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THE SYSTEM :

NITROSYLSULPHURIC ACID - SULPHURIC ACID - WATER

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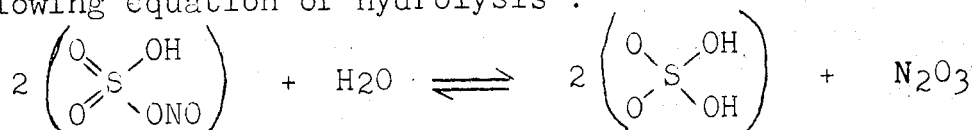
The presence of nitrosylsulphuric acid during the manufacture of sulphuric acid by the lead chamber process was reported by LUNGE (1), since when numerous investigations on the system in question have been made by very many authors.

The observations formulated on the subject of this system have been put forward principally by HANTZSCH and BERGER (2), who drew attention to the instability of nitrosylsulphuric acid in aqueous solutions of sulphuric acid; and by LUNGE, ZALOZIECKI and MARCHLEWSKI (3), SOREL (4), MATSUI (5), SANFOURCHE (6) and others, who have measured the partial pressures resulting from this instability and which form the basis of all procedures for the manufacture of sulphuric acid employing oxides of nitrogen as catalyst. SAENGER (7) gives ample details on this subject, but it all reduces to the reactions and concentrations employed in the lead chamber process.

The object of this first communication is a study of the system envisaged but at the concentrations and under the conditions applying in plant used for the manufacture of sulphuric acid by the K. CHK. ROF process.

In principle, the solutions examined are those of 10, 15, 20, 25, 30 and 35% nitrosylsulphuric acid in aqueous solutions of sulphuric acid of 70, 75, 80 and 85% strength. Concentrations below 70% of sulphuric acid are characterised by remarkable instability, decomposing very rapidly even at ambient temperatures. Acids above 85% concentration give rise to solutions so stable that they present hardly any practical interest.

The investigation made by us reduces to the ascertainment of the partial pressures of the gas produced in accordance with the following equation of hydrolysis :



and to determining the effect of the variables temperature and the composition of the system.

We employed the static method over the range 10° to 90°C.

EXPERIMENTAL.

The sulphuric and nitric acids employed by us for the preparation of the various solutions were of reagent quality, complying with the conditions specified by the Committee on Reagents of the American Chemical Society (8).

Nitrosylsulphuric acid was prepared by passing pure gaseous sulphur dioxide into fuming nitric acid, and the crystals obtained, after draining by centrifuging, were kept in a desiccator over sulphuric acid. Analysis was carried out in accordance with the methods of LUNGE (9) and the small quantities of nitric acid were determined by the method of KILTHOFF (10).

The dissolving of the necessary quantities of nitrosylsulphuric acid in adequate amount of sulphuric acid yields solutions which present points of interest.

With acids which are rich in water the solutions were made at low temperature in order to avoid the effect of heat of solutions and of hydrolysis; those containing little water were made by warming the sulphuric acid solution. When made, the solutions were carefully analysed in order to classify them definitively and make any corrections.

Apparatus with glass membranes was employed to make the measurements and to fix the zero we used two systems: one described by F. DANIELS (11) in which we varied the electrical circuit by using an electronic relay, instead of that of the author, which enables us to light a strong lamp by the single passage on very few milliamperes and the other was that described by LEDENBURG-LEHMANNSCHEIN (12) using an optical system. With these glass manometers the precision was ± 0.1 mm Hg.

The measuring manometer enabled a reading of 0.1 mm by means of a vernier. The arrangement of the apparatus is as shown in Fig. 1.

The temperature was maintained to within $\pm 0.01^\circ\text{C}$ by means of a thermostat. The vacuum was obtained by means of a rotary pump at the commencement, and at the end an oil diffusion pump was employed which enabled pressures lower than 0.001 mm. Hg to be obtained.

The solution was introduced via the tubulure 1 into the receptacle by means of a glass funnel. It was then cooled in carbon dioxide snow to -40°C and the vacuum made on both sides of the flexible glass membrane, the solution being left under vacuum for 30 minutes at the temperature indicated. It was then warmed to about 10 - 15 to eliminate dissolved gases and again cooled until bubbles were no longer visible. The tubulure 1 at the lamp was then closed and the whole assembly placed in the thermostat.

The values for the partial pressure due to hydrolysis were measured while the temperature was raised by 10° stages from 10°C , stability being achieved at each stage (i.e. three readings agreeing within ± 0.3 mm. during a period of 15 minutes).

During the experiment it was found that the period of permanence at the given temperature was the greater as the values for the partial pressure rose, so that the curves were displaced slightly in a vertical direction.

It was also observed that measurements made as the temperature falls were different from those made under rising temperature, the difference becoming less the longer the period for obtaining equilibrium. For example: a pressure measured at 40°C

was found to be 34.2 mm.; after the temperature had been raised to 60°C the figure was found to be 35.6 mm., which value after one hour had fallen to and become stabilised at 34.7 mm.

These phenomena had previously been reported by SAENGER (loc. cit.) and are explained by the thermal effects of decomposition not being completely reversible. In effect, we can say that the hydrolysis reaction gives rise to derivatives other than those theoretically derivable from equation (1) and that the velocity of equilibration from right to left is not the same as from left to right, usually less.

The partial pressures given are the total pressures, i.e. of the system. The values for sulphuric, water and nitric vapours present are such that we have neglected them, without seeking to ascertain that for the nitrous compounds, since we do not know the influence of the dissociation and cannot calculate them. Further, the values are very small and displace the curves very slightly in a parallel direction following SAENGER (loc. cit.)

From the results of these experiments we have interpolated the results given in the tables and represented in the graphs. Verification of these experimental results has been obtained using the formula of A EUCKEN (13) and the results of this check are given in tables a) and the corresponding figures.

The partial pressure of the gas and the concentration of nitrosylsulphuric acid are so related that for the same solvent the pressure increases as the given concentration of nitrosylsulphuric acid increases. Figures 2, 3, 4 and 5 represent the variation, which is practically a straight line. The slopes of these lines, as determined by experiment, give the coefficient for rise of pressure for each isotherm.

The relationship between the partial pressure of the gas and the water content of the nitrosylsulphuric acid solution is reflected in figures 6, 7, 8 and 9 from which one sees quite clearly the logical consequence that the higher pressures correspond to the larger quantities of water contained therein. One can thus set a limit on the average of these figures to the details of work relative to the recuperation of nitrous products or the denitration of the acids. The lines AB thus delimit two zones which we can term zones of denitration and of nitration.

The relationship between the temperature and pressure is of the form shown in figures 10, 11, 12 and 13, very similar to the foregoing. The pressure is the greater the higher the temperature of the nitrosylsulphuric acid solution. Their relationship appears simple for by taking as ordinates the logarithms of the pressure instead of the pressure itself, the pressure-temperature relationships are almost straight lines. The expression of EUCKEN (loc.cit.) which expresses the relation between the temperature and pressure of the vapour is as follows:

$$\ln P = -L_0 / RT + \ln T + C$$

where

- T = Temperature °K
- R = Gas constant
- C = a constant
- L₀ = Molecular heat of vapourisation
- Ln = Napierian logarithm.

Substituting the values ;

$\text{Log } P = L_0 / 4.571 T + \text{Log } T + C$ from which one obtains

$$L_0 - 4.571 CT = 4.571 T \text{Log } T/p$$

making $y = 4.571 T \text{Log } T/p$

$$\text{and one obtains the value of } C = \frac{(y_2 - y_1)}{4.571 (T_1 - T_2)}$$

The results of the formula give the values of C, which enable L_0 to be calculated, and from these two values that of P.

The tables a) give some of these values found by calculation in the manner indicated.

From these values and in view of the good agreement with the results of experiments shown in Table 1, it is found that the mathematical expression given may be used to calculate and deduce the intermediate values should one so desire.

The relationship between L_0 and the concentration of the nitroso complex cannot be expressed mathematically with the ease and range that it is preferred to employ in graphic representation for interpolation.

From the work presented in this first note we can deduce the following conclusions :

1. The vapour tension of solutions of nitrosylsulphuric acid increases with the temperature and the water content of the solution.
2. There exist two fairly well defined zones where the velocity of hydrolysis indicates easy denitration or energetic nitration.
3. The values for the partial pressure of solutions of nitrosylsulphuric acid in the concentrations investigated can be expressed by the following simple relationship:

$$\text{Log } P = -L_0 / 4.571 T + \text{Log } T + C$$

4. The values of L_0 and C appear to become somewhat less as the content of water and nitrosylsulphuric acid becomes greater.

TABLE I.

Sulphuric Acid solution. 70% H₂SO₄. D = 1.610 @ 20°C.

Conc SO ₄ HNO	Pressure of nitrous gases in mm. Hg at temps:								
	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C
5%	4.5	5.5	9.1	15.5	23.5	32.2	54.0	89.2	140.1
10%	6.2	9.0	14.2	23.8	36.0	55.1	86.3	131.0	200.0
15%	8.9	11.9	19.0	32.0	49.8	78.3	118.7	176.0	260.0
20%	11.3	15.0	25.1	40.0	63.2	101.0	151.0	219.2	320.0
25%	13.2	17.5	29.3	48.5	76.7	124.0	183.1	263.1	381.0
30%	15.8	20.0	33.2	56.9	91.1	147.0	227.9	307.1	442.0
35%	18.1	23.0	38.5	65.1	104.2	165.0	247.6	351.0	503.0

Sulphuric Acid solution. 75% H₂SO₄. D = 1.669 @ 20°C.

5	2.3	3.1	4.0	5.0	7.1	10.5	12.5	18.0	27.5
10	2.5	3.5	5.5	7.5	11.2	17.5	23.5	33.5	53.0
15	2.9	4.0	6.8	9.8	15.5	24.3	35.0	49.2	78.5
20	3.2	4.7	7.9	12.2	19.5	31.2	46.5	64.5	103.5
25	3.5	5.2	9.0	14.5	23.5	38.1	57.5	80.5	118.5
30	3.8	6.0	10.1	17.0	27.5	45.0	69.5	96.5	155.0
35	4.1	6.5	11.0	19.7	31.5	51.5	81.5	111.5	179.1

Sulphuric Acid solution. 80% H₂SO₄. D = 1.814 @ 20°C

5	0.7	0.9	1.3	2.0	2.8	4.8	5.9	7.9	12.2
10	1.3	1.8	2.5	3.6	5.0	7.8	10.3	14.3	20.0
15	1.7	2.6	3.7	5.1	7.3	10.5	14.5	20.3	28.2
20	2.4	3.5	4.8	6.7	9.5	13.2	19.0	26.2	36.2
25	3.0	4.2	6.0	8.2	11.7	16.1	23.3	31.8	44.0
30	3.6	5.0	7.3	9.8	13.9	19.2	27.5	37.5	53.0
35	4.2	5.7	8.4	11.5	16.2	21.7	32.0	43.8	62.3

Sulphuric Acid solution. 85% H₂SO₄. D = 1.778 @ 20°C

5	0.2	0.3	0.6	0.9	1.3	2.2	2.8	3.9	5.7
10	0.4	0.7	1.1	1.6	2.4	3.8	5.0	7.5	11.2
15	0.7	1.2	1.6	2.3	3.6	5.4	7.3	11.1	16.5
20	0.9	1.6	2.1	2.9	4.7	7.1	9.6	14.6	21.8
25	1.3	2.0	2.7	3.7	5.8	8.7	11.8	18.2	27.1
30	1.6	2.4	3.3	4.4	6.9	10.3	14.2	21.8	34.1
35	1.8	2.8	3.9	5.1	8.0	12.0	16.4	25.3	39.2

Table a)

Pressure found			C	L ₀	Pressure calculated			SO ₄ HNO	H ₂ SO
20°C.	50°C.	90°C.			20°C.	50°C.	90°C.		
9.0	36.0	200.0	4.92	8599	9.1	36.2	198.2	10%	70%
15.0	63.2	320.0	5.13	8614	15.1	63.1	322.1	20%	"
20.0	91.1	442.0	5.50	8927	20.1	91.5	442.3	30%	"
1.8	5.0	20.0	3.71	7542	1.8	4.2	20.1	10%	
3.5	11.2	53.0	4.68	8669	3.5	10.0	53.1	20%	"
4.7	19.5	103.5	5.15	9158	4.5	19.3	102.2	30%	"
1.8	6.0	20.0	2.73	6618	1.7	4.2	20.1	10%	
3.5	9.5	36.2	2.85	6390	3.5	9.5	36.2	20%	"
5.0	13.9	53.0	3.07	6479	4.6	13.8	53.6	30%	"
0.7	2.4	11.2	3.12	7716	0.7	2.3	11.2	10%	
1.6	4.7	21.8	3.14	7009	1.6	6.6	21.6	20%	"
2.4	6.9	34.1	3.38	7321	2.4	6.9	34.3	30%	"

RESUME.

The total vapour pressures have been investigated for solutions of nitrosylsulphuric acid (10 to 35%) in aqueous solutions of sulphuric acid (70 to 85%) at temperatures between 10 and 90°C.

The apparatus employed in these determinations is described.

The results obtained in this investigation have enabled graph to be constructed, showing the increase of vapour pressure of the system with increasing concentration of water, of nitrosylsulphuric acid and of temperature. The equation suggested by Eucken relating vapour pressure with temperature :

$$\text{Log P} = \frac{-L_0}{4.571 T} + \text{Log T} + C$$

where L₀ represents the molecular heat of vapourisation and C is an empirical constant,

has been applied with satisfactory results.

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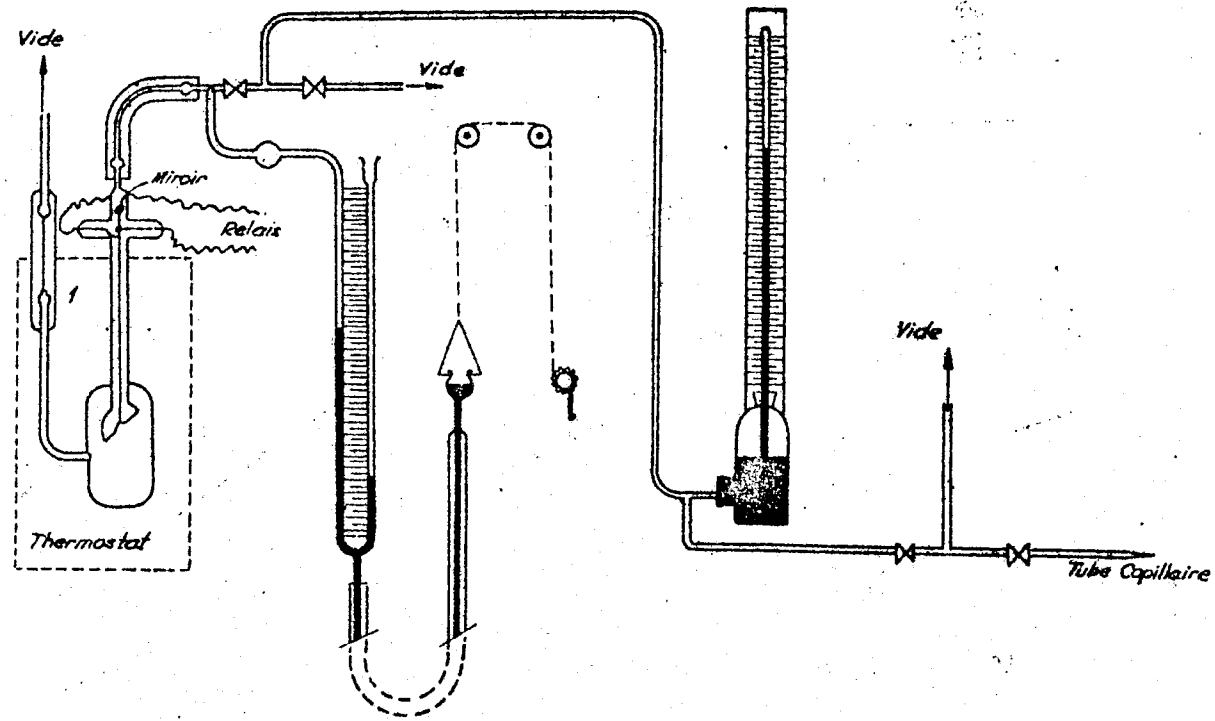


fig. 1.

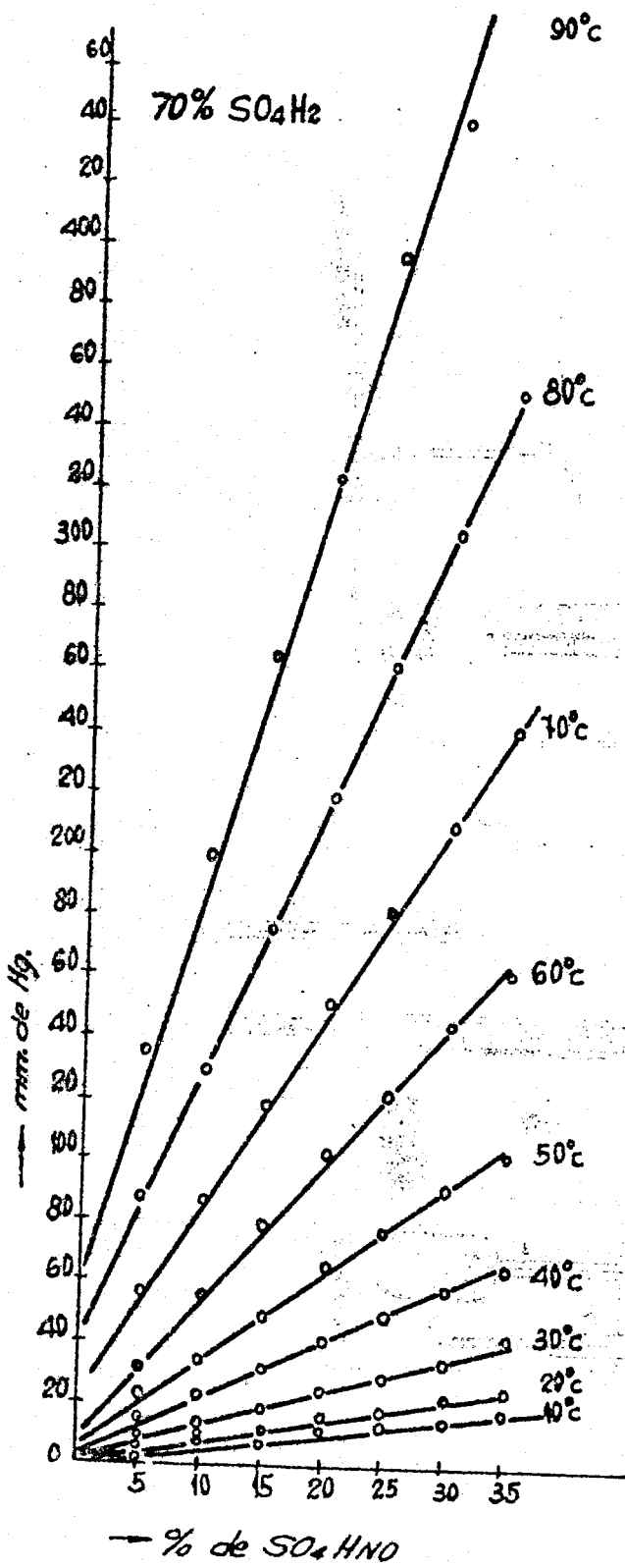


fig. 2

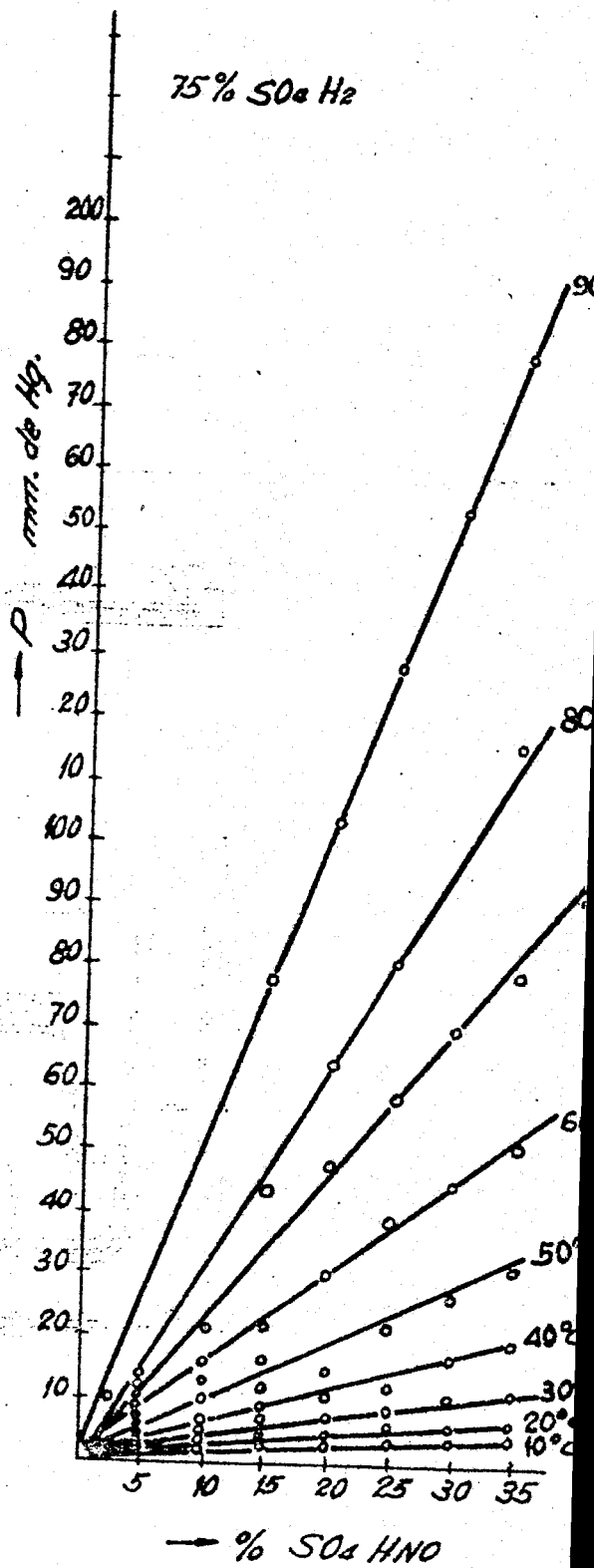


fig. 3

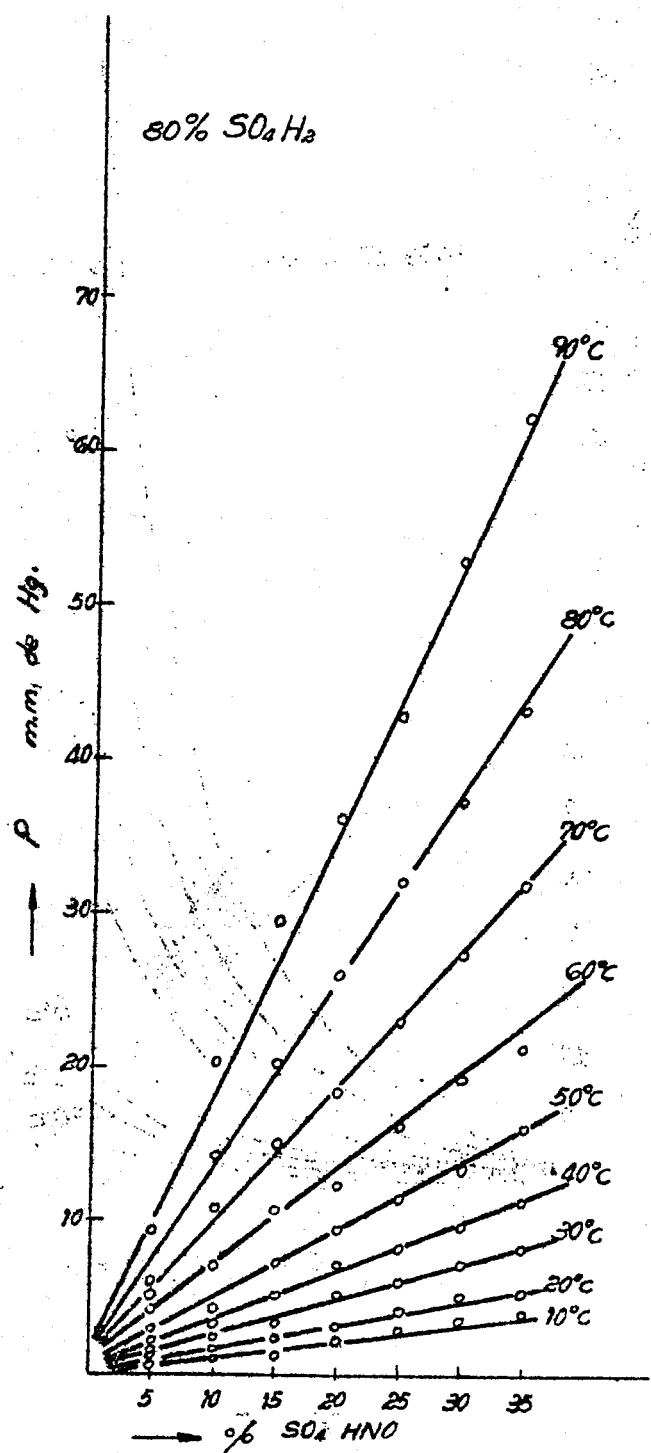


fig. 4

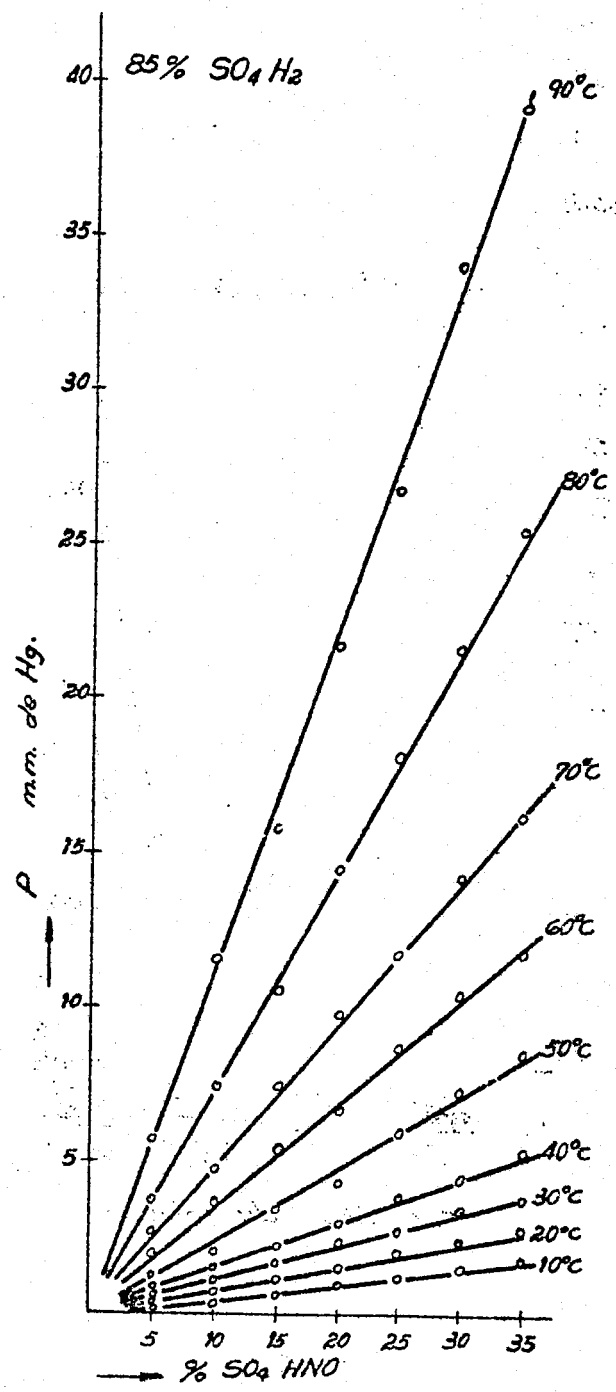


fig. 5

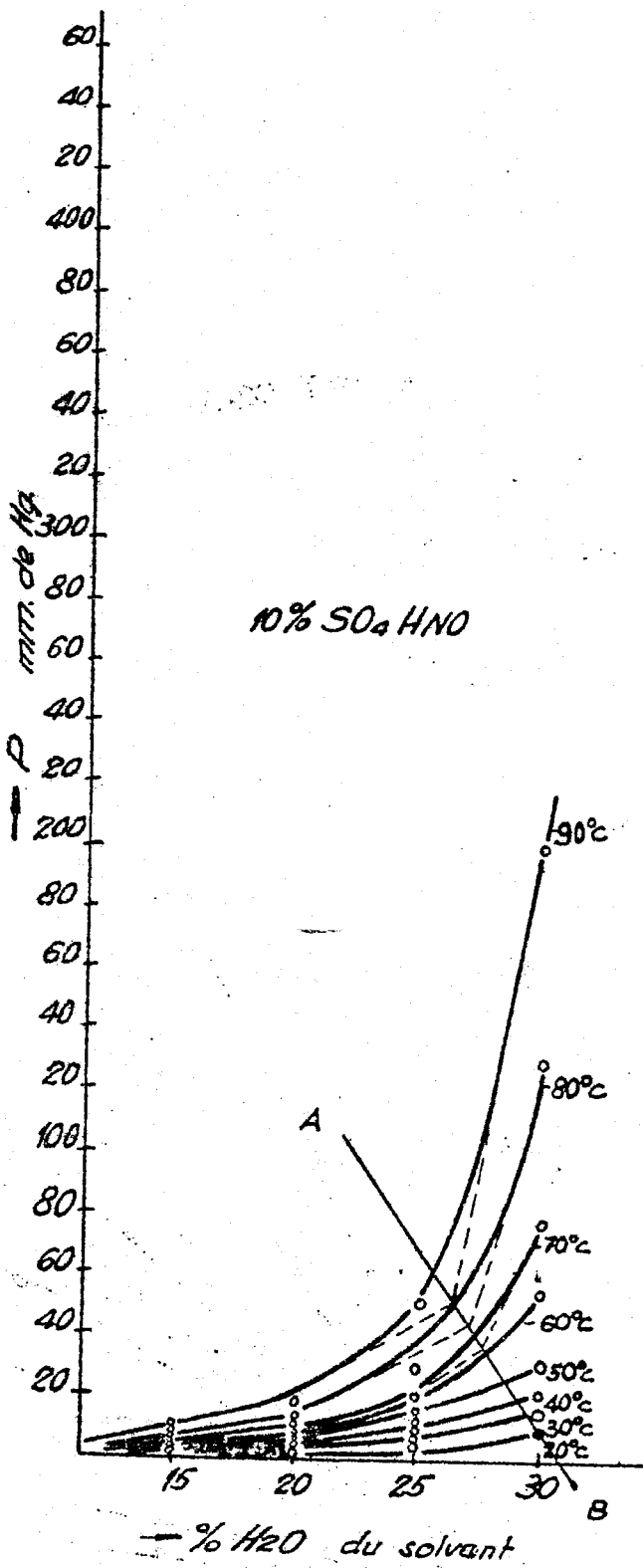


fig. 6

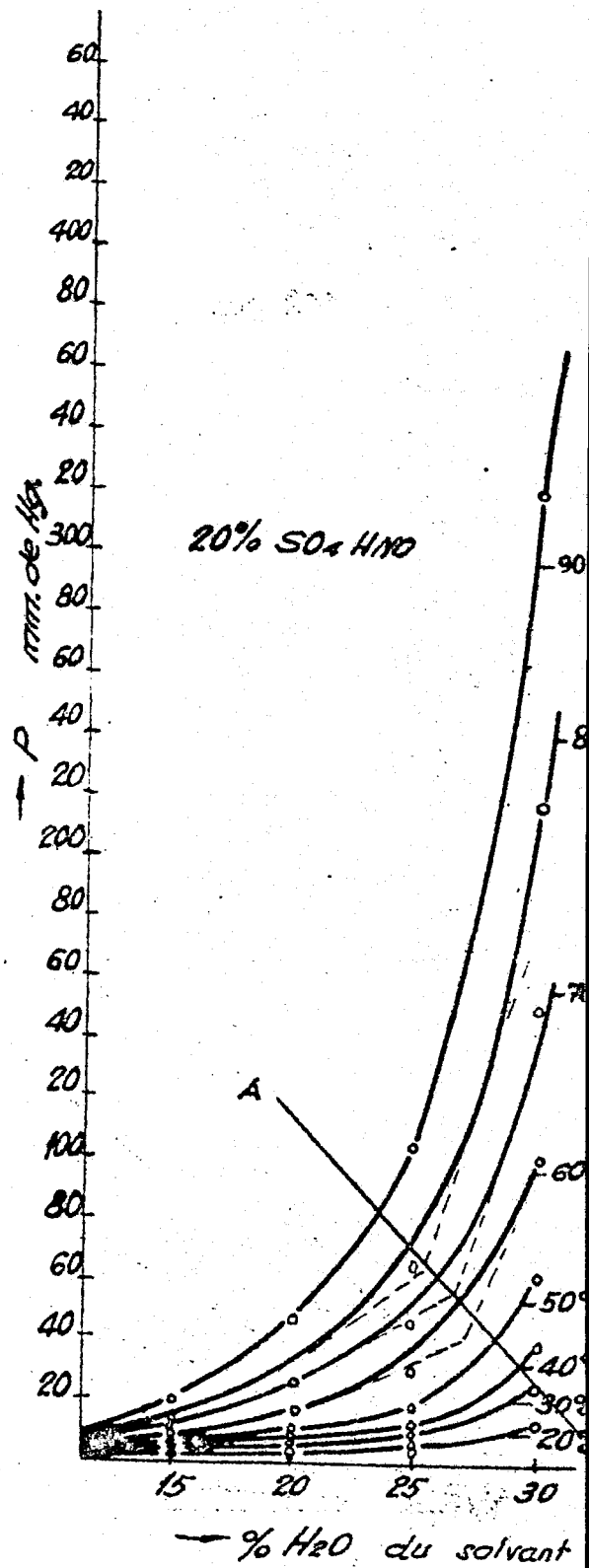


fig. 7

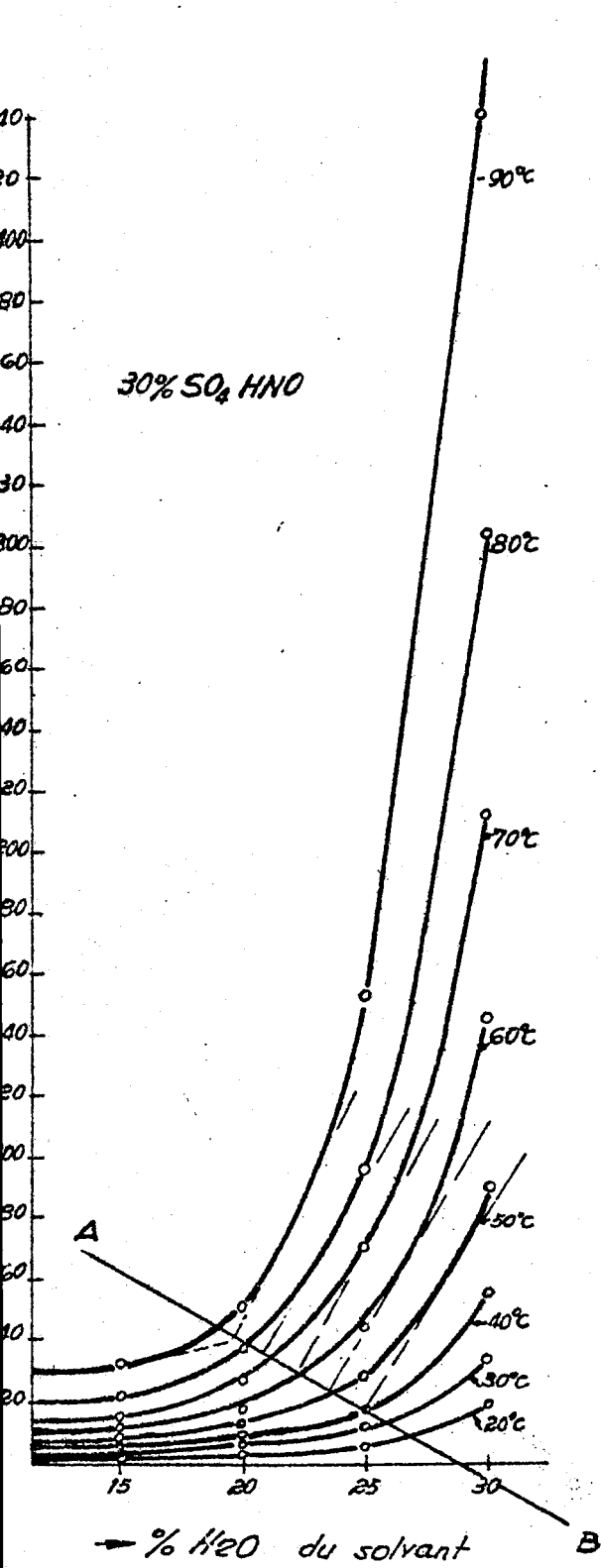


fig. 8

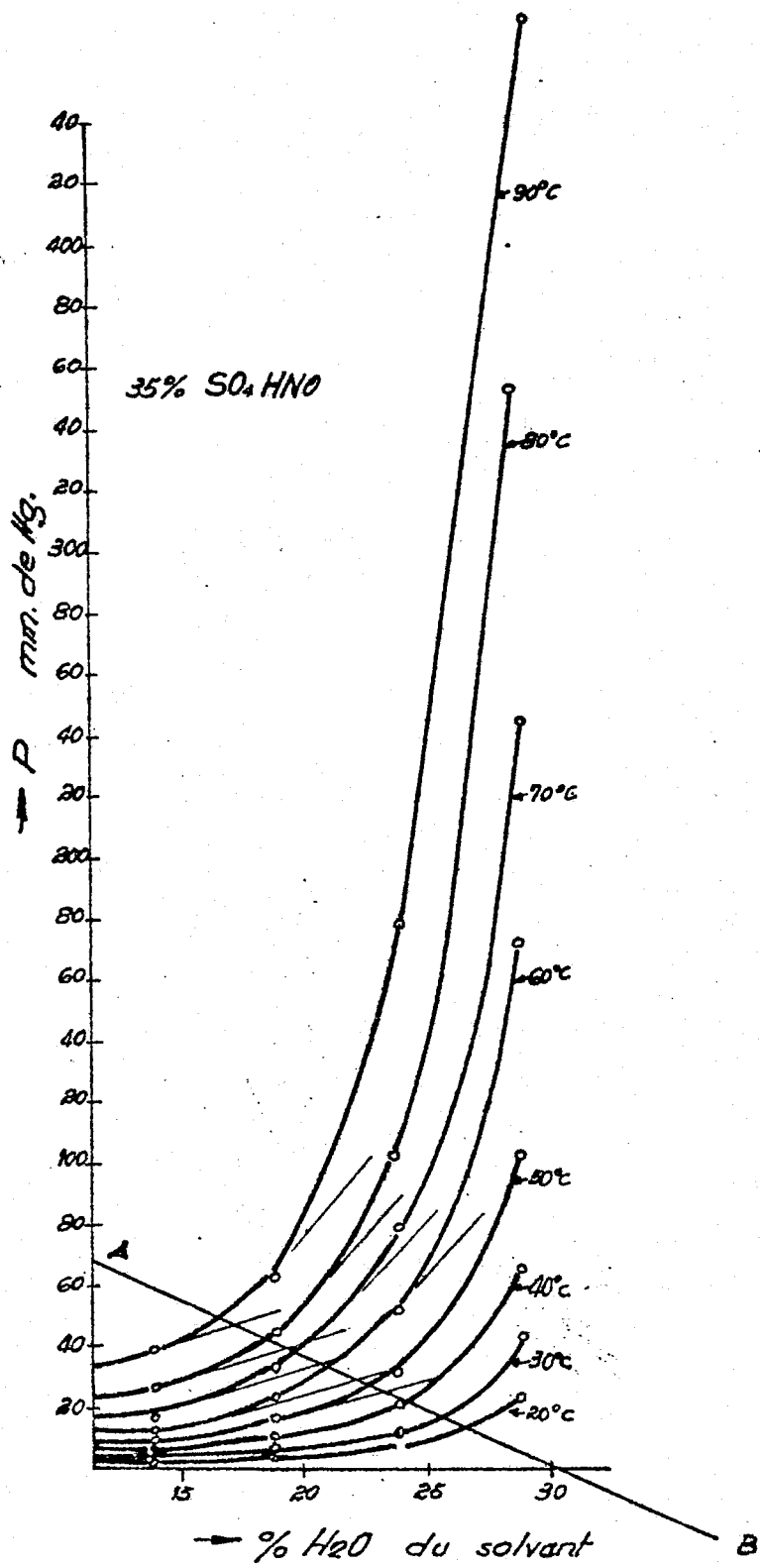


fig. 9

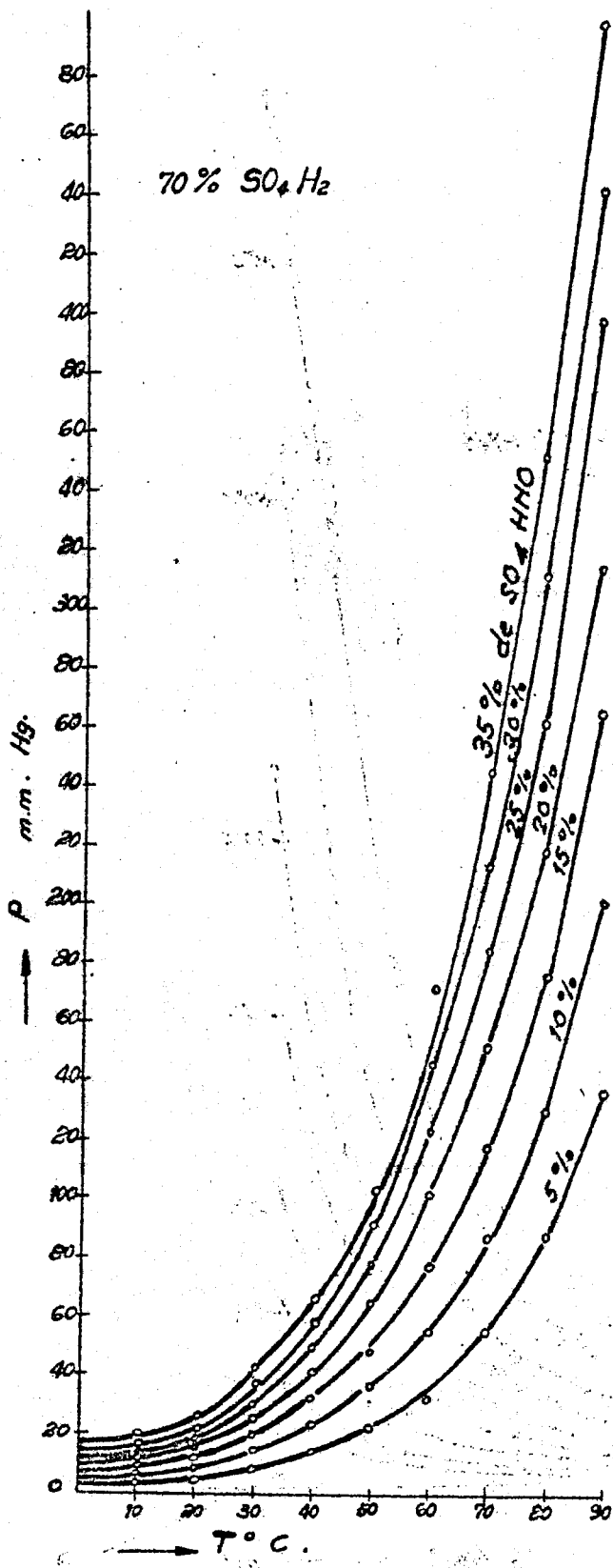


fig. 10

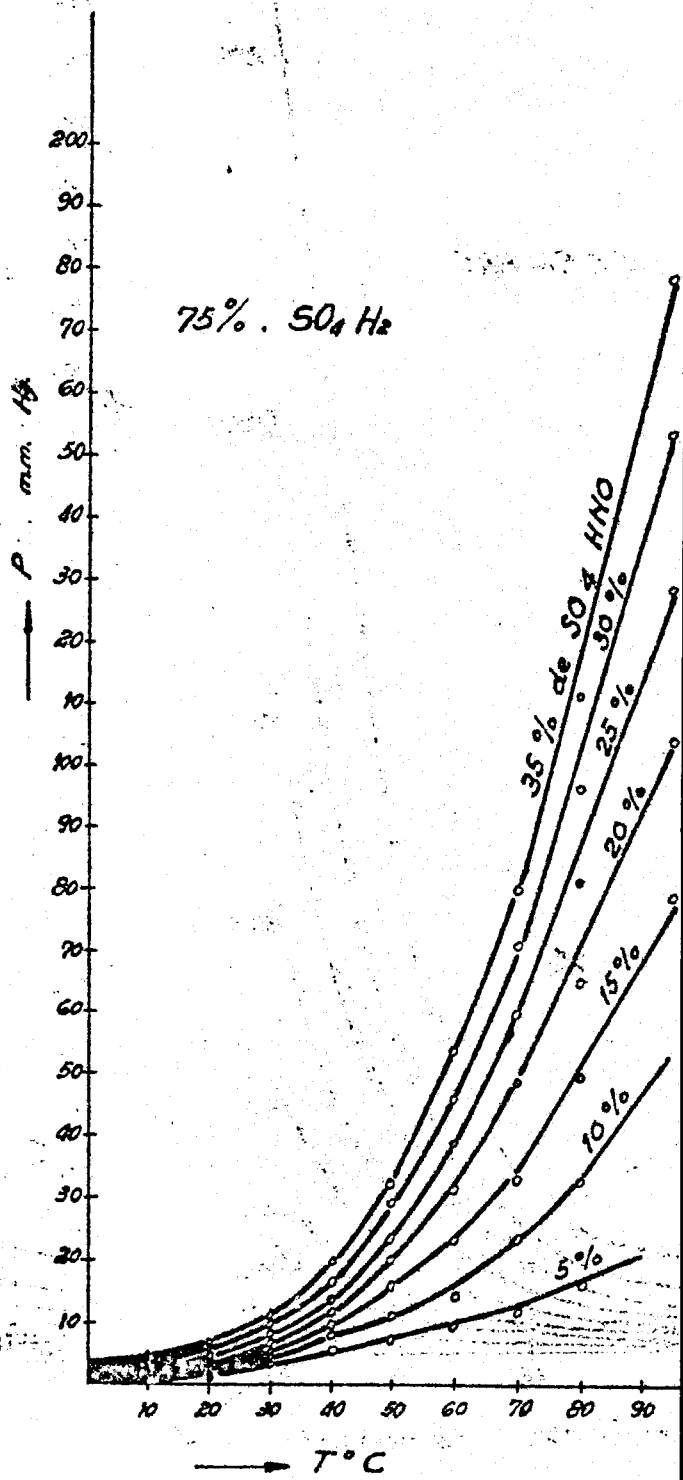


fig. 11

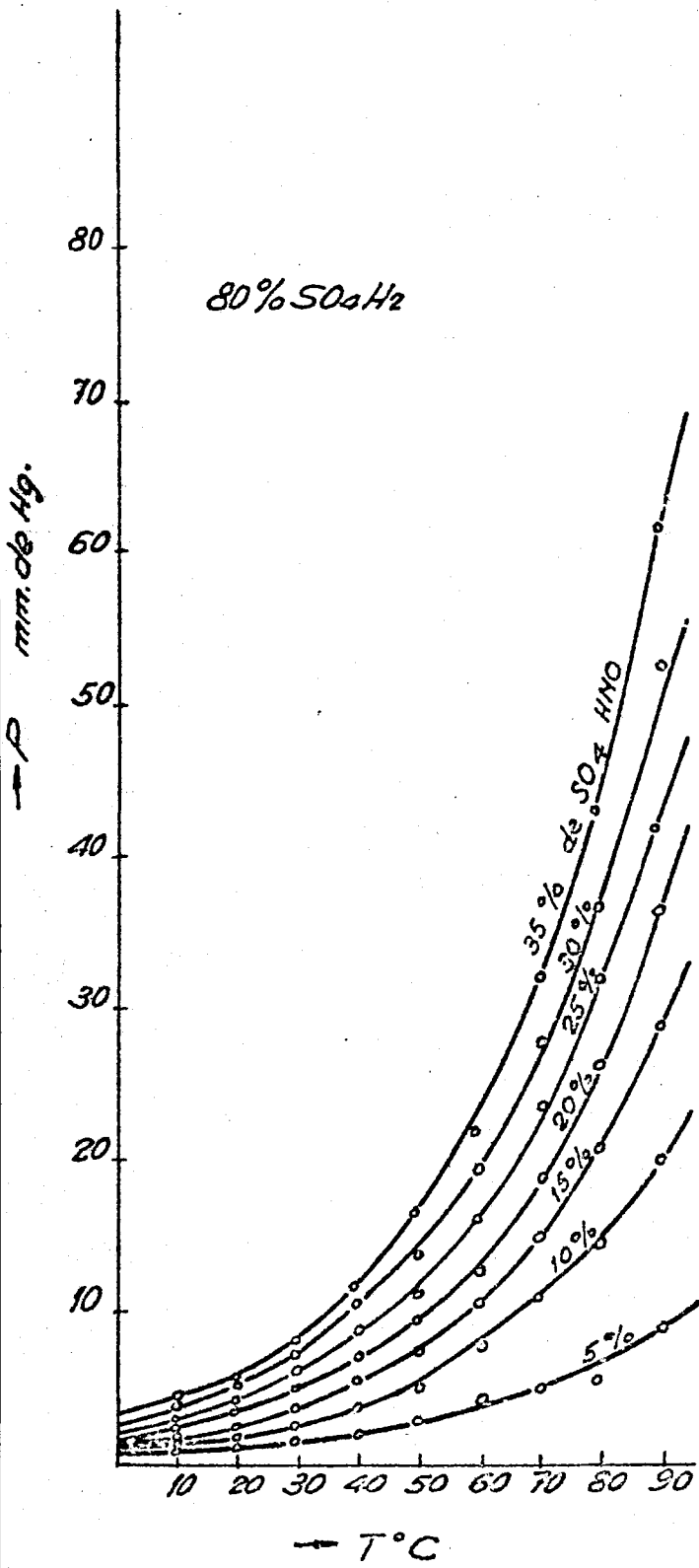


fig. 12

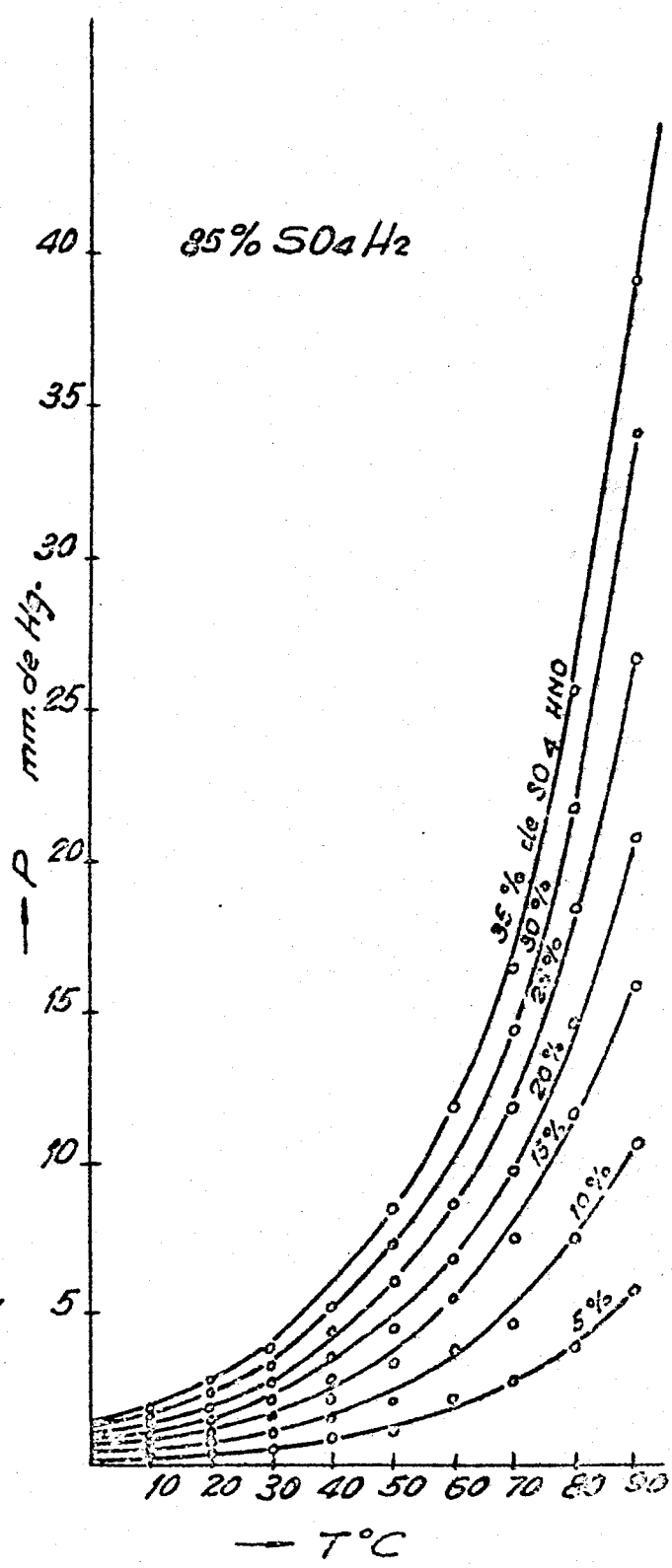


fig. 13