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## TECHNICAL MEETINGS - WIESBADEN

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### A CONTRIBUTION TO THE STUDY OF THE SPEED OF THE TRANSFORMATION OF SO<sub>2</sub> INTO SULPHURIC ACID UNDER THE PRODUCTION CONDITIONS OF THE KACHKAROFF PROCESS

by F. Sandalinas and R. Loste,  
Sociedad Anonima Cros, Spain.

#### INTRODUCTION

The purpose of the present work was to study the influence of the concentration of N<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in nitrous acids on the speed of the conversion of SO<sub>2</sub>, in the Kachkaroff process, and also its variation in accordance with the temperature, in order to obtain experimental data to assist us in designing and assessing the relevant industrial apparatus.

The "Nitroses" from which free nitric acid was absent and with which our work was carried out were prepared by dissolving crystals of acid sulphate of nitrosyl in sulphuric acid of variable concentration. The concentration of the sulphuric acid used varied from 70 to 85%, and the quantity of dissolved HNO<sub>3</sub> crystals was such that the concentration of N<sub>2</sub>O<sub>3</sub> was kept between 2.99 and 10.44% in the prepared nitrose, any nitric acid which it might contain being eliminated by passing SO<sub>2</sub> gas through it and by analytical verification, the nitrose being given the desired composition. Other tests besides these were performed, quantities of free nitric acid being added to the nitrose in order to study the effect of this new constituent on the conversion of the SO<sub>2</sub>.

The operating-temperature was kept between 55 and 85°C.

The nomenclature adopted in our work to identify the various nitroses consists of two figures separated by a hyphen and enclosed in parentheses; the first indicates the concentration of the acid in which the acid sulphate of nitrosyl has been dissolved, while the second indicates the percentage-content of HNO<sub>3</sub> in the nitrose obtained. "Nitrose (80-20)"

means that it contains 20% of acid sulphate of nitrosyl, the solvent acid having 80% of  $H_2SO_4$ .

#### CONDITIONS FOR EXPERIMENT

The composition of the gas was kept constant in all the tests, being: 7.5% of  $SO_2$ , 11.29% of  $O_2$  and 81.21% of  $N_2$ . The said gas is heated by being passed through a glass tube fixed in an electric furnace, up to the reaction-temperature, passing through the bottom to the reaction-tower.

The reaction-tower has a cross section of  $12.56 \text{ cm}^2$  and a height of 20 cm, and contains glass fillers. The approximate area for contact between gas and liquid was estimated to be equivalent to the geometrical dimensions of the filling plus the interior of the tower, although strictly speaking our calculations should have been based on the moist area, the true contact-surface, and under the conditions described this amounts to  $1,324 \text{ cm}^2$ . The feed of the acid takes place at the top of the reaction-tower, the "irrigation-flow" amounting to 70 cc per min. The reaction-temperature was kept constant by means of a thermostat with a water-bath and a temperature-regulator.

Other details of the apparatus are shown in Fig. 1.

The experiment consisted of determining the percentage of  $SO_2$  converted per unit contact-time, this being understood to mean the quotient of the height of the tower divided by the supposed linear speed of the gas. The conversion was measured for each nitrose, with various contact-times and temperatures.

The  $SO_2$  in the gas, at the inlet to the tower, was analysed by iodometry, and we accepted deviations of  $\pm 0.3$  in respect of the theoretical percentage. The  $SO_2$  in the outlet gases is determined by absorption in an NaOH solution, after the gas has been made to pass through a glass filter-plate, supplemented by a space filled with glass wool, completely submerged in ice, in order to purify the gas by removing from it the little drops which it always carries along with it. This precaution is indispensable, and its efficacy was duly verified. The  $SO_2$  absorbed was determined by the  $BaSO_4$  gravimetric method, after oxidation.

In the course of each test, the composition of the nitrose could be regarded as constant, in view of the considerable volume of liquid returned to the cycle, as was duly verified. Before each series of tests was performed, the composition of the nitrose was adjusted to the value desired, variations of  $\pm 0.5$  in respect of the theoretical composition being regarded as acceptable, both in the acid and in the  $HNOSO_4$  content. The conditions for the experiments were determined by reproducing, on a laboratory scale, the operating-data which apply to an industrial apparatus.

The results of the experiments are given in Tables 1 - 6 and in the graphs in Figs. 2 - 9.

Table 1 gives the  $SO_2$  conversion values for nitroses in which the concentration of solvent acid is constant, and equal to 80%, the nitrous content being varied between 10 and 35% of  $HNOSO_4$ , the temperature between 55 and 85°C, and the

contact-time between 6.04 and 15.15 sec. The irrigation-flow of the nitrose was 70 cc per min.

Table 2 shows the conversion-values of  $\text{SO}_2$  (%) for acids of which the nitrous content is constant (20% of  $\text{HNO}_3\text{SO}_4$ ) when varying the concentration of the solvent sulphuric acid from 70 to 85%, likewise for various temperatures and contact-times. Irrigation-flow of nitrose: 70 cc per min.

Table 3 shows the  $\text{SO}_2$  conversion values obtained when varying the free  $\text{HNO}_3$  in the nitrose (80 - 10), for different contact-times and temperatures, the irrigation flow of the nitrose being 70 cc per min.

Table 4 gives the  $\text{SO}_2$ % conversion values for the acid (80 - 10) without free  $\text{HNO}_3$  for different contact-times and temperatures, the values obtained by experiment being compared with those extrapolated for  $\text{HNO}_3 = 0$ , according to the data in Table 3. Delivery-rate of nitrose: 70 cc per min.

Table 5 shows the  $\text{SO}_2$ % conversion values for the acid (80 - 10), for various temperatures and contact-times, between 7.51 and 60.6 sec., for the kinetic study as indicated later.

Finally, Table 6 gives the values of the speed-constant for the nitrose (80 - 20) at various temperatures.

TABLE I

Nitrose (80-10). N<sub>2</sub>O<sub>3</sub>% 2.99

Contact-time in sec: ..... 6.04      7.51      10.05      15.55

°C Temperature:					
55		17.8	25.5	35.5	54.5
65	Conversion %	23.0	31.5	41.7	59.2
75		28.2	37.5	47.7	64.0
85		33.2	43.5	53.7	69.0

Nitrose (80-20). N<sub>2</sub>O<sub>3</sub>% 5.98

°C Temperature:					
55		24.0	33.5	49.7	63.0
65	Conversion %	32.5	41.2	54.2	66.8
75		39.5	49.0	58.7	70.7
85		45.5	57.5	66.3	77.7

Nitrose (80-25). N<sub>2</sub>O<sub>3</sub>% 7.45

°C Temperature:					
55		33.0	41.5	52.5	65.0
65	Conversion %	39.5	48.5	59.8	70.0
75		46.5	57.0	67.0	75.0
85		53.0	65.2	74.3	82.5

Nitrose (80-30). N<sub>2</sub>O<sub>3</sub>% 8.97

°C Temperature:					
55		44.5	47.5	58.3	69.5
65	Conversion %	50.2	55.0	63.7	75.0
75		55.0	63.0	69.2	80.8
85		61.5	71.7	75.0	86.2

Nitrose (80-35). N<sub>2</sub>O<sub>3</sub>% 10.44

°C Temperature:					
55		45.5	49.0	58.8	69.0
65	Conversion %	52.0	56.5	64.5	75.5
75		57.0	64.5	71.0	81.8
85		65.0	72.5	77.5	88.0

TABLE 2

Contact-time in sec: .....	6.04	7.51	10.05	15.15
<u>Nitrose (70-20). N<sub>2</sub>O<sub>3</sub>% 5.98</u>				
Temperature:				
55	78.5	80.4	84.2	92.1
65	82.5	84.5	91.0	94.2
75	92.0	95.3	95.8	97.0
85	98.8	99.0	99.2	99.5
<u>Nitrose (75-20). N<sub>2</sub>O<sub>3</sub>% 5.98</u>				
Temperature:				
55.	44.0	51.3	63.1	84.0
65	57.3	66.1	74.5	91.3
75	76.1	82.5	89.5	97.0
85	88.2	96.5	98.1	99.3
<u>Nitrose (85-20) N<sub>2</sub>O<sub>3</sub>% 5.98</u>				
Temperature:				
55	15.5	25.1	34.0	50.0
65	20.1	27.7	40.5	54.1
75	24.3	36.3	45.5	57.2
85	30.8	40.4	48.5	61.1

TABLE 3

Nitrose (80-10) with free HNO<sub>3</sub>

<u>Contact-time in sec.</u>	<u>HNO<sub>3</sub> (free), %</u>	<u>Temperature, °C</u>			
		55	65	75	
30.30	0	73.1	79.2	81.5	
30.30	0.5	77.1	85.5	95.5	T %
30.30	1.0	81.0	92.3	100	
30.30	1.5	86.2	98.4	100	
15.15	0	52.2	59.9	67.3	
15.15	0.5	58.5	68.4	84.4	T %
15.15	1.0	65.1	77.6	100	
15.15	1.5	71.2	87.9	100	
10.05	0	37.2	44.6	45.3	
10.05	0.5	44.1	54.3	61.9	
10.05	1.0	51.4	64.2	79.6	T %
10.05	1.5	58.0	74.4	97.0	
7.51	0	30.0	34.5	37.4	
7.51	0.5	37.1	44.3	54.0	
7.51	1.0	44.2	53.5	71.0	T %
7.51	1.5	51.1	63.3	87.2	

TABLE 4

Nitrose (80-10) without free HNO<sub>3</sub>. Conversion %

Contact-time in sec.	Temperature in °C.	Found in experiments.	Found by extrapolation.
15.15	55	54.5	52.2
15.15	65	59.2	59.9
15.15	75	64.0	67.3
10.05	55	35.5	37.2
10.05	65	41.7	44.6
10.05	75	47.7	45.3
7.51	55	25.5	30.0
7.51	65	31.5	34.5
7.51	75	37.5	37.4

TABLE 5

Nitrose (80-20). N<sub>2</sub>O<sub>3</sub>% 5.98

Temperature in °C	Contact-times in sec.					
	60.6	43.4	30.3	15.15	10.05	7.51
	Conversion %					
55	98.61	96.02	90.33	66.62	50.51	42.41
65	100	99.84	93.85	74.01	59.20	46.26
75	100	99.92	96.81	80.93	66.84	53.21
85	100	100	98.31	86.10	71.07	58.15

TABLE 6

Specific speed-constants

Nitrose (80-20)

N<sub>2</sub>O<sub>3</sub>% 5.98

Temperature in °C.	Gradient of straight line.	K sec <sup>-1</sup>
55	- 32.23	7.14 · 10 <sup>-2</sup>
65	- 24.44	9.42 · 10 <sup>-2</sup>
75	- 19.93	11.50 · 10 <sup>-2</sup>
85	- 16.65	13.83 · 10 <sup>-2</sup>

## ASSESSMENT OF RESULTS

The values shown in Tables 1, 2, 3 and 4 must be regarded as qualitative, since the measurements were not reproducible with sufficient accuracy to enable them to be regarded as absolute, as the tower-irrigation conditions adopted were in accordance with industrial data and it was difficult to maintain a contact-surface irrigated to an equal extent in all the tests. The values shown are averages from the results obtained in the experiments, the latter being very useful for drawing conclusions, from a "semi-quantitative" point of view, on the influence exerted by the factors mentioned over the conversion of  $\text{SO}_2$ , but it would not be correct to take the said measurements as a basis for mathematical equations covering the influences observed.

### (a) Influence of temperature:

To bring out the effect of the temperature, we have drawn two graphs (Figs. 2 and 3), showing the temperatures along the abscissae and the conversion-percentages along the ordinates. In one of them (Fig. 2) we have shown the values corresponding to one group of nitroses with the same concentration of solvent acid 80%  $\text{H}_2\text{SO}_4$  and with variable percentages of  $\text{HNO}_3\text{SO}_4$  (between 10 and 35%).<sup>4</sup> The points shown correspond to the data in Table 1 for the time of contact of 15.15 sec. In the other (Fig. 3) we have shown, for a constant nitrous-content of 20% in  $\text{HNO}_3\text{SO}_4$ , the ratio between the conversion-percentage and the various concentrations of solvent acid (75-80 and 85% of  $\text{H}_2\text{SO}_4$  - data in Tables 1 and 2).

These graphs show that:

(1) The conversion increases in linear proportion to the temperature.

(2) The effect of the temperature is independent of the concentration of the acid, and also of the nitrous content, within the range studied.

(3) The increase in the conversion is of the order of 5% for every 10 degrees of temperature, within the range studied.

### (b) Influence of nitrous content:

Fig. 4 shows the variation of the conversion-%, as a function of the nitrous content, expressed as a % of  $\text{N}_2\text{O}_3$  on the axis of the abscissae, for a constant concentration of solvent acid (80%  $\text{H}_2\text{SO}_4$ ) and different temperatures, for a contact-time of 15.15 seconds.

This graph shows that:

(1) The conversion increases with the nitrous content of the acid. The increase is in linear proportion thereto.

(2) The more nitrous the acid, the less will be the increase in conversion.

(3) It appears that from a 9% content of  $\text{N}_2\text{O}_3$  onwards, any further increase in its nitrous content results in no appreciable effect.



(c) Influence of the dilution of the acid:

In Fig. 5 we have shown graphically the variation of the  $\text{SO}_2$  conversion % as a function of the concentration of the solvent acid, for a constant  $\text{N}_2\text{O}_3$  content of 5.98%, equivalent to 10% of  $\text{HNO}_3$ , at various temperatures and for a contact-time of 10.05 sec.

In Fig. 6 we have shown the above-mentioned variation, but only at a temperature of  $55^\circ\text{C}$ , and with various contact-times, for an  $\text{N}_2\text{O}_3$  content of 5.98%.

From these graphs it follows that:

(1) The conversion increases very conspicuously with the dilution of the solvent acid.

In our opinion, the increase is not linear, and the greater the dilution of the acid, the greater is the increase. This is the conclusion we should reach if the curves representing the phenomenon were those shown by continuous lines on our graphs, but the existence of points clearly deviating from them, prevents us from concluding definitely that this is the case. But the fact that, with rare exceptions, these points correspond to very considerable conversions, where the errors are more noticeable, leads us to believe that these points, or rather those corresponding to a 70%  $\text{H}_2\text{SO}_4$  content in the solvent acid, are misleading, and that curves should be obtained similar to those given but with a more pronounced curvature. Our present experiments are being directed towards the clarification of this phenomenon.

NITROSES WITH FREE NITRIC ACID

When adding nitric acid to the nitroses, in quantities varying from 0.1 and 1.5%, we found that the conversions increased considerably and that the increase bore a linear relationship to the percentage of free  $\text{NO}_3\text{H}$  in the nitrose. We studied the nitrose (80-10), with free nitric acid in the temperature-range  $55-75^\circ\text{C}$  and for gas-liquid contact-times of 30.3, 15.15, 10.05 and 7.51 sec., measuring the conversions for each temperature and contact-time, as a function of the free  $\text{HNO}_3$ , present in the nitrose; its percentage was determined, for each measurement, by analysis with the nitrometer, and with permanganate. Combining the resulting data with the percentage of free  $\text{HNO}_3$ , we obtain three groups of straight lines for the temperatures of  $55.65$  and  $75^\circ\text{C}$ , and the greater the increase in temperature, the greater is the gradient of these lines (see Fig. 7).

The increase is surprising, since the quantities of  $\text{HNO}_3$  added do not result in a total content of nitrogen compounds sufficient to explain it. As we have stated, the influence of the free  $\text{HNO}_3$  in the nitrose is the more marked the greater the working-temperature; thus, if the nitrose (80-10), at  $55^\circ\text{C}$ , is given an addition of 1% of  $\text{HNO}_3$ , the  $\text{SO}_2$  converted exceeds that converted by the nitrose (80-20). At  $65^\circ\text{C}$  an addition of 0.5% of free  $\text{HNO}_3$  - and at  $75^\circ\text{C}$ , an addition of 0.2% is sufficient.

In Table 3, as has been indicated, we give the % conversions of  $\text{SO}_2$  for the acid (80-10) with free  $\text{HNO}_3$ , and the values given have been obtained by interpolating in the straight lines in Fig. 7. By extrapolation for  $\text{HNO}_3 = 0$ , we obtain the conversion

values corresponding to the said nitrose in the absence of free nitric acid, and these values are compared in Table 4 with those obtained by experiment and already indicated in the foregoing. This fact once again confirms the absence of free nitric acid in the nitroses prepared as stated above.

### CONTRIBUTION TO THE KNOWLEDGE OF THE KINETICS OF THE PROCESS

Having succeeded in our object, i.e. that of obtaining data on the process, with a view to its application in industry, we will re-examine the data and conclusions set out, seeing that the process takes place in a simpler manner than was to be foreseen. We abandoned the conditions required for industrial data and carried out fresh tests in order to obtain strict agreement between the measurements and to provide a basis for a more complete study. Analysing our previous experimental conditions we found, as we had assumed already, that the irrigation of the tower did not result in an even distribution and in a constant renewal of the liquid layer; to free ourselves of this influence of the irrigation and to ensure the previous conditions, we gave the tower the maximum irrigation possible and introduced minor modifications in our operating technique in the light of previous experience. Under these conditions, the results obtained, even if of the same order as the previous results, are sufficiently reproducible and accurate to enable them to be adopted as a basis for a more conscientious study.

With the acid (80-20) we repeated the measurements, extending them to new contact-times (Table 5). When the contact-times were drawn against the logarithm of the percentage of SO<sub>2</sub> unconverted, this produced straight lines for each temperature. This experiment corresponds to a kinetically homogeneous process of the first order. That is to say, even if the process of determining the SO<sub>2</sub> for the nitrose and the subsequent chemical reaction represents theoretically a process which deviates from the simple and homogeneous processes, and is in fact extremely complex, it behaves as if it were a homogeneous mechanism of the 1st order. The simple mathematics of these processes can be applied in order to obtain equations of undoubted interest.

The specific speed-constant for a homogeneous process of the first order is

$$K = \frac{2.303}{t} \log \frac{a}{a-x} \quad (1)$$

wherein  $a$  is the initial concentration of SO<sub>2</sub> and  $x$  the decrease after the interval  $t$ . From (1) we obtain:

$$t = \frac{2.303}{K} \log (a-x) + \frac{2.303}{K} \log a,$$

which is the general equation of these straight lines obtained in the experiment; the gradient of this straight line thus enables the value of  $K$  to be found. Table 6 shows how  $K$  has been calculated. Its values fluctuate between  $7.14 \times 10^{-2}$  for 55°C and  $13.83 \times 10^{-2}$  sec.<sup>-1</sup> at 85°C.

Equation (1) can also be expressed as follows:

$$K = \frac{2.303}{t} \log \frac{1}{1-R},$$

where  $R$  is the quantity converted.

The said equation enables the value of R to be calculated when that of K is known, and the latter can be ascertained as indicated, selecting the desired contact-time, which is governed by the height of the tower, the cross section of the tower and the gas flow rate to be adopted. The value of R will be:

$$R = (1 - 10^{-\frac{Kt}{2.303}}),$$

and  $100 R =$  conversion %.

To express the influence of the temperature on the reaction speed, we endeavoured to see whether the Arrhenius Equation

$$\ln K = - \frac{R}{RT} + \text{const.}$$

was satisfactory, when

K is the specific speed-constant,  
E the activation-energy, in cal./mol.,  
R the constant of the gases, in cal/°/mol., and  
T the absolute temperature.

The said equation requires the graph of  $\ln K$  as a function of  $1/T$  to be a straight line. The points we have shown in Fig. 9 actually do confirm this.

From the gradient of the said straight line we obtain the value of E, which, for nitrose (80-20), has a value of 2,210 cal/°/mol. The ordinate at the origin gives us the constant for the Arrhenius equation, and its value for this nitrose is 2.78.

We can now simplify the Arrhenius equation for the nitrose (80-20), this being

$$\log K = - \frac{481}{t} + 2.78,$$

which gives us the value of K for any temperature in the range under examination.

E and K are data of a complex phenomenon, but not as we are accustomed to consider them in the theory of kinetics. They will depend on the area of the fillings of the tower, even though the influence of the latter tends to have a limit, which substantially corresponds to the area adopted by us.

Our object is to ascertain whether what has been observed in the case of the nitrose (80-20) still obtains in the case of the other nitroses, and within what ranges and for what values, as regards the factors which affect the course taken by the process.

The results obtained are in accordance with those given in the works consulted ( 1 to 4 ) referring to general principles. For the data and scope of the kinetic problem we had to refer to the Russian literature on the subject. The work described there takes a different course from the simple method adopted by us. For the authors in question do not maintain constancy in the content of nitrous compounds in the acid, and therefore have to deal with two different terms as regards concentration, i.e. that relating to the concentration of  $SO_2$  and that relating to the concentration

of the nitrous compounds considered as a whole, or of those corresponding to the hydrolysis of  $\text{HNO}_2$  (active nitrous content). Furthermore, they calculate the specific speed-constants in accordance with Velopolsky's equation (7), based on a complex absorption process, with subsequent chemical reaction. The calculation of the value of K by this equation presupposes a knowledge of physical constants and of magnitudes which are difficult to calculate by experiment and which do not appear to have been evaluated in their work. In the absence of concrete data it has been impossible to give any comparison and assessment of results.

#### SUMMARY

(1) For an acid of a given concentration, the higher the temperature and the greater the concentration of  $\text{HNO}_2$  in the acid, the greater will be the speed of oxidation of the  $\text{SO}_2$ . It appears that above a 9%  $\text{N}_2\text{O}_3$  content, a further increase in  $\text{N}_2\text{O}_3$  does not produce any appreciable effect.

(2) For an acid with a constant nitrous content, the more diluted the acid, the greater will be the speed of the reaction.

(3) Free nitric acid in a "nitrose", in quantities of 0.1 to 1.5%, increases the speed of the reaction in an extraordinary and inexplicable manner, in view of the very insignificant increase in nitrogen compounds which it implies. The greater the temperature, the more marked will be this influence; for each temperature, the increase is linear, and it is proportional to the concentration of free  $\text{HNO}_3$  in the nitrose.

(4) As regards the process for a nitrose (80-20), it has been found in experiments that even if it is very complex in itself, for the temperature-range and experimental conditions described it behaves in the same way as a homogeneous process of the first order.

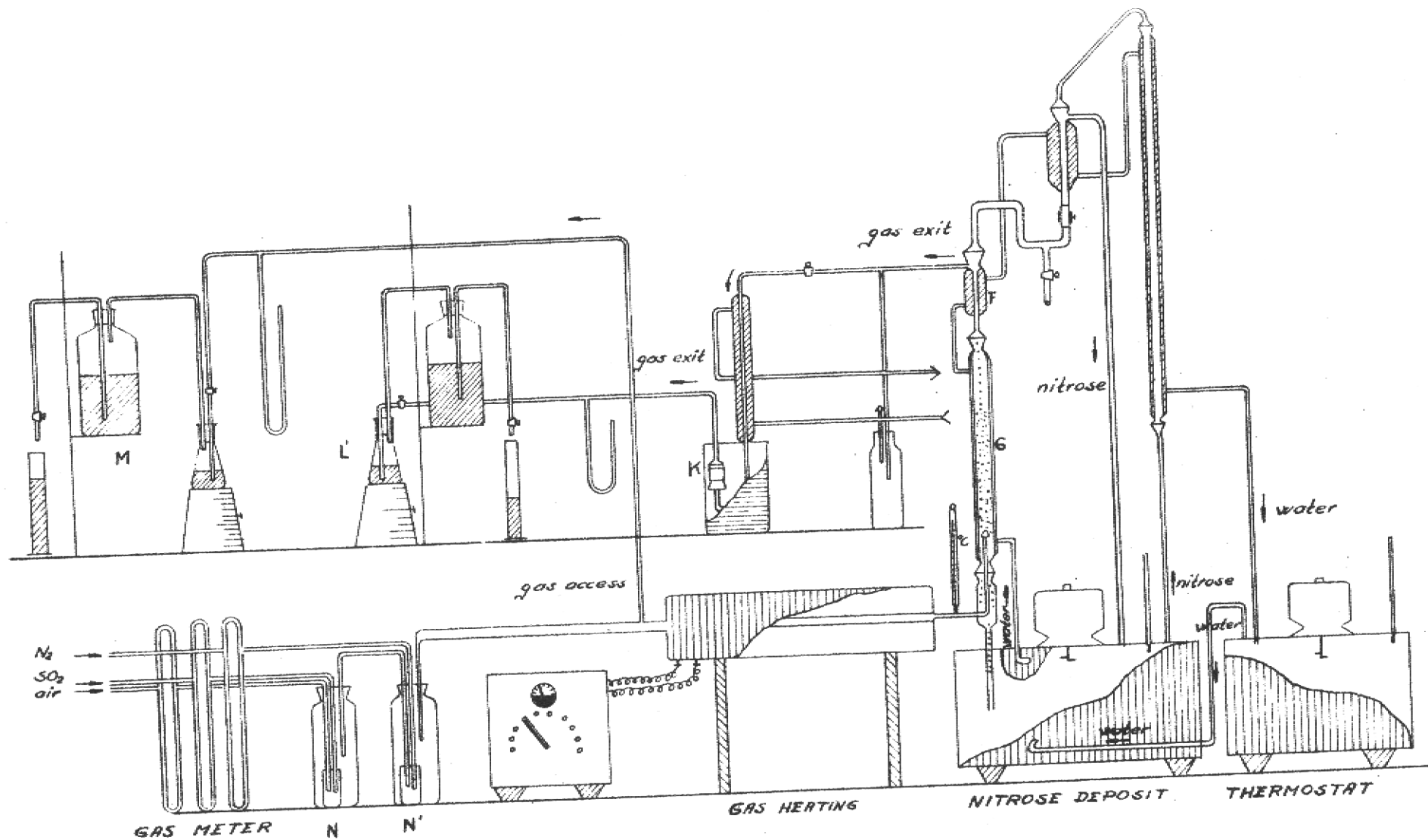
(5) The specific speed constant has been calculated by this means, and the influence of the temperature on the value of K satisfies the Arrhenius equation; the curve for  $\log K$  as a function of  $1/T$  is a straight line.

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Ny N' = Mixers gas  
 G = Reactor  
 K = Gas filter (exit)

M = Reich for analysing gas access  
 L' = Reich for analysing gas exit

Fig. 1

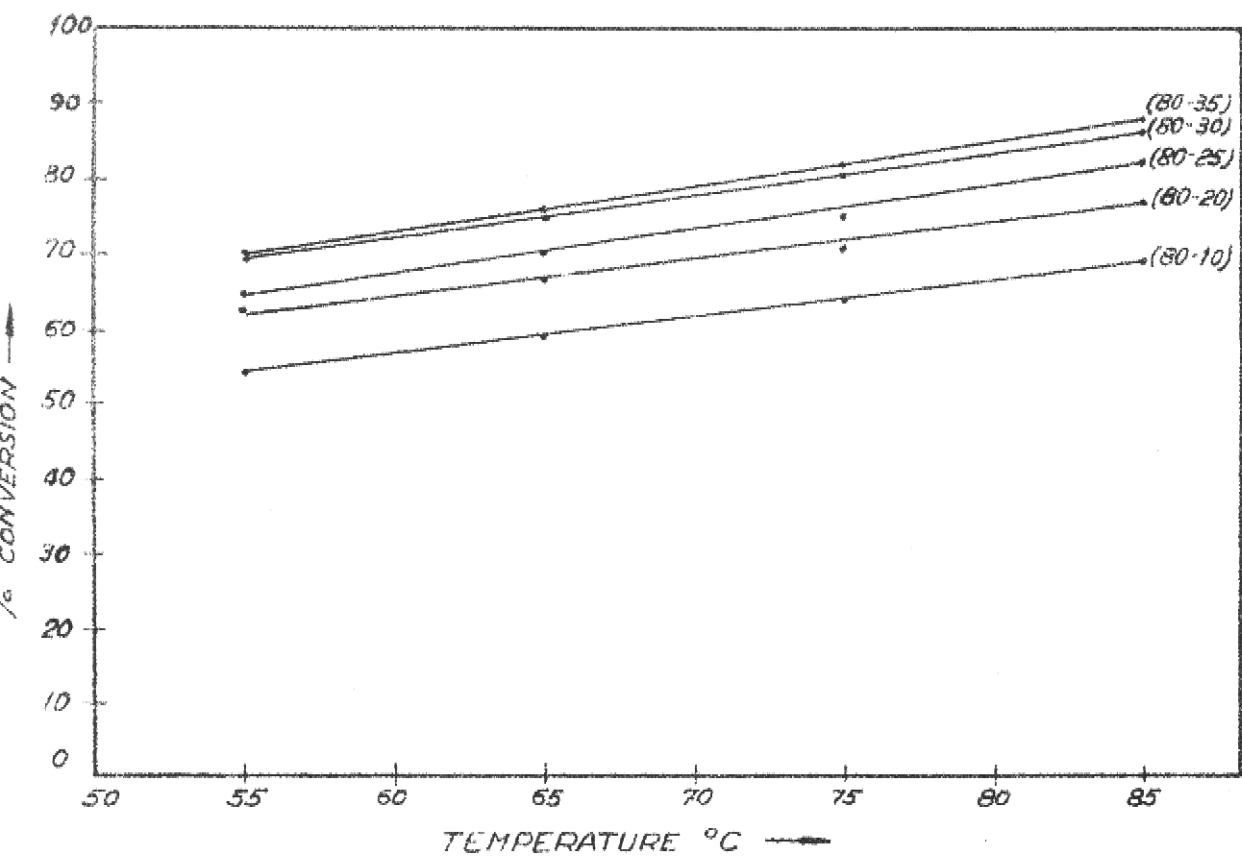


Fig. 2.  
Temperature effect.

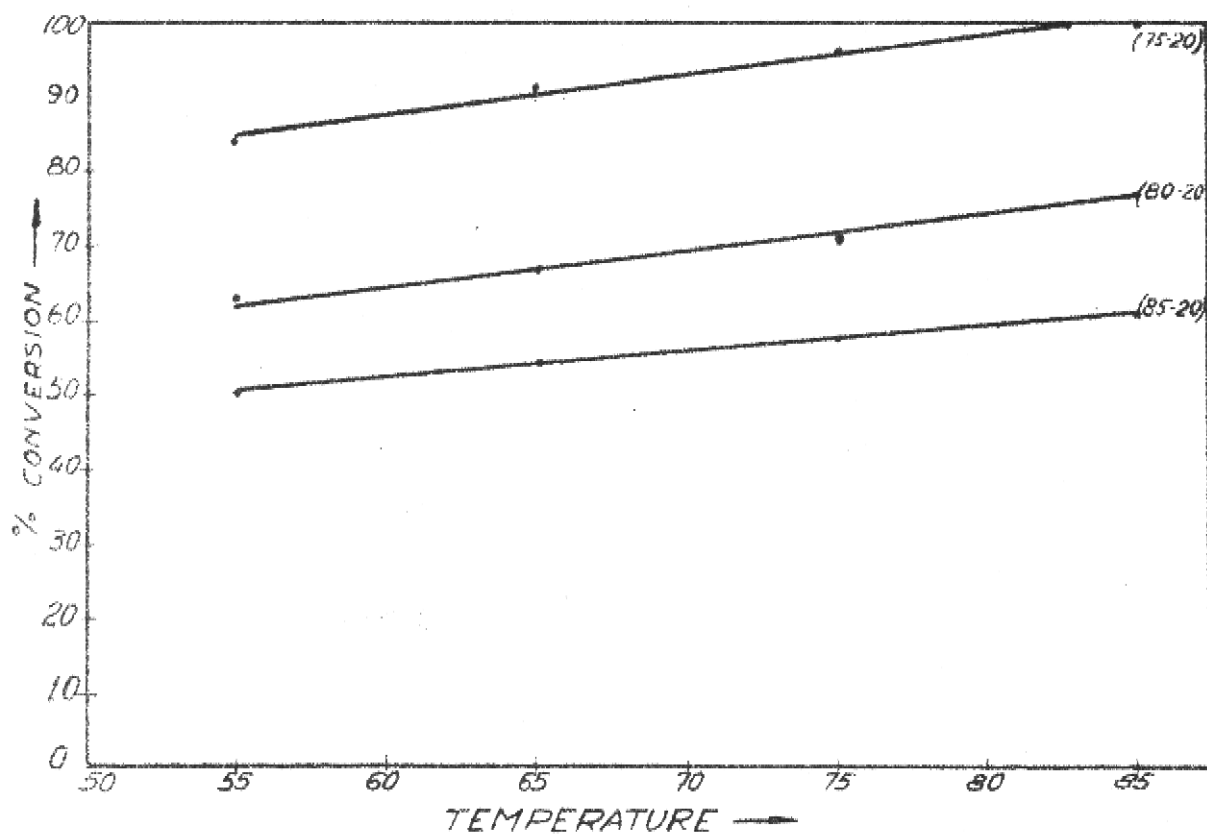


Fig. 3.  
Temperature effect.

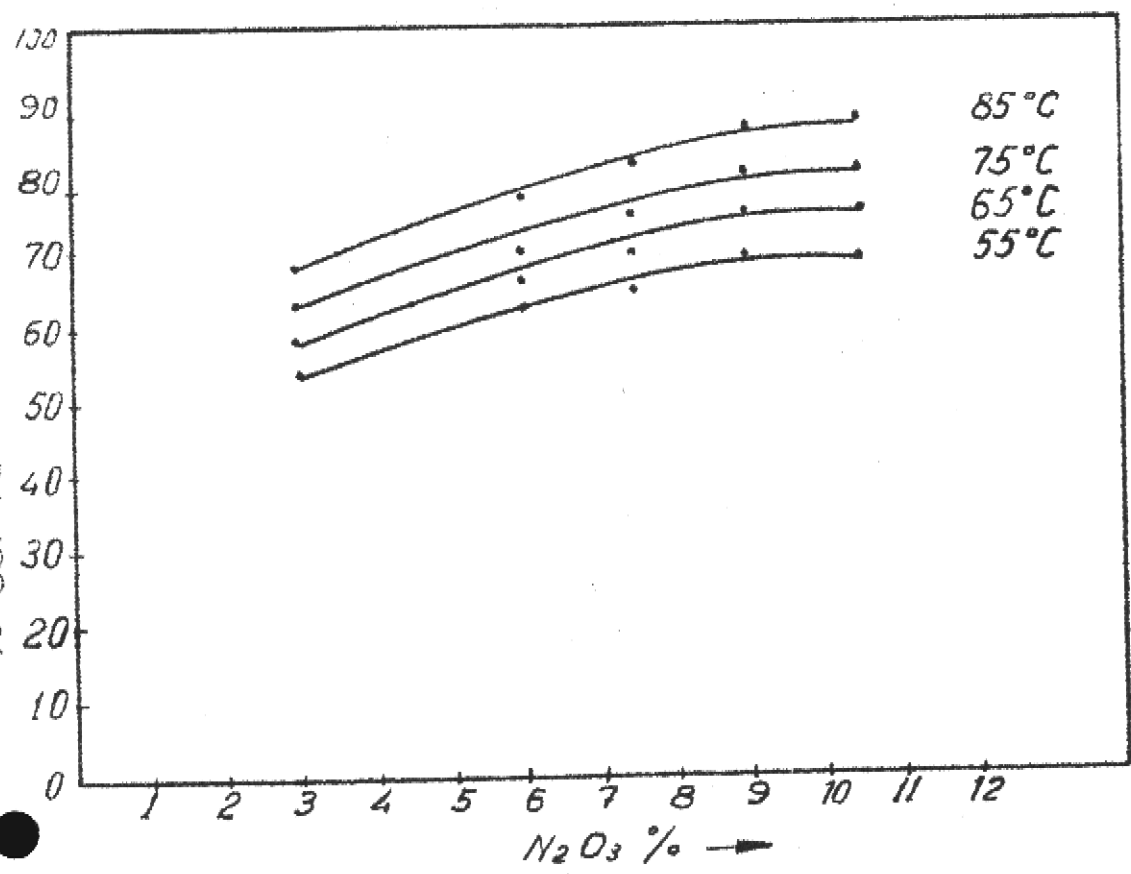


Fig. 4.  
Nitrosity effect.

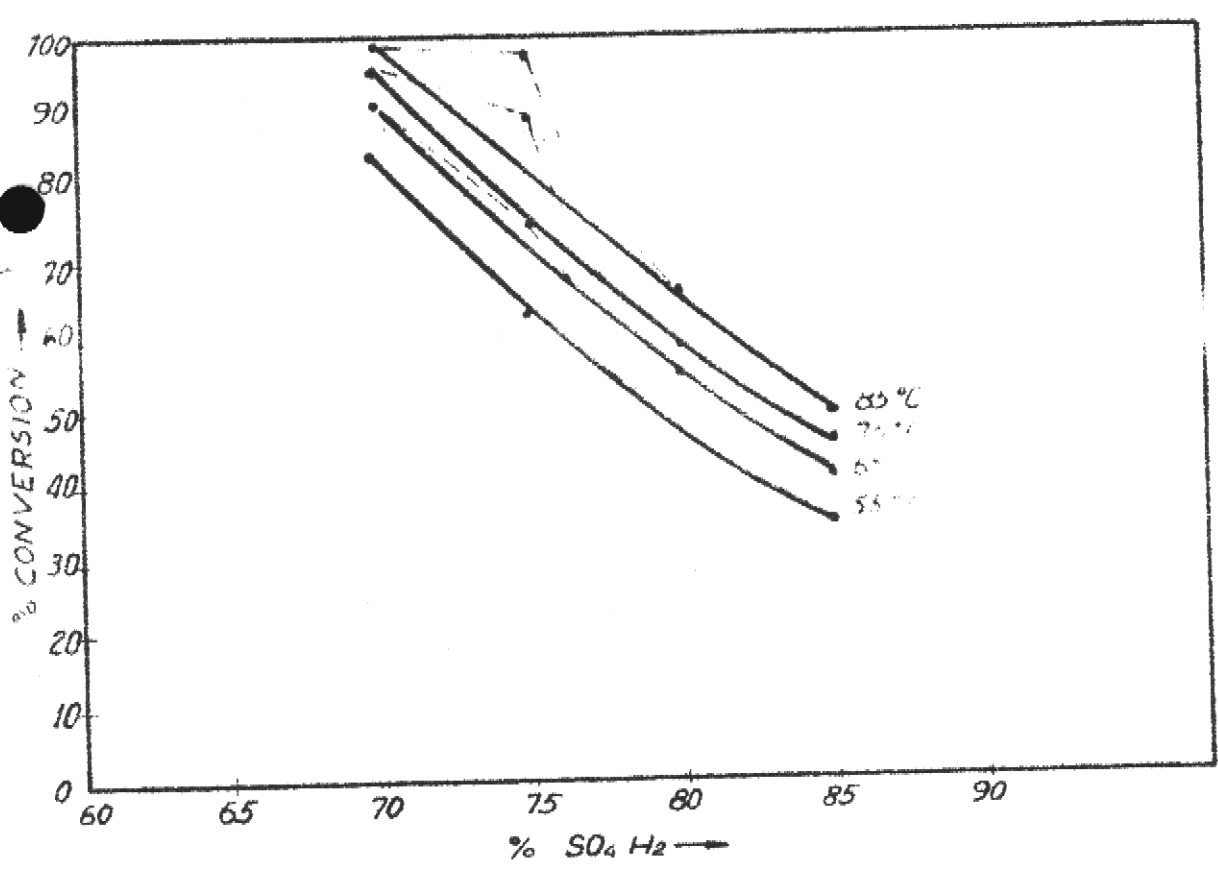


Fig. 5  
Effect of dilution of acid.



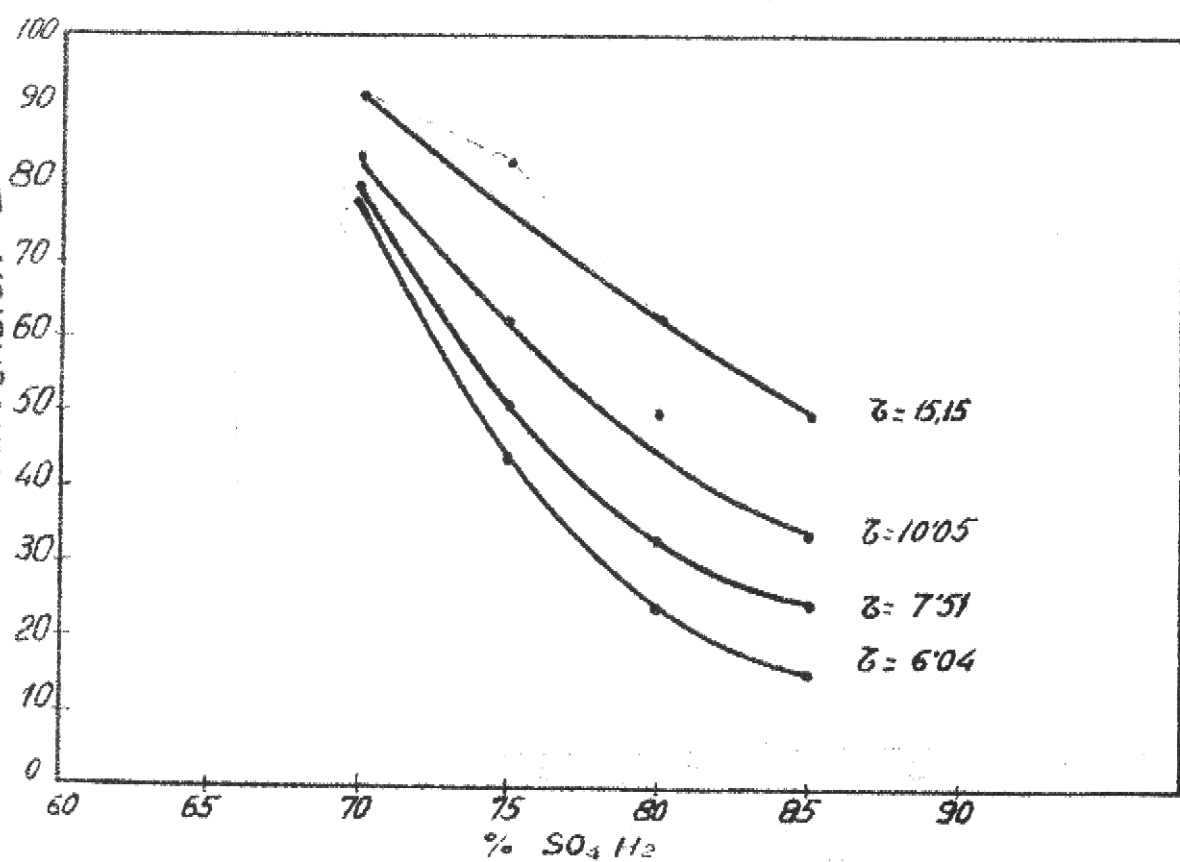


Fig. 6.  
Effect of dilution of acid.

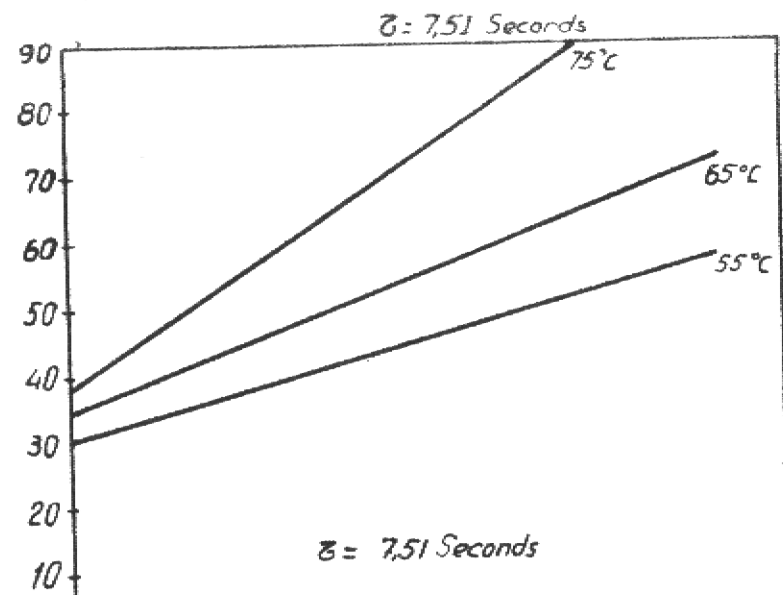
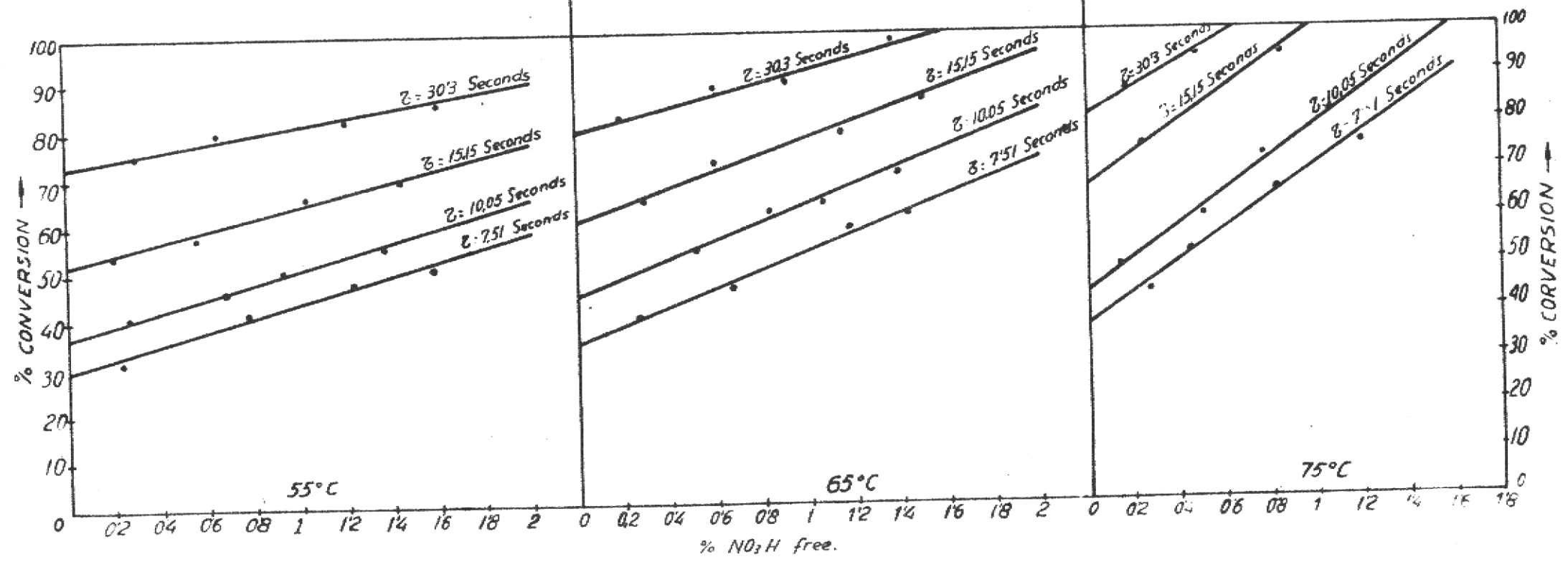


Fig. 7.  
Influence of nitric acid,  
free in the nitrose.



Nitrose = 80.20

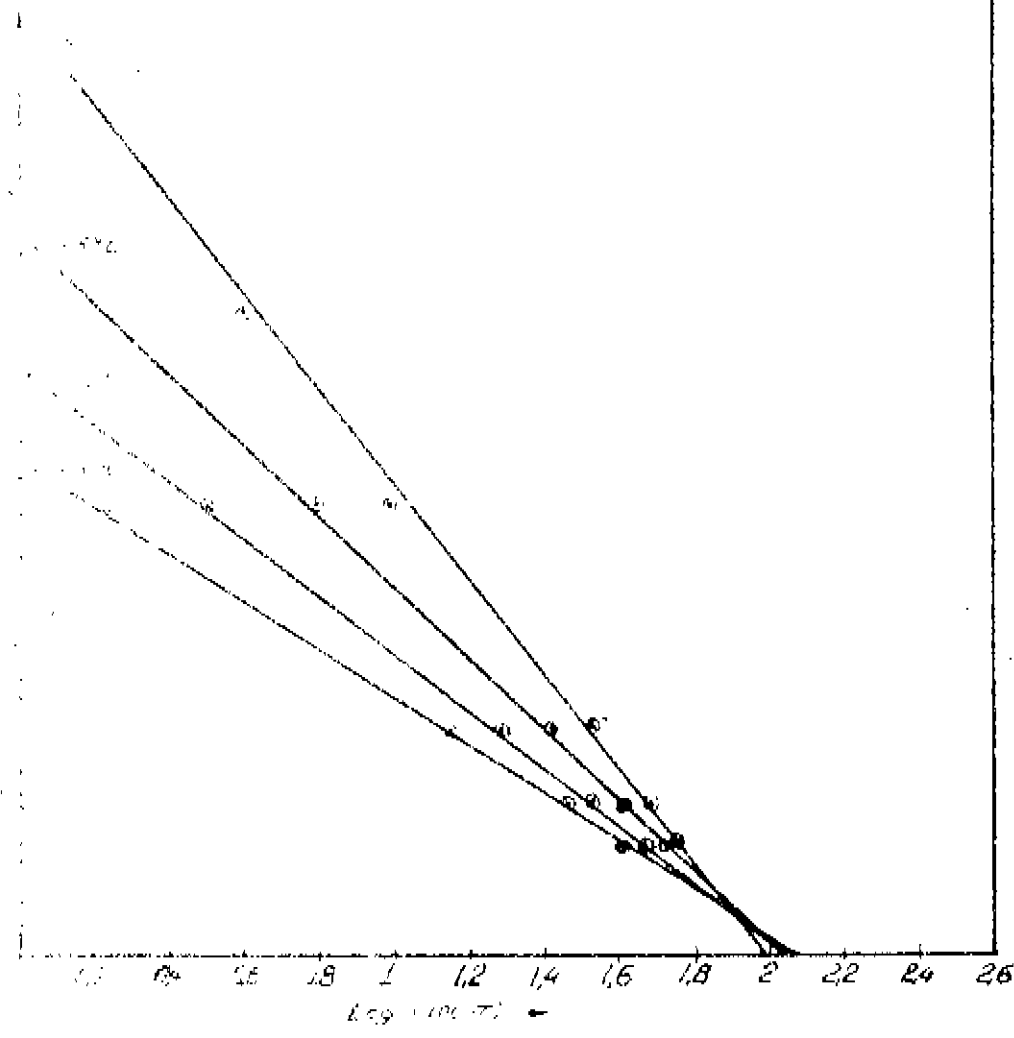


Fig. 8.  
Kinetics of the process.

Nitrose = 80.20

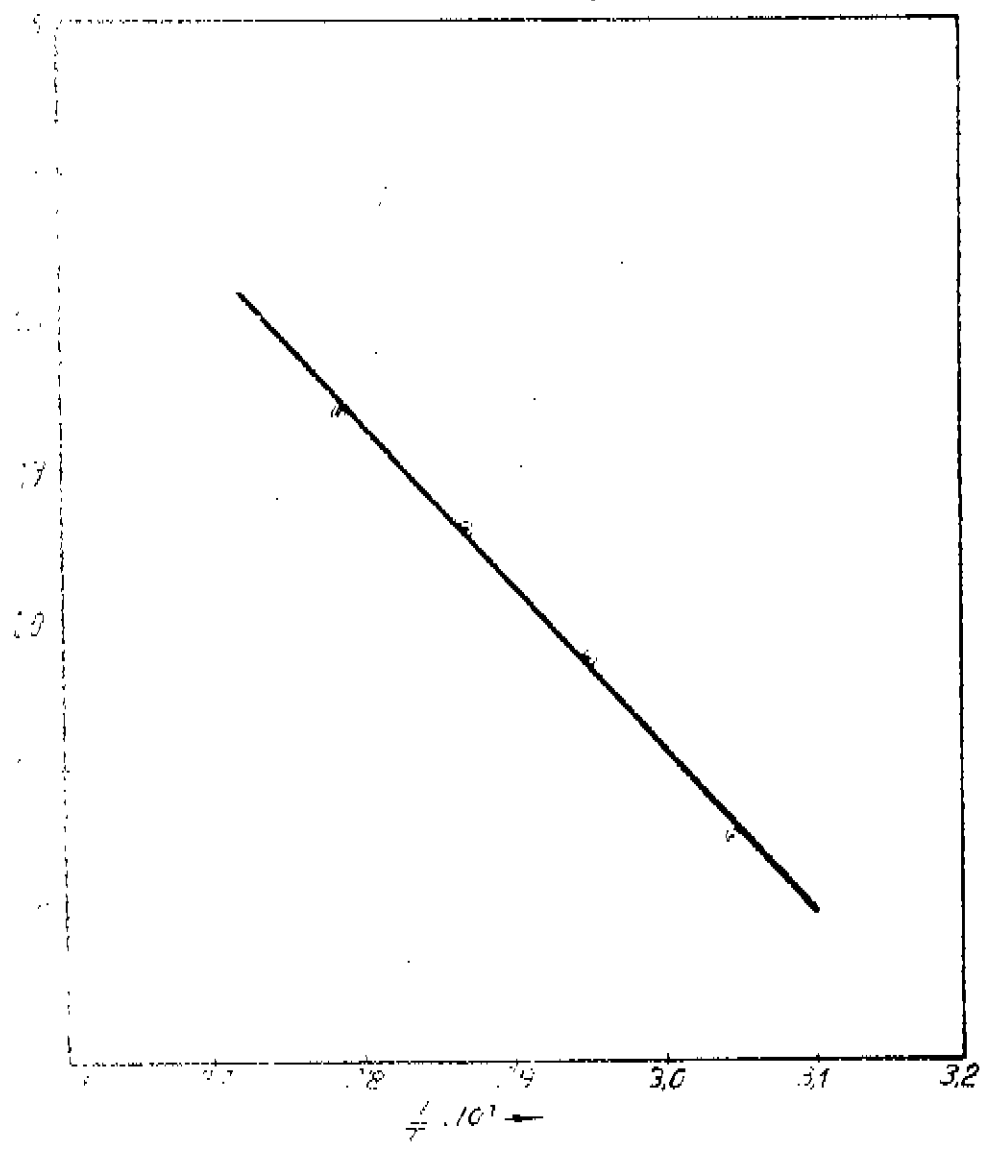


Fig. 9.  
Arrhenius' equation.