THERMODYNAMIC EXPLANATION OF SPONTANEOUS NITROGEN-OXIDE FORMATION EXPERIENCED ON A PLASMA TREATED CATALYSTS

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ABSTRACT

It has been observed at the plasmachemical transformation of powdered catalysts that the surface of the particles undergoes structural and chemical changes. Powdered α-chromium-oxide, after having been treated in reductive and inert plasmas, showed strong warm-up with simultaneous formation of nitrogen-oxides when exposed to air. On the basis of thermodynamic considerations, two reaction-pathways seem to be possible for the formation of nitrogen-oxides.

1. INTRODUCTION

It has been observed at plasmachemical treatment of solid powders that the surface of the particles undergoes structural and chemical alterations /1/. Powdered α-chromium/III/-oxide showed strong warm-up with simultaneous generation of nitrogen-oxide fumes when exposed to air after having been treated in reductive and inert plasmas /2/. No mentioninig of the pyrophoric character of the chromium-oxides has been found in the literature. At the same time, it was found that chromium/III/-oxide shows catalytic activity in several chemical reactions /3/ and can chemisorb nitrogen as well as oxigen /4/. It could be thought on the basis of the above mentioned observations that the formation of nitrogen-oxide fumes can be explained by a catalytic reaction between nitrogen and oxigen. In order for getting acquinted with the supposed reaction pathways, physical, chemical and catalytic properties of treated and untreated catalysts were studied, and thermodynamic analysis of the nitrogen-oxigen system was carried out in order to find those reaction conditions which make the happening of the reaction possible.

2. PLASMACHEMICAL TREATMENT OF THE CATALYST

For the plasmachemical treatments a plasmatron of own make was used. Main components of the plasmatron are the cathode rod /tungsten/ and the anode funnel/copper/. Between the two electrodes a direct current arc was established. The heat content of the plasma is proportional with the intensity of the current in the arc and with the voltage between the electrodes. The specific heat content of the plasma can be calculated from the heating power and from thespace velocity of the plasma-generating gas, under considering also the energy applied for cooling

the electrodes. The plasma generating gas was introduced partly through the permeated cathode, partly tangentially into the space above the anode-funnel. The gas heated up by the electric current streams through the hole in the anode funnel. Chromium-oxide is added to the plasma-generating gas introduced through the cathode and is transported through the plasmatron by the gas. Leaving the anode-funnel, the plasma is cooled down partly by adiabatic expansion, partly by cooling with liquid nitrogen. The catalyst particles leaving the anode-funnel with high velocities, fall into liquid nitrogen and consequently are cooled down quickly.

3. PREPARATION AND PRETREATMENT OF THE CATALYST

Preparation of chromium/III/-oxide.
The catalyst was prepared from chromium/III/-nitrate through chromium/III/-oxide gel.
Preparation of chromium/III/-oxide gel:
60 g $Cr/NO_3/_3.9H_2O$ and 60 g urea are dissolved in 4 litres of water. The solution is boiled until a well observable precipitate appears /about 3 hours/. The precipitated green solid is filtered, washed and dried at 383K.
Chromium/III/-oxide gel was calcined at 850°C for 6 hours in air.
The fraction with particle size 0,23-0,5 mm of the chromium/III/-oxideprepared in the above described procedure was used as catalyst.
Conditions of the plasma treatment:

Intensity	100 A
Voltage	20 V
Space velocity	1200 l/h

Activation of the catalyst samples:
Cca. 0,5 g samples were used for each measurement; the catalyst sample was weighed in with 4 decimal accuracy, then heated at 300°C in a vacuum of 10^{-6} bar for one hour and subsequently treated in hydrogen atmosphere at 350°C for 0,5 hour.

4. CHARACTERIZATION OF THE CATALYTIC ACTIVITY BY MEASURING THE INITIAL RATE OF THE ORTHO-PARA HYDROGEN CONVERSION

The ortho-para hydrogen conversion can occur according to two different mechanisms /Leffler,5/:
1. Dissociative mechanism: The hydrogen molecule dissociates to it's atoms and the atoms recombinate in a composition corresponding to the equilibrium at the given temperature;
2. Magnetic mechanism: In strong magnetic fields the spin of the proton can be inverted /and the reaction is realised in this way/.

The reactions happening according to the two different mechanisms can be separated when the rate of the hydrogen-deuterium exchange is also measured besides the rate of the ortho-para hydrogen conversion. The number of hydrogen molecules transformed according to the dissociative mechanism is - disregarding the kinetic isotopeffect - namely identical with the number of molecules participating in the hydrogen-deuterium exchange during the same time period.

Consequently, the difference between the rate of

the ortho-para hydrogen conversion and that of the hydrogen-deuterium exchange can be attributed to the ortho-para conversion happening according to the magnetic mechanism. Selwood /6/ has shown that below 60°C the rate of the hydrogen-deuterium exchange is neglectible compared to the rate of the ortho-para conversion. This means, that at low temperatures the conversion happening according to the magnetic mechanism is dominating on α-chromium/III/-oxide catalyst. The magnetic conversion was investigated by several researchers. Swenson /7/ found the process to be first order for ortho hydrogen.

The rate of the reaction proceeding according to the magnetic mechanism depends greatly on the structure, preparation and pretreatment of the catalyst /8/. The investigations conducted by Selwood /8/ demonstrated that the rate of the ortho-para conversion as a function of the temperature has a characteristic shape depending on the structure of the catalyst in the vicinity of the Neel-point.

Our measurements were carried out in a flow-through reactor. The surface area of the catalyst was 10 m^2/g, as measured by BET nitrogen adsorption The rate values determined under this conditions can be seen in Table 1.

Table 1.

	untreated /mol/m^2s/	plasma treated initial /mol/m^2s/	plasma treated constant /mol/m^2s/
0°C	$1,08.10^{-6}$	$1,49.10^{-6}$	$1,30.10^{-6}$
60°C	$1,14.10^{-7}$	$1,30.10^{-6}$	$8,50.10^{-7}$
-196°C	$2,21.10^{-7}$	$1,74.10^{-7}$	$1,74.10^{-7}$
$\frac{k_o}{k_{60}}$	7,5	1,15	1,52

The reaction rates measured with untreated α-chromium/III/-oxide are smaller than those measured by Selwood /9/. The reasons of this observation are not cleared yet. The relative ratios of the reaction rates measured at different temperatures and the behaviour of the catalyst in the vicinity of the Neel-point correspond to the data found in the literature.

The activity of the treated catalyst has shown different changes at different temperatures. The change in activity at -196°C - a slight decrease in activity - is not significant. Similarly, the small increase in activity at 0°C is also not important. The activity of the treated catalyst measured at 0°C has shown a slight decreaseduring repeated reaction-rate measurements and then became constant. The activity increase of about one order of magnitude observed at 60°C is very interesting. Comparing the reac-

tion the reaction rates at 0°C and 60°C /that is, below and above the Neel-point/ we can come to the conclusion that the activity increase attributable to the alteration of structure characteristics - that is, the reaction rate increase measured in the paramagnetic domain /at 60°C/ - is not effective in the antiferromagnetic domain. The behaviour of the catalyst is like it had lost it's antiferromagnetic arrangedness - it's activity does not change in the vicinity of the Neel-point - but the structural changes enhance the approachability of the active centres.

5. THERMODYNAMIC ANALYSIS OF THE NITROGEN-OXIGEN SYSTEM

For calculating the thermodynamic equilibrium of the studied nitrogen-oxigen system, a computer program was written which was suitable to calculate the equilibrium composition of a gas-mixture consisting of an arbitrary number of components on the basis of the thermodynamic data of the gases. /An ideal mixture of ideal gases was postulated./ On the basis of a literature study, for carrying out such a general calculation, only the free-enthalpy minimation method seemed to be suitable. The calculation method was transformed into a computer program written in BASIC for the WANG 2200 computer of the Department of Chemical Technology.

Controll of the program

In order to controll the program, several runs were made for reactions where equilibrium constants were known from the literature, e. g.:

1. $N_2 + O_2 = 2NO$
2. $NO_2 = NO + 1/2\ O_2$
3. $N_2O_4 = 2NO_2$
4. $N_2 + 3H_2 = 2NH_3$

With the help of the program, isobars and equilibrium constants were calculated for different temperatures. The temperature plots of the equilibrium constants were compared with the literature data. It could be established, that the calculated results fit well with the literature data; that is, the program works well. In addition to the above mentioned reactions, the temperature dependence of the equilibrium compositions of the nitrogen-monoxide, nitrogen-dioxide, nitrogen-trioxide and nitrogen-tetroxide systems were also calculated, and these results showed also good correspondence with the literature data. The mentioned equilibria were calculated also for an elevated pressure. The results showed that the equilibria are shifted towards the expected directions.

Results of the calculations

At the thermodynamic analysis of the nitrogen-oxigen system we were striving for completeness, but regarding the limited memory capacity of the computer, we could not consider all compounds resulting from all possible combinations of nitrogen and oxigen. Thus, formation of compounds having the smallest standard heats of formation - like nitrogen-trioxide, dinitrogen-trioxide, nitrogen-tetroxide and nitrogen-pentoxide - was excluded from

the calculations. Concentrations of these compounds in the temperature range above 300-400 K are negligible. At higher temperatures, these nitrogen-oxides undergo transformations into nitrogen-oxides with higher heats of formation /like e.g. nitrogen-monoxide, nitrogen-dioxide/.
Thus, the following components were taken into consideration in the calculations:
1. nitrogen 2. oxigen 3. atomic nitrogen 4. atomic oxigen 5. nitrogen-monoxide 6. nitrogen-dioxide 7. nitrogen/I/-oxide.
Equilibrium compositions were calculated at the following atomic ratios:

$$N : O = 4 : 1$$

$$N : O = 1 : 1$$

$$N : O = 1 : 4$$

at 0,1; 1 and 10 bar total pressure in the temperature range 1500-6000 K in steps of 200 K. /Fig. 1,2 and 3./

During the calculations, some limits of applicability of the program also turned out: when the difference between the two nearest mole numbers is greater thun 5-6 orders of magnitude, or when the change of the total mole number is smaller than 10^{-6}-10^{-7} then the computer could not register such small differences. As a consequence of this imperfection in the program, we could not obtain reliable results for the temperature range below 1500 K. Nevertheless, the fact that in this temperature range all the mole fractions of the other components are negligible compared to the concentration of nitrogen and oxigen, could be firmly established.

The effects of the studied parameters on the equilibrium of the nitrogen-oxigen system can be summarized as follows:

1. Effects of temperature:
   Three different, well separated ranges can be observed on the diagrams:
   - Between 0 and 2000 K molecular nitrogen and oxigen are stable and concentrations of the other components are negligible.
   - Between 2000 and 4500 K the concentration of atomic oxigen shows a sharp increase. The concentrations of nitrogen-monoxide and nitrogen-dioxide reach their maximums and start to decrease slowly.
   - Between 4500 and 6000 K the concentration of atomic nitrogen shows a sharp increase on the cost of molecular nitrogen and nitrogen monoxide. The stabilization of the atomic oxigen concentration can be observed.
2. Effects of pressure:
   Elevation of the pressure increases the concentration of nitrogen-monoxide but at a constant N/O ratio the maximum of nitrogen-monoxide concentration is shifted towards higher temperatures. Elevation of the pressure enhances formation polyatomic molecules /nitrogen-dioxide, nitrogen/I/-oxide/. It can be stated in general that elevation of the pressure is disadvantageous because it supresses the decomposition of molecular nitrogen.

3. Effect of nitrogen-oxigen ratio:
   A maximal value of nitrogen-monoxide formation can be observed at a N/O=1 ratio /which is identical with the stochiometric composition/. A decrease of nitrogen/I/-oxide concentration was found with increasing N/O ratios.

On the basis of thermodynamic analysis it has been found that nitrogen oxides formation can't produced from molecular nitrogen and oxigen either on the surface of a catalyst. The possible reaction pathways were searched for through wich the exothermic nitrogen-oxigen reaction on the plasma treated surface of the catalyst can proceed, the followes:

1. The more probable pathway -
   Chemisorption of atomic nitrogen on the surface of the high temperature catalyst, formation of surface compounds consisting of chromium, oxigen and nitrogen atoms, followed by reaction with molecular oxigen when exposed to air.
2. The less probable pathway -
   Chemisorption of atomic oxigen on the surface of catalyst followed by the reaction of this species with the nitrogen of air. This reaction can be excluded in that case when the liquid nitrogen has no oxigen content.

6. SUMMARY

From among the possible methods for measuring ortho-para hydrogen conversion, the most convenient was chosen and this method was applied for our measurements. α-chromium/III/-oxide was prepared from $Cr/NO_3/_3.9H_2O$ by urea precipitation. A portion of the catalyst was exposed to heat-treatment in argon plasma. The change in the activity of the catalyst was characterized by the initial reaction rate of the ortho-para hydrogen conversion measured at -196, 0 and 60°C /10,11/. It has been established, that as a result of the plasmachemical treatment, the catalyst suffered structural changes and, as a consequence of these changes, the active centers became more approachable for hydrogen. The almost one order of magnitude change in the activity of catalyst experienced at 60°C can be explained in this way. At the same time, taking into consideration that at 0°C only a slight activity increase could be observed, it can be stated that the antiferromagnetic arrangedness of the catalyst has decreased, as a result of the plasmachemical treatment.

On the basis of a literature study, a mathematical model was set up and a computer program was written to calculate the thermodynamic equilibrium composition of gasmixtures. Thermodynamic analysis of th nitrogen-oxigen system was carried out for the parameter ranges in question. Formation of nitrogen oxides on plasma treated and quenched α-chromium/III/-oxide possible goes on the way that product of adsorbed atomic nitrogen and surface oxigen and chorium atoms react to molecular oxigen of air when exposed to air. There is no well-founded explanation for connection between the catalytic activity in o-,p-hydrogen conversion reaction and the formation of nitrogen oxides.

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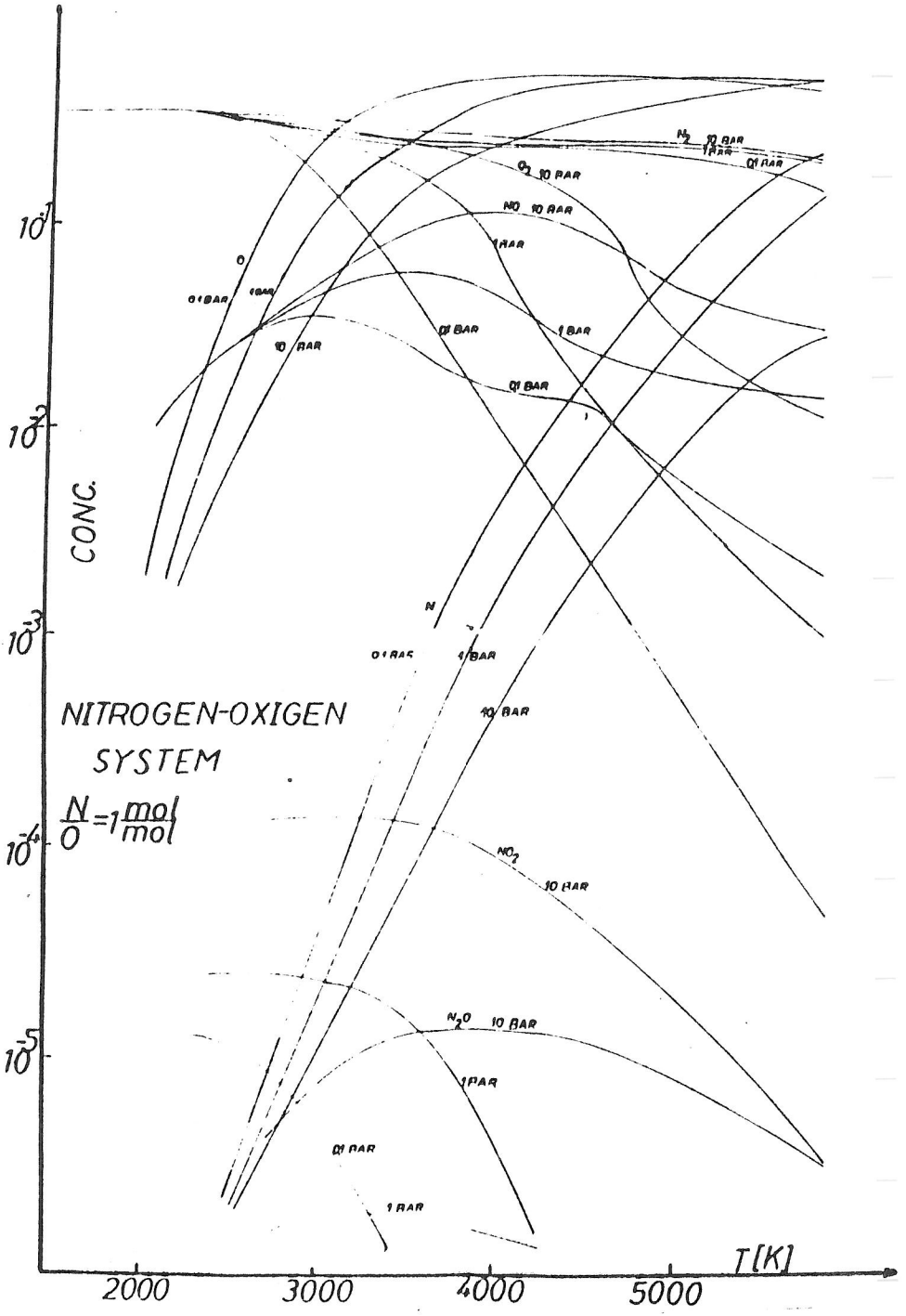
CONC.
NITROGEN-OXIGEN
SYSTEM
N/O = 1 mol/mol
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3000
4000
5000
10 BAR
1 BAR
0.1 BAR
NO
NO2
N2O
N

Figure 1.

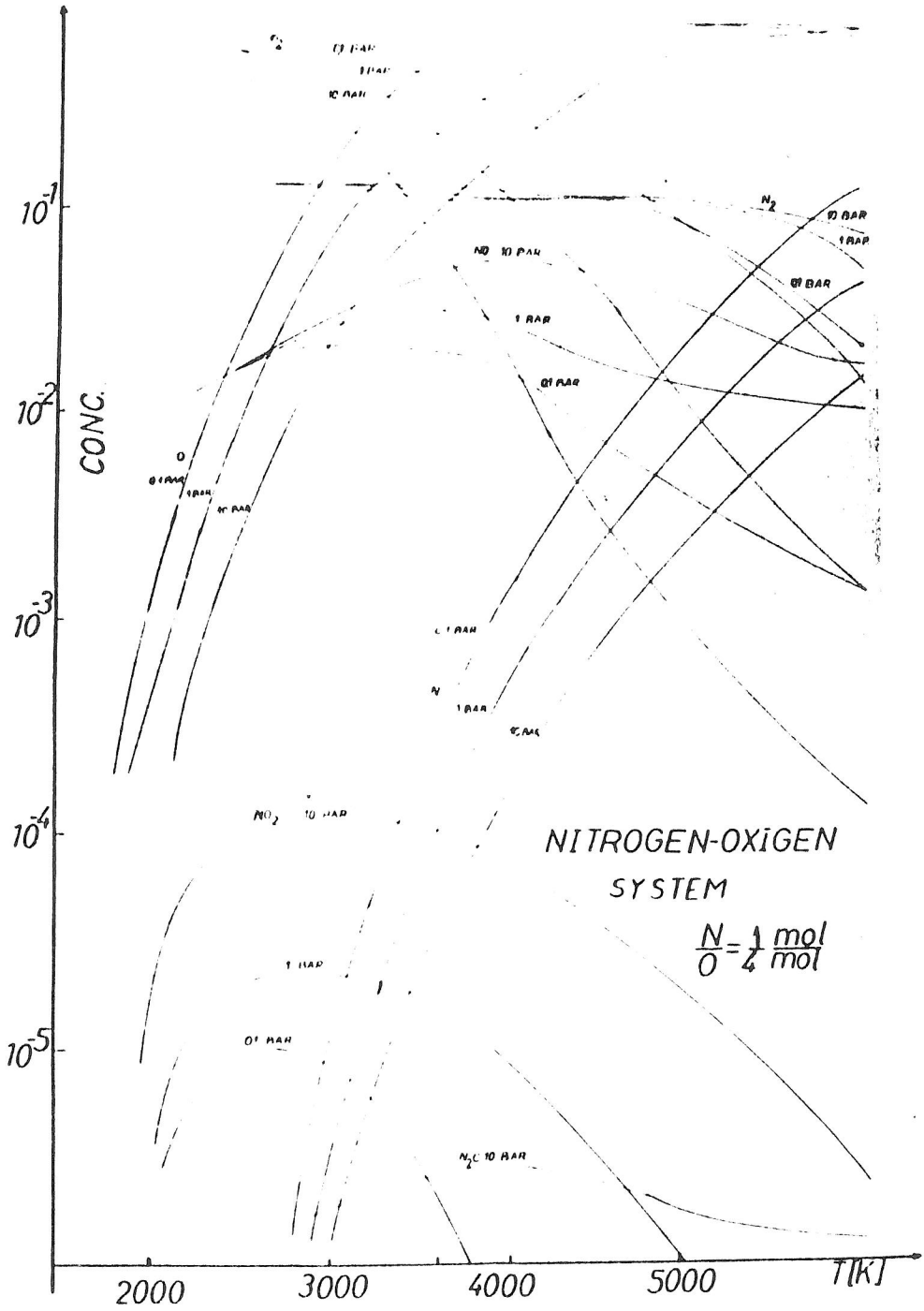
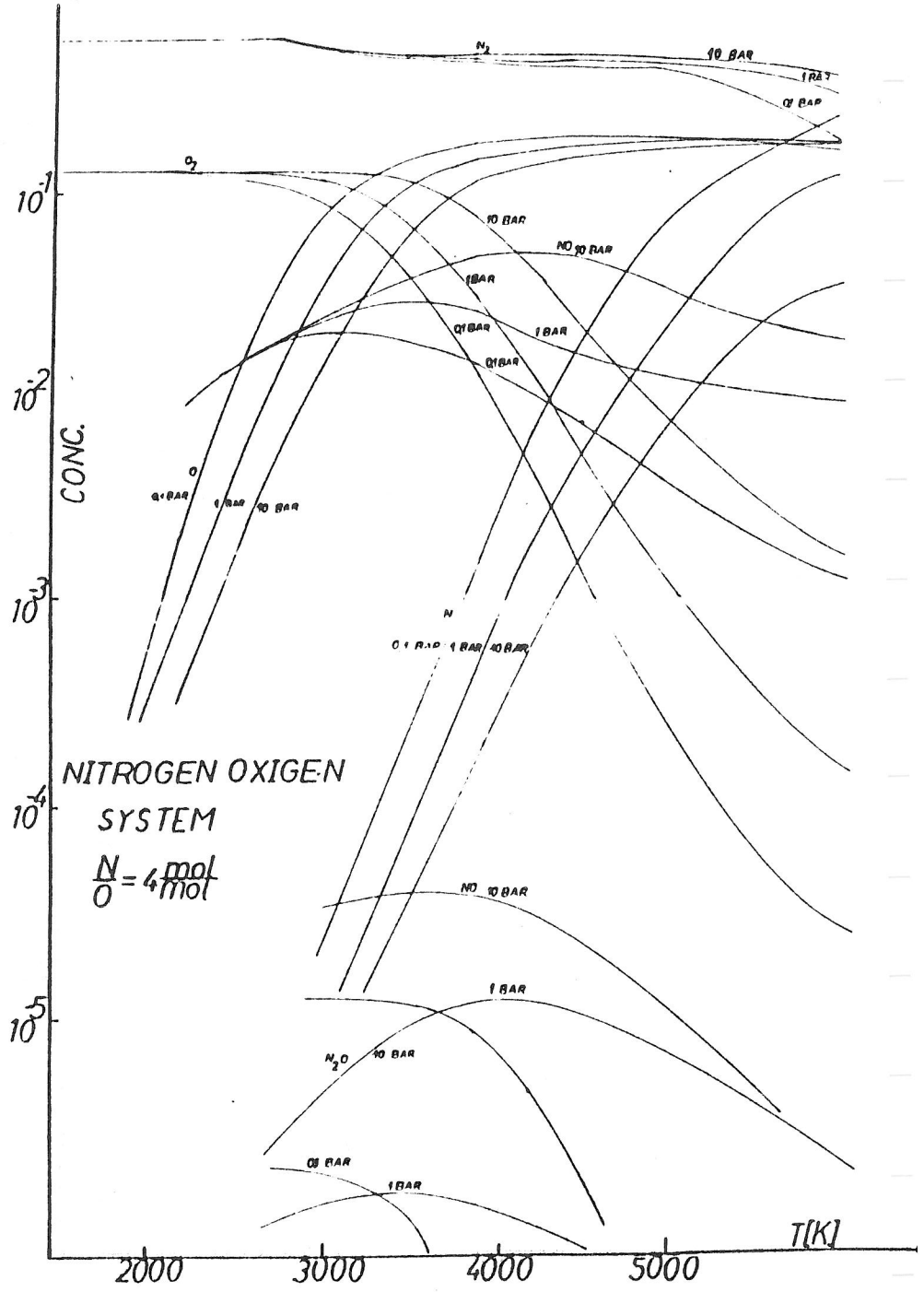

CONC.
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
2000
3000
4000
5000
T[K]
N_2
NO 10 BAR
1 BAR
0,1 BAR
O
NO_2 10 BAR
N_2O 10 BAR
NITROGEN-OXIGEN
SYSTEM
$\frac{N}{O} = \frac{1}{1} \frac{mol}{mol}$

Figure 2.


CONC.
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10^{-2}
10^{-3}
10^{-4}
10^{-5}
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O_2
10 BAR
NO 10 BAR
1BAR
0.1BAR
1 BAR
0.1BAR
O
0.1BAR
1 BAR
10 BAR
N
0.1 BAR
1 BAR
10 BAR
NITROGEN OXIGEN
SYSTEM
$\frac{N}{O} = 4\frac{mol}{mol}$
NO 10 BAR
1 BAR
N_2O
10 BAR
0.1 BAR
1BAR
2000
3000
4000
5000
T[K]

Figure 3.