Report A-94

I

PRODUCTION OF D_2O FOR USE IN THE FISSION OF URANIUM

Report by Harold C. Urey, Aristid V. Grosse,
and George Walden, June 23, 1941

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Introduction

Approximately last February 1, Dr. R. H. Fowler, British scientific liaison officer in the United States, brought to our attention certain experiments by Drs. Halban and Kowarski, showing that a mixture of ordinary uranium oxide and D_2O resulted in an increased production of neutrons over the number produced by a primary source, thus indicating that if the mass of uranium oxide and heavy water were large enough, uranium fission would become a chain reaction and spontaneous. This indicated the need for the production of D_2O in the amounts of the order of magnitude of tons. Up to this time some 180 kilos of heavy water have been produced by the Norsk Hydro-Elektrisk Kvaelstofaktieselskab in Norway, which has served mostly as the source of this material for the whole world. Before the invasion of Norway this supply had been transported to Paris. At the time of the invasion of France, Halban escape from France to England with this water, and made experiments in England.

The electrolytic method for the production of D_2O has been studied by Professor Otto Maass of Montreal, and more recently by Prof. Hugh S. Taylor of Princeton University. The large electrolytic plant at Trail, British Columbia, might be made to produce 70-100 kilograms of D_2O at costs that are difficult at present to estimate. However, tons of material would require years of production by this method. Professor Taylor is giving further consideration to the possibility of this development as a means of getting immediate supplies of D_2O.

The distillation of water might also be used for the production of D_2O, but an estimate made by Professor Dodge of Yale University some years ago, showed that this could not be done even on a very large scale, for less than something like 20¢ or 30¢ a gram, making the cost somewhere between $200,000 and $300,000 a ton of heavy water. A recent survey of this made by Professor Dodge showed that the cost of plant would be very large, as well as the cost of operation.

The best method which we know for the concentration of D_2O from natural water where it exists to the extent of one part in 5750 parts of light water, is by the chemical exchange method which has been used successfully in the case of the nitrogen, carbon and sulfur isotopes. The method proposed consists in making use of the supplies of hydrogen which are used for the manufacture of ammonia in the United States. Ordinarily the method is to pass water into a counter-current system (an elongated vessel filled with a suitable catalyst) and then use this water for the production of hydrogen by the usual coke-water process. The hydrogen thus produced would be circulated counter-currently to the water in the reaction vessel filled with the catalyst, and after this be used for the manufacture of synthetic ammonia. This process will result in increased concentration of D_2O in the hydrogen and water involved in the manufactured process, just as has been found in similar reactions involving the other isotopes (reprints covering this previous work are attached). A plant producing 270 tons of ammonia per day has about 2 1/2 tons of D_2O in the water used for this production during one month operation. The process outlined above should make possible the removal of two-thirds of this material as a maximum. The theory of this process has been worked out by Cohen and a reprint of the theory is attached.[1]

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[1] It must be modified slightly for use on this process, due to the fact that the heavy hydrogen is concentrated in the liquid phase, namely, the water rather than in the gaseous phase, while the reverse was true in the process considered by him. Modification is easily made by changing the signs of his quantities ζ and L throughout the treatment. We shall refer to this theory later.

This prospective method for the production of D_2O in amounts of the order of a ton per month, depends upon the development of suitable catalysts for establishing equilibrium between the hydrogen gas and water with respect to the heavy hydrogen exchange between the two in accordance with the following reaction:

$$H_2O+HD=HDO+H_2.$$

Such catalysts were studied some five or six years ago by F. Farkas, L. Farkas and M. Polanyi, working in England, and publishing their results largely in the <u>Transactions of the Faraday Society</u>. The catalysts found by them were platinum, palladium, and the bacillus coli; these are substances which are known to give satisfactory hydrogen electrodes. This early work was not done in a way which gave us much indication as to what could be done under the conditions needed for our process. It indicated that in the case of platinum and palladium, a reaction could be brought one-half of the way to equilibrium in a matter of minutes, and that this half-time did not change markedly with pressure. These figures apply to the platinum and palladium catalysts, with every indication that the platinum was the better of the two. The speed of the reaction in the case of the bacillus coli was very much slower. The equilibrium constant of this reaction is reported to be between 3 and 3.7.

This brief review shows that the general method for the separation was well understood as the result of the studies on other isotopes, but that the problem was to secure a catalyst of the proper activity, in order to establish the equilibrium between hydrogen and water. The work that has been done in our laboratories here was concerned with the development of such suitable catalysts.

Before effective work could be begun on this it was necessary to improve our methods for the analysis of isotopic mixtures. In this we had the help of Dr. A. O. C. Nier of the University of Minnesota, who visited us and made a new tube for our mass spectrometer which we have used for the analysis of deuterium samples. In addition to that we have used **the interferometric** method which was developed some ten years ago for this problem. After some difficulty with these analytical methods the work has gone forward rapidly. Considerable progress in the development of such catalystis has been secured.

Experimental Methods

1. At Atmospheric Pressure.

Tests at atmospheric pressure and below are made by placing the catalyst in a vertical tube through which are circulated simultaneously water, and hydrogen containing 2-3% deuterium. The gas circulation can be either concurrent or countercurrent with the water circulation. Both gas and water circulations are accomplished by means of rubber tube pumps. Included in the gas circuit is a manifold connecting through stopcocks and interchangeable glass joints with a set of sample tubes.

The method of operation is as follows: The catalyst is placed in the tube along with a sufficient amount of water for the run. The system including the sample tubes is then evacuated. The stopcocks communicating with the sample tubes are then closed, the circulating pumps started and the deuterium containing hydrogen admitted to the rest of the system. The apparatus is so arranged that these manipulations can be accomplished swiftly so that the zero time of the run is sharply established. Samples of gas are withdrawn at measured time intervals by opening successively the cocks to the evacuated sample tubes. These were then removed to the mass spectrometer for analysis.

Due to the large number of analyses necessary we have found it convenient to erect another testing apparatus similar to the one described but with an electroscope included in the gas circuit. The gas used here contains radioactive H^3 as well as deuterium and the exchange of the former can be followed by means of the electroscope. The rate of exchange of H^3 was compared on some runs with that of H^2.

2. At Super-Atmospheric Pressures

The apparatus used for the pressure runs consists of a pressure chamber of either copper or steel to contain the catalyst. This is connected through a valve with a cylinder of electrolytic hydrogen, and through another valve with a sample receiver and vacuum pump. The sample received consists of a glass bulb of such capacity that when the gas in the catalyst chamber is expanded into it the pressure is about 1 atmosphere. Connected to the bulb by a stopcock and interchangeable joint is a sample bulb.

The experimental procedure is as follows: The catalyst is placed in the chamber and wet with heavy water containing about 10% deuterium. This water is somewhat diluted by the water contained in the catalyst. The amount of added water is so regulated that the catalyst is thoroughly wet but not flooded. The chamber is then connected with the rest of the apparatus, evacuated, the exit valve is closed, and gas is then admitted from the hydrogen cylinder through a diaphragm valve which fixes the pressure to a predetermined value measured by a pressure gauge. This arrangement allows the chamber to fill very rapidly so that the zero time is sharply defined. The entrance valve is closed after about 30 seconds, and after a suitable time interval the entire gas change is blown off into the evacuated bulb, thus allowing complete mixing of the gas in the pockets around the valve seats, and a sample for analysis is then drawn off into the evacuated sample bulb. The chamber is then evacuated, refilled, and after another time interval emptied and sampled again. In this way data for a kinetic run is obtained by repeated runs for different times. Kinetic considerations show that the rate of approach to equilibrium is independent of the direction from which the equilibrium is approached, so that the rates here are directly comparable with those obtained in the atmospheric pressure runs.

Catalytic Life.

The change of catalyst activity with time is a consideration of primary importance. This has been followed at atmospheric pressure by setting up duplicate apparatus so that tubes containing catalyst samples can be kept in continuous contact with hydrogen, and the kinetic runs repeated without bringing the catalyst in contact with the air. In the pressure apparatus the connectors with the catalyst chamber are made with flanged unions, so that at the end of the run the pressure chamber can be filled to pressure and stored in a thermostat. The chambers can at any time be reconnected and kinetic runs repeated without admitting air.

<u>Kinetics</u>. It has been found experimentally that the rate of exchange obeys the following equation:

$$\ln \frac{n_\infty - n}{n_\infty - n_0} = Kt$$

where t is the time, and n_0, n, and n_∞ are the mole fractions of deuterium in the gas phase at zero time, at time t, and infinite time, respectively.

The reaction being studied is

$$H_2O + HD \underset{k}{\overset{\alpha k}{\rightleftarrows}} HDO + H_2$$

and the velocity constants are as taken as indicated by the arrows. Cohen's equations (See J. Chem. Phys. <u>8</u>, 589 (1940) apply to the static case considered here if λ and L are set equal to zero and the equations integrated. This gives

$$\ln \frac{n_\infty - n}{n_\infty - n_0} = - \frac{kc^C(h+H\alpha)t}{hH},$$

In this equation k is the kinetic constant, c and C are the concentrations of hydrogen and water in <u>moles</u> per cc of the pure substances, h and H are the moles of hydrogen and water per cc. of the working system, and α is the fractionation factor ($\sim$3). Thus the observed constant K is in terms of these symbols - $\frac{kc^C(h+H\alpha)}{hH}$.

The theory also shows that

$$\ln \frac{N \quad -N}{N \quad -N_o} = - \frac{kcC(h+H\ )t}{hH}$$

where N_o, N, and N   are the mole fractions of deuterium at the beginning of the reaction, at time t and at infinite time, respectively. c and h are both proportional to the hydrogen pressure while C and H are not dependent on pressure. If H   h as in our experiment, K, reduces to

$$\frac{-\ kcC}{h}.$$

The half time of the reaction is the time required for $\frac{n \quad -n}{n \quad -n_o}$ to become equal to 1/2 and thus if t 1/2 represents this half time,

$$kcC = \frac{h}{t_{1/2}} \ln 2.$$

Thus the static experiments secure this quantity, kcC, needed for the discussion of the flowing system to be considered later.

Catalysts for Exchange Reactions

The exchange reaction between heavy hydrogen and water takes place extremely slowly, and therefore has to be speeded up by catalysts in order to be of practical value. In order to accomplish this it is necessary to find substances that will activate both water and hydrogen and at the same time will not interfere with one another. While the activation of water can be accomplished comparatively simple by the use of such substances as aluminum hydroxide, silicic acid, and other hydrates, the activation of the hydrogen molecule is much more difficult. The same problem of activating hydrogen is encountered in hydrogenation catalysts and in catalysts for the hydrogen electrode. From all the elements of the periodic system the noble metals, i.e., Pt, Os, Ir, Hu, Bd and Pd, are therefore the most likely to succeed as catalysts for this reaction. In our work most of the efforts were devoted to developing platinum and palladium containing catalysts, since these two metals are the cheapest of the lot. Catalysts containing other metals, such as iron, nickel and cobalt, copper and silver, chromium, zinc, and aluminum, were tried, but found to have practically no activity. The possibility of finding other metals or other catalysts with the above mentioned metals, (excepting of course, the noble metals), is not likely, but by no means excluded. A certain amount of effort will be devoted to finding catalysts free from noble metals.

It was found that catalysts containing palladium and platinum could be prepared with a noble metal content of from about 0.5% to 0.05% which showed high catalytic activity.

Their catalytic performance depends on the very large number of chemical and physical factors, the chemical factors being first the support used for the noble metal, the method of preparation of the catalyst and the intentional or unintentional impurities present in the gas or water. The performance furthermore depends upon such physical factors as the total pressure of the system, the temperature of the reaction and the age or length of performance of the catalyst. In view of the short time available these factors could not all be evaluated with the desired thoroughness and the results so far available cover the ground only in a preliminary fashion. Before discussing the behavior of individual catalysts it might be worth while to give some experimental data illustrating these different effects.

1. Law of rate exchange.

As has been mentioned in the theoretical part, the rate of this reaction follows a monomolecular kinetic law. Experimental results proving this for our particular case are given in Figures 1 and 2, which demonstrate nicely the straight-line relationship between time and the logarithm of the difference between the equilibrium concentration and the actual concentration at any particular moment, both at atmospheric and super atmospheric pressure.

2. Effect of pressure.

According to theory the rate constant, K, should be independent of pressure. The experimental data support this requirement of theory, although not in a perfectly satisfactory manner. (This may be partly due to the fact that the activity of the catalyst is not constant, but changes with time. See paragraph 4.) The catalysts have been tried at pressures from 1 to 75 atmospheres. It was found that although the concentration of hydrogen is 50 times greater at 50 atmospheres, the rate constant K or the half life the reaction, which is proportional to it, is approximately the same as at 1 atmosphere pressure.

Experimental results on the different catalysts at 50 atmospheres pressure and 25°C are given in Table 1.

Table 1.

No. of catalyst (For description of catalysts see Table 2.)	Initial Standard half-time in minutes
1	8
6, II	16
<u>11</u>	12
14, II	11.5

3. Effect of temperature.

Practically all of our experiments were run at 25°C. Some, however, were run at lower and higher temperatures. At lower temperatures, such as 0°C, it was found that the rate of deterioration of the catalyst with time, i.e., the aging was very much slower but at the same time the activity of the catalysts or the rate of the exchange reaction is slowed down by a very substantial factor. The reverse is true at higher temperatures, i.e., the rate of the reaction is increased but the deterioration is very rapid.

4. Effect of time or aging.

Most catalysts show two time effects. Under "time effect" we understand the change in the performance of the catalyst as it ages under the experimental conditions. Most catalysts show initially a very high activity which disappears more or less rapidly, usually from a few minutes to about an hour. After this rapid initial decrease the further decrease is only very slow. This slow rate of decrease of catalyst activity or the second time effect is illustrated in Figures 3 and 4 for two representative catalysts at 1 and 50 atmospheres pressure respectively. This slow aging is one that has great practical significance and a lot of effort is being devoted to decrease it.

5. Revivification of the catalyst.

In many cases the activity of our catalysts can be brought to substantially its original level by passing air or oxygen over it or other oxidizing substances. However, this revivification is only short lived. At present only a small number of experiments were devoted to studying the effect of oxygen, although it is recognized that it may have an important bearing on the performance of the catalyst if it could be made continuous.

6. Other chemical effects.

It was found that small concentrations of acids or alkalies in the water decreased the catalytic activity of the catalyst, although only to a comparatively small degree. High concentrations of acids, for instance of hydrochloric acid, may completely ruin the activity of the catalyst as is illustrated in Figure 5.

In some instances it was found that the catalyst activity is affected to a high degree by the material of the walls of the experimental tube. For instance, steel in some high pressure experiments, was found to decrease the activity of the catalyst.

Discussion of Various Catalysts

Twenty-four catalysts containing small amounts of palladium and platinum on a number of varying supports, such as alumina, silica, magnesia, alumina-silica mixtures, were tried. Various methods of deposition of the noble metals and precipitation or impregnation, were tried. They are described briefly in Table 2, under "Method of Preparation." In the last column of this table a figure is given describing the activity of the catalyst. The activity is expressed as the time required for the reactants present in the catalyst volume to reach half of the equilibrium value and will be referred to as the standard half-time. All half-times given in this table were determined at 1 atm. pressure and at 25°C, using radio-hydrogen as a tracer.

It is not possible at this time to make any general conclusions as to the best methods of preparation, but the experimental evidence shows that by dispersing platinum or palladium metal very finely on a water activating base material, it is possible to prepare catalysts with the desired qualities. Taking all factors into consideration, including of course high pressure results, catalysts No. 1, 6, 11, 14 and perhaps 23, appear at present to be most promising. Efforts will be made to keep the performance of the catalyst as steady as possible. In order to do so intelligently, however, additional data on the performance of the presently available catalyst over longer periods of time will be necessary.

Table 2

Number	Composition	Method of Preparation	Initial Standard Half-time, in Minutes for H^3 at 25°C and 1 atm. H_2
1.I & II	0.1% Pt on AlO.OH	Impregnation with H_2PtCl_6 reduction with H,COONa	5-8
2	0.5% Pt on AlO.OH	Impregnation with H_2PtCl_6, reduction with H_2 gas at 175- 250°C.	40
3	0.3% Pd on AlO.OH	Impregnation with $Pd(NO_3)_2$; reduction with H_2-gas at 25°C	90
4	0.3% Pd on AlO.OH	Impregnation with $Pd(NO_3)_2$; reduction with H,COONa	10
5a	0.2% Pt + 0.1% Pd on AlO.OH	Imp. with H_2PtCl_6+$Pd(NO_3)2$; reduced with H.COONa	10
6,I & II	0.1-0.4% Pt on SiO_2-gel	Imp. with H_2PtCl_6; reduced with H.COONa	5-7
7	0.4% Pt + Sn on SiO_2-gel.	Impreg. with H_2PtCl_6; reduced with $SnCl_2$	0.35-6.5
8	0.4% Pd + Sn on SiO_2-gel	Impreg. with $Pd(NO_3)_2$; reduced with $SnCl_2$	3-30
9	Pure SiO_2-gel	Commercial product	abs.inactive
10	Trace of Pt on magnesite	Impreg.with H_2PtCl_6 and reduction with H.COONa; Pt does not stick to $MgCO_3$	very slow
11	0.4% Pt on Uncalcined $Al(ON)_3$ SiO_2-gel	Impreg. with H_2PtCl_6 and reduced with H.COONa	3-8.5
12	0.4% Pt on calcined Al_2O_3-SiO_2	Impreg. with H_2PtCl_6 and reduced with H.COONa	7-20
13	1% Ag. on SiO_2-gel	Precipitated AgCl on gel & reduced	inactive

Table 2 (continued)

Number	Composition	Method of Preparation	Initial Standard Half-time, in Minutes for H^3 at atm. H_2
14,I % II	0.2% on SiO_2-gel	Impreg. with colloidal Pt solution	6-8
15	3% Pt on $A(OH_3)_3$	Pt reduced by NaCOOH from Cat. I, II, and precip. $Al(OH_3)$	45' at 50 atm.
16	Pure H_2 $Pt(OH)_6$ on AlO.OH	Prepared from Na_2PtCl_6 and deposited on AlO.OH and reduced by H_2 at 50 atm.	Very slow
17	0.1% Pt on $Al(OH)_3$	Colloidal Pt, coprecipitated on $Al(OH)_3$	To be tested
18	0.7% Pt on $Al(OH)_3$	" "	To be tested
19	Loew's Pt on $Al(OH)_3$	Loew's Pt does not stick to $Al(OH)_3$!	Discarded
20	1.5% Pt on $Al(OH)_3$	Coprecipitated Pt and $Al(OH)_3$ with $NH_2.NH_2$ and NH_3	To be tested
21	13% Pt and $Al(OH)_3$	" "	Slow
22	0.2% Pt +$Al(OH)_3$ on AlO.OH	Coprecipitated Al(OH)+ Pt with $NH_2.NH_2$ and NH_3 deposited on AlO.OH	18'
23	0.2% Pt on Alo.OH	Impregnated AlO.OH with H_2PtCl_6 and reduced with $NH_2.NH_2$, HCl	18.5'
24	0.1% Pt on Pumice	Commercial catalyst	50'

Price of Catalysts

The price of catalysts is mainly determined by the concentration of the noble metal. The price of palladium (sponge) at the present time equals about $0.85 per gram, and platinum $1.15 per gram. The price of the base material equals about 25¢ per pound of alumina, $1.50 per pound of silica-gel and about 2¢ per pound for magnesia. From these figures the material price of most of these catalysts can be readily calculated. For instance, the price of catalysts Nos. 1 and 14, II, would equal, respectively, $0.77 and $2.54 per pound. The cost of catalyst preparation cannot be accurately estimated at this time, but, based on past experience, it should be of the order of 25¢ per pound of catalyst. Taking this into consideration and keeping in mind the fact that the apparent densities of these two catalysts are 0.75 and 0.66, the price per cubic foot of catalyst should be $48 and $115, respectively.

Conclusion

Catalysts costing from $50 to $150 per cubic foot are now available, which will catalyze the exchange reaction between water and hydrogen with a standard half-time of the order of 10 minutes. These catalysts are comparatively easy to prepare on an industrial scale. Their performance does decrease during periods of the order of weeks or months, and efforts will be made to remedy this.

On the whole, the results obtained so far look promising, and there is every reason to expect that substantial improvements both in initial activity of the catalysts and in the steadiness of their performance with time will be obtained if a sustained effort will be made toward this objective.

At the time our work began on this Dr. David Rittenberg of the College of Physicians and Surgeons, was working on the catalysis of this reaction by the use of bacillus coli. We helped him some with this work but to date it has been found that the cultures are difficult to prepare and their catalytic activity low and not reliable. Half times of the order of 90 minutes have been secured at times. Further work is being done in attempts to develop better cultures for this purpose.

Plan for Pilot Plant

The success thus far with catalytic materials, though we have not secured as active and as desirable catalysts as we finally wish for this work, nevertheless has been sufficiently successful to lead us to consider the possibility of pilot plants which could be built and operated parallel to continuing development of catalytic materials. In order to accomplish this we have secured the advice of Mr. Thomas C. Chilton of E. I. du Pont de Nemours & Co., and have had the cooperation of Mr. Russell, Vice-President of the Standard Oil Co., of New York, and Dr. Murphree and Dr. Sweeney of the Standard Oil Development Co. Two of us (G. W. and H.C.U.) have visited the development laboratories of Louisiana at Baton Rouge, to see whether suitable plant facilities could be secured for this pilot plant development. Though the final plans have not been made, it would appear that such a pilot plant is feasible and can be put into operation within a month of the time that the contract is let. Further details in regard to this development will be reported in a short time.

Using the theory of Cohen, calculations have been made on the probable size of a large plant necessary for this process. Due to the success of the high pressure experiments, it appears that 200 atmospheres can be used with advantage for this work. The catalysts with which we are working will cost in the neighborhood of \$50-\$150 per cubic foot, and for this reason as well as the cost of pressure apparatus it is highly desirable to keep the cubical contents of the plant down as much as possible. Since hydrogen gas mixed with nitrogen gas in a ratio of 3 to 1 is supplied at total pressures up to 750 atmospheres in the ammonia synthesis plants, it is possible to use up to pressures of this order of magnitude without the necessity of additional compression in order to secure the extraction of heavy hydrogen from this hydrogen. So far our calculations have been made on the assumption that 200 atmospheres partial pressure of hydrogen would be used. Since experiments at this writing have only been made up to 50 atmospheres, further extrapolations of the results would hardly be justified. In making these calculations we have assumed a catalyst with an activity such that the half time will be ten minutes and that the equilibrium constant for the exchange reaction is 3. A redetermination of this equilibrium constant will be made shortly, but up to the present time the development of active catalysts seemed to be the more important. We have assumed that what is desired is a ton of D_2O per month in order that a matter of tons can be produced in not too long a time, and we have assumed in these calculations that the rate of production of the plant is 270 tons per day of ammonia, since this was given to us as the capacity of the Morgantown plant of the du Pont Company, which is being built for the production of synthetic ammonia for the government, this being a reasonable sized plant to postulate.

Cohen's theory when modified for this process by changing the signs of the symbols ℓ and L in his formulae. This results in a negative flow, P, and if this is to be considered positive, his symbol θ must be used with changed sign. Then

$$\frac{N_o}{N_Z} = \frac{1-\alpha\theta}{e-\rho Z-\theta},$$

Where N_0 is the mole fraction of deuterium at the bottom of the countercurrent catalytic chamber, N_Z the mole fraction in natural water $\frac{1}{5750}$, α is the fractionation factor taken as 3, and Z the length of the apparatus. θ and μ are defined by the equations

$$\theta = \frac{\Gamma}{L-\Gamma} \quad \frac{1}{1-\alpha} ,$$

$$\mu = -\frac{kcC}{L} \quad (1-\alpha) \quad (1-\alpha\theta),$$

where L is the flow downward through the column per unit cross section, Γ the amount of product withdrawn from the apparatus per unit cross section and kcC is a constant which must be determined from the static experiments of the preceeding section. If the half time is 10 minutes and the value of kcC is at 1 atm. pressure and is proportional to the pressure as nearly as can be decided by our present experiments. Equation (1) can be solved for $\frac{kcCZ}{L}$,

$$\frac{kcCZ}{L} = \frac{1}{1-\alpha)\ (1-\alpha\theta)} \quad \ln \quad \frac{1-\alpha\theta + \alpha\theta\frac{N_0}{N_Z}}{\frac{N_0}{N_Z}}$$

If numerator and denominator of the left hand member are multiplied by the cross sectional area, A, ZA is the volume of the apparatus and LA is the total feed to the apparatus.

The following table gives the calculated values of $\frac{kcCZ}{LA}$ for various values of N_o and of the total production of D_2O (PN). The numbers in parentheses are the values of these numbers divided by the production.

No. Tons D_2O per month	1	1.25	1.375	1.5
N. .001	1.132 (1.132)	1.271 (1.02)	1.370 (1.00)	1.52 (1.01)
.002	1.56 (1.56)	1.75 (1.40)	1.88 (1.36)	2.08 (1.39)
.003	1.70 (1.70)	2.00 (1.60)	2.11 (1.54)	2.39 (1.59)

Taking the value 1.56 for 1 ton per month and N_o equal to .002 and the value of kcC as 14×10^{-5} for 200 atms. and a half time of 10 min. in moles per cc. and per min. and the total flow, LA, equivalent to 270 tons of ammonia per day is 5850 cu. feet of catalyst space. Thus the total cost of catalyst will run to about $600,000. At present estimates of cost of the apparatus and cost of modification of an ammonia plant have not been made.

Future Development.

It is obvious that every effort should be bent toward improving the catalysts available for the size of the apparatus needed decreases as the catalytic activity increases.

We believe this is not an unlikely development for more active catalysts have been secured from time to time but their lives have not been sufficiently long to make them satisfactory. Further work is proceeding in this direction.

Experiments at higher pressures, 200 to 750 atmospheres, are now in progress. Gases actually used for ammonia synthesis should be used in our experiments instead of pure hydrogen gas. Samples of mixtures of nitrogen and hydrogen are being supplied to us by the du Pont Company.

Work on a pilot plant should be started immediately in order to test the calculations outlined above. Plans for this will be presented shortly.

A chemical engineer should study the present ammonia plant designs with the object of their modification to permit their use in connection with the process discussed here.

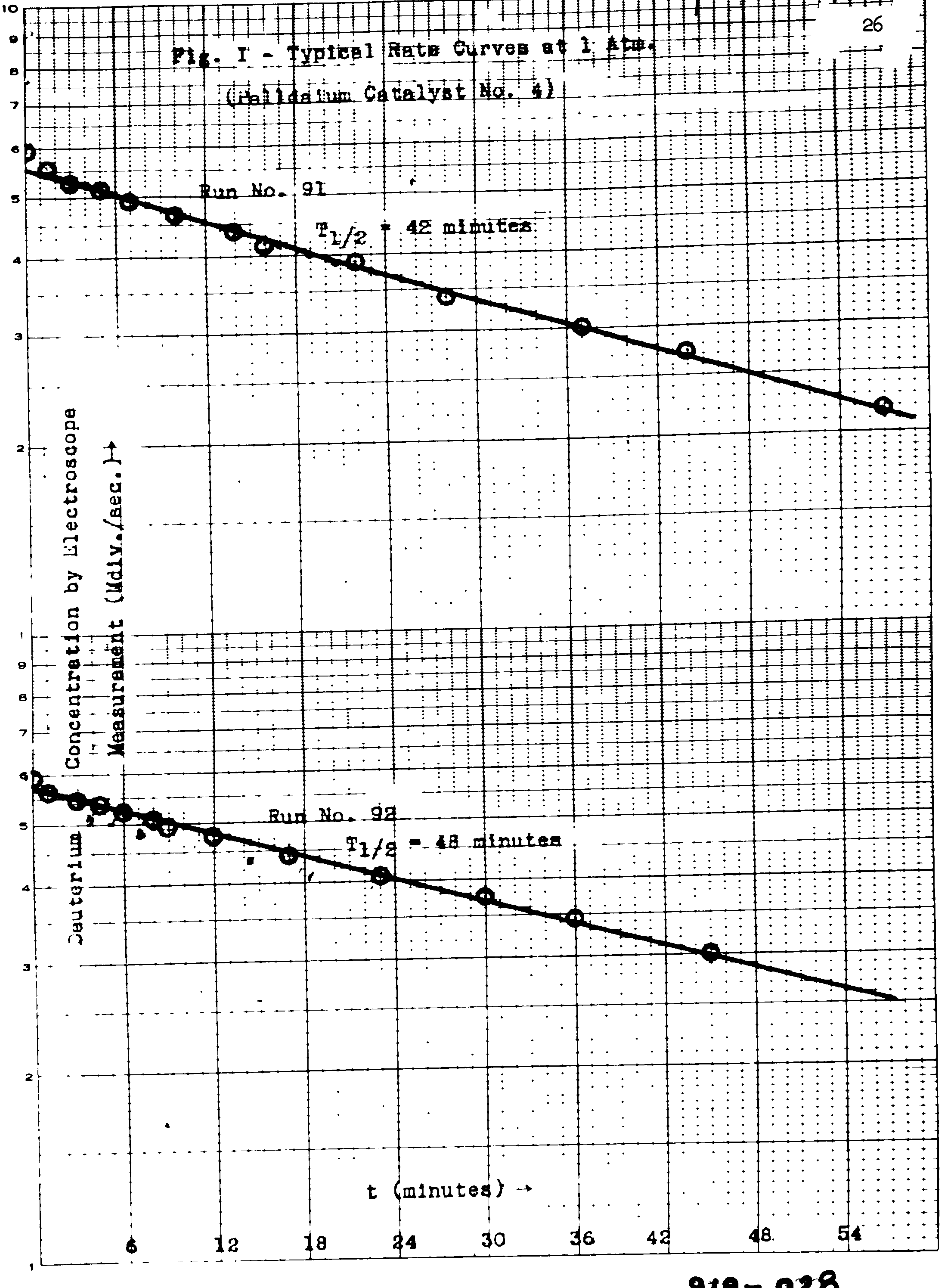

Fig. I - Typical Rate Curves at 1 Atm.

(Palladium Catalyst No. 4)

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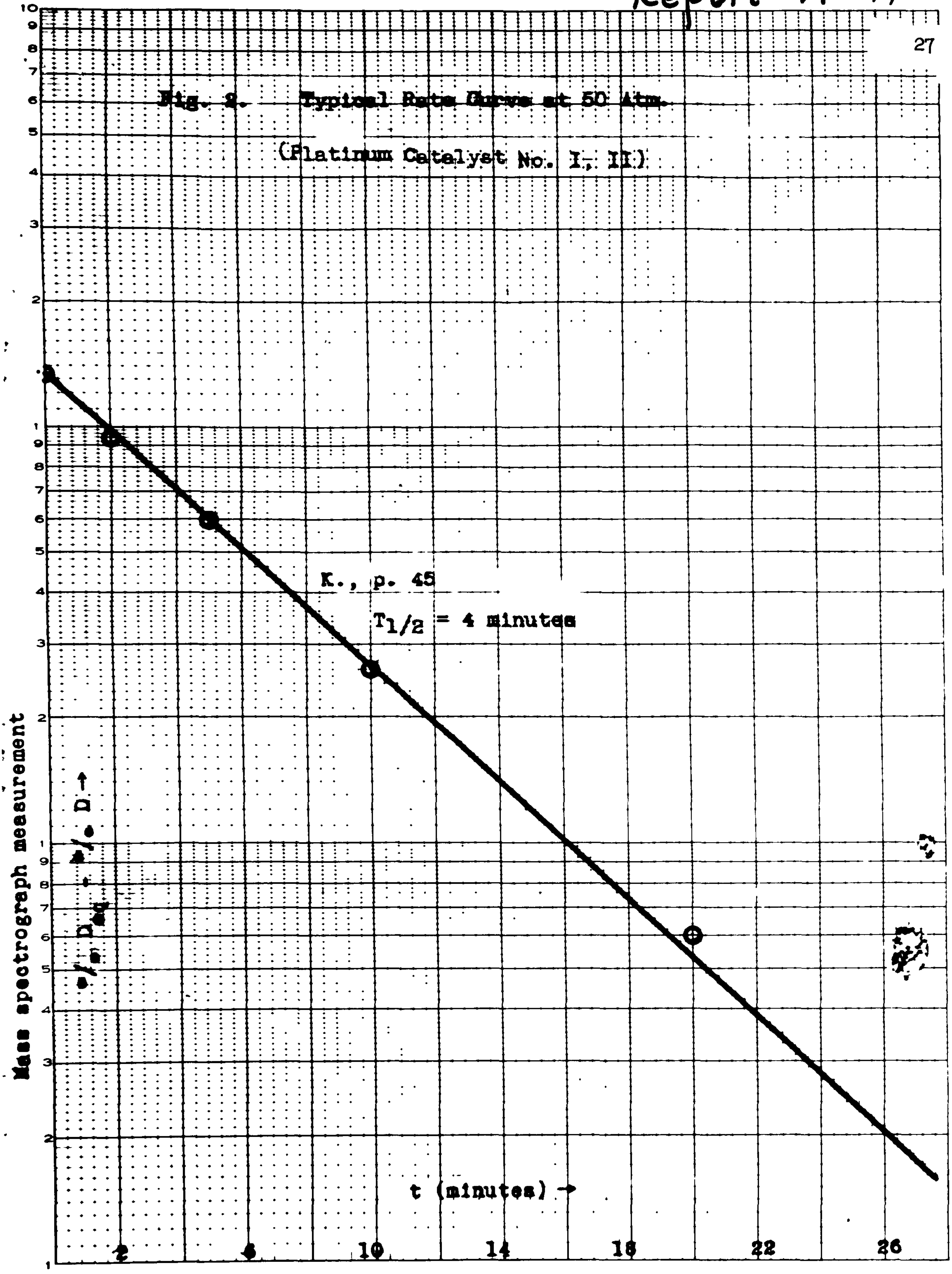


Fig. 2. Typical Rate Curve at 50 Atm.

(Platinum Catalyst No. I, II)

K., p. 45

$T_{1/2}$ = 4 minutes

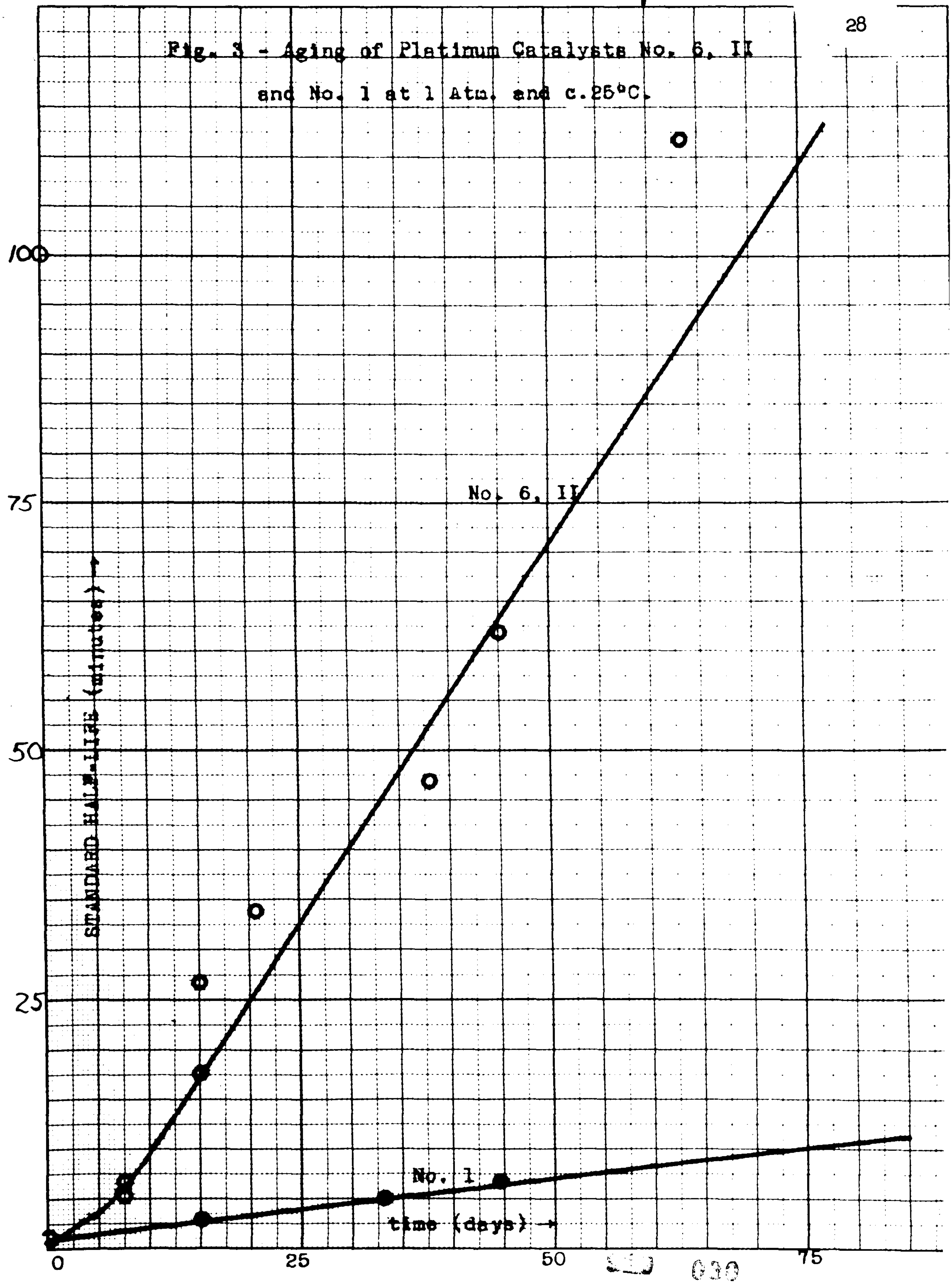
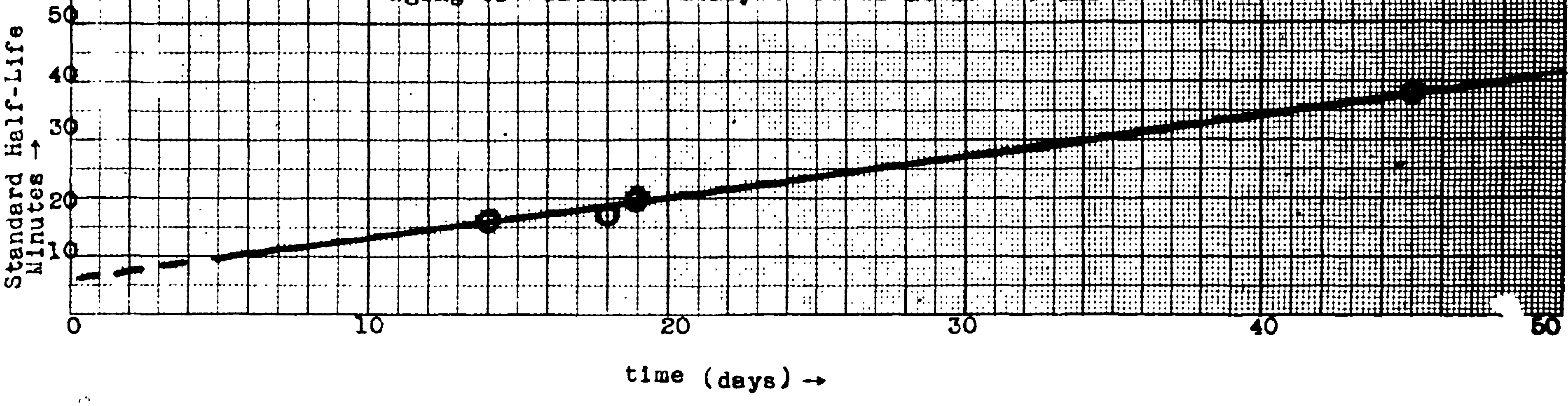


Fig. 3 - Aging of Platinum Catalysts No. 6, II and No. 1 at 1 Atm. and c.25°C.

Fig. 4

Aging of Platinum Catalyst No. 11 at 25° C. and 50 Atm.



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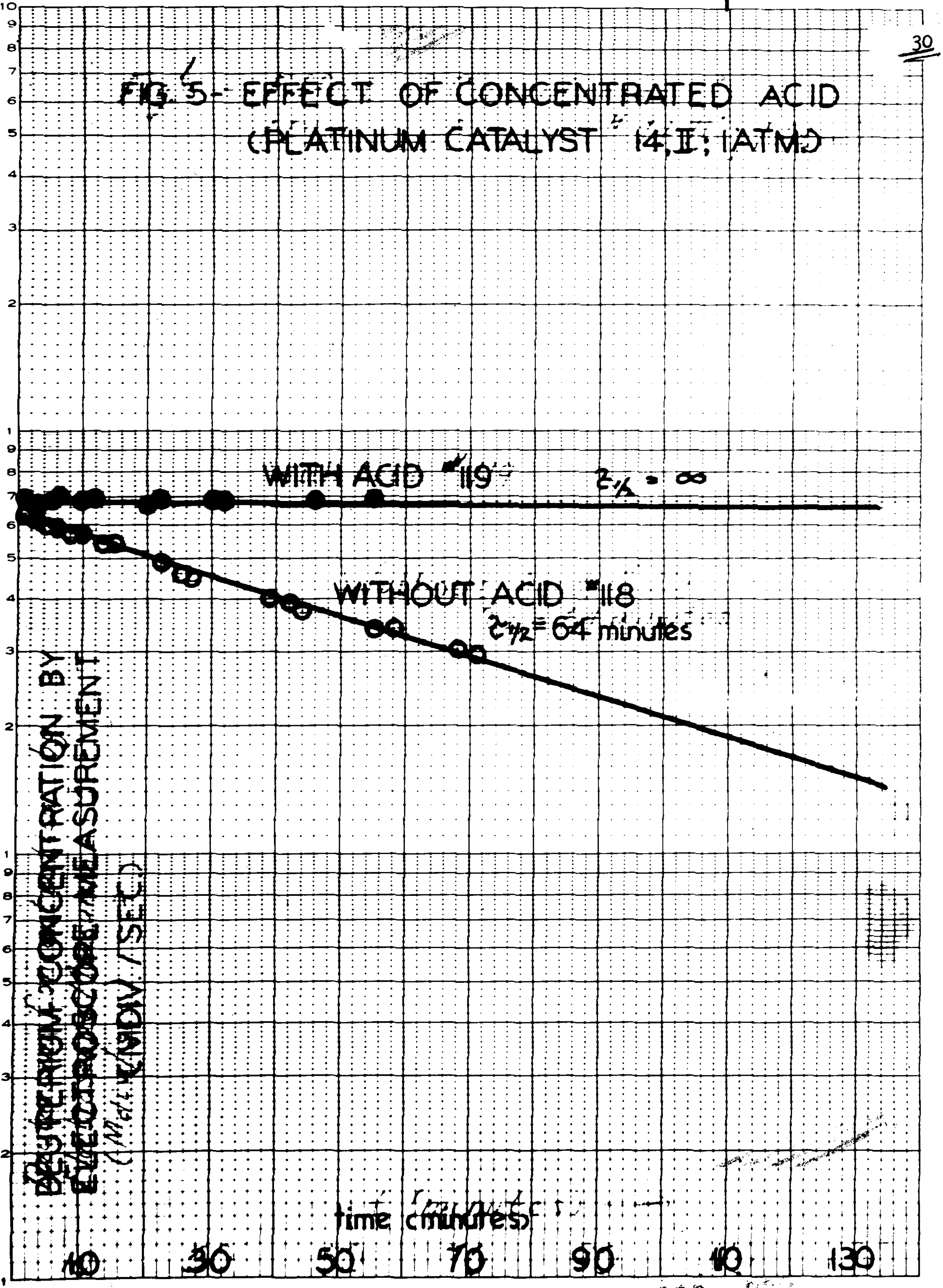

FIG. 5 - EFFECT OF CONCENTRATED ACID (PLATINUM CATALYST #14,II; 1 ATM)