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**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

A contribution to the study of the
reaction of sulphurous anhydride
with nitrous acids

(continuation)

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Introduction

The purpose of this work is to continue the study of the way in which gases containing sulphurous anhydride react with nitrous acids of varying composition, both as regards their nitrous content and the strength of the sulphuric acid used in their preparation.

A start had already been made to this study in a previous work by using gases with an SO_2 content of 7.5% and nitrous acids operating with a counter-current system with a reactor consisting of a glass tower filled with rings of the same material. After studying the influence of various factors, such as the concentration of the sulphuric acid and the N_2O_3 content, temperature and the presence of free NO_2H , the process was studied kinetically and it was found possible to consider that with nitrous acid (80-20) and within the range studied, the reaction took place on the whole as though it were a reaction of the first order. The chief drawback of the equipment then used was that the contact surface considered, which served as the basis of the study, was clearly not accurate, since it was noted that the distribution of the acid used was insufficiently uniform or complete. We wondered whether this surface could be kept constant throughout all the tests and whether we could reproduce it at will. In order to solve this question we prepared three towers, all identical as regards their measurements and the type and quantity of filling used, wetting them simultaneously with the same acid and feeding in the same gas. The results of the numerous tests carried out

under identical conditions of temperature and throughput revealed a considerable dispersal period which, although sufficient for a qualitative and comparative study to be made, did not enable this to be performed with the thoroughness required in considering a type of reaction as complex as the one in question. We carried out further tests, altering the characteristics of the filling, but failed. In view of the results obtained, we decided to replace the packed tower by a wet-wall tower of the type we shall describe later, with which we established a known contact surface that enabled us to obtain true and acceptably reproducible data. In this work, therefore, we shall outline the results obtained.

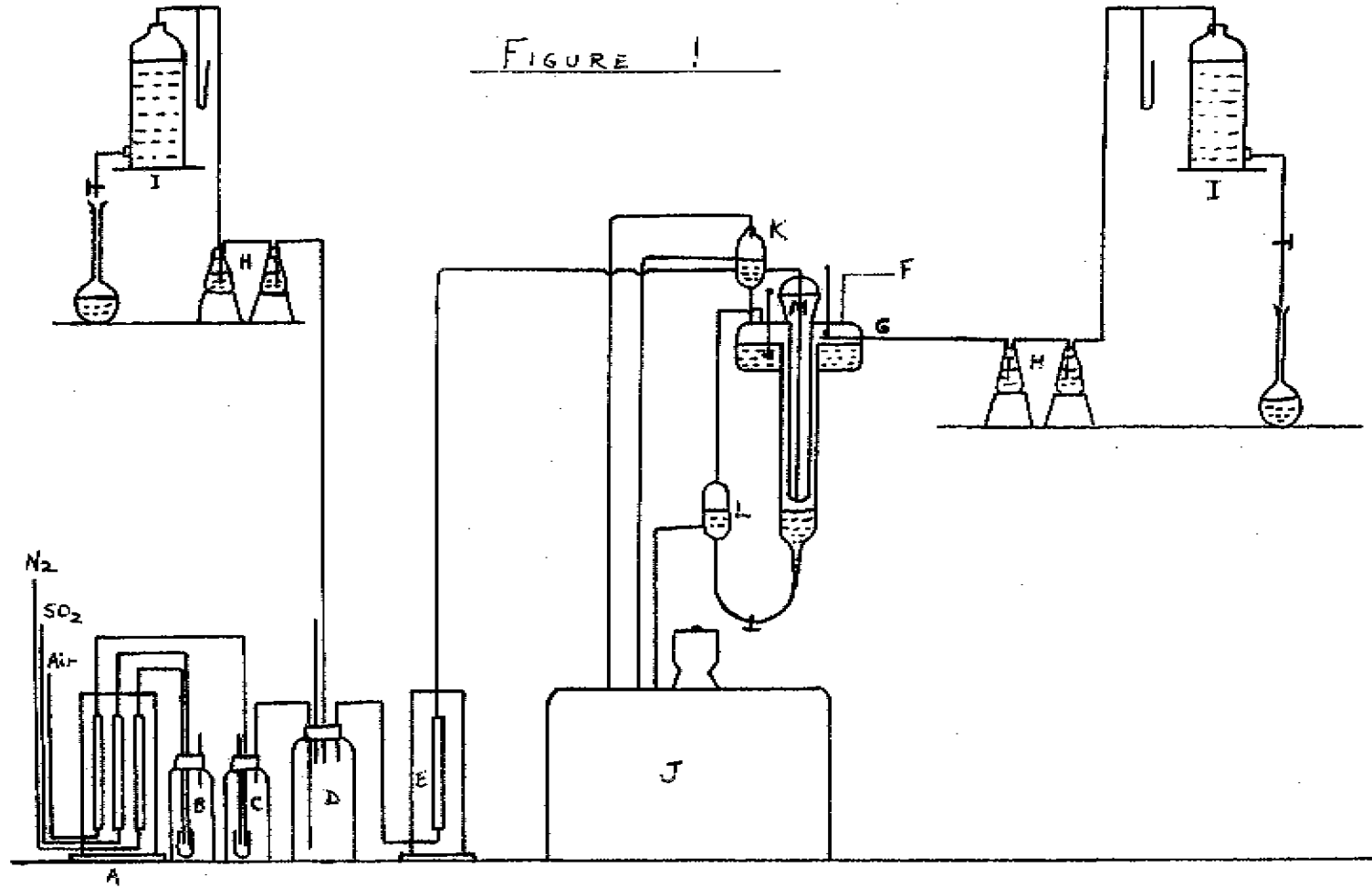
Equipment

Figure 1 is a schematic representation of the equipment we used. For reasons of maximum simplicity, we have omitted the heating systems consisting of a thermostat, heating chambers and resistances enabling us to keep the whole apparatus at the required working temperature. In fact, the lay-out of all these items is the same as that indicated in our previous work.

The gases, SO_2 , nitrogen and air, obtained from a purification system, are introduced into discharge meters (A), where the rate of flow of each is fixed so that the mixture of the required composition flows at 5 litres per minute. Mixing takes place in the mixing flasks (B), (C) and (D). flask (D) has three discharge outlets which may be adjusted by means of taps. One of these taps allows the gas to flow into another discharge meter (E), by which we fix the rate of flow at the required value according to the time of contact. One of the other outlets is used for taking samples for analysis, while the third outlet pipe enables excess gas to be discharged.

On leaving the meter (E), the gases, which already have the required composition and rate of flow, are led to the reaction column which they enter through the top of a glass cylinder (M) fitted concentrically with the column, which leads the gases down to within one cm. of the surface of the nitrous acid, which serves to shut off the column at the base; the gases then begin to travel in counter-current to the nitrous acid flowing on the

FIGURE 1



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walls and, finally, emerge into the wide part at the top of the column. After this point has been reached, the gases leave by way of outlet (F). A sheet of glass (G), almost a capillary is fitted at the upper limit of the reaction chamber, i.e., immediately above the level of the nitrous acid, and, by means of this, samples of the tail gases are drawn off for analysis.

The same system of analysis is used for head and tail gases; this consists of Erlenmeyer flasks (H) placed on magnetic shakers, and Mariotte flasks(I).

(J) is the tank from which the nitrous acid is pumped to container (K); an overflow valve fitted to the latter and leading back to (J) serves to keep the level of the nitrous acid constant. The lower part of this container is connected to a glass tube which leads to the bottom of the tank forming the enlargement of the upper part of the reaction column. The rate of flow or discharge of the nitrous acid is determined by the fixed height of container (K) and the diameter of the tubing, and a tap fitted to this tubing enables us to adjust this flow so that it remains constant for each nitrous acid and each temperature. The level of the nitrous acid rises until it reaches the upper edge of the column, which is bevelled and emery-papered, whereupon it flows onto the inner walls of the column, covering them completely and thus providing a constant contact surface.

The lower part of the column is connected to tank (L) by means of a flexible plastic tube which serves to fix the level of the nitrous acid inside the column, thus delimiting the contact surface and forming a hydraulic seal for the gases. From this tank (L), the nitrous acid returns to the general tank (J). A tap is fitted between these two tanks for taking samples of the nitrous acid and measuring its rate of flow.

Characteristics of the reaction column

The dimensions of the reaction column are as follows at the area of contact:

Internal radius	2 cm
Height	20 cm
Lateral surface	251.33 cm ²
Volume of the chamber	251.33 cm ³

The lateral surface and the area of one section, i.e., 263.9 cm², constituted the contact surface.

As mentioned during our description of the equipment, the gases were introduced into the column by way of a glass cylinder concentric with the column, which reached to 1 cm. from the surface of the nitrous acid in the bottom. We operated with three such cylinders of differing diameters, and were thus able to alter the ratio between the contact surface and the volume of the gas chamber. The details of these cylinders were as follows:-

Column No.	1	2	3
External radius	0.517	1.00	1.52 cm
Height	19.0	19.0	19.0 cm
Volume	15.96	55.79	137.94 cm ³

The working volume will therefore be the volume of the empty tower less that occupied by the cylinder inside it. If we divide the contact surface by this volume we obtain the operating "Surface/Volume" ratio, which we shall represent by ϕ , and arrive at the following values for each unit:

	1	2	3
ϕ	1.12	1.37	2.33 cm ⁻¹

Experimental data

The nomenclature we have used for naming each nitrous solution takes the form of two numbers, separated by a dash and enclosed in brackets. The first number shows the concentration of sulphuric acid in which the nitroxyl acid sulphate is dissolved, and the second indicates the percentage of the latter by weight. Thus, "nitrous solution (85-20)" contains 20 grs. of nitroxyl acid sulphate and 80 grs. of sulphuric acid of 85% H₂SO₄ concentration.

The nitrous solutions were prepared by dissolving H₂SO₄ crystals (obtained by the action of SO₂ on nitric and sulphuric acid)

in the required concentration of sulphuric acid.

The range of concentration of the acid studied was from 70 to 85%.

The nitrous content varied from 10 to 35% of HNO_3 , which corresponds to between 3 and 10.5% of N_2O_3 .

We worked within a temperature range of from 30 to 90°C.

Contact time was varied between 3.7 and 40 seconds.

The linear speed of the gas varied between 0.5 and 5.4 cms. per second.

In all the tests, the throughput of the nitrous solution was at the rate of 2.5 litres per minute.

We kept the composition of the gases constant as follows:

7.5% SO_2 , 11.29 O_2 , and 81.21 $\text{N}_2 = 100\%$

The experiments consisted in ascertaining the percentage of SO_2 converted in relation to the operating time under different conditions.

Methods of analysis

A permanent check was kept on the nitrous solutions by verifying their analysis by acidimetry and permanganimetry and by checking, at the start of our operations with each solution, that they were free from nitric acid. We compared the result of the permanganimetric analysis with the corresponding determination achieved with a nitrometer.

The gravimetric method was used to determine the gases both at the head and the tail. We operated as follows: after washing the pipes with the gas, we slowly and simultaneously took one litre of head and tail gas which we passed through two absorbers containing a solution of NaOH, the second of which served to verify that all the SO_2 had been absorbed by the first absorber. The volume of the gas sample taken was measured by the corresponding Mariotte flasks. The alkaline solution, treated with bromine water and afterwards with hydrochloric acid, immediately enabled us to determine the SO_2 in the form of Ba.SO_4 .

We allowed a tolerance of $\pm 0.3\%$ on the percentage

of SO_2 at the head and of $\pm 0.5\%$ in the composition of the nitrous solution, both as regards the H_2SO_4 and the nitrous concentration.

Presentation of results

We are presenting the results of the experiments in two ways simultaneously, i.e., as the percentage of transformation (T%) and as a coefficient of speed of transformation (K) expressed as weight of SO_2 absorbed by the nitrous solution per unit of surface area and unit of contact time.

$$K = \frac{X}{S \cdot t.}$$

in which X = kg. of SO_2 absorbed

S = contact surface in m^2

t = time in hours.

The table of results shows the mean values of at least three results obtained from each of our experimental determinations. In certain cases, up to ten readings were taken during experiments carried out on different days to study the reproducibility of the results obtained; with the exception of a few values which deviated from the average figure shown, all the experimental readings taken were generally within a dispersal range of ± 1 .

TABLE OF RESULTS - I

$$\sigma = 1.37 \text{ cm}^{-1}$$

Temperature $^{\circ}\text{C}$	30	50	70	90	30	50	70	90
	Conversion %				k.10 ³			
Contact time								
sec.	<u>NITROUS SOLUTION (80-10)</u>							
5	16.1	-	17	-	181	-	191	-
10	30.8	30	27.8	30.8	173	168	156	173
20	49	-	49.3	-	138	-	139	-
30	57.9	56.4	58.7	59.9	108	105	109	112
40	63.5	-	65	-	89	-	91	-
	<u>NITROUS SOLUTION (80-20)</u>							
5	14.7	-	20.1	-	165	-	226	-
10	26.7	33.1	37.5	43.9	150	186	210	247
20	45.9	-	55.5	-	129	-	156	-
30	55.6	60.4	65.8	71.4	104	113	123	133
40	64.7	-	74.	-	90	-	103	-

TABLE OF RESULTS (Continued)

$$\sigma = 1.37 \text{ cm}^{-1}$$

Temperature °C	30	50	70	90	30	50	70	90
	Conversion %				k.10 ³			
Contact time sec.	<u>NITROUS SOLUTION (80-25)</u>							
3.7	11.7	13.2	15.7	-	167	200	238	-
5	14.-	18.9	22.-	-	157	213	247	-
10	25.9	32.6	39.4	45.-	146	183	221	253
15	37.2	43.3	49.-	-	139	162	183	-
20	43.8	50.5	57.7	-	123	141	162	-
25	48.8	55.8	61.5	-	110	124	138	-
30	54.8	60.8	65.8	74.-	104	116	125	140
40	64.3	70.2	75.7	-	90	98	106	-
	<u>NITROUS SOLUTION (80-35)</u>							
5	12.9	-	25.3	-	146	-	281	-
10	23.8	33.4	44.1	57.-	134	187	246	319
20	40.5	-	61.1	-	113	-	171	-
30	50.9	63.5	73.5	84.8	97	121	140	161
40	61.-	-	81.-	-	85	-	113	-
	<u>NITROUS SOLUTION (70-25)</u>							
5	48.5	-	-	-	545	-	-	-
10	68.6	-	-	-	384	-	-	-
20	82.3	-	-	-	230	-	-	-
30	90.3	-	-	-	171	-	-	-
40	-	-	-	-	-	-	-	-
	<u>NITROUS SOLUTION (75-25)</u>							
5	29.4	-	40.-	-	330	-	450	-
10	45.7	49.9	59.-	64.9	258	280	330	364
20	64.9	-	80.-	-	182	-	224	-
30	73.4	80.7	86.7	90.-	131	146	155	162
40	78.2	-	90.6	-	109	-	126	-

TABLE OF RESULTS (Continued)

$$\epsilon = 1.37 \text{ cm}^{-1}$$

Temperature °C	30	50	70	90	30	50	70	90
	Conversion %				k.10 ³			
Contact time	NITROUS SOLUTION (85-25)							
sec.								
5	10.1	-	14.2	-	112	-	157	-
10	21.2	22.8	23.5	24.2	117	128	130	134
20	36.3	-	42.9	-	101	-	120	-
30	48.8	51.7	53.4	56.2	88	92	97	101
40	55.5	-	59.7	-	78	-	83	-

TABLE OF RESULTS - II

Nitrous Solution	Contact time sec.	Conversion %			K.10 ³		
		$\epsilon \text{ cm}^{-1}$			$\epsilon \text{ cm}^{-1}$		
		1.12	1.37	2.33	1.12	1.37	2.33
(80-18)	10	24.1	30.8	44.1	173	166	146
	30	52.2	57.9	73.1	120	108	80
(80-20)	10	23.9	26.7	43.	165	150	143
	30	50.8	55.6	68.1	117	104	75
(80-25)	10	21.	25.9	42.	145	146	145
	30	50.5	54.8	69.9	116	104	77
(80-35)	10	20.6	23.8	41.	142	134	136
	30	47.	50.9	69.	108	97	76
(70-25)	10	60.3	68.6	77.5	416	384	258
	30	-	90.3	-	-	171	-
(75-25)	10	38.5	45.7	57.8	265	258	192
	30	65.8	73.4	83.5	151	131	92
(85-25)	10	15.3	21.2	30.3	105	117	101
	30	42.	48.8	59.7	96	88	65

Examination of results

I. General conversion curves

Graphs 1 and 2 show the percentage values of conversion (T) against the contact time in seconds, thus providing a series of curves which tell us the dependency or relationship between these two values.

Graph 1 represents a group of nitrous solutions of varying nitrous concentration and with constant concentration of the sulphuric acid solvent, at 30 and 70°C. It may be noted that the conversion yield rises as the contact time is increased; the relationship is not linear but the relative increase in conversion decreases as the contact time increases. For contact times of more than 20 seconds duration, the relative increase is practically constant regardless of the nitrous content and the temperature of the solution. When the contact time is less than 20 seconds, the relative increase depends upon the nitrous content and temperature; for equal nitrous concentrations temperature produces a positive effect on the relative increase in conversion, and this effect is greater, the higher the nitrous concentration. If the latter amounts to no more than 10% of HNO₂ SO₄ temperature has practically no effect at all. For equal temperatures the nitrous concentration produces contrary effects depending upon the temperature; thus, the nitrous concentration has a positive effect at 70°C and a negative effect at 30°C.

Graph 2 expresses the same idea but represents a group of nitrous solutions in which the nitrous concentration is constant (25% HNO₂ SO₄) and the concentration of the sulphuric acid solvent variable, also at 30 and 70°C. This shows the positive and non-linear effect of the contact time upon conversion. For contact times of more than 20 seconds, the relative increase may be considered as constant, regardless of the concentration of the acid and the temperature. In the case of contact times of less than 20 seconds, the relative increase is greater the higher the temperature and the lower the concentration of the acid.

II. Influence of the linear speed of the gas.

Graphs 3 and 4 show the values of the coefficient of speed

K, in relation to the linear speed of the gases expressed in cms/second.

Graph 3 represents a group of nitrous solutions of varying nitrous contents and with acid of equal concentration, at 30 and 70° C. In Graph 4, the nitrous content of the group represented is constant (25% HNO₃) and the concentration of the acid variable; this group, too, is at 30 and 70° C.

If we examine these graphs, we find that the coefficient of the speed of conversion increases with the linear speed of the gas; this increase is not itself linear, but decreases as the speed of the gas is increased towards certain limit values.

The relative increase in K with the linear speed of the gases depends upon the temperature, the nitrous content, and the concentration of the acid. T° C always produces a positive effect upon the relative increase of K, all the more so in fact as the nitrous content increases and the concentration of the acid decreases; thus, in the case of (80-10), temperature has no effect. Temperature also has practically no effect when the nitrous content is 25% HNO₃ and the concentration of the acid is more than 80%. When the nitrous content and temperature are constant, the dilution of the acid has a positive effect on the above mentioned relative increase, and when the concentration of the acid and the temperature are constant, the nitrous content produces contrary effects according to the temperature. An increase in the nitrous content has a positive effect when the acid has a concentration of 80° C, while, at 30° C, the effect of the nitrous content on the relative increase in K is negative.

The limit values of K are obtained with gas speeds which are lower, the lower the temperature, the higher the acid concentration and the larger the nitrous content.

III - Influence of temperature

In order to demonstrate the influence of temperature, we have drawn Graphs 5, 6, 7, 8 and 9 from the tables of data.

Graphs 5-a and 5-b show the values of %T against T° C, and Graphs 5-c and 5-d show the values of K against T° C. The nitrous solutions represented in 5-a and 5-c have an HNO₃

content of 25% and an acid concentration varying between 70 and 85% for contact times of 10 and 30 seconds; 5-b and 5-d show solutions with 80% acid concentration and a nitrous content of between 10 and 35% HNO_2 also for contact times of 10 and 30 seconds.

Graphs 6 show the values of %T against $T^{\circ}\text{C}$ for various solutions with a solvent sulphuric acid concentration of 80% and various HNO_2 contents; each with contact times of 5, 10, 20, 30 and 40 seconds. Graphs 7 represent the same idea, but the values of T% have been replaced by K values.

Finally, Graphs 8 and 9 show the same idea as 6 and 7 respectively but for nitrous solutions of varying acid concentrations and a constant HNO_2 content of 25%.

When examined, Graphs 5 reveal the following: with the exception of solution (80-10), in which an increase in temperature has no effect on the degree of conversion or the coefficient of speed, in all the other solutions, when the temperature is raised, T% and K increase linearly within the range of 30-90 $^{\circ}$ studied. The effect of temperature increases the higher the nitrous content becomes and the greater the dilution of the acid, although it appears in the latter case that when the acid concentration of the nitrous solution is below 80% H_2SO_4 the effect of temperature is already constant, and that for acid concentrations of approximately 90%, the temperature has no effect on the degree of conversion.

According to Graphs 6 and 8, for any given nitrous solution, the effect of temperature on the degree of conversion increases with the contact time, i.e., as the linear speed of the gases is reduced. However, this increase tends to find its limit, which is reached sooner the more concentrated the acid solvent used and the lower the nitrous content becomes. In all the solutions studied, this limit was obtained at a contact time of 10 seconds, which corresponds to a linear speed of 2 cms/second for the gases.

According to Graphs 7 and 9, the effect of temperature on

the coefficient of speed increases as the contact time is reduced, i.e., as the linear speed of the gas is increased; this effect is accentuated the more the sulphuric acid solvent is diluted and the higher the nitrous content becomes.

IV - Influence of the nitrous content

Graphs 10 show the values of the nitrous content, expressed as percentages of HNO_3 and N_2O_5 against the corresponding K values in the case of 10-a, and against the percentage conversion values in that of 10-b, for solutions with sulphuric acid containing in each case an 80% concentration of H_2SO_4 , for temperatures between 30 and 90° C and contact times of 10 and 30 seconds.

It is found upon examination that the influence of the nitrous content depends upon the temperature. At a temperature which we estimate at about 45° C, the nitrous content has no effect on conversion. At temperatures of over 45° C, the effect of the nitrous content on the degree of conversion and the coefficient of speed is positive: these values increase in linear progression with the nitrous content, and increasingly so the higher the temperature is raised. Below 45° C the effect is negative. The degree of conversion and the coefficient of speed decrease in linear progression with the nitrous content, and this decrease is more rapid, the lower the temperature becomes.

The effect of the nitrous content on the coefficient of speed increases as the contact time is reduced, i.e., as the speed of the gases increases. The effect of the nitrous content on the degree of conversion is practically constant over the range of contact times studied.

If we extrapolate for a nitrous content = 0, we find that in the case of a sulphuric acid with an 80% concentration of H_2SO_4 , the coefficient of speed for the absorption of SO_2 decreases as the temperature is raised.

V - Influence of the dilution of the acid

In Graphs 11, we have shown the concentration of H_2SO_4 against the degree of conversion (T%) in the case of 11-b, and against K in that of 11-a, for nitrous solutions with a HNO_3 50%.

content of 25% in the temperature range of 30-90° C and for contact times of 10 and 30 secs.

It is noted that the dilution of the acid solvent has a positive effect on the degree of conversion and the coefficient of speed. At low temperatures and within the range studied, the increase is small initially but rapidly increases. At temperatures of more than 50° C, the increase takes place rapidly from the beginning and may be considered as linear within the range in question.

The effect of acid dilution on the degree of conversion is constant over the range of time studied, while its effect on the coefficient of speed increases in inverse proportion to the contact time, i.e., the higher the speed of the gases becomes.

VI - Influence of σ

Graph 12 shows the values of the degree of conversion against those of σ for all the nitrous solutions studied at 30° C and for contact times of 10 and 30 seconds. It may be noted here that an increase in σ produces a positive effect on the degree of conversion which, in the range studied, may be considered as practically linear and constant for all the solutions.

Graph 13 shows σ against the values of the coefficient of speed for all the solutions considered at 30° C and for contact times of 10 and 30 seconds. It is found from these graphs that the effect of σ depends upon the solution concerned or, rather, on the concentration of its acid. If this is greater than 80% H_2SO_4 there is hardly any effect regardless of the nitrous content; if less than 80%, an increase in σ has a negative effect on the coefficient of speed which becomes more pronounced the more the acid is diluted. When the contact time is increased, i.e. when the speed of the gases is reduced, there appears a slight negative influence on the part of the nitrous solutions concerned, although they revealed no influence at all at higher gas speeds.

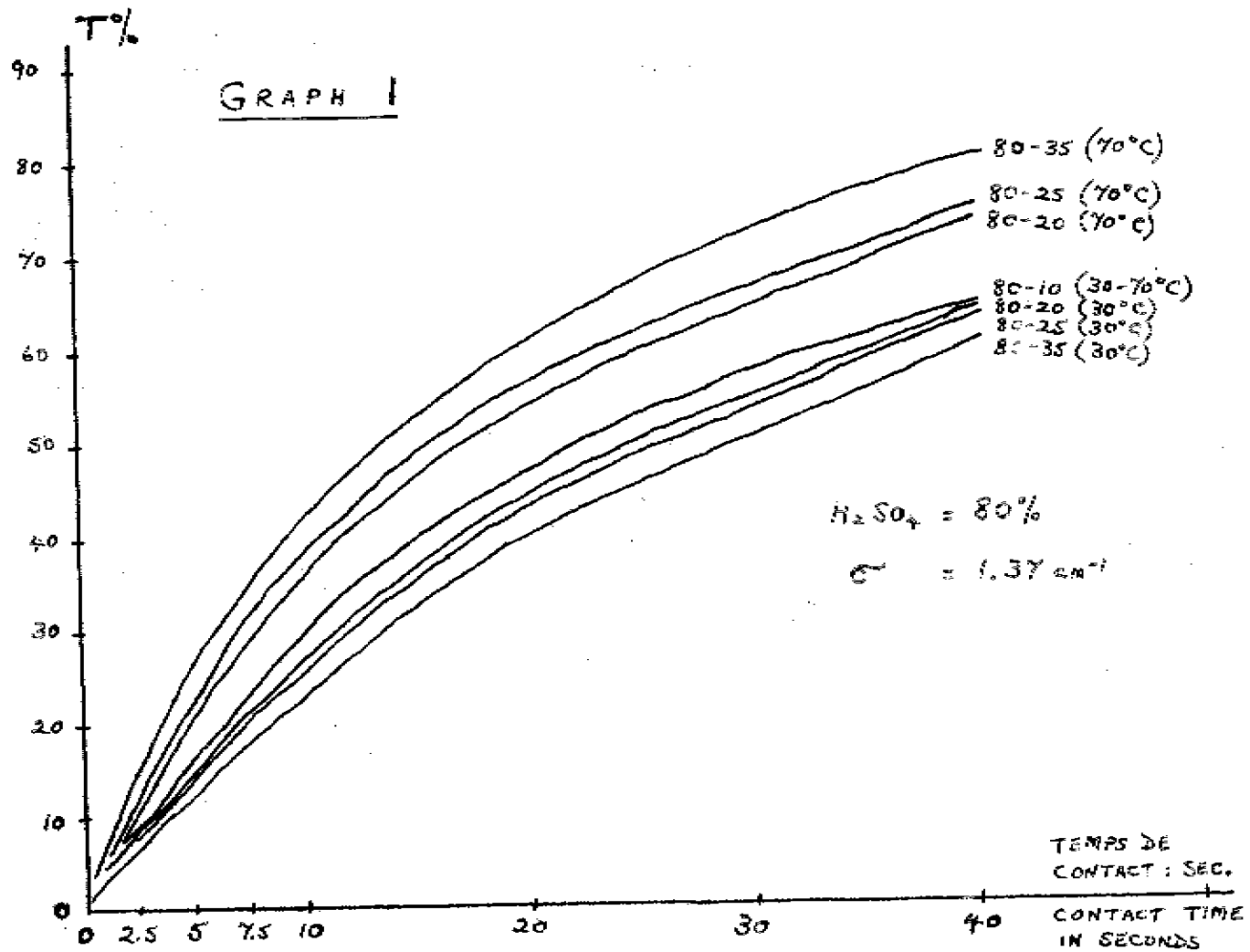
Besides the above experiments, we have also carried out a few tests in which the oxygen content of the gases was raised from 11.29 to 19.42%, the SO_2 content being kept constant.

These tests were all conducted with nitrous solution (80-25), at 30 and 70° C and with various contact times; and we have to report that this modification of the oxygen content has no influence whatsoever on the degree of conversion.

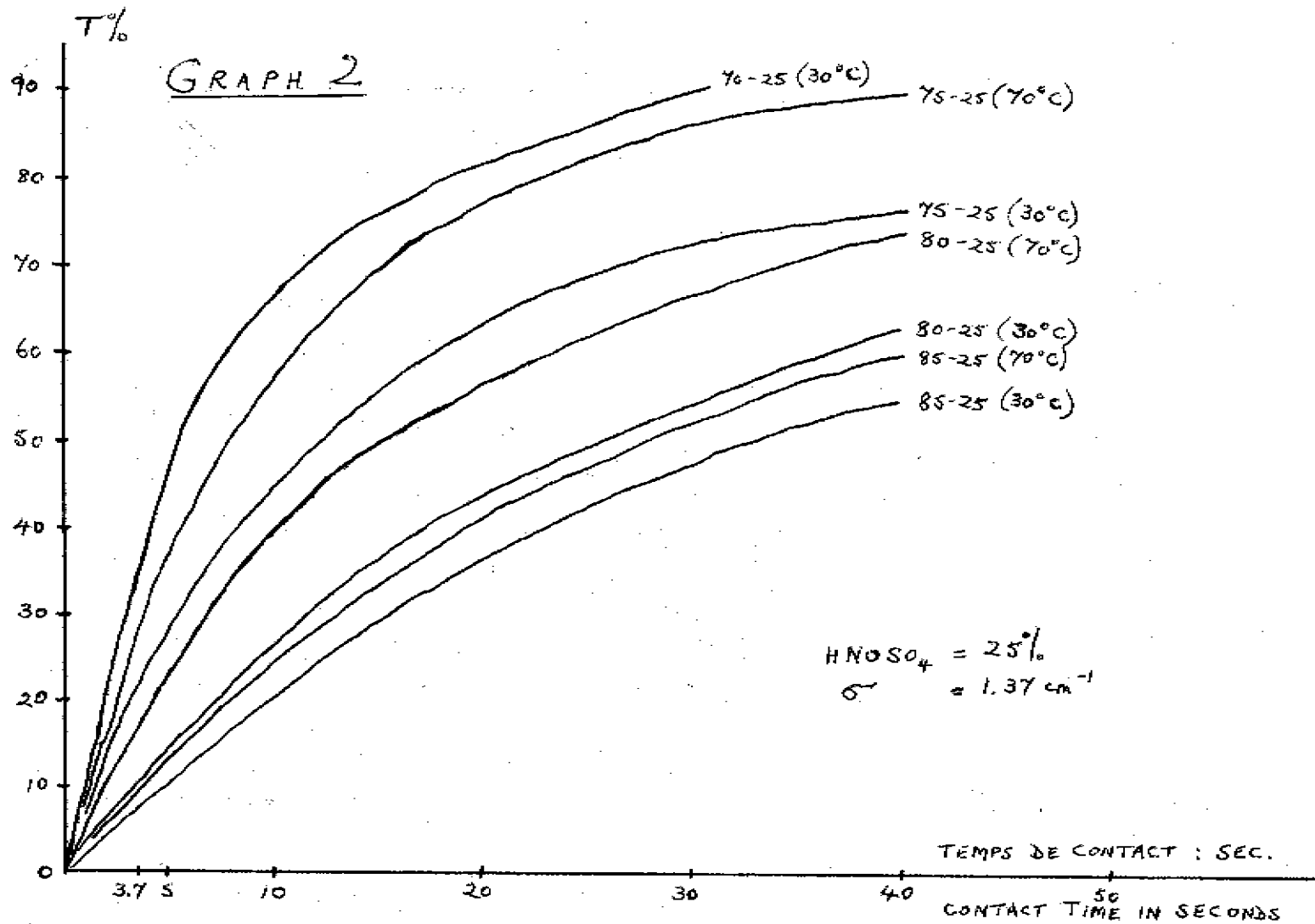
SUMMARY

We have studied the influence of various factors, such as the linear speed of the gases, the temperature, nitrous content, concentration of the acid solvent and the operating surface/volume ratio, on the conversion of SO_2 when gases containing 7.5% SO_2 are reacted with nitrous acids, and we have arrived at the following conclusions:

1. - The coefficient of speed increases with the linear speed of the gas, tending towards limit values attained at speeds which are lower, the lower the temperature, the higher the concentration of the acid used and the higher the nitrous content of the solution.
2. - The degree of conversion and the coefficient of speed increase in linear progression with the temperature; this increase becomes sharper the higher the nitrous content rises and the more the acid is diluted. Temperature has no appreciable influence in the case of nitrous solution (80-10) and hardly any in that of solution (90-25).
3. - The nitrous content produces contrary effects according to the temperature, when the sulphuric acid solvent has an 80% concentration of H_2SO_4 . At temperatures of more than 45° C, the nitrous content has a positive effect and, at lower temperatures, a negative effect.
4. - Dilution of the acid solvent has a marked positive effect on the degree of conversion and the coefficient of speed.
5. - The effect of the surface/volume ratio depends upon the concentration of the acid solvent. When this is greater than 80% H_2SO_4 there is no appreciable influence on the coefficient of speed. In the case of acids of lower concentration, the effect is negative and becomes increasingly pronounced the lower the concentration falls.

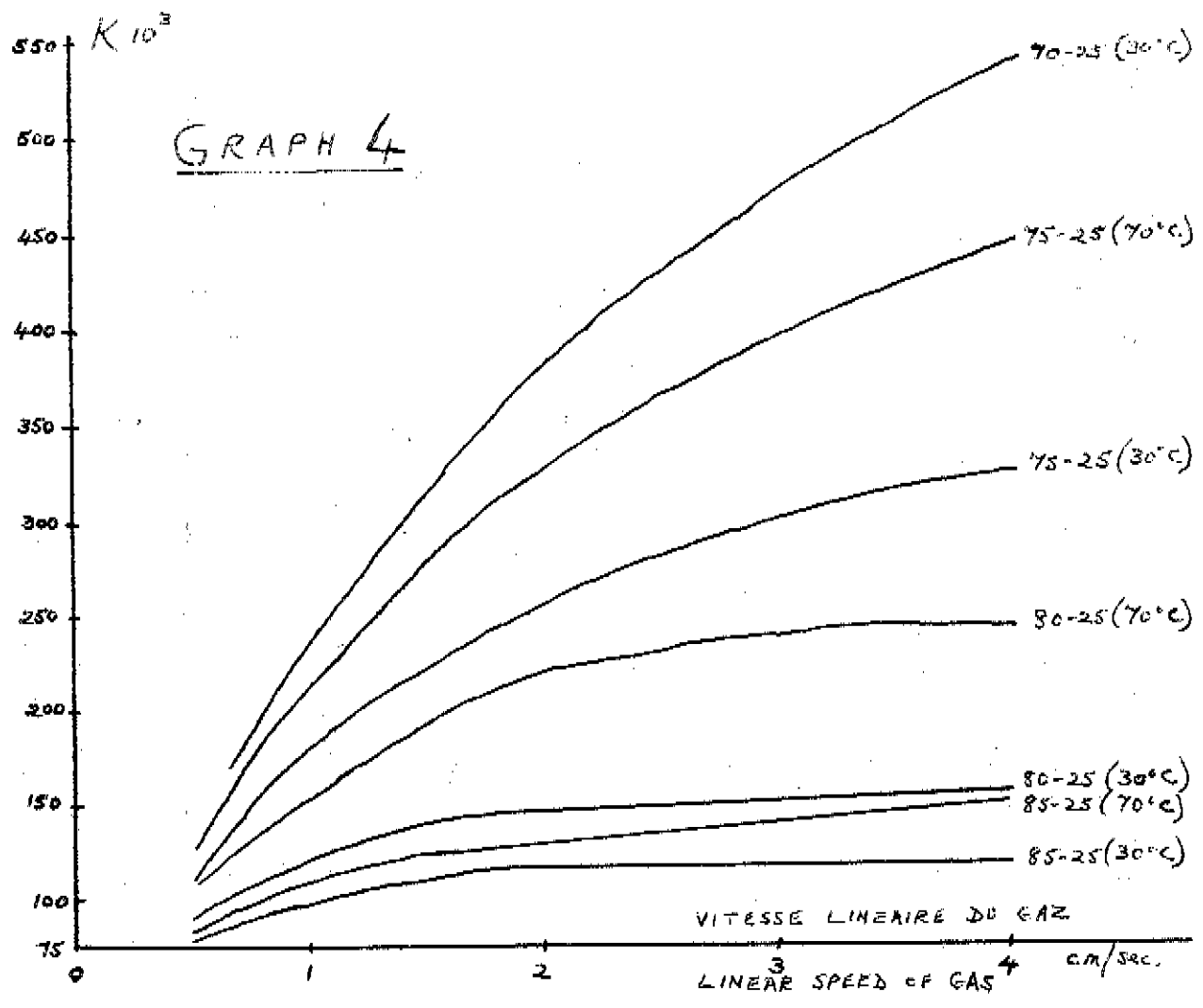
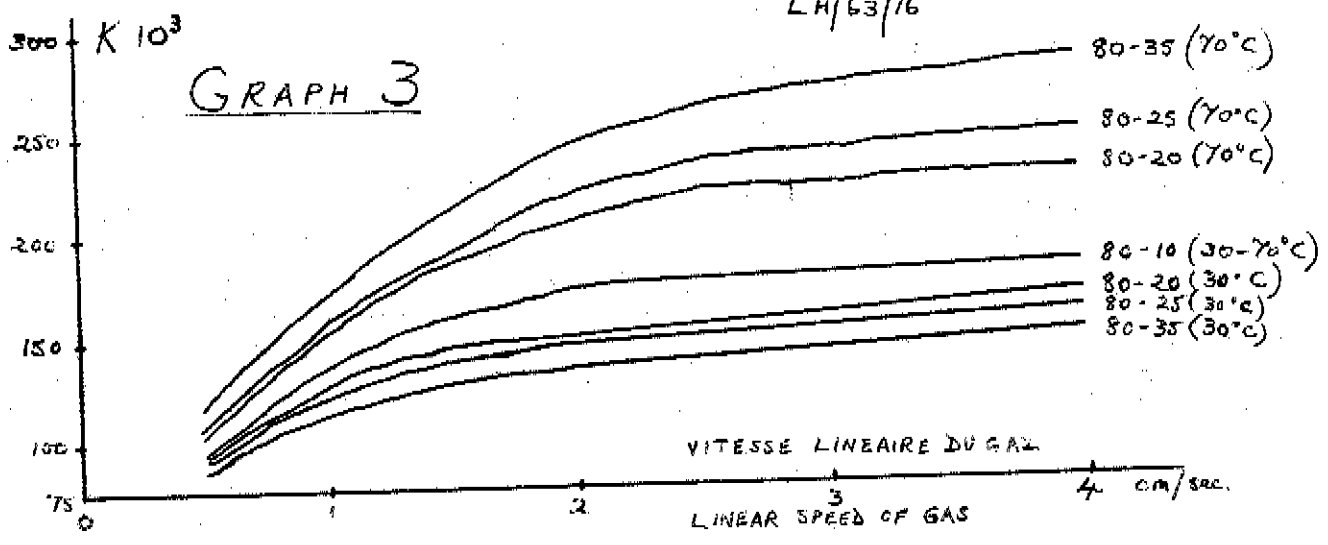


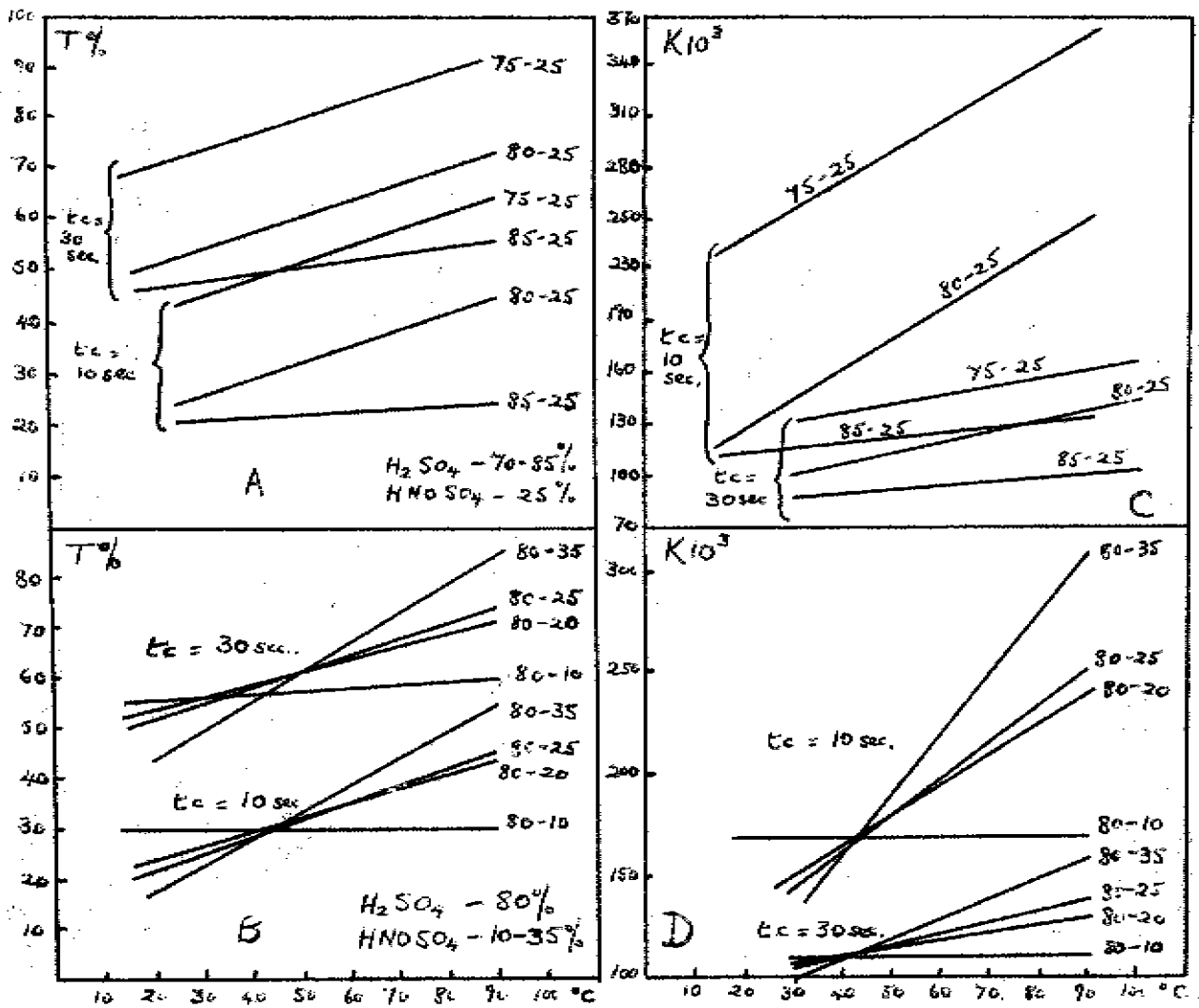
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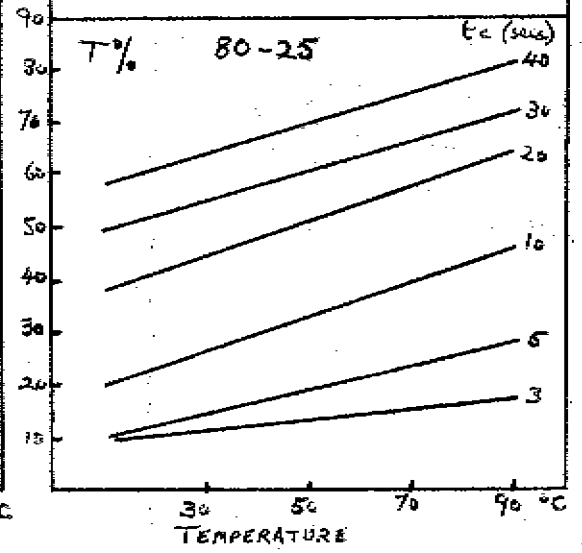
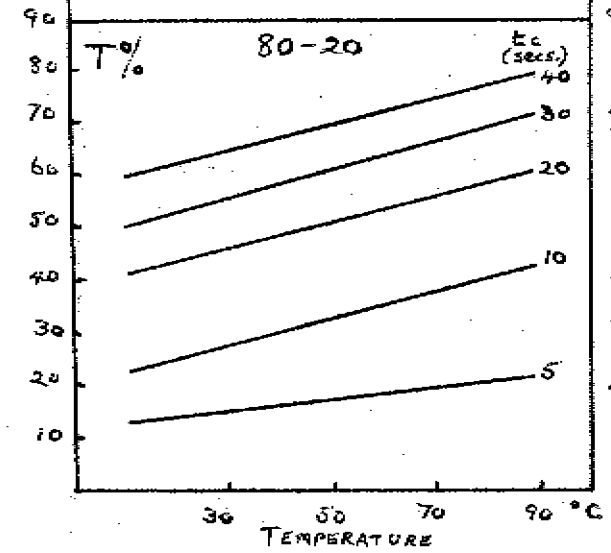
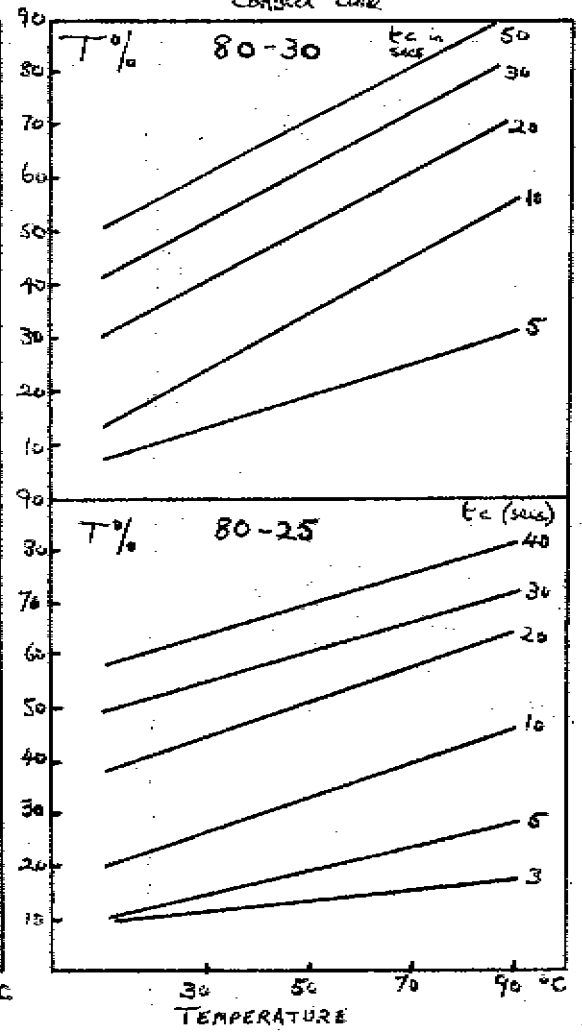
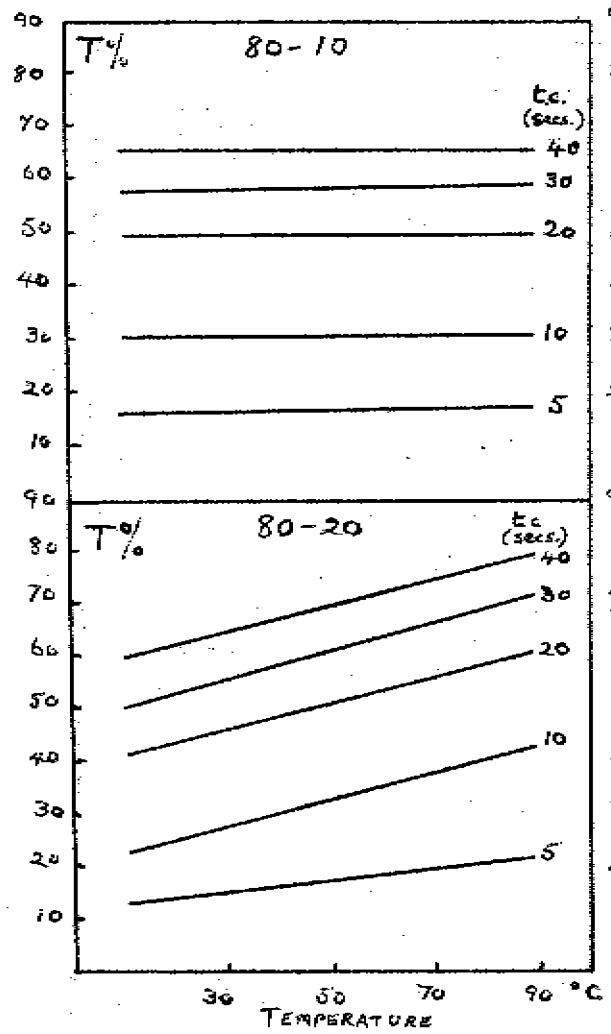


GRAPH 5

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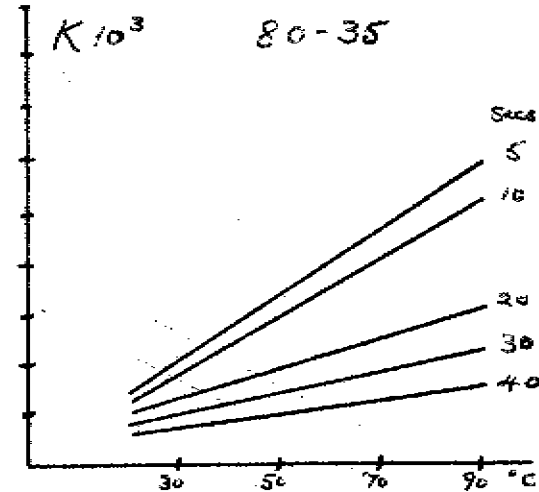
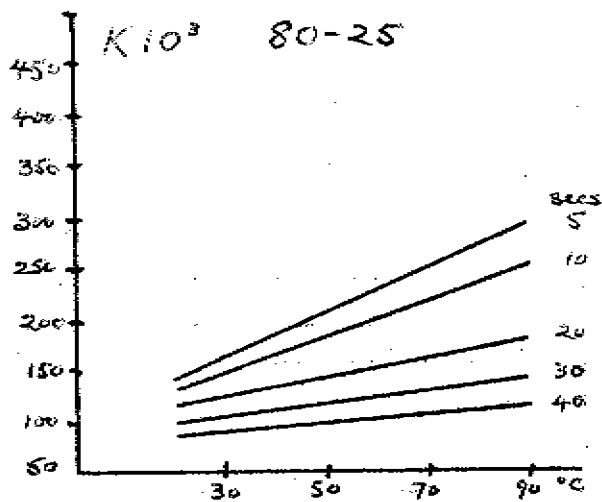
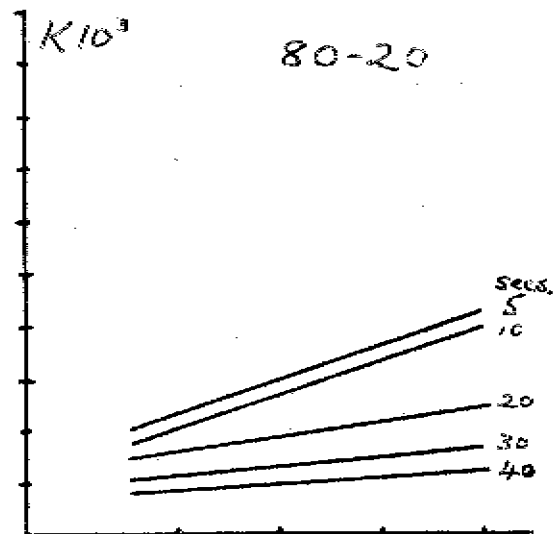
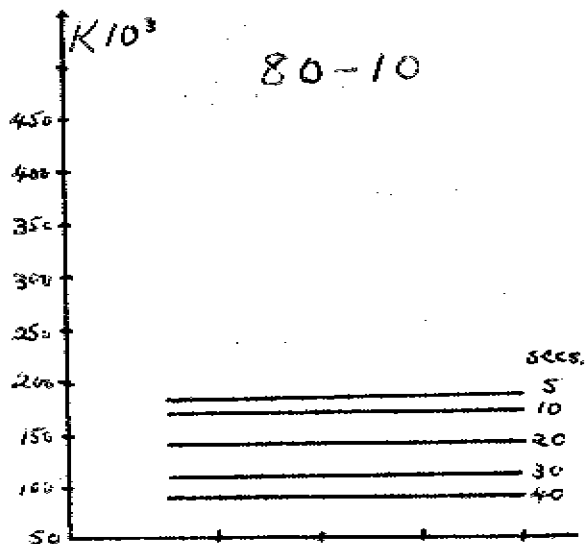
GRAPH 6

$t_c = \text{Temps de contact} = \text{contact time}$



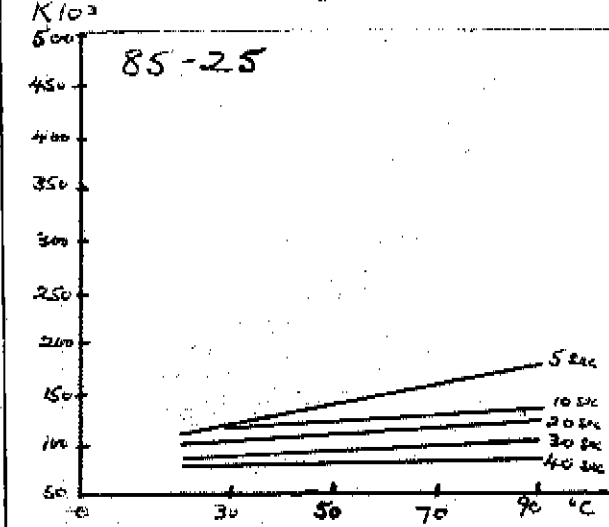
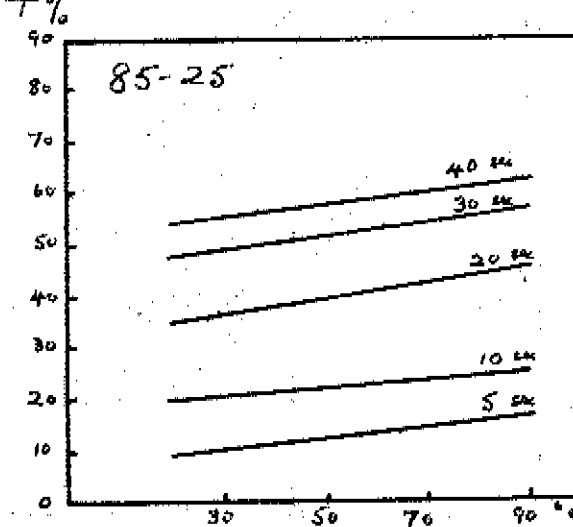
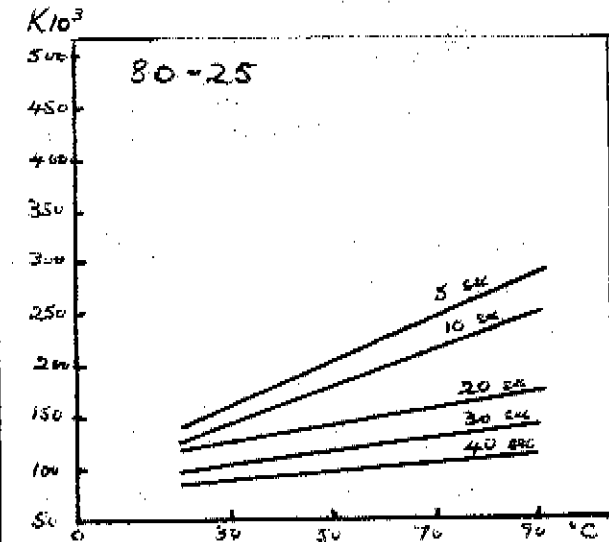
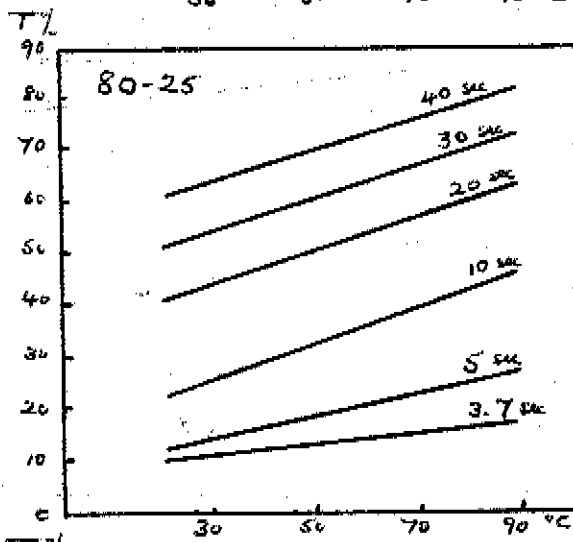
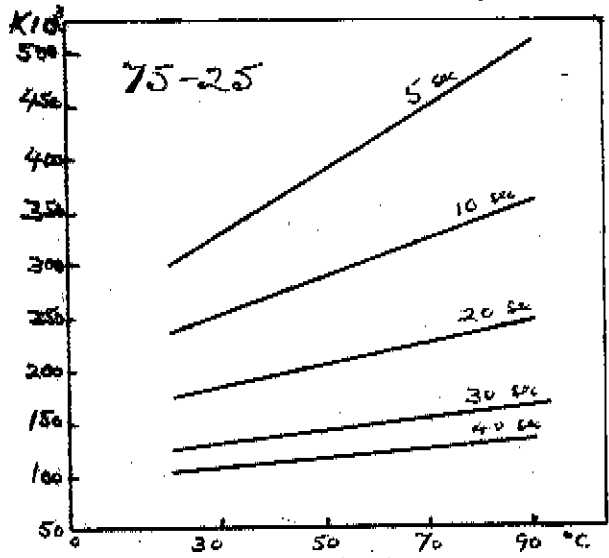
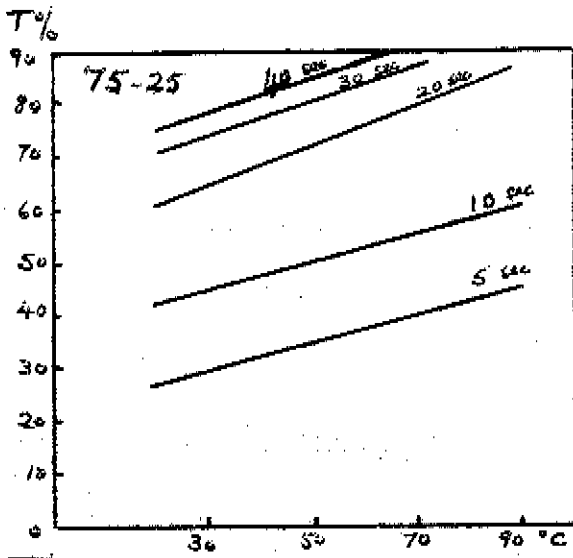
LH/63/16

GRAPH 7



TEMPERATURE

L.H./63/16



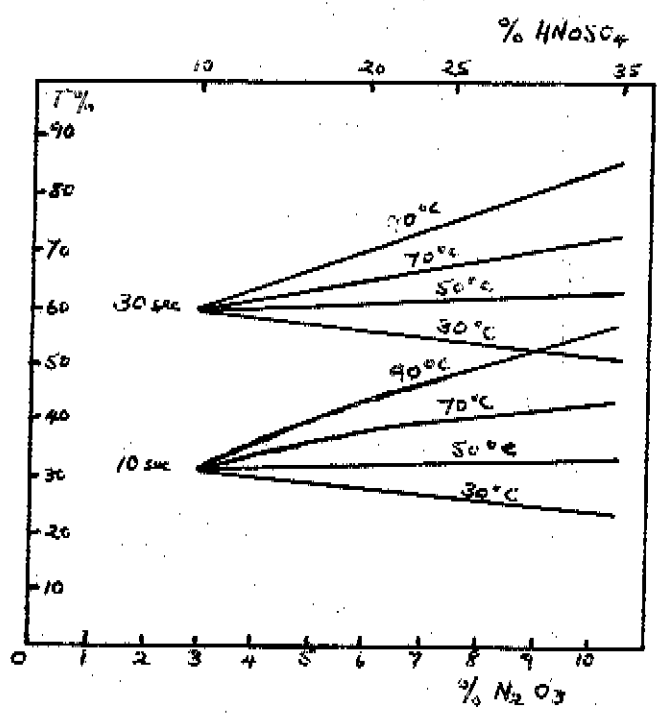
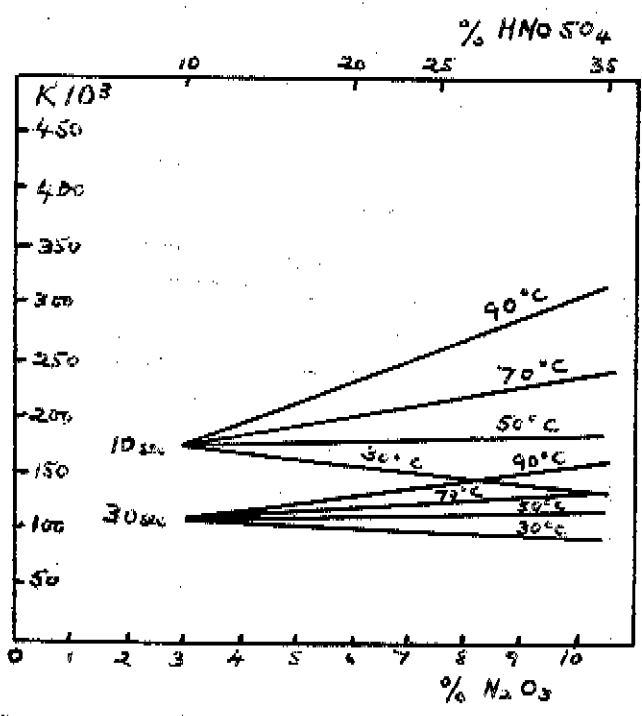
GRAPH 8

GRAPH 9

bH/63/16

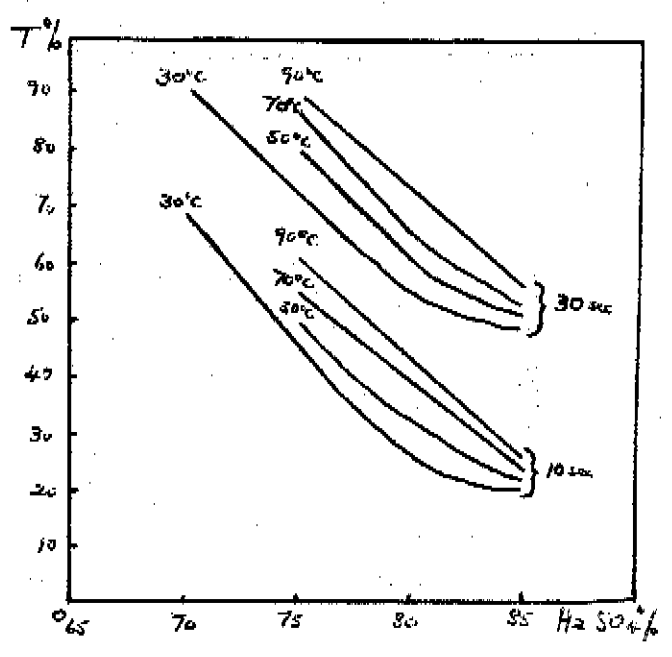
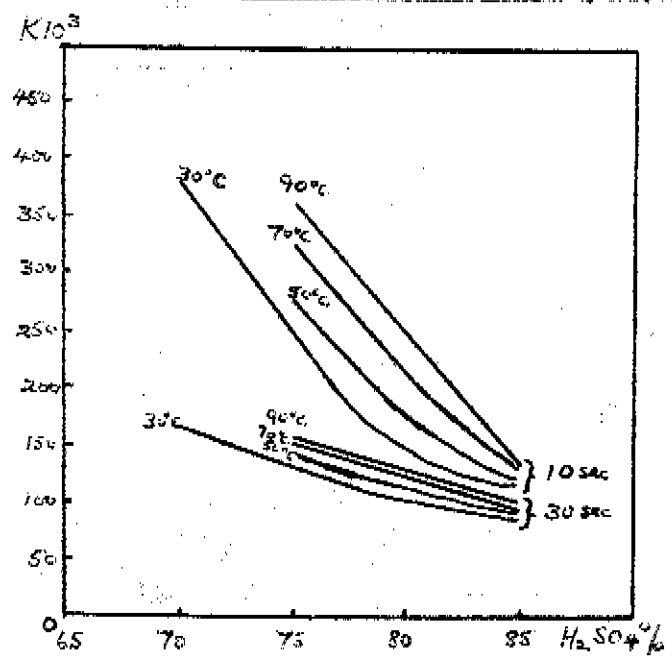
GRAPH 10 - INFLUENCE OF NITROUS CONTENT
INFLUENCE DE LA NITROSITE

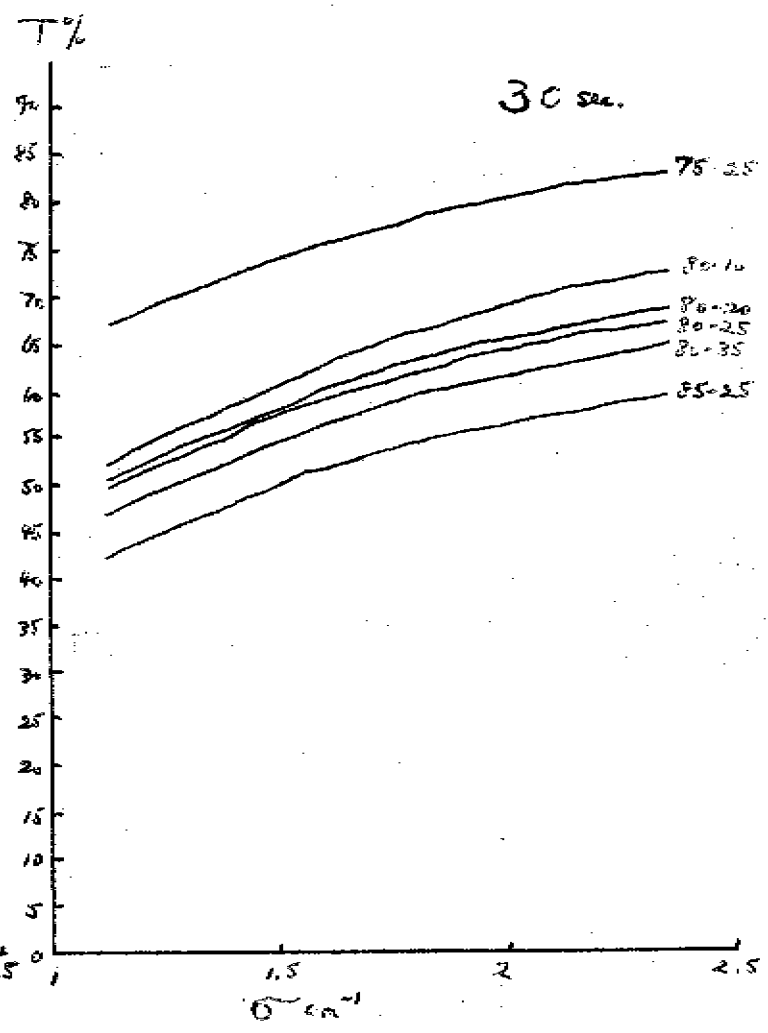
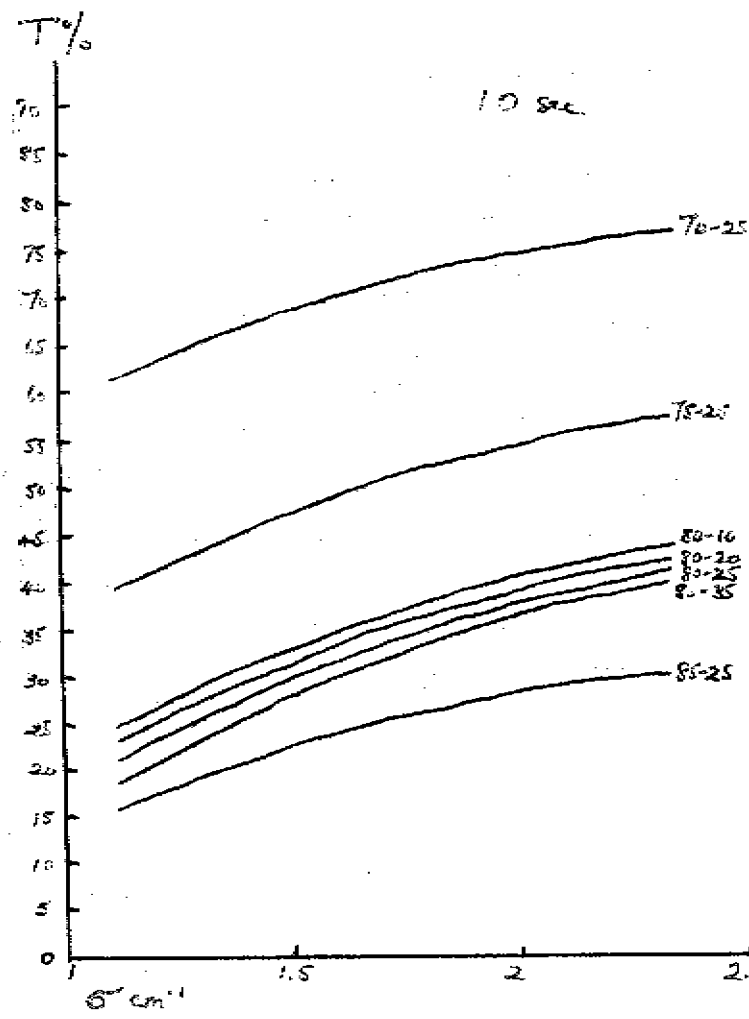
$H_2SO_4 = 80\%$



GRAPH 11 - INFLUENCE DE LA CONCENTRATION DU H_2SO_4
INFLUENCE OF H_2SO_4 CONCENTRATION

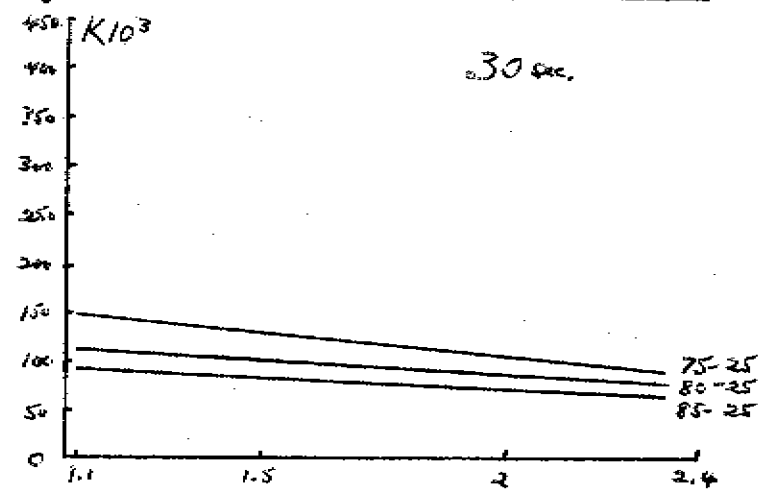
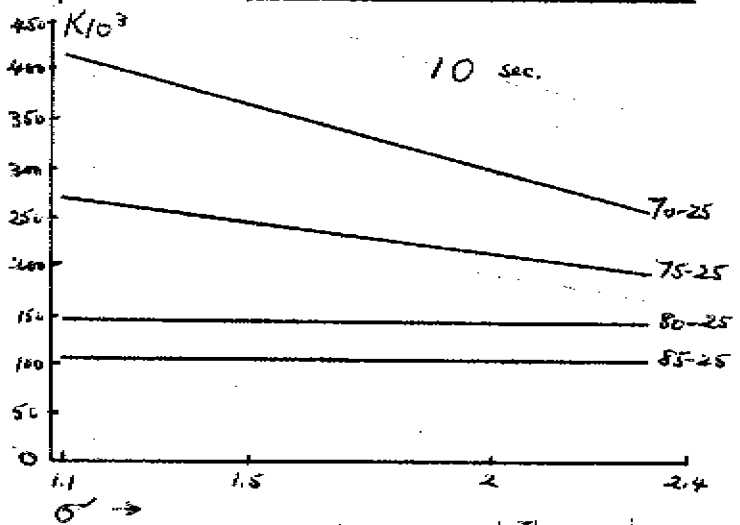
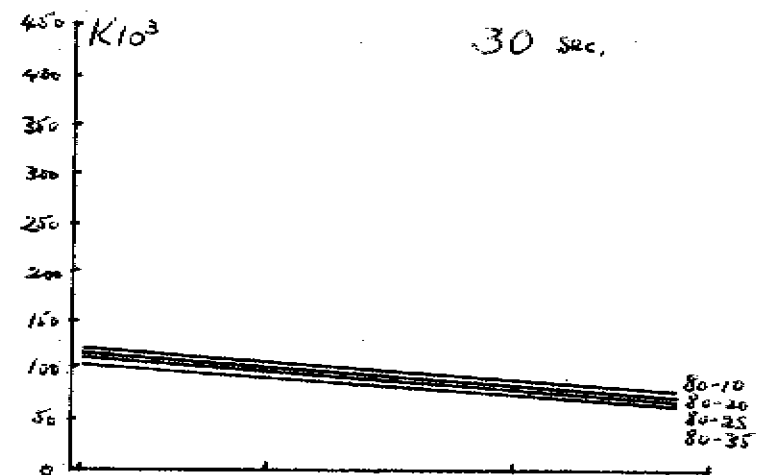
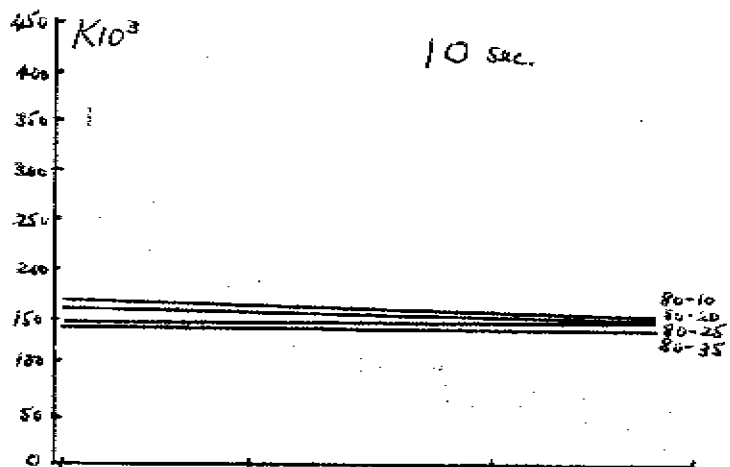
$HNO_3O_4 = 25\%$





GRAPH 12 - INFLUENCE OF σ 30°C

LH/63/16



GRAPH 13 - INFLUENCE OF σ 30°C

9/59/H7

DISCUSSION

MR. J. A. VALDES (Spain) : The paper I have the honour to present is a second report concerning the reaction of sulphurous anhydride with nitrous acid. It is a subject which has received much study, but which remains obscure in certain aspects. We consider it to be of great interest, not only for the improvement of the operation of the Kaschcaroff process, in which we are particularly interested, but also for all chamber processes of sulphuric acid manufacture. In this work, we have restricted ourselves to presenting an account of the experimental measures we have carried out. We believe that some of the conclusions we have arrived at, though they may seem strange, can be of great value. We have worked out a general theory of this process which enables us, we believe, temporarily to explain these conclusions. But our limited experience, which is confined to this process - which, although it may seem in certain cases to be simple, is basically a very complex process - obliges us not to relate our theory in the present work but to wait until our subsequent investigations confirm it or enable us to carry out the necessary modifications, so that we may put it forward more successfully on another occasion. I hope that this will be at the next technical conference of this Association. Nevertheless, I am at your disposal to answer your questions.

MR. V. SARKKA (Finland) : The paper by Mr. Sandalinas and Mr. Valdes relates how numerous experiments were effected to determine the influence of various factors on the reaction between SO_2 and nitrous acids. The results are stated both graphically and in tables. The graphs give a particularly clear picture of the influence of the different factors. The authors paid special attention to the selection of their equipment and have been very successful in choosing a wet-wall tower as the reaction column.

The reaction studied is essential to the manufacture

of chamber-process sulphuric acid. Exact knowledge of the conditions affecting it is, in practice, of direct significance.

Although this paper is on the whole very clear, there are a few points requiring elucidation :-

1. The authors have carried out experiments on the effect of oxygen content on the conversion. I should like to know whether any experiments have been made on the influence of the SO_2 content.
2. The preparation of the nitrous solutions is outlined at the bottom of page 4. Could Mr. Valdes give more details of this preparation ?
3. Study of the results reveals that increasing the nitrous content has a positive effect upon the conversion at temperatures above $45^{\circ}C$ and a negative effect below this temperature. It is apparent that a distinct change occurs to some essential factor in the reaction at $45^{\circ}C$. It would be of great interest to learn the nature of this phenomenon.

MR. J. A. VALDES : With regard to the effect of the gas composition, I must admit that we began this work by examining factors other than this one. We have not yet arrived at this point in our investigations: the effect of gas composition is still to be studied. But as a result of certain circumstances, we have already carried out some measurements by varying the O_2 content in our system between 2 and 11%. These measurements have been carried out on nitrous solutions with 80% sulphuric acid and a variable nitrosity. The results have been practically identical, but we cannot yet make the generalisation that the O_2 content has no influence.

With regard to the preparation of the nitrous solutions, we have reacted the gases containing sulphurous anhydride with a sulpho-nitric mixture. The acid nitrosyl sulphate formed was crystallised at low temperature, and after being drained off it was recrystallised in sulphuric acid, then drained off again and then dissolved in sulphuric acid of the desired concentration. The absence of nitric acid was verified by comparing the analytical permanganometric

result with the determination of total nitrogen by the nitrometer. If any traces remained, we eliminated them with sulphurous anhydride.

The third question is much more complicated. To give a full reply, I should describe all the factors which affect the reaction. I cannot describe all these details without revealing the general theory which we have accepted temporarily for these reactions. This would require too much time. Nevertheless I shall try to give a brief reply.

The conversion of sulphurous anhydride by nitrous acid may be considered as comprising several phases, the completion of which implies three different physical processes. The co-ordination of the effect of these processes will determine the speed of conversion. They are as follows:

- the conveyance of the molecule to be absorbed from the gas to the surface of the liquid.
- the process of optimising the gas/liquid contact area, for which an equilibrium must be established.
- the conveyance of the molecule to be absorbed, or of the compounds formed, towards the interior of the liquid.

These three processes determine the speed of a purely physical absorption and, it should be added, the speed of completion of the equilibrium of the chemical reactions taking place on the surface and in the interior of the liquid, and of the reactions which can take place in the gaseous phase. We can divide the total resistance of the process into three partial resistances: the resistance of the gaseous phase, the purely physical resistance of the liquid phase, and another resistance which we shall call chemical and which occurs in the liquid phase and results from the equilibrium reactions taking place. Under our own working conditions, the resistances which dominate the process are the latter two. If the temperature is low, the dominating resistance is the physical resistance of the liquid surface layer. This increases with nitrosity, but beyond a certain temperature - about 45°C - the resistance which dominates the process is that which we call chemical and which decreases with nitrosity. We thus

apply the effect of nitrosity with that produced by temperature. But the phenomenon which actually takes place is really much more complicated than this.

MR. A. C. VAN ES (Netherlands) : I notice from the paper that there is a very pronounced effect on the reaction velocity produced by the speed of the gas. Was the gas stream in your apparatus of a laminar or a turbulent nature ?

Secondly, could you give any information as to the optimum proportion of oxygen to sulphur dioxide in your gases? I ask this in view of the fact that in contact sulphuric acid plants there is a very well known excess of oxygen which must be obtained in order to achieve a good conversion.

MR. J. A. VALDES : According to the details we have calculated, relating to the speed of the gas flow, the rate of flow of the nitrous solution, the temperature and the physical constant of the nitrous solution, we believe the system to be totally laminar. In a previous work, we operated with a packed tower, precisely in order to determine the conditions of turbulent system corresponding more closely to the actual conditions found in an industrial plant. But we changed this tower, because, under these conditions, measurements are not always reproducible, and this we considered to be necessary for the verification of the effect of the various factors.

As far as the effect of the gas composition is concerned, the only experiments we have carried out are those which I mentioned in my reply to the first question of Mr. Sarkka.

MR. O. JENSEN (Denmark) : You have found that the conversion increases quantitatively with the temperature, at higher nitrous contents, but that there is no effect when the nitrous content is below a certain value which depends on the acid concentration. Is the explanation of this of the same nature as the reply you gave to Mr. Sarkka?

MR. J. A. VALDES : Without going into detail, the explanation of this phenomenon is of the same nature as that which I gave to the question put by Mr. Sarkka.
