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SECOND NOTE ON VAPOUR PRESSURES

IN THE

SYSTEM $H_2SO_4 - NOHSO_4 - H_2O$

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INTRODUCTION

In a previous paper we made known the experimental data collected in the laboratory of the Sociedad Anonima Cros on the subject of vapour pressures in the system $H_2SO_4 - NOHSO_4 - H_2O$. As a continuation of this work, we proposed to raise the temperature limit as we thought it would be useful to have data at higher temperatures.

A further reason for carrying on this work was to check the results and compare them with those published in the literature as a result of the work done by various researchers, particularly Varlamov (1) and Kunin & Surov (2), because the nitrous products which they studied had a similar composition to those found in the acids prepared and studied by us.

Having carried out this work and compared the results, we discovered a significant difference between our values and those obtained by the various authors we studied whose vapour pressures were considerably lower.

This is undoubtedly a difficult problem since even the values of the co-efficient of Henry's Law are not acceptable; but there is no doubt that phenomena which we do not know about occur in the solutions and that careful work is required to elucidate them and eliminate their influence on the pressure we wish to measure. Nor is it any easier to criticize the results from the thermodynamic point of view because these values as a rule obey the laws of physical chemistry when we would have expected them to be more complex.

Finally, we believe that the measurement techniques used in earlier work were inadequate to obtain the desired results.

VAPOUR PRESSURES IN THE SYSTEM $H_2SO_4 - NOHSO_4 - H_2O$.

In this continuation of our previous paper we have studied the temperature range between 20 and 130°C, and the composition of the nitrose solutions we prepared was that obtained by dissolving 10, 20, 25, 30, 35 % solutions of nitrosylsulphuric acid in 70, 75, 80, 85 % H_2SO_4 . We again prepared the nitrose solutions by the method described in our earlier paper, that is, preparing nitrosylsulphuric acid crystals by the action of sulphur dioxide on a mixture of nitric and sulphuric acids, centrifuging the crystals so obtained and storing them in a desiccator over sulphuric acid until required. As it was necessary to dissolve these crystals in sulphuric acid of the required concentration, remove traces of nitre by passing SO_2 through, and perform an analysis to confirm the absence of free HNO_3 , we prepared the most concentrated $NOHSO_4$ solution in the required acid strength and obtained the remaining nitrose solutions by dilution.

When the nitrose solutions were ready, we passed through them a current of N_2 at room temperature so as to avoid any effects due to heat or hydrolysis, checking the composition immediately afterwards and correcting it if necessary. The content of nitrogen oxides was determined by the permanganate method and measured with the nitrometer; in a few cases not more than 0.05% nitric acid was found, while in most cases it was zero. In these conditions, we assumed that the nitrose solutions contained no free HNO_3 .

The procedure of the static method was carried out with the apparatus described in our first paper, while some vapour pressure determinations were duplicated using the dynamic method which we are at present studying in this laboratory. The apparatus used for operating the dynamic method is shown in Fig. 1.

The nitrogen supplied from the cylinder N passes successively through the damper 1, the Fresenius flask 2 containing calcium chloride, the flask 3 filled with glass wool, the oven 4 containing copper fillings to remove traces of oxygen,

the pressure regulator 5, and the flasks: 6 vacuum, 7 & 8 containing 20% potassium hydroxide, 9 vacuum, 10 containing sulphuric acid, 11 with glass wool, rheostat 12, flask 13 with sulphuric acid and 14 with glass wool. After this scrubbing, the gas passes into the saturator which consists of 6 tubes with porous glass bottoms filled with glass beads and rings to give a closer contact between the gas and the nitrose. These tubes are immersed in an oil bath maintained by means of a N.B. Coloras thermostat at a temperature constant within 0.01°C . At the saturator exit the tubes are kept in a closed oven at 50 to 60°C to prevent condensation and the gases are then passed to the absorption system which consists of four wash bottles containing the reagent to fix the nitrogen oxides. The amount of gas passed through the system was measured by means of the flask 15, allowance being made for the pressure drop in the apparatus when calculating the vapour pressure.

After the saturators we inserted a two-way valve to enable us to pass the gases through the secondary system S so as to be able to flush the apparatus with nitrogen and to adjust the speed of the gases before commencing the measurements. The absorbers also have a direct nitrogen inlet for flushing.

Before taking the measurements, we had to consider the choice of reagent for the absorbers, the analytical method to be used and the rate at which the gases should pass through to ensure that its nitrogen oxides content should be in equilibrium with the nitrose.

As absorbents we used solutions of NaOH, Na_2CO_3 1 N and concentrated H_2SO_4 . We avoided using alkaline solutions with a caustic base because silica was present as an impurity and it interfered with the results obtained in the colorimetric determination of nitrates by the phenol disulphonic acid method. Following Kudryavtsev's working method (3), concentrated H_2SO_4 has the advantage of enabling us to determine the water vapour pressure by weighing the absorbers and making a combined analysis with permanganate.

We used the following analytical methods: for the determination of N_2O_3 absorbed by the alkaline solutions, we used colorimetric determination with Griess's reagent (4) which was remarkably sensitive. Hydrogen peroxide was used to oxidize the nitrogen oxides to nitrates and a quantitative analysis by the phenol disulphonic acid method (5). We also used the method of reduction to ammoniacal nitrogen using Devarda's alloy (6) to determine the total nitrogen oxides, or used brucine (7) for the colorimetric determination of nitrates, but these methods proved less sensitive than the phenol disulphonic acid method. The nitrogen oxides absorbed by the concentrated H_2SO_4 were determined as NOHSO_4 by the permanganate method, together with the determination of excess permanganate with oxalic acid. The nitrogen absorbed as HNO_3 was determined by the Bowman Scott method (8) as modified by

C.L. Johnson (9) and applied by us in a more dilute form than that shown in the sample graph, with known quantities of HNO_3 of the order of those contained in the absorbent solutions based on strong sulphuric acid.

The rate at which the gases should pass through was chosen to give us the highest values which were also the most constant among the various measurements we carried out; we found that the optimum rate was 1,500 cc/hr and that the values obtained were practically constant with variations of $\pm 15\%$ and a tendency to rise or fall as the rate increased or diminished in relation to the chosen rate.

The vapour pressure values found by the static method in the group of nitroso solutions we prepared are given in Table I. A comparison of the values shown in this table with those of other authors shows that our values are higher. In point of fact, a direct comparison is not possible because of the differences in the composition of the solutions and in temperatures. Thus, we find that Pozin & Florinskaya (10) use the dynamic method over the range 30 to 60°C with acid strengths 70.9 to 76.87% H_2SO_4 and a N_2O_3 concentration varying from 0.092 to 0.583 mols/litre, with references to Berl & Saenger (static method) using 73.28 to 78.04% H_2SO_4 and N_2O_3 from 0.125 to 0.225 mols/litre, and Sanfourche & Rondier (dynamic method) using 76.2% H_2SO_4 with N_2O_3 at 0.202 mols/litre. Further, Tikhonov uses 70.9% H_2SO_4 with 0.583 mols/litre N_2O_3 , all lower strengths than any of ours, which range between 0.648 and 2.665 mols/litre N_2O_3 . Another point is that even H_2SO_4 concentration is not expressed in a standard form, as some authors refer to the starting acid which is subsequently enriched by the addition of N_2O_3 for the preparation of nitroso, while others refer to total H_2SO_4 present in the nitroso, both free and combined with N_2O_3 in the nitrosylsulphuric acid, and yet another way of referring to it is as the strength of the sulphuric acid in which nitrosylsulphuric acid is dissolved to obtain nitroso. Very serious errors of interpretation may result from comparing results without allowing for these differences.

Kudryavtsev (3), who carried out his experiments with acids with N_2O_3 content ranging from 0.5 to 6% and H_2SO_4 from 70 to 95.2% by the dynamic method at temperatures from 30 to 150°C, can be more readily compared with us. This author gives values for the H co-efficient for acids containing 71.43 - 73.27 - 76.48 - 82.00% H_2SO_4 when used to dissolve NOHSO_4 (the author does not in fact express them in this way, but we have calculated the values to correspond with our way of expressing the composition of the nitroso solutions). Using the dynamic method, we have found that these values do not represent the total pressure of the nitroso but only that of the N_2O_3 , which he appears to have expressed already as $\text{NO} + \text{NO}_2$. Therefore, we require to deduct from our values the partial pressure of the solvent, and divide by the % N_2O_3 content to find the value of N for each temperature and acid strength. We cannot calculate the partial

pressure due to the solvent because we do not know the variation of the vapour pressure of the solvent relative to the amount of nitrosylsulphuric acid dissolved, nor its dissociation and variation with the temperature. According to Kunin & Surov (2), if the system is regarded as a solution of nitrosylsulphuric acid in concentrated sulphuric acid, the water vapour pressure equals that of the starting acid and this also applies, although less obviously, when the acid is 75% H₂SO₄. Berl & Saenger also suggest that no correction need be carried out, but this is doubtful except in the case of nitroses with a low N₂O₃ content where the correction would be negligible.

We have worked out a correction factor according to Raoult's Law, taking into account the number of mols of nitrosylsulphuric acid and of H₂SO₄ and allowing for the molecules of water included in the sulphuric acid and working out the appropriate molar fraction. We consider the correction we have applied as approximate only and made for the sole purpose of this comparison. Accordingly we calculated the values shown in Table II. which represent the vapour pressure after subtracting the values for the solvent; dividing by the % N₂O₃ content, we deduced from these values the values of the co-efficient H of Henry's Law which we give in Table III.

The following are the H values found by Kudryavtsev:

<u>% H₂SO₄</u>	<u>Temperature</u>					
	<u>40</u>	<u>60</u>	<u>80</u>	<u>100</u>	<u>120</u>	<u>130</u>
71,41	0,671	1,751	3,912	-	-	-
73,27	0,62	1,577	2,807	4,797	7,950	10,058
76,48	0,25	0,707	1,555	3,080	4,99	6,108
82,17	0,08	0,19	0,448	0,869	1,752	2,125

Thus, it appears that our results are from 4 to 7 times higher than Kudryavtsev's. Varlamov's results also showed significant differences from ours. In this case, the author uses acids of the following composition:

	<u>% H₂SO₄</u>	<u>% N₂O₃</u>	<u>Mols/litre N₂O₃</u>
1	70,90	2,73	0,583
2	72,62	3,43	0,742
3	75,89	3,45	0,766
4	76,06	5,36	1,19

which are equivalent to acids of the type:

	<u>% H₂SO₄ solvent</u>	<u>% NOHSO₄</u>
1	70,26	9,12
2	72,04	11,46
3	75,72	11,52
4	75,81	17,91

and gives the values for pressure and coefficient H for temperatures between 40 and 80; of these, we shall quote only

the H values for acids 1 and 2 at 40°C, 3 at 80°C and 4 at 60°C which are respectively:

1.22 0.68 1.92 0.72

which correspond approximately to results obtained by us of the following order:

4.6 3.6 8.5 4.22

once more, 4 to 6 times higher.

Finally, we come to Kunin & Surov's results; they worked with higher N_2O_3 concentrations and their results can only be compared at 138°C, which is nearest to our maximum of 130°, as the other data were obtained at 159, 173 and 198°, temperatures well above those used by us.

The acids which Kunin & Surov worked with are equivalent to $NOHSO_4$ concentrations from 13.54 to 35.20. It is impossible to make a direct comparison, but our values are certainly more than double theirs.

In some cases one may question whether the authors in carrying out their experiments by the dynamic method made allowances for the dissociation of the N_2O_3 into NO and NO_2 , or for the corresponding association of NO_2 to N_2O_4 . Without doubt, the majority of authors allow for the presence of N_2O_3 only in the gaseous phase; however, when we obtained our first results by the dynamic method we noted the presence of nitrogen oxides in the gaseous phase at a degree of oxidation in excess of N_2O_3 and which we took to be N_2O_4 although the analysis did not show the presence of free nitric acid in the nitrose solutions. We also obtained values for water vapour pressure, following Kudryavtsev's working method, and we found that they differed little from the values calculated from the pure solvent according to Raoult's Law and that they were in agreement with the hypothesis we made and referred to above.

Generally speaking, when using the dynamic method we used an acid of 54.35% H_2SO_4 , 30.60% $NOHSO_4$ and 15.05% H_2O , free of nitric acid, or the equivalent of 30.60% nitrosylsulphuric acid dissolved in sulphuric acid of 78.31% H_2SO_4 .

The vapour pressure of this acid measured by the static method gives the following values:

°C	20	40	62	80	97.5
mm. Hg	2.0	7.4	26.5	48.6	82.5

and by the dynamic method at the same temperatures:

mm. Hg	0.09	0.60	2.22	3.88	16.00
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while our calculated values were:

mm. Hg	0.10	0.43	1.58	4.92	13.59
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(the last two sets of values are not too different)

The vapour pressures of the nitrogen oxides were:

mm. Hg	1.47	4.99	13.66	38.35	53.87
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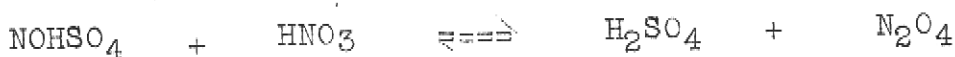
which added to the water vapour pressures give a total of:

mm. Hg	1.57	5.32	15.88	42.23	69.87
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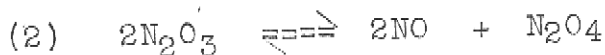
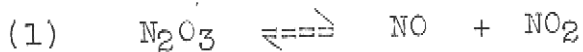
which is less than the total pressures we determined by the static method. We should suppose this to be due to lack of saturation of the gases, although constant values were obtained. However, the values we obtained using the dynamic method are different from those obtained by the static method, and are similar to the values given in the literature to which we have referred.

We can only assume, since we found forms of nitrogen oxide with a higher valency than that corresponding to N_2O_3 , that we have to do with nitroses containing free nitric acid, although in very small amounts, since the analyses did not show its presence except in a few isolated cases and in amounts less than 0.053%, as already stated.

We concluded that in the gaseous phase we had N_2O_4 in addition to N_2O_3 and that this came from the reaction:



in which case we must allow for all the equilibria:



in order to give adequate expression to the analytical values and to interpret them in terms of partial vapour pressures. In this case, the following group of equations would enable us to find the values corresponding to the components:

$$h + x + y + z + w = a$$

$$\frac{x}{y z} = b \quad \frac{x^2}{w y^2} = c \quad \frac{w}{z^2} = d$$

hence:

x =	partial pressure of	N_2O_3
y =	"	NO
z =	"	NO_2
w =	"	N_2O_4
h =	"	H_2O

- a = total pressure obtained experimentally (static method)
 b = dissociation constant of (1)
 c = " " " (2)
 d = " " " (3)

We have not given any equations for calculating the pressures because the purpose of this work is merely to anticipate those values which may subsequently require to be modified or augmented when our studies have supplied all the necessary data for a complete critical examination.

TABLE I. Pressures in mm. Hg
 Sulphuric acid solvent with 70% H₂SO₄ Density at 20°C 1.670

%NOHSO ₄	Temperature							
	20	40	60	80	100	120	130	133
10	6.8	18.2	38.0	107.5	227.5	400.8	-	663.4
20	11.4	29.5	73.8	175.3	352.0	604.3	-	-
25	13.5	36.5	90.8	204.0	422.0	729.8	-	-
30	15.2	42.0	106.0	230.0	495.0	-	-	-
35	18.8	65.4	158.4	303.4	576.4	-	-	-

Sulphuric acid solvent with 75% H₂SO₄ Density at 20°C 1.669

10	2.3	6.9	16.5	39.2	96.9	178.4	-	256.9
20	3.9	11.0	26.5	65.0	150.0	304.5	-	459.2
25	5.3	14.5	36.8	87.5	190.5	387.5	-	569.2
30	6.4	17.5	43.5	104.2	230.0	440.5	-	621.2
35	7.7	22.0	53.0	126.5	285.0	525.0	-	-

Sulphuric acid solvent with 80% H₂SO₄ Density at 20°C 1.778

10	0.8	1.8	4.5	10.8	26.9	60.0	95.0	-
20	1.2	2.9	6.6	17.0	40.0	98.0	150.0	-
25	1.4	3.5	7.9	19.5	47.0	110.0	170.0	-
30	1.6	3.8	9.4	21.5	52.0	123.7	185.0	-
35	2.1	5.1	12.5	32.0	76.0	190.0	273.9	-

Sulphuric acid solvent with 85% H₂SO₄ Density at 20°C 1.814

10	0.7	1.5	3.0	6.1	12.0	27.5	-	40.0
20	1.1	2.4	4.3	8.5	17.5	37.5	-	54.0
25	1.2	2.5	4.8	9.5	20.2	44.6	-	63.0
30	1.4	2.9	5.5	11.4	24.1	52.5	-	75.0
35	1.5	3.2	6.3	12.7	27.6	59.9	-	88.1

TABLE II.

Vapour pressures for the nitroso solutions after subtracting the values for the solvent, calculated according to Raoult's Law.

70% H ₂ SO ₄		Temperature						
%NOHSO ₄	20	40	60	80	100	120	130	133
10	6.26	15.78	38.52	82.11	165.56	260.38	-	436.3
20	10.91	27.31	66.13	153.23	296.93	477.22	-	-
25	13.04	34.43	83.55	183.13	369.98	609.62	-	-
30	14.76	40.04	99.15	210.3	444.95	-	-	-
35	18.39	49.17	119.6	284.98	529.6	-	-	-

75% H ₂ SO ₄								
10	2.05	5.88	12.93	28.43	68.17	109.71	-	139.27
20	3.69	10.10	23.34	55.45	124.53	243.61	-	354.93
25	5.09	13.65	33.84	78.56	166.66	320.51	-	471.61
30	6.21	16.71	40.73	95.85	207.73	387.26	-	530.09
35	7.52	21.27	50.45	118.80	264.46	475.89	-	-

80% H ₂ SO ₄								
10	0.73	1.46	3.18	6.50	14.35	27.81	44.64	-
20	1.14	2.60	5.42	13.16	28.79	69.28	105.61	-
25	1.34	3.22	6.79	15.89	36.48	83.06	127.61	-
30	1.54	3.53	8.36	18.13	42.18	98.44	145.41	-
35	2.05	4.85	11.54	29.87	66.87	166.62	237.11	-

85% H ₂ SO ₄								
10	0.68	1.39	2.56	4.49	7.11	14.32	-	15.64
20	1.08	2.31	3.72	7.01	13.11	25.68	-	32.14
25	1.18	2.41	4.26	8.15	16.06	33.47	-	42.42
30	1.38	2.82	4.99	10.13	20.22	42.05	-	55.69
35	1.49	3.12	5.83	11.52	23.99	50.18	-	70.12

TABLE III.

Values of the coefficient H deduced from Table II.

		<u>Temperature</u>							
<u>70% H₂SO₄</u>		20	40	60	80	100	120	130	133
%NOHSO ₄									
10	2.09	5.26	12.86	27.46	55.33	87.09	-	-	145.9
20	1.82	4.56	11.05	25.62	49.65	79.80	-	-	-
25	1.74	4.60	11.16	24.48	49.32	81.50	-	-	-
30	1.67	4.46	11.05	23.44	49.60	-	-	-	-
35	1.75	4.69	11.41	27.21	50.58	-	-	-	-
<u>75% H₂SO₄</u>									
10	0.685	1.96	4.31	9.50	22.79	36.69	-	-	45.67
20	0.615	1.68	3.90	9.27	20.82	40.73	-	-	59.35
25	0.680	1.82	4.52	10.50	22.28	42.84	-	-	63.04
30	0.692	1.86	4.54	10.68	23.15	43.18	-	-	59.09
35	0.718	2.03	4.81	11.34	25.25	45.44	-	-	-
<u>80% H₂SO₄</u>									
10	0.244	0.468	1.06	2.17	4.79	9.30	14.86	-	-
20	0.190	0.434	0.906	2.20	4.79	11.58	17.66	-	-
25	0.179	0.430	0.907	2.12	4.87	11.10	17.05	-	-
30	0.171	0.393	0.943	2.02	4.81	10.87	16.21	-	-
35	0.195	0.462	1.00	2.85	6.38	15.91	21.68	-	-
<u>85% H₂SO₄</u>									
10	0.227	0.464	0.789	1.50	2.37	4.78	-	-	5.23
20	0.180	0.386	0.622	1.17	2.19	4.29	-	-	5.37
25	0.144	0.322	0.569	1.08	2.14	4.47	-	-	5.67
30	0.153	0.314	0.556	1.12	2.25	4.68	-	-	6.20
35	0.142	0.297	0.556	1.10	2.19	4.79	-	-	6.69

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Appareil pour déterminer les tensions de
vapeur de solutions de SO_4HNO en SO_4H_2

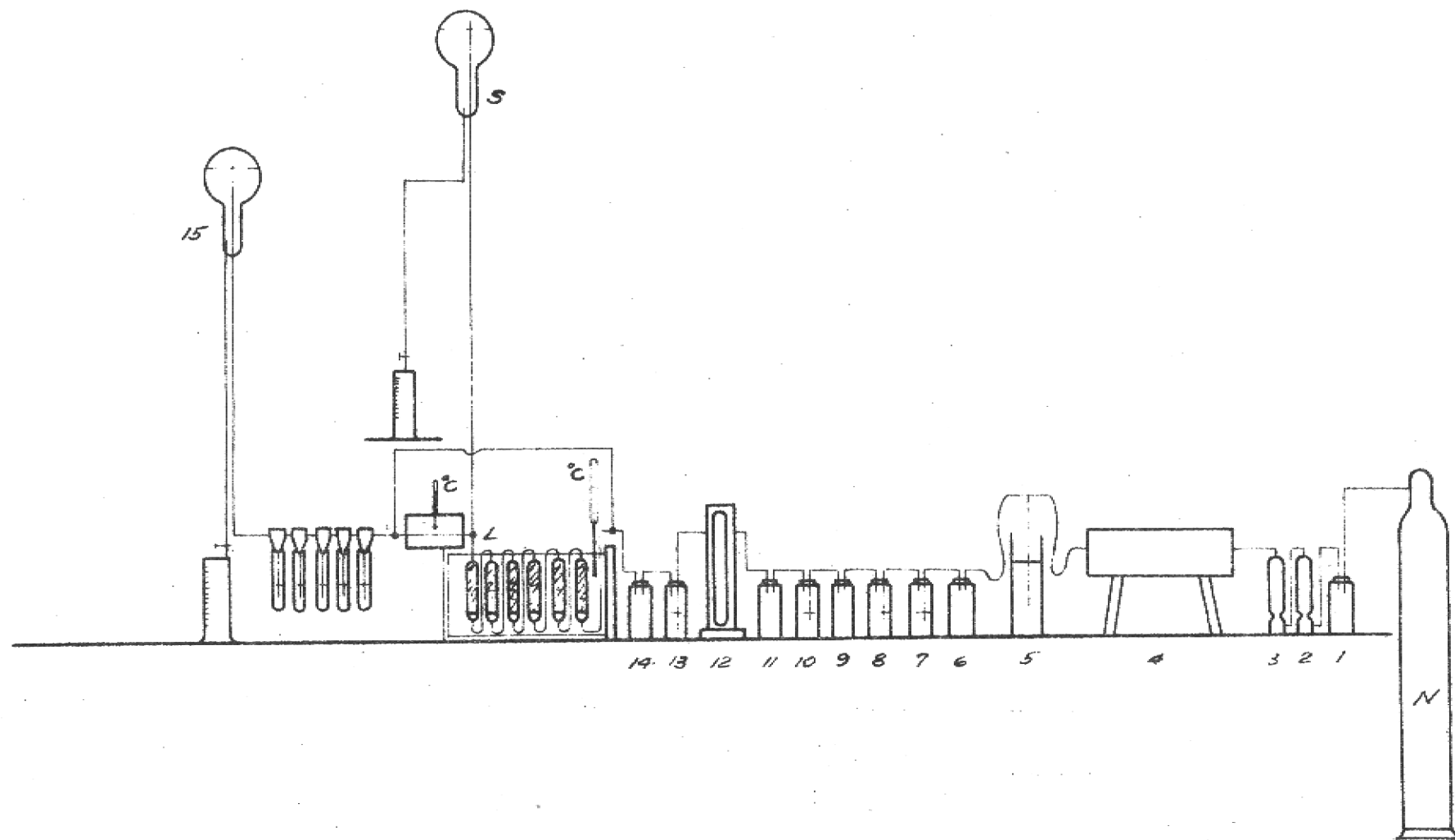


Fig. - 1