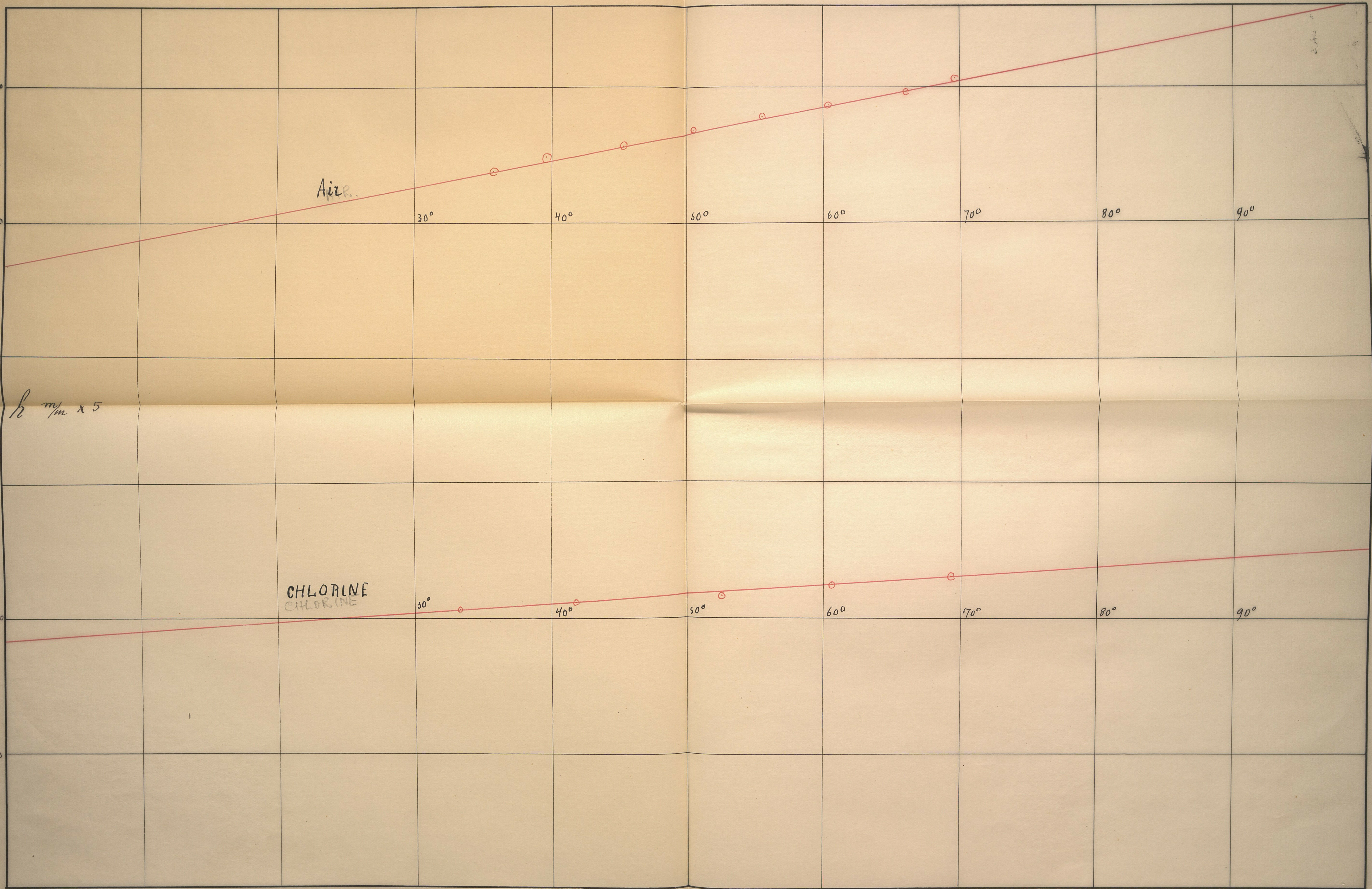

300
250
200
150
100
50
h m/m x 5
Air
AIR.
30°
40°
50°
60°
70°
80°
90°
CHLORINE
CHLORINE
30°
40°
50°
60°
70°
80°
90°

Diagram. 2.


300
250
200
150
100
50
Vol. cm³/min
N.T.P.
30°
35°
40°
45°
50°
55°
60°
65
70°
75°
80°
85°
90°
h m/m
200
25.
30.
35.
40.
45.
50.
55.
60.
65.
70
D 2

Diagram 3.

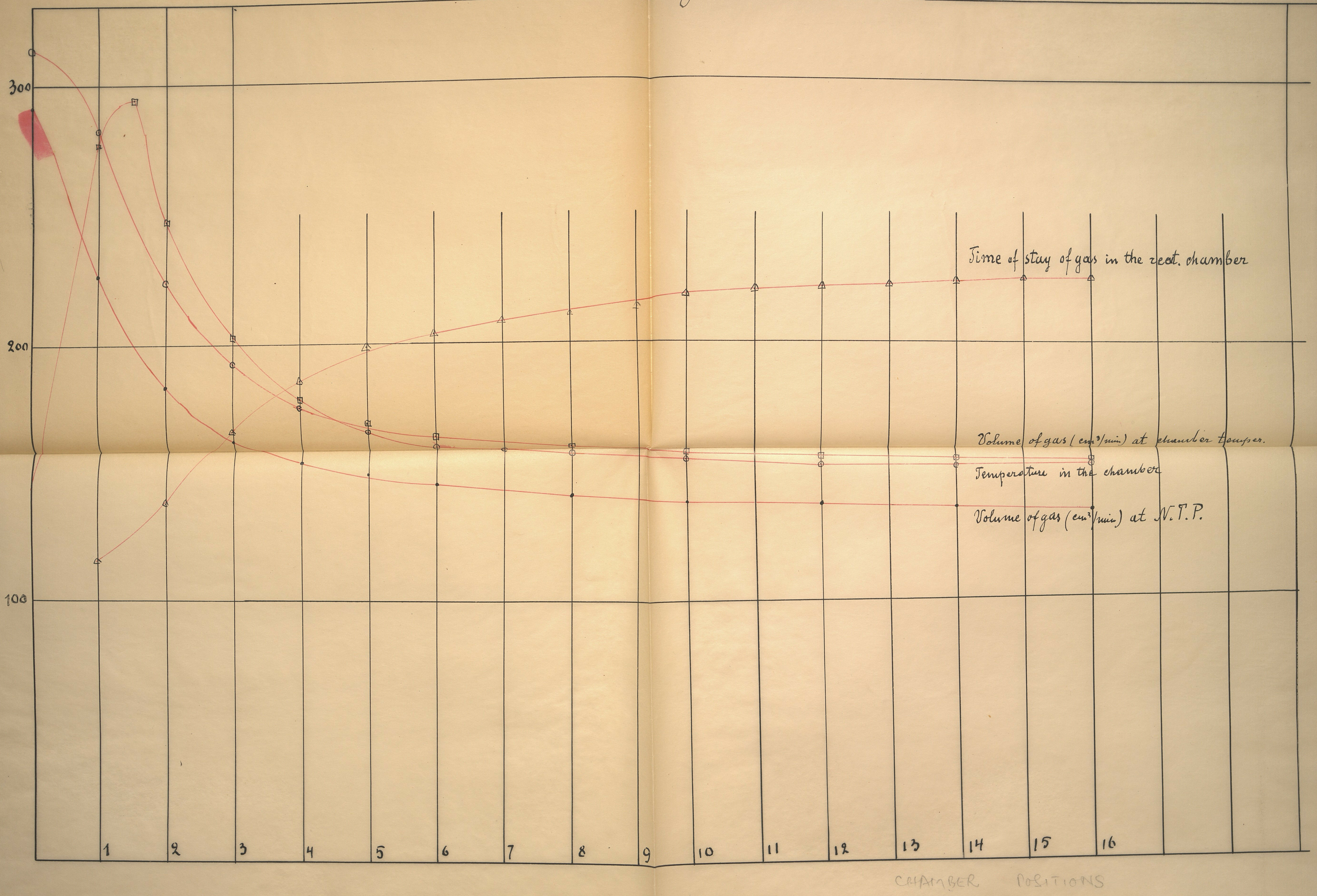

300
200
100
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
Time of stay of gas in the react. chamber
Volume of gas (cm³/min) at chamber temper.
Temperature in the chamber
Volume of gas (cm³/min) at N.T.P.
CHAMBER POSITIONS

Diagram 4.

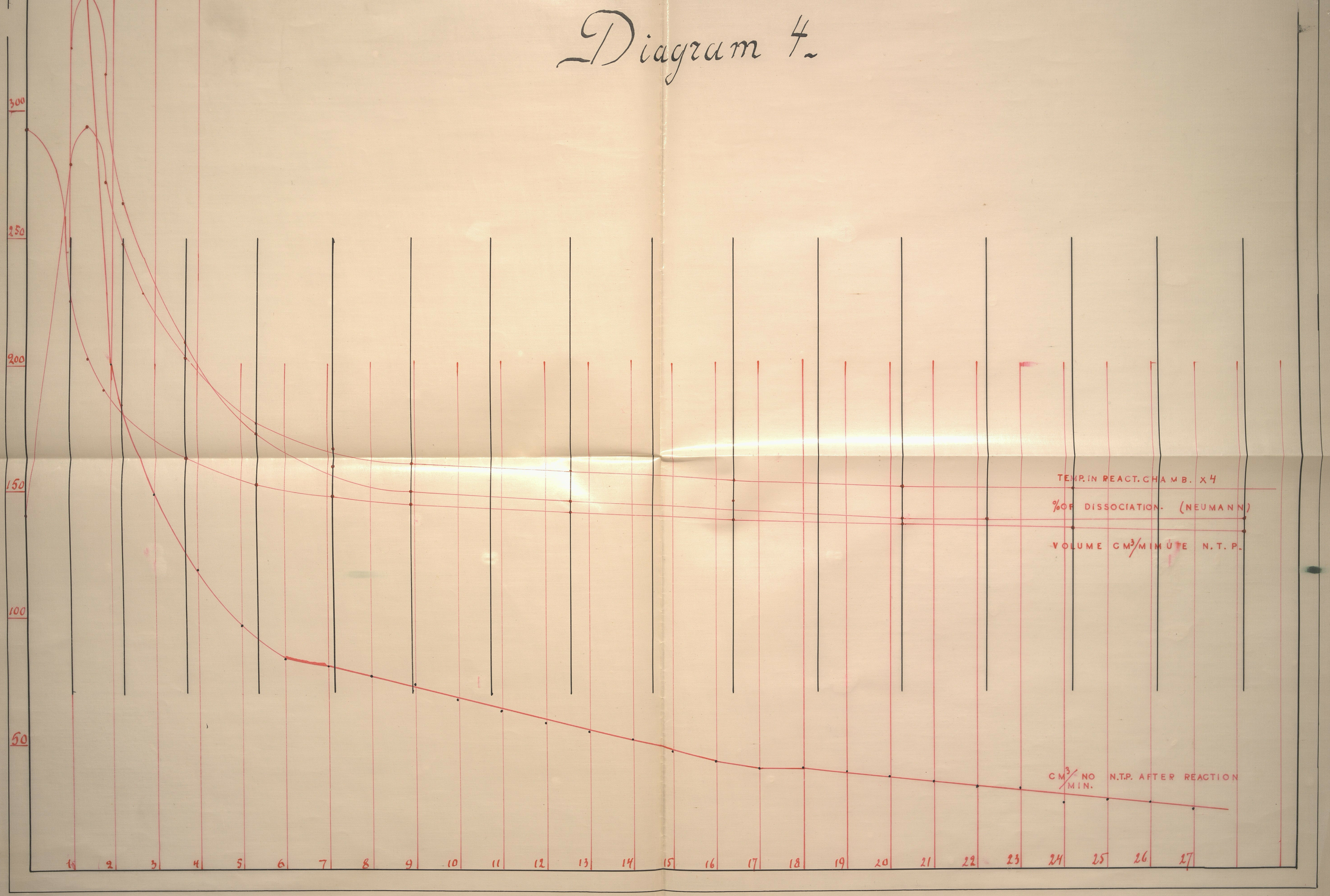

300
250
200
150
100
50
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
TEMP. IN REACT. CHAMB. X 4
% OF DISSOCIATION. (NEUMANN)
VOLUME CM³/MIMUTE N.T.P.
CM³/MIN. NO N.T.P. AFTER REACTION

Fig. 1.

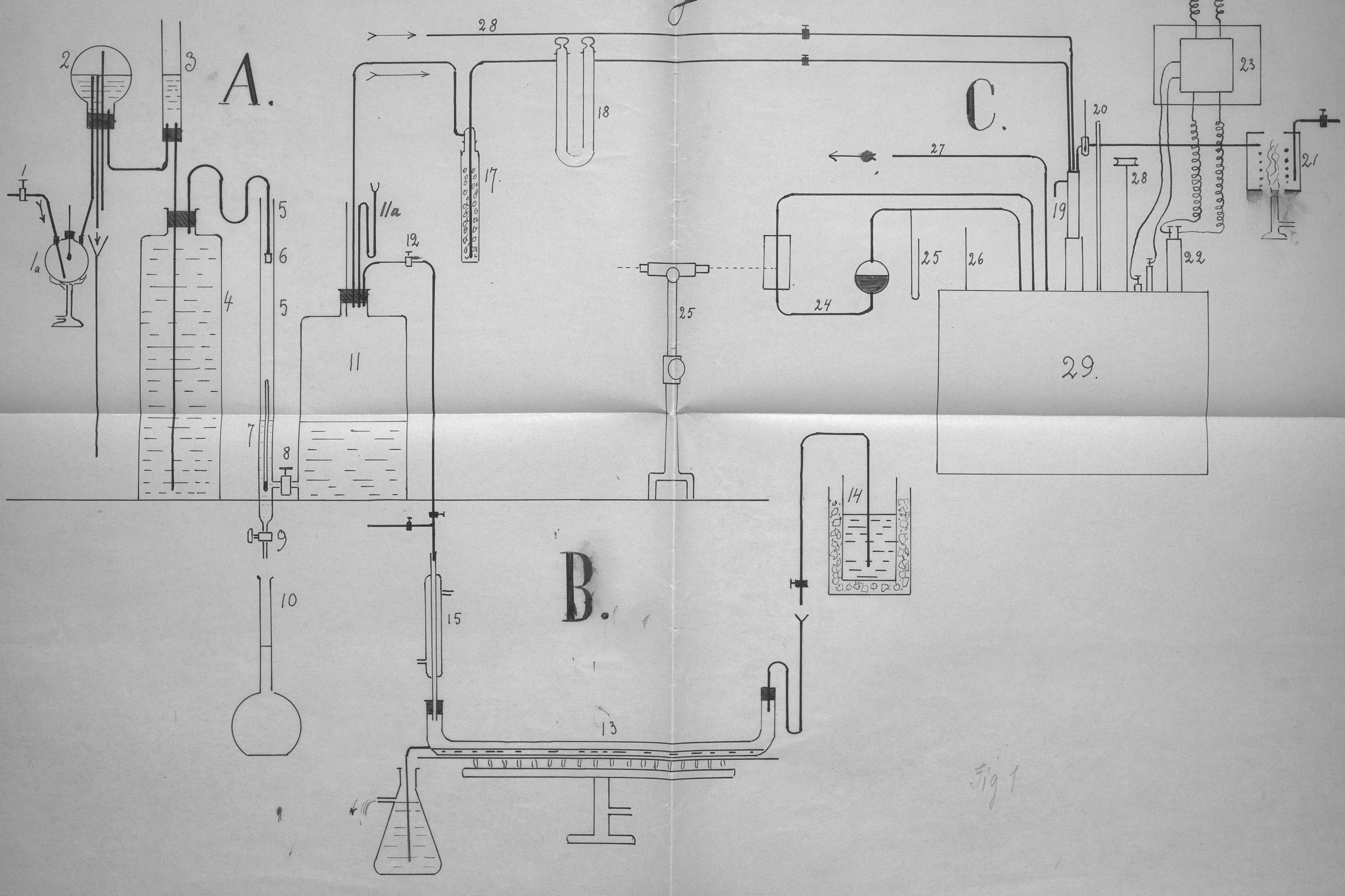
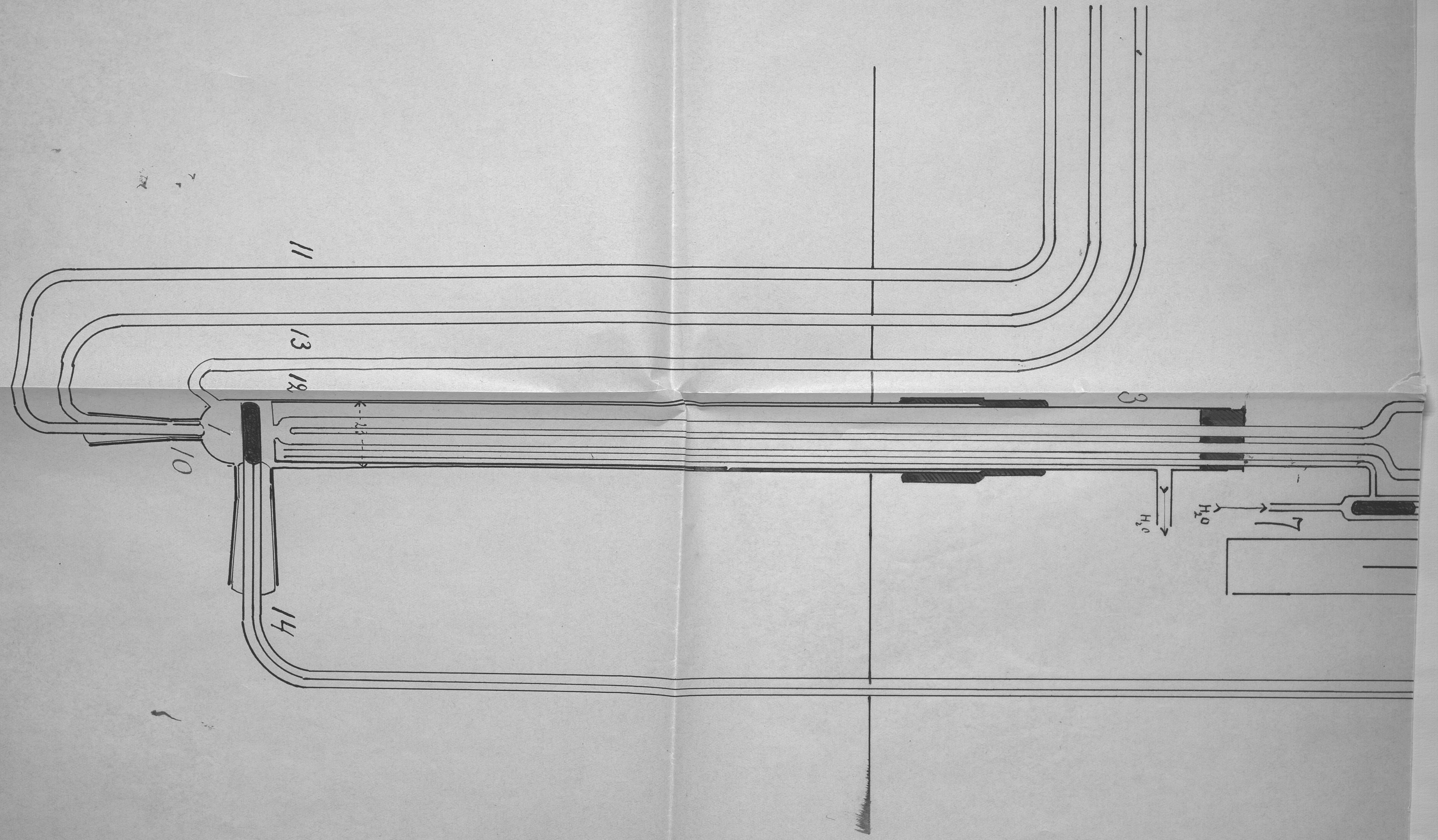

A.
1
1a
2
3
4
5
6
5
7
8
9
10
11
11a
12
28
17
18
25
B.
15
13
14
C.
20
27
28
19
21
23
22
24
25
26
29.

Fig 1


11
13
12
1
10
3
14
H_2O
H_2O
7

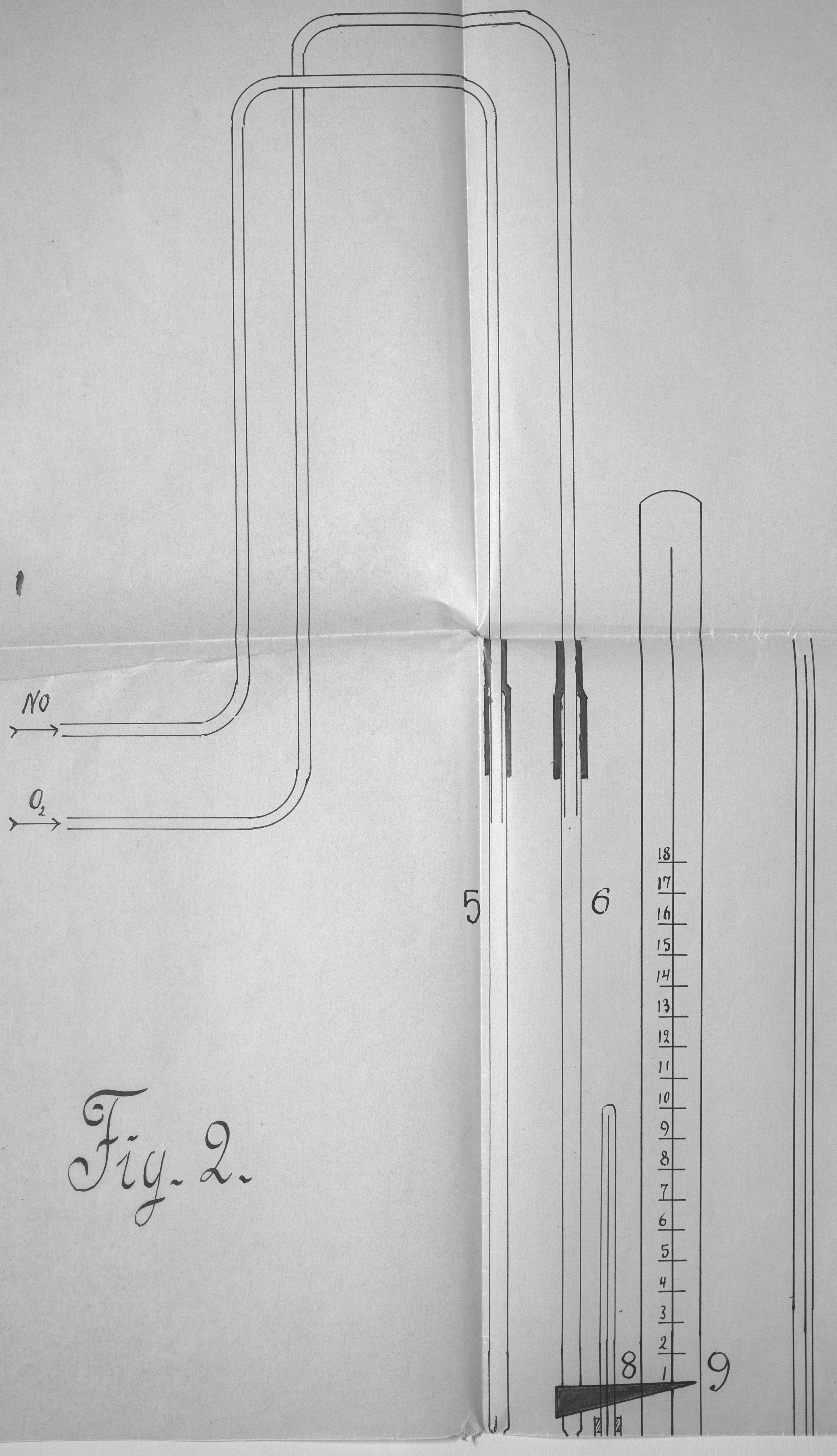


Fig. 2.