

ON THE KINETICS OF THE DECOMPOSITION OF AMMONIA ON QUARTZ SURFACE

By Z. G. SZABÓ and M. ÖRDÖGH

Institute of Inorganic and Analytical Chemistry, The University, Szeged

(Received September 10, 1957)

The decomposition of the ammonia has been studied on quartz surface at 640 and 740° C. Experiments at 640° C — that so far is not available in the literature — have been undertaken to a more detailed investigation.

It has been established, that the nitrogen, one of the reaction products has no effect on the reaction at all, the hydrogen, however, influences the course of the process to a great extent owing to its strong adsorption.

Having determined the seemingly apparent order of reaction the most likely rate equation of the process has been established.

The pretreatment with water-vapour and oxygen does not influence permanently the behaviour of the quartz surface. The reaction is greatly inhibited by the presence of oxygen.

The study of the mechanism of the primary act of oxidation processes, more exactly that of the oxygen addition reactions, is from theoretical, as well as from practical point of view, one of the problems of the utmost kinetical importance. To this end was chosen *inter alia* the study of the oxidation of ammonia under possibly homogeneous conditions. It is empirically shown that oxygen undergoes reaction with different substances hardly, or even not directly, only with their decomposition products. Such a process seemed to be the non-catalyzed oxidation of ammonia, too. This might be evidenced also by the experimental fact that the temperature at which the rate of the oxidation of ammonia is readily measurable corresponds approximately to that at which the rate of its decomposition also becomes appreciable.

Although the study of the process $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$ is rather extended to different surfaces, literature data on the decomposition on quartz surface are rather scanty. Therefore, it was necessary to study, prior to the oxidation experiments, the decomposition of ammonia on quartz surface at temperatures corresponding to those of oxidation.

The decomposition of ammonia on quartz surface shows an extraordinary sensitivity to the changes in surface of the reaction vessel. This process was investigated by C. N. HINSHELWOOD and R. E. BURK [1] in two different vessels. They obtained for the adsorption capacities very strikingly different data. The reduced rate was *e.g.* in the one bulb the half of that found in the other one. At the nearly same temperatures (1268° and 1261° K) the half period proved to be 9 sec in the one, and 790 sec in the other case. According to the view of the authors the extreme sensitivity of the quartz surface

was responsible for the deviation of their experimental results from those of M. BODENSTEIN and F. KRANENDIECK [2] who had found that the products forming during the reaction, both nitrogen and hydrogen, inhibit the process, while on premixing these gases no inhibiting effect could be observed. HINSHELWOOD and BURK could not reproduce these experiments, on the contrary, they found that hydrogen formerly introduced exerts inhibiting action to the same extent as that formed in the course of the reaction.

M. BODENSTEIN and F. KRANENDIECK studied the heterogeneous decomposition on quartz surface within the temperature range of 780—800° C. In their opinion the decomposition rate of ammonia corresponds neither to mono-, nor to bimolecular reaction, which may be interpreted on the basis of inhibiting influence of the reaction products.

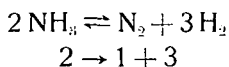
On the other hand, according to the data of HINSHELWOOD and BURK the decomposition of ammonia is a monomolecular process and can be represented by the expression $k[\text{NH}_3]\{1-c[\text{H}_2]\}$. Not only the mixture consisting of nitrogen and hydrogen formed at the reaction but also hydrogen previously introduced *inhibits* the decomposition. Up to the highest (1050° C) temperature studies no indication of homogeneous thermal decomposition of ammonia was observed.

J. A. CHRISTIANSEN and E. KNUTH [3] studied the decomposition at low pressure (2—7 cm Hg) and similarly regarded the process as monomolecular heterogeneous reaction. The rate is dependent, on a large scale, on the pretreatment of the vessel. On introducing water vapour into the reaction products, then suddenly cooling it, the intermediary NH could be, now and then, detected in form of hydroxilamine.

Our experiments were carried out under static conditions at the lowest temperature possible not yet investigated at. The experimental equipment was the kinetic apparatus commonly used, made of natron glass with exception of the quartz reaction wessel. To the stop cocks, as well as to the ground glass joints we applied Apieson grease the tension of which was about 10^{-7} mm Hg.

Preparation of the experimental substances. Ammonia gas was prepared from ammonium chloride with conc. sodium hydroxide. The evolving ammonia was let go through freshly ignited lime. Ammonia thus obtained was of about 99—99,8% purity. Hydrogen, oxygen and nitrogen gases were acquired from tanks, after washing and drying with sodium hydroxide, water, conc. sulphuric acid and calcium chloride respectively. In addition, nitrogen was let go through a tube heated to 350° and filled with copper sponge.

Experimental results. The experiments were carried out at 640° and 740° C. The pressure of the gas introduced into the vessel was approximately 50, 100, 150, 200 mm Hg. From the data available (initial pressure p_0 , total pressure observed, p , rise in pressure Δp) on the basis of equation



the concentration of the ammonia, hydrogen and nitrogen can be calculated for each total pressure.

The reaction rates increased with increasing initial pressure; the increase is linearly proportional to the initial pressure; the half period is about 4 minutes.

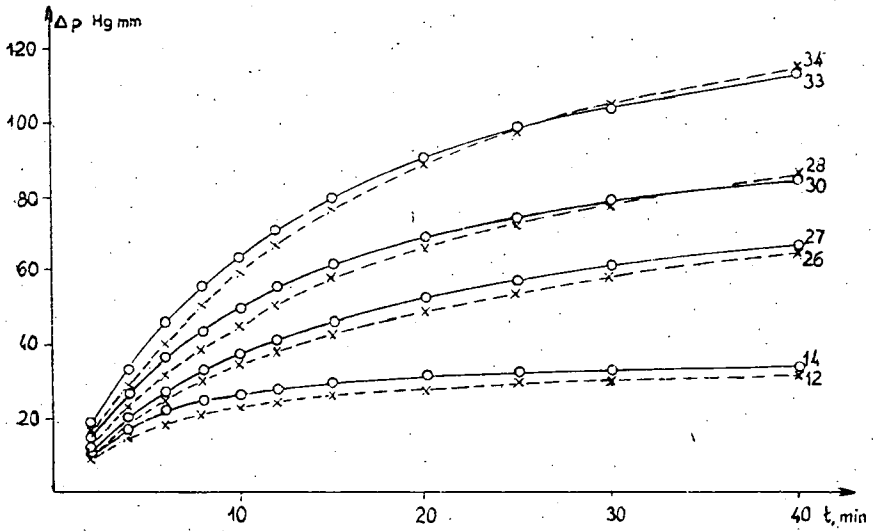


Fig. 1

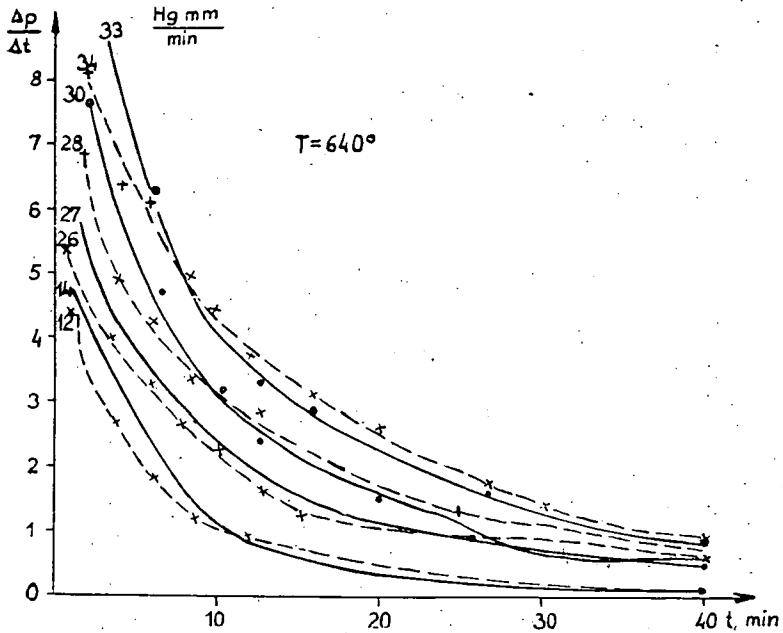


Fig. 2. $T = 640^{\circ}\text{C}$, 12. $p_0 = 45,3$ mm Hg, 14. $p_0 = 49,8$ mm Hg,
 26. $p_0 = 102,3$ mm Hg, 27. $p_0 = 99,9$ mm Hg,
 28. $p_0 = 150,5$ mm Hg, 30. $p_0 = 152,1$ mm Hg,
 33. $p_0 = 200,3$ mm Hg, 34. $p_0 = 197,5$ mm Hg

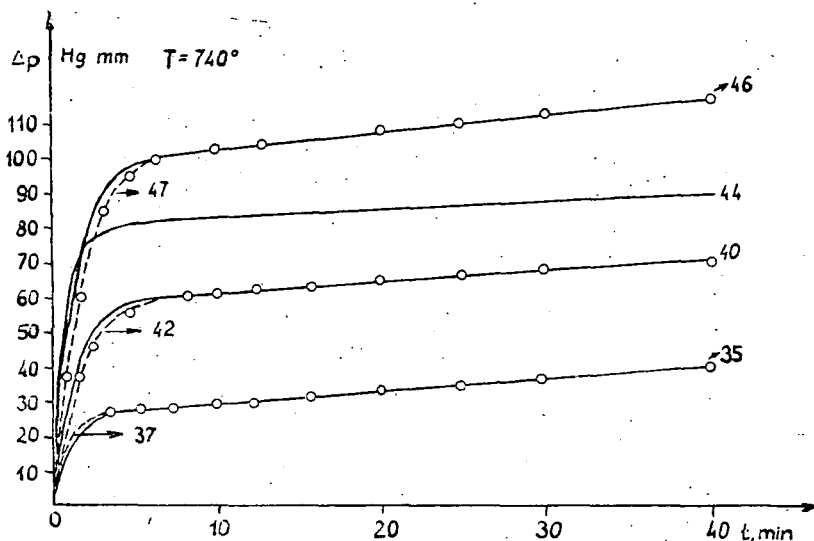


Fig. 3. 35. $p_0 = 50,8$ mm Hg, 37. $p_0 = 49,3$ mm Hg,
40. $p_0 = 101,8$ mm Hg, 42. $p_0 = 101,0$ mm Hg,
44. $p_0 = 151,1$ mm Hg, 46. $p_0 = 199,3$ mm Hg,
47. $p_0 = 201,1$ mm Hg

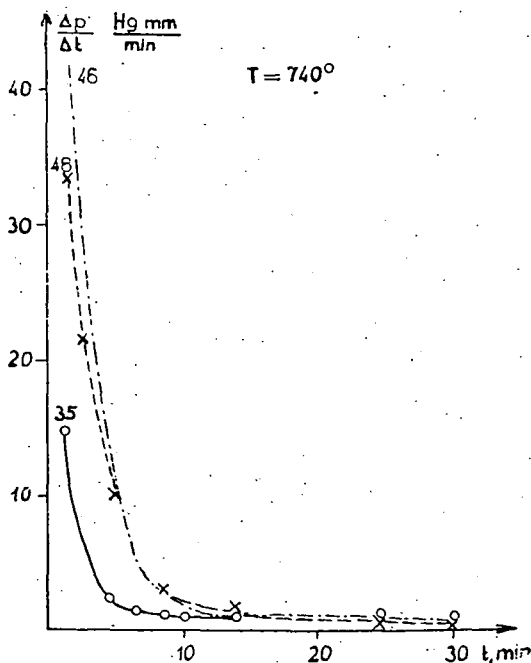


Fig. 4. $T = 740^\circ\text{C}$, 35. $p_0 = 50,8$ mm Hg, 43. $p_0 = 153,8$ mm Hg, 46. $p_0 = 193,3$ mm Hg

The pressure rise (mm Hg)-time (min.) relation is graphically illustrated by the curves of Fig. 1. The dashed and the solid lines represent parallel experiments.

Fig. 2 represents the reaction rate-time relations.

Fig. 3 and 4 similarly illustrate the relations pressure rise-time, reaction velocity-time at 740°C . At this temperature most of the reaction runs down in a few minutes. The pressure rise afterwards is of rather small amount, the reaction rate acquires a low but constant value.

The order of reaction: The matter being about heterogeneous reaction, on the basis of the data obtained the apparent order of reaction was to be found. At 740°C temperature the fraction of the gas, which transforms at a definite time, is independent of pressure thus the reaction seemed

to be of first order at this temperature. At 640°C this fraction varies considerably. However, being the rate not independent of pressure, the order of reaction must be somewhere between 0 and 1. On calculating from Eq.:

$$v = k[\text{NH}_3]^n$$

the value of k and n was tried to find on the way of successive approximation. Since it is the ammonia for which the order is wanted, the value of k may vary within one experiment, it is only important that it must not be dependent upon the pressure.

At 740°C calculating by Eq. $-d[\text{NH}_3]/dt = k[\text{NH}_3]$ we got such a rate constant which was independent of pressure but which decreased within the same experiment.

$$k_t = v/[\text{NH}_3]$$

Table I.

t = 740°C

No.	$p_{0\text{NH}_3}$	2'	4'	6'	8'	10'
38.	49,0	0,212	0,057	0,064	0,019	0,025
36.	52,0	0,217	0,068	0,040	0,031	0,012
41.	100,1	0,262	0,101	0,036	0,018	0,010
44.	151,1	0,257	0,070	0,022	0,007	0,008
48.	153,1	0,204	0,097	0,034	0,018	0,008
45.	200,7	0,185	0,102	0,049	0,024	0,015

Since among the literature data on the decomposition of ammonia on quartz surface the lowest temperature is 780°C and the reaction is even at this temperature of first order, the study of these reactions was not continued. The experiments carried out at 640°C were studied in details. Calculating with equation

$$-\frac{d[\text{NH}_3]}{dt} = k[\text{NH}_3]^{\frac{1}{2}}$$

at 640°C we obtained within the experimental errors constant k values:

$$k = v/[\text{NH}_3]^{\frac{1}{2}}$$

Table II.

t = 640°C

No.	$p_{0\text{NH}_3}$	2'	4'	6'	8'	10'	12'
17.	54,3	0,652	0,512	0,419	0,345	0,247	0,197
16.	55,5	0,604	0,509	0,348	0,295	0,264	0,179
27.	99,9	0,600	0,493	0,416	0,348	0,298	0,242
25.	102,8	0,475	0,371	0,311	0,281	0,241	0,199
26.	102,3	0,542	0,443	0,381	0,313	0,274	0,206
29.	149,9	0,555	0,486	0,455	0,379	0,358	0,292
28.	150,5	6,577	0,445	0,385	0,321	0,297	0,235
30.	152,1	0,663	0,514	0,447	0,346	0,312	0,254
32.	178,2	0,603	0,510	0,435	0,380	0,342	0,305
34.	197,5	0,586	0,488	0,483	0,413	0,366	0,319
31.	199,5	0,541	0,468	0,433	0,364	0,319	0,276
33.	200,3	0,678	0,584	0,503	0,403	0,338	0,294

With heterogeneous reaction the extent of adsorption is of decisive importance, which may be weak, medium or strong. All the three cases may be expressed in first approximation by the LANGMUIR's adsorption isotherm. The rate of the chemical reaction is proportional to the fraction of the surface which is covered by the reacting gas; the reaction is in case of weak adsorption of first order, with strong adsorption of zero order, and in the case of moderately strong adsorption, according to the equation: $dx/dt = kp/(1+bp)$, which can be approximately represented by $dx/dt = kp^n$ (where n will be a *real* fraction properly chosen) it is between 1 and 0.

In the case of decomposition of ammonia the latter possibility will be realized, *i. e.*, the adsorption is at 640°C of medial strength.

The effect of reaction products. The dropping of the rate constants within one reaction cannot be brought about by the inverse reaction through the reformation of ammonia.

The adsorption isotherm applied in the calculation of the order of reaction did not take, however, into account the presence of reaction products, although it is well known that the reaction product strongly adsorbing, decreases the apparent order of reaction. It is thus possible that the order of reaction which is first one at 740°C, becomes, at lower temperatures of lower order not because ammonia is adsorbed more strongly — although, undoubtedly also this is, to a certain extent, the cause — but for the reaction products, occupying more and more the sites of ammonia on the surface, act to lower the order.

Hydrogen is adsorbed firmly by quartz surface. The measurements of the ionization potential of the adsorbed hydrogen, further the measurements by electron interference method show that hydrogen is, on the different surfaces, strongly, *quasi* chemically adsorbed [5]. On this basis can be interpreted the strong inhibiting effect of hydrogen, especially when taking into account that hydrogen is formed during the reaction in a rather great amount. This will be, undoubtedly, the cause of the decrease of the rate constants within one reaction.

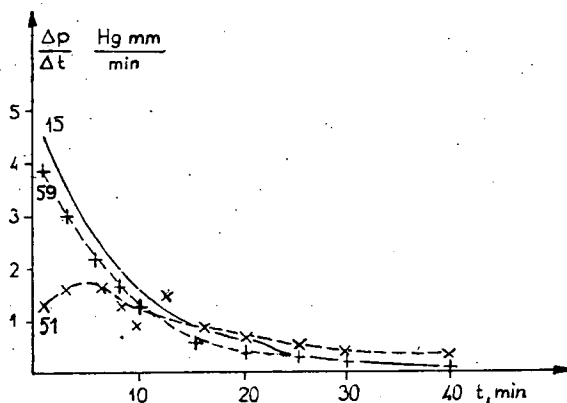


Fig. 5

In order to study the inhibiting effect of hydrogen the decomposition of ammonia was studied in experiments adding excess hydrogen to the reacting gas. In a part of the experiments hydrogen and ammonia were mixed and introduced into the vessel. Then the reaction velocity decreased relating to the experiments carried out with pure ammonia gas.

Afterwards, first hydrogen was introduced into the evacuated vessel and ammonia only after 5—6 min. The rate of reaction then decreased more considerably. These are illustrated in Fig. 5 where the three reaction velocities are plotted as functions of the time. Curve 15 represents the decomposition of pure ammonia, 59, that of ammonia premixed with hydrogen and 51 is that of ammonia in the case when hydrogen was previously introduced into the vessel.

As to the change of the curve of the reaction velocity it was similar to that carried out with pure ammonia, however, the rate was much lower. The rate constants calculated from Eq. $k = v/[\text{NH}_3]$ were, in the first period of the experiment, constant then decreased. These rate constants were independent even of the pressure but were strongly influenced by the amount of added hydrogen. The increase of the concentration of hydrogen decreased the value of the constant and *vice versa*.

Table III.

$$k_e = v/[\text{NH}_3]$$

$$t = 640^\circ\text{C}$$

No.	p_{H_2}	$p_0\text{NH}_3$	2'	4'	6'	8'	10'	$\text{NH}_3:\text{H}_2$
50.	74,2	55,7	0,0275	0,0388	0,0396	0,0379	0,0236	2:3
54.	74,9	98,8	0,0318	0,0358	0,0300	0,0271	0,0308	4:3
52.	75,4	102,1	0,0274	0,0272	0,0246	0,0323	0,0291	4:3
55.	74,6	138,5	0,0323	0,0320	0,0293	0,0264	0,0234	2:1
74.	78,3	146,9	0,0273	0,0221	0,0211	0,0225	0,0222	2:1
76.	155,9	152,5	0,0117	0,0149	0,0142	0,0161	0,0116	1:1
75.	154,7	159,3	0,0103	0,0142	0,0146	0,0143	0,0118	1:1
57.	37,0	52,1	0,0651	0,0548	0,0822	0,0550	0,0579	2:1,5
56.	37,4	53,4	0,0449	0,0481	0,0491	0,0485	0,0488	2:1,5

From these experiments it follows that hydrogen inhibits the reaction by that that from the surface of the catalyst — here the quartz glass — displaces, through its firmer adsorption, the ammonia molecules. It is thus understandable that the rate and the rate constants are at the beginning of the reaction really constant, being only a smaller fraction of the active quartz surface on which the decomposition of ammonia may occur, the other part of it is covered by hydrogen. Hydrogen forming during the decomposition does not increase considerably the amount of hydrogen formerly added; it is

thus clear why its retarding effect is always of the same extent. A considerably amount of ammonia being, however, already decomposed, the shift in the ratio of hydrogen formed in the reaction, as well as of the remaining ammonia, cannot be further on neglected. From here on the inhibiting effect increases. It is to be seen that in the rate equation assumed the first power of the concentration of ammonia is applied. It seems to be evident that in the presence of such a great amount of hydrogen the rate of reaction is controlled by the velocity of diffusion.

Experiments were carried out to make certain whether the course of the reaction is influenced by the presence of nitrogen. These experiments were arranged similarly to those carried out in presence of hydrogen. Nitrogen was formerly introduced into the vessel in such a quantity that would form in the case if the total amount of ammonia would react. There were also experiments carried out in which nitrogen and ammonia were premixed and then introduced into the vessel. The addition of nitrogen did not alter the course and the rate of the reaction in either case.

Nitrogen exerted, however, an inhibiting effect in these experiments, in which the amount of nitrogen formerly added was rather large, about 100 mm Hg, as a consequence of which, the reaction velocity considerably decreased. Nitrogen was, however, in these experiments present, in such a large quantity, as to inhibit as an inert gas, ammonia to diffuse towards the quartz surface, thus slowing down the reaction. Its effect is, accordingly, different than that of hydrogen; the latter occupies the active surface, while nitrogen does not adsorb at least at places of the surface, which are active. Until some 150 mm Hg pressure ($\text{NH}_3 : \text{N}_2 = 2 : 1$) the rate of the reaction is the same as in the case without nitrogen. At the same ratio but at a total pressure of 300 mm Hg nitrogen exerts already an inhibiting effect, the value of the rate is much lower but decreases within one experiment to such a negligible extent that it can be as constant regarded.

Rate equation. Since the experiments showed that it is the hydrogen which among the reaction products, strongly inhibits the course of the reaction, to the detailed discussion of the rate equation also the effect of hydrogen is to be taken into account.

Supposing that ammonia weakly, hydrogen firmly is adsorbed, consequently, the adsorption coefficients of the two substances differ from each other considerably, the following equation can be applied:

$$\frac{dx}{dt} = k \frac{p_{\text{NH}_3}}{p_{\text{H}_2}}$$

i. e., the rate is inversely proportional to the pressure of the reaction product. Calculating, however, on the basis of this equation, the experiments carried out at different pressures did not show a satisfactory agreement.

It is yet to be supposed that both, ammonia and hydrogen strongly adsorb, although not to the same extent, taking into consideration the fact too, that the rate is proportional to the total pressure, we arrive at the equation

$$r = \frac{dx}{dt} = \frac{k p_{\text{H}_3\text{N}}}{b_{\text{H}_3\text{N}} p_{\text{H}_3\text{N}} + b_{\text{H}_2} p_{\text{H}_2}} p_0$$

On transforming the equation

$$\frac{b_{\text{H}_3\text{N}}}{k} + \frac{b_{\text{H}_2}}{k} \cdot \frac{p_{\text{H}_2}}{p_{\text{H}_3\text{N}}} = p_{\text{e}}/r$$

$$\xi + A\eta = B.$$

This equation — the calculating of the single constants — cannot be solved exactly. Assuming, however, ξ as constant we obtain also for η constant values as within one experiment, as between the different series at varying initial pressure. Thus the kinetics of the decomposition can be described really by the equation above.

In order to study, whether the treatment with water vapour influences the action of the wall, *i. e.*, whether it causes a permanent change in the case if it is let stand for a long time in the vessel, some 15 mm Hg water vapour were introduced and let stand at the temperature of the experiments. Thereafter the vessel was pumped out as usually then the decomposition reaction studied again. The rate of decomposition rose something but not considerably.

Thereafter, when the rate of decomposition again became stabilized about 280 mm Hg oxygen were introduced into the evacuated vessel and let stand for three days similarly at the temperature (650°) of the experiments. Then, after pumping out of oxygen, it was found that the rate of the next decomposition reaction increased more than twice of that of the former one. This phenomenon may be attributed to that that oxygen has oxidized, during that rather long time and at high temperature, the impurities present in the vessel, it exerted, however, on the surface no lasting effect,

which could retard the reaction after having oxygen evacuated. The very presence of oxygen in the decomposition reaction of ammonia does exert a considerable retarding effect. Fig. 6 illustrates the rate of a reaction in comparison with one, to which 28 mm Hg oxygen was added. As it is shown, in presence of oxygen the reaction hardly sets in and becomes only later appreciable.

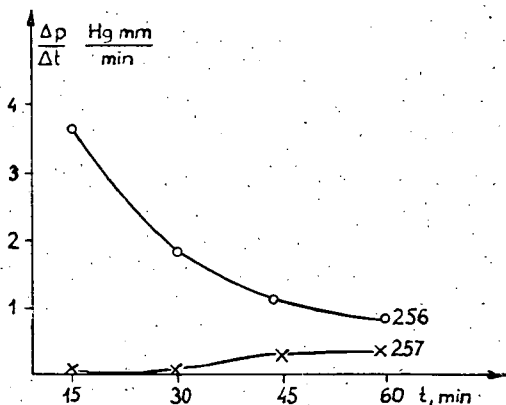


Fig. 6

References

- [1] Hinshelwood, C. N., R. E. Burk: *J. Chem. Soc.* **127**, 1105 (1925).
- [2] Bodenstein, M., F. Kranendieck: *Nernstfestschrift* (Halle a. S., 1912), p. 99.
- [3] Christiansen, J. A., Knuth Eggert: *Kong. Dansk. Vidensk. Selsk., Mat.-fysiske Medd.* **13**, Nr. 12—18. S.-Ref. Zblatt. **I**, 1172 (1936).
- [4] Schwab, G. M., H. S. Taylor, R. Spence: *Catalysis from the Standpoint of Chemical Kinetics* (D. van Nostrand, New York, 1937), p. 223.
- [5] Schwab, G. M., H. S. Taylor, R. Spence: *Catalysis from the Standpoint of Chemical Kinetics* (D. van Nostrand, New York, 1937), p. 254.