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The Heterogeneous-catalytic Activation of Nitrogen and Oxygen Molecules

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Data on the activation of molecular nitrogen on metals and metal nitrides have been analysed and compared with the previously observed regular features of the activation of oxygen on oxide catalysts. The similarity in the mechanisms of the isotopic exchange of O_2 and N_2 makes it possible to examine from a single viewpoint questions relating to the prediction of catalytic action in reactions involving these molecules.
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I. INTRODUCTION

A large number of papers have been devoted to the study of the reactivity of oxygen. The results of these studies have been summarised in a number of reviews, including a recently published work[1] dealing with the catalytic activation of oxygen. The activation of nitrogen has been much less extensively studied, although this question is of equal theoretical and practical interest and importance.

In the examination of the problem of the activation of nitrogen, it is necessary first of all to take account of the exceptionally high bond energy in the N_2 molecule, which is greater than the energy of practically all other chemical bonds. This feature creates two difficulties. The first is associated with thermodynamic restrictions, since no other bonds which might be formed by nitrogen are capable of replacing the energy expended in the rupture of the original nitgrogen–nitrogen bond. As a result, the range of thermodynamically "allowed" reactions in which the nitrogen molecule may be involved is very narrow. Apart from metals, hydrogen is practically the only substance with which molecular nitrogen reacts (to give ammonia), although the course of even this reaction is complicated by the equilibrium conditions. The non-existence of a wide range of reactions is the main reason why the chemical properties of the nitrogen molecule have been insufficiently studied.

The second difficulty is kinetic in character, and is related to the need to activate such a strong bond; this can be explained in terms of the concept of energy compensation, formulated in Ref.2. In chemical transformations, bond rupture takes place in the starting materials, making it necessary to overcome a definite energy barrier E, which in the limit may correspond to the sum of the energies of the broken bonds ΣD_i. In fact, however, such high values of E are not observed, since on moving along the reaction path, some of the energy required for the rupture of the old bonds is compensated by the energy liberated in the simultaneous formation of new bonds. The extent of the compensation is the decisive factor determining the rate of a chemical reaction.

It is this phenomenon that reveals the essential feature of catalytic action. The catalyst, forming part of the activated complexes of the principal stages, increases the degree of compensation η

$$\eta = \frac{\sum D_i - E}{\sum D_i}$$

and thus lowers the activation energy of the reaction.[2] It is clear that the higher the energies of the bonds involved in the reaction, the more efficient the catalyst must be from the viewpoint of energy compensation in order to ensure a given reaction rate. Thus for example in the dissociative adsorption of a molecule A_2, the activation energy of adsorption will represent the non-compensated part of the dissociation energy $D(A_2)$:

$$E = (1 - \eta) D(A_2) ,$$

Thus for equal values of η, the activation energy of the adsorption of nitrogen will be almost twice that of oxygen, in view of the corresponding difference in the values of $D(N_2)$ and $D(O_2)$ (Table 1). This probably also explains the fact that there are only a few catalysts capable of activating nitrogen, whereas catalytic properties in reactions involving molecular oxygen are shown by a wide range of different chemical substances.[3]

The activation of molecules in a reaction is usually due to a weakening of a bond as a result of electron transfer in a particular direction. From this viewpoint, however, the positions of the orbitals in the nitrogen molecule are extremely unfavourable. The energy of the highest occupied orbital is −15.3 eV, which corresponds to the exceptionally high ionisation potential of the nitrogen molecule (1500 kJ mole^{-1}). On the other hand, the nitrogen molecule has a high first

unoccupied orbital, and electron transfer to this orbital is also energetically unfavourable, since it requires the expenditure of 352 kJ mole^{-1}.[4] It is thus difficult to bring N_2 into a reactive state either by transferring electrons to the molecule or by withdrawing electrons from it.

The values of the dissociation energies (D), ionisation potentials (I), and electron affinities (A) for the N_2 and O_2 molecules[5] are compared in Table 1.

Table 1. Characteristics of the nitrogen and oxygen molecules.

Molecule	D, kJ mole^{-1}	I, kJ mole^{-1}	A, kJ mole^{-1}
N_2	942	1500	−352
O_2	494	1163	42

The activation of nitrogen is particularly important in the synthesis of ammonia. Because of its great practical interest, the synthesis of ammonia is one of the few reactions which has attracted the close attention of scientists over a long period of time. There is hardly another reaction for which such a large number of varied catalysts has been tested.

If reference is made strictly to the activation of nitrogen, however, the synthesis of ammonia can hardly be regarded as a comprehensive test reaction. In the first place, in this case it is necessary to activate not only nitrogen but also hydrogen. In the second place, as shown below, some catalysts which are able to convert the nitrogen molecule into a reactive state are unstable in the presence of H_2, although their study is extremely important for an understanding of the general features of the activation of nitrogen.

From this viewpoint, a unique position is occupied by the method of isotopic exchange, which makes it possible to study the activation of molecules of a given kind in "pure" form, without the introduction of any additional components into the system. When applied to a diatomic gas, this method requires the study of two independent reactions taking place under conditions of adsorption equilibrium or hetero-exchange, that is the redistribution of the isotopes between the surface (s) and the gas phase:

$$^{15}N^{15}N+{}^{14}N_s\rightarrow{}^{14}N^{15}N+{}^{15}N_s$$

and homomolecular exchange, that is the redistribution of the isotopes between molecules of the gas phase:

$$^{14}N^{14}N+{}^{15}N^{15}N\rightarrow 2{}^{14}N^{15}N\ .$$

This raises the important question of whether the activation of nitrogen with respect to these simplest reactions is typical of its activation with respect to other reactions, in particular the synthesis of ammonia. The very first study by Taylor[6] in 1939 detected a qualitative relationship; it was found that the isotopic exchange and the synthesis of ammonia take palce in the same temperature range. Subsequent studies confirmed repeatedly that catalytic activities in the reactions of isotopic exchange and the synthesis of ammonia always change in the same sense.[7,8] Isotopic exchange has been little used to study the activation of nitrogen, and has been used chiefly to investigate the mechanism of the synthesis of ammonia. Thus most published studies have been carried out using iron or promoted iron catalysts, which are the most active and whose practical value far exceeds that of all other catalysts.

The fact that there have been insufficient systematic studies probably explains the absence of reviews of the isotopic exchange of nitrogen, apart from the brief summaries in Refs. 8 and 9. This is probably also related to a large extent to the low reliability of the results, particularly those obtained in the study of metals. This last feature is due primarily to the fact that metallic catalysts, both in the synthesis of ammonia and more particularly in isotopic exchange, are very sensitive to the degree of preliminary reduction and to the presence of oxygen-containing poisons.[10-12]

The catalytic properties in the isotopic exchange of N_2 have been studied not only for Fe but also for the following metals: Cr, Co, Ni, Cu,[7] Mo,[13-15] Ru,[16,17] Ta,[18] W,[6,14,19] Re,[14,20] and Os.[21] Many of the studies are qualitative in character, and give information only on the temperature range in which exchange was observed. Reliable data which might be reduced to comparable conditions have apparently been obtained only in a few comparatively recent studies and are restricted to two metals, Fe[10,17,22] and Ru.[17]

More reliable data on the isotopic exchange of N_2 have been obtained on metal nitrides. In addition to Mo_2N, studied earlier,[22] a fairly wide range of nitrides, including those of Li, Cu, the alkaline earth metals, the lanthanides, and uranium have now been studied in this reaction. Compared with metals, it is easier to obtain reliable results using nitrides, since these catalysts are not highly sensitive to the presence of oxygen-containing poisons.[23-25]

Thus a fairly large amount of experimental material has now been published, and in subsequent sections an attempt will be made to analyse this material and to compare it with the regular features previously established for the activation of O_2 on oxides.

II. THE ISOTOPIC EXCHANGE OF OXYGEN AND REACTIONS INVOLVING EXTENSIVE OXIDATION

Extensive isotopic-exchange studies of the activation of molecular oxygen on metal oxides have been carried out.[1,26-30] These studies have played a decisive role in establishing the regular features of extensive oxidation reactions. Rigorous kinetic equations have been derived for the redistribution of the isotopes in simultaneous hetero-exchange and homo-exchange,[31-33] and these have stimulated considerably the subsequent development of the method.

Depending on the number of surface oxygen atoms taking part in the exchange act, three types of exchange are possible in an M–O_2 system: 1) without the participation of surface oxygen, 2) with the participation of one surface oxygen atom, and 3) with the participation of two surface oxygen atoms. Analysis of the kinetic relationships makes it possible to calculate the rates for these types of exchange (w_1, w_2, w_3), which are related to the observed rates of hetero-exchange, w_r, and homo-exchange, w_k, as follows:[31-33]

$$w_r=w_2/2+w_3 \qquad (1)$$

$$w_k=w_1+w_2+w_3\ . \qquad (2)$$

All three types of exchange are observed on oxides under different conditions, but the case of greatest interest for catalysis corresponds to the mechanism of exchange of the third type, which is the predominant type (and often the only type) at high temperatures, that is the range in which

oxidative reactions take place. This exchange is limited by the equilibrium dissociative adsorption and desorption of oxygen, and it can be regarded as resulting from the reversible dissociation of a surface layer of the oxide. From Eqns.(1) and (2), for the third typd of exchange, $w_r = w_k$.

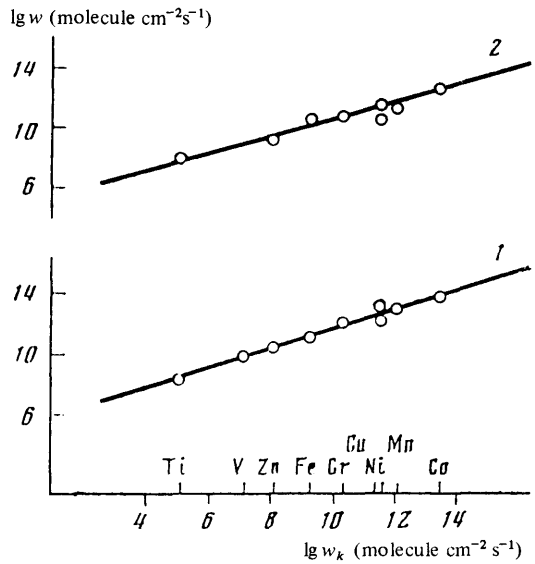


Figure 1. Comparison of the rates of the oxidation of hydrogen (*1*) and methane (*2*) with the rate of the isotopic exdhange of oxygen w_k on oxides.[34]

Comparison of the catalytic properties of a wide range of oxides in the isotopic exchange of O_2 and in extensive oxidation reactions showed changes in the same sense, illustrated in Fig.1. This is a general relationship, and is observed for the oxidation of not only hydrogen and methane, but also CO, NH_3, acetylene, benzene, and other substances.[34] Subsequent studies established the essential features of this relationship. Thus the nature of the limiting stage is the same in all cases, and, as in isotopic exchange, is related to the removal of oxygen from the catalyst surface.[35] Although the rates of the oxidation of different substances may differ considerably, the same regular feature is always observed: the activation energy of the reaction is lower, and its rate higher, the smaller the heat of adsorption of oxygen $q(O_2)$ on the catalyst surface:

$$E = E_0 + \alpha q(O_2) \,. \qquad (3)$$

Eqn.(3) shows that a certain fraction α of the heat of adsorption appears in the activation energy of extensive oxidation E. This regular behaviour is also seen in oxidative reactions on catalysts of other types, in particular metal carbides.[36]

The strength of the bond formed by oxygen with the catalyst surface also plays an important role in reactions of partial oxidation.[3,37]

The dependence of the activation energy of isotopic exchange $E(O_2)$ on $q(O_2)$ is even more direct than in the case of oxidative reactions. It can be seen from Fig.2 that for oxides characterised by the third type of exchange, the equality $E(O_2) = q(O_2)$ is observed, and this makes the isotopic-exchange method particularly effective for the study of the reactivity of surface oxygen, since it makes it possible to characterise quantitatively the heat of adsorption of O_2.

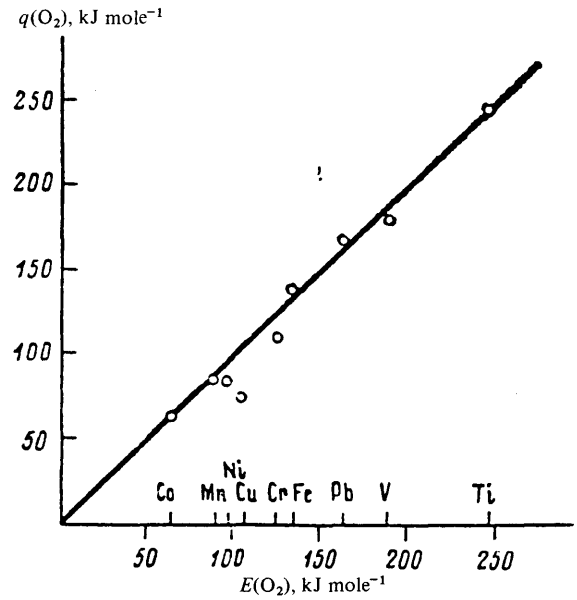


Figure 2. Relationship between the activation energy of isotopic exchange and the heat of adsorption of oxygen on metal oxides.[28]

The dependence of the rate and the pre-exponential factor for isotopic exchange on the heat of adsorption of oxygen is shown in Fig.3 (from the data in Refs.38 and 39).

The regular features observed make it possible to use data on the isotopic exchange of oxygen to predict the catalytic properties of oxides in extensive oxidation reactions and make it of considerable interest to attempt to establish a corresponding relationship between the isotopic exchange of nitrogen and the synthesis of ammonia.

III. NITRIDES AS AMMONIA SYNTHESIS CATALYSTS

Attempts to use metal nitrides as catalysts for the synthesis of ammonia were made as early as the end of the last century.[40] In the early studies, insufficient attention was paid to the phase and chemical composition of the specimens after the experiments, and the catalytic activity was usually attributed to the metal.[41] Subsequent studies showed that under the conditions of the synthesis of ammonia, some metals are converted into their nitrides, among which uranium nitride was found to be a highly active catalyst.[42] It was on uranium nitride, and also on metallic osmium, that Haber was first able to obtain high yields of ammonia which left no doubt about the promising possibilities provided by the catalytic method for the synthesis of NH_3.

Since the nineteen-sixties, there has been an increase in interest in nitrides as ammonia synthesis catalysts. This has also been related to the problem of the applicability of ideas about the mechanism of the synthesis, developed mainly in the study of iron catalysts, to catalysts of other classes. The

basic information on the catalytic properties of nitrides in the synthesis of NH_3, obtained since 1960, is given in Table 2. The data for a doubly promoted iron catalyst are also given for comparison. It can be seen that most of the nitrides studied are transition metal nitrides. The interest in nitrides of this class is related to the fact that transition metals and their compounds usually show an increased catalytic activity in redox reactions.[49,50]

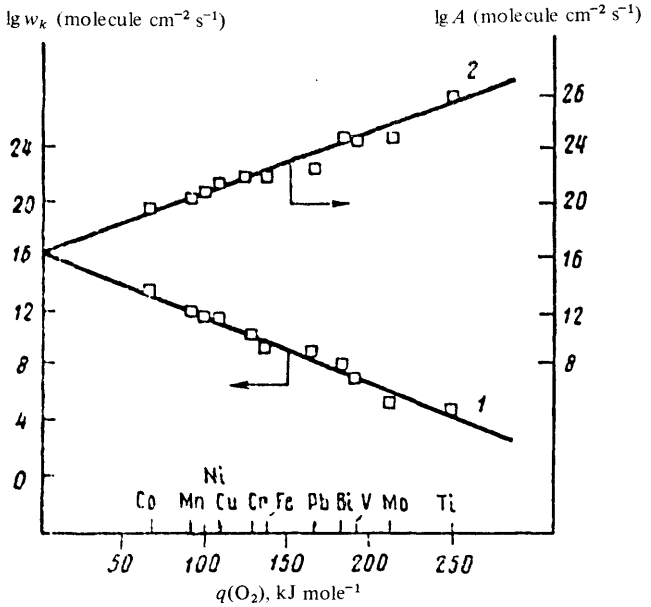


Figure 3. Dependence of the rate (*1*) and the pre-exponential factor (*2*) for the isotopic exchange of O_2 on oxides at 573 K and a pressure of 1.33 kPa on the heat of adsorption of oxygen.

The reaction of ammonia synthesis is reversible, and its rate is considerably reduced by ammonia. This makes it difficult to compare the activities of different catalysts. For a quantitative comparison it is often necessary to have data on the values of the rates at the same temperature, pressure, and NH_3 concentration at the outlet from the reaction vessel.[51] For the nitrides studied, this comparison in many cases is impossible, because of the large differences in the NH_3 concentration. Nevertheless, it is qualitatively clear that all the nitrides given in Table 2, including transition metal nitrides, with the exception of UN_x, have a low catalytic activity. The most active of them, Mo_2N, to which the largest number of studies has been devoted (including Ref. 52, where it was observed for the first time that the ammonia synthesis mechanisms on Mo_2N and on an iron catalyst are the same), is much less active than promoted iron.

A noteworthy feature is the large difference in the rates of ammonia synthesis on uranium nitride. The α-U_2N_3 specimen studied in Ref. 47 was found to be less active by several powers of ten than the UN_x specimen studied by Haber.[42] Similar differences were observed in the study of the isotopic exchange of N_2.[53] An α-U_2N_3 specimen prepared by the direct reaction of the metal with nitrogen at 972 K was also found to be 10^4–10^5 times less active than a specimen with the composition $UN_{1.70}$, prepared under milder conditions by nitriding the hydride, previously obtained from the metal. The values of the heat of adsorption of nitrogen on these specimens differ by 120 kJ mole^{-1}. This marked dependence of the adsorption and catalytic properties of uranium nitride on the chemical composition for similar crystal structures is extremely unusual, and its explanation requires further studies.

Table 2. The synthesis of ammonia on metal nitrides at 673 K.

Catalyst	s, m^2 g^{-1}	p, kPa	[NH_3], vol.%	$10^{-10}\,w$, molecule cm^{-2} s^{-1}	Refs.
BN *	—	98	—	—	[43]
Ti_2N	0.21	98	$6.6\cdot10^{-4}$	6.2	[43]
TiN	0.44	98	$2.0\cdot10^{-4}$	0.9	[43]
VN	0.32	2250	$1\cdot10^{-3}$	0.3	[44]
Cr_2N	0.1	98	$2.8\cdot10^{-3}$	5.5	[43]
CrN	0.06	98	$5.4\cdot10^{-5}$	0.2	[43]
FeN **	—	98	—	—	[45]
Ge_3N_4 **	—	98	—	—	[43]
ZrN	0.08	98	$5.3\cdot10^{-4}$	13	[43]
NbN	0.06	98	$2.0\cdot10^{-4}$	0.9	[43]
Mo_2N	13.5	20	—	0.8	[46]
Mo_2N	2.7	98	$1.2\cdot10^{-2}$	8.9	[43]
Mo_2N ***	5.0	98	$5.4\cdot10^{-2}$	150	[22]
HfN	0.06	98	$2.0\cdot10^{-4}$	8.9	[43]
UN_x	—	9600	2,5	920****	[42]
α-U_2N_3	4.1	2940	$2.5\cdot10^{-2}$	4.9	[47]
Fe *****	10.5	98	$1.85\cdot10^{-1}$	67	[48]

Symbols: s is the specific surface, p the pressure of the stoichiometric mixture, [NH_3] the ammonia concentration, and w the rate of the synthesis of ammonia.

*Inactive.

**Decomposes.

***At 748 K.

****Approximate estimate.

*****Doubly promoted iron catalyst.

The attention of research workers has recently been drawn to the so-called ionic nitrides, formed by the electropositive elements of groups I, II, and III of the periodic system.[54] These elements have an increased reactivity with respect to nitrogen. Of particular interest is lithium, which is the only element that reacts vigorously with N_2 even at room temperature to give the phase Li_3N.

Various alkaline earth metals (Ca, Sr, Ba) react with nitrogen to give not only the nitrides M_3N_2 but also other stable compounds, namely the subnitrides (M_2N) and pernitrides (M_3N_4, MN_2), which show a number of interesting properties. In the subnitrides, the bonds between the metal atoms are partly preserved, as indicated by the metallic character of their electrical conductivity,[55,56] so that these compounds are similar to the metal-like nitrides of the *d* elements. The pernitrides, on the other hand, contain an N–N bond, so that the hydrolysis of these compounds leads to the partial liberation of hydrazine instead of NH_3. The possibility of obtaining hydrazine by this method probably stimulated a number of studies of the physicochemical properties of nitrogen-containing compounds of the alkaline earth elements.[57–59]

The possible formation of various chemical compounds with nitrogen suggests that the nitrides of this class may be interesting materials from the viewpoint of the activation of molecular nitrogen. Their study has followed two directions: 1) the study of the activation of molecular

nitrogen and its state on a surface by isotopic exchange;[24,25,60-63] 2) the study of the synthesis of ammonia as a reaction for which the activation of nitrogen is the limiting stage.[25,53,61]

These studies open up the possibility of determining how general are the regular features established for oxides, molecular oxygen, and oxidative reactions, and whether they are applicable to other reactions and systems.

The subsequent analysis, in addition to ionic nitrides, will also consider catalysts based on Fe,[22] Ru,[17] and Mo_2N,[22] for which sufficiently reliable data on the isotopic exchange of N_2 and the synthesis of NH_3 are available. Among the catalysts based on Fe and Ru, the examination will be restricted to the simplest systems consisting of metallic iron and ruthenium without promoting additives.

IV. THE KINETICS AND MECHANISM OF THE ISOTOPIC EXCHANGE OF NITROGEN

The nitrides of the metals of groups I, II, and III of the periodic system are most frequently understood to be the stoichiometric compounds with the compositions M_3N, M_3N_2, and MN respectively.[54,64] Detailed studies have shown, however, that in a number of cases these compounds cannot be obtained at all.[65] Table 3 shows that the stoichiometry of the nitrides in fact does not always correspond to the composition expected on the basis of classical ideas. Moreover, some of these nitrides (strontium and barium nitrides and uranium nitride with the approximate composition $UN_{1.70}$) in general have a variable chemical composition, which changes considerably with change in the conditions.[53,60]

Table 3. Kinetic characteristics of the isotopic exchange of nitrogen (573 K, 52 Pa).

Catalyst	Crystal structure: type of lattice	Crystal structure: a, Å	$\varkappa_3$	x_{exch}	n	$E(N_2)$, kJ mole^{-1}	lg w (molecule cm^{-2} s^{-1})	lg A	Refs.
Li_3N	cubic	5.50	1.0	x_v	0.4	175	6.9	23.0	[66]
Cu_3N *	cubic	3.815	—	—	—	—	—	—	[66]
$MgN_{0.6}$**	FCO	9.9525	—	—	—	—	—	—	[25]
$CaN_{0.5}$	anti-Mn_2O_3	11.463	0.6	0.7	0.7	130	8.0	20.0	[25]
$SrN_{0.5}$	—	—	0.8	60	0.8	55	11.4	16.3	[66]
$BaN_{0.6}$	—	—	0.7	50	0.7	50	11.3	15.9	[60, 62]
LaN	NaCl	5.288	~0.1	0.5	—	—	—	—	[25]
CeN	NaCl	5.021	1.0	3.0	0.5	130	8.0	19.8	[24]
PrN	NaCl	5.151	~0.1	0.5	—	—	—	—	[61]
ErN	NaCl	4.84	~0.1	0.3	—	—	—	—	[61]
α-U_2N_3	Mn_2O_3	10.644	1.0	x_v	0.5	225	4.4	24.9	[63]
$UN_{1.70}$	CaF_2	5.30	0.9	x_v	0.5	105	10.0	19.9	[53]
Mo_2N	—	—	1.0	x_v	0.5	155	6.3	20.8	[22]
Fe	—	—	1.0	—	0.5	130	9.4	21.2	[22]
Ru	—	—	—	—	0.7	125	7.6	19.0	[17]

Symbols: x_v is the quantity of nitrogen in the catalyst specimen, A is the pre-exponential factor.
*Decomposes.
**Inactive up to 973 K.

The principal results of studies of the kinetics and mechanism of the isotopic exchange of nitrogen can be summarised (Table 3). In general, all three possible types of exchange are observed on nitrides. As in the case of oxides, however, the change by the third type of mechanism most frequently predominates (its proportion $\kappa = w_3/w_k$ is equal or close to 1). Thus exchange takes place chiefly as a result of the reversible dissociation of the surface layer of the nitride. Exceptions are the nitrides of lanthanum, praseodymium, and erbium, which have a very low catalytic activity and have not been studied in detail.

The same regular feature is also observed for metallic catalysts. The isotopic exchange on Fe takes place only by the third type of mechanism.[22] A detailed analysis of the kinetics of exchange on Ru has not been carried out, but the similarity in the rates of hetero-exchange and homo-exchange indicates that the third type of exchange also predominates in this case.[17]

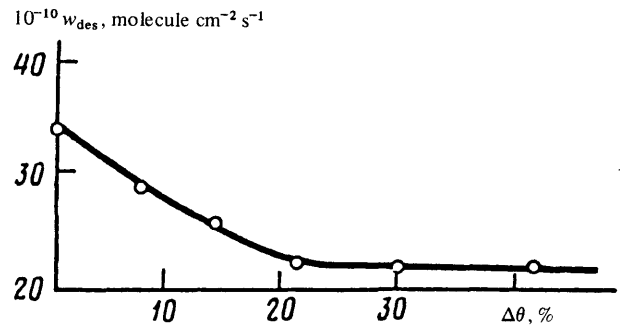


Figure 4. Dependence of the rate of desorption of nitrogen at 593 K on the quantity of nitrogen removed from the surface of $BaN_{0.62}$ (% of a monolayer).

Many nitrides, particularly those with variable chemical composition, show a high mobility of the nitrogen atoms in the crystal lattice. Thus for Sr and Ba nitrides,[60] the quantity of nitrogen taking part in exchange, x_{exch}, amounts to 50–60 surface monolayers at 550 K. This means that the "movement" of nitrogen to a depth of several tens of monolayers takes place more rapidly than exchange between the surface and the gas phase. In the case of the nitride $UN_{1.70}$[53] at this temperature, the exchange involves all the nitrogen of the solid phase ($x_{exch} = x_v$). The high rate of self-diffusion of nitrogen makes it impossible to determine whether the surface is uniform or non-uniform, since in either case the rapid movement means that the nitrogen on all parts of the surface acquires an equal probability of exchanging with the gas phase. The very fact that rapid movement takes place, however, indicates that if there is any non-uniformity, it can hardly be clearly defined. This is confirmed by experiments on the desorption of nitrogen from a barium nitride surface, the results of which are given in Fig. 4.[62] The rate of desorption shows an extremely weak dependence on the quantity of nitrogen removed, and after 20% of the nitrogen of the surface monolayer has been removed, its subsequent removal does not lead to any decrease in the rate of desorption. This is related to the fact that, as a result of the high rate of diffusion, a change in the degree of surface covering is compensated by the migration of nitrogen from the bulk of the $BaN_{0.62}$.

According to Ref. 67, self-diffusion also takes place at a high rate in the adsorbed layer of nitrogen on the surface of a promoted iron catalyst. For oxides, the mobility of oxygen is less characteristic. Among oxides, however, there are

also catalysts (MoO_3, V_2O_5) in which movement takes place throughout the entire volume, although this occurs at much higher temperatures.[28]

The kinetic order n of the exchange of nitrogen can be considered. For oxygen on oxides characterised by the third type of exchange, the order of the reaction is generally close to 0.5.[68] Table 3 shows that this regular feature is also observed for nitrogen. This pressure dependence was explained[68] by assuming that the limiting stage of the third type of exchange is the reversible dissociative adsorption of nitrogen

$$N_2+[\ ]+(\ )\rightleftarrows[N]+(N) \qquad (4)$$

to give firmly bound [N] and weakly bound (N) surface forms. These forms are present in equilibrium, as a result of rapid transformation:

$$[N]+(\ )\rightleftarrows[\ ]+(N)\,.$$

Since isotopic exchange takes place under conditions of adsorption equilibrium, the rate of exchange w_3 can be expressed as the rate of adsorption or desorption, and, in accordance with Eqn.(4), is described by the expression

$$w_3=k_a p(1-\theta_1)(1-\theta_2)=k_d\theta_1\theta_2 \qquad (5)$$

where p is the nitrogen pressure, and k_a and k_d the rate constants of adsorption and desorption respectively.

Assuming Langmuir adsorption at a high degree of covering of the surface by the firmly bound form ($\theta_1 \cong 1$) and a low degree of covering by the weakly bound form ($\theta_2 \ll 1$), it follows from Eqn.(5) that

$$w_3=\frac{k_a}{b_1^{0.5}}p^{0.5}$$

where b_1 is the adsorption coefficient for the firmly bound form. This dependence of the reaction rate on the nitrogen pressure corresponds to the experimentally observed order of the exchange reaction by the third type of mechanism.

A detailed explanation was also given in Ref.69, where it was assumed that the exchange takes place via the following stages:

$$N_2+[\ ]\rightleftarrows[N_2] \qquad (6)$$

$$[N_2]+[\ ]\rightleftarrows 2[N]\,. \qquad (7)$$

If stage (6) is slow, this also leads to a reaction of order 0.5 with the condition that $\theta[N_2] \ll 1$ and $\theta[N] \cong 1$. The assumption that molecular adsorption is the rate limiting stage can hardly be correct, however.

The higher orders observed on various nitrides, and also on metallic ruthenium, can probably be attributed to additional contributions from the mechanisms of the first and second types.

Thus there is an extensive analogy between the mechanism of the exchange of N_2 and O_2. The specific features of N_2, however, are superimposed on its exchange and a number of characteristics, revealed chiefly at low temperatures. An example is provided, in particular, by the so-called low-temperature exchange.

Most oxides, previously subjected to vacuum treatment at 673–873 K, after cooling are capable of bringing about homomolecular exchange by the first type of mechanism at a high rate. This exchange, which takes place with a very low activation energy, is due to the existence of anion vacancies on the surface and is observed at reduced temperatures down to liquid-nitrogen temperature. The mechanism of the low-temperature exchange probably involves a redistribution of the bonds in a four-atom complex consisting of two adsorbed diatomic molecules.[1] There is only a very small quantity of oxygen in the molecular form on the oxide surface, and it generally cannot be detected experimentally.

In the case of nitrides, the formation of anion vacancies as a result of the removal of nitrogen on high-temperature vacuum treatment does not lead to low-temperature exchange. It cannot be observed on metallic catalysts either.[70] This is apparently due to the much greater stability of the N_2 molecule, compared with O_2, which makes a redistribution of the bonds between nitrogen atoms in the low-temperature range impossible.

This is also probably responsible for another characteristic feature of nitrides. Some of them, namely Sr_2N and $BaN_{0.62}$, at low temperature are capable of binding a considerable quantity of nitrogen in the molecular form,[62] and the state of this nitrogen will be examined in the next section.

V. THE MOLECULAR FORM OF ADSORBED NITROGEN

Comparison of the rates of the separate stages with the rate of the catalytic process as a whole provides an effective method for studying the mechanism of reactions, and is particularly widely used in the study of oxidative processes.[71] The homomolecular exchange of nitrogen involves the following stages: adsorption; surface processes leading to a redistribution of the isotopes: and desorption.

Isotopic exchange is studied under conditions of adsorption equilibrium, when the rates of the adsorption and desorption stages are equal. The ratio between the rate of the reversible adsorption (desorption) and the rate of the surface processes is one of the factors determining the reaction mechanism. It was the comparison of the rate of desorption with the rate of isotopic exchange that made it possible to establish an interesting characteristic feature of Sr and Ba nitrides with respect to molecular nitrogen.[62]

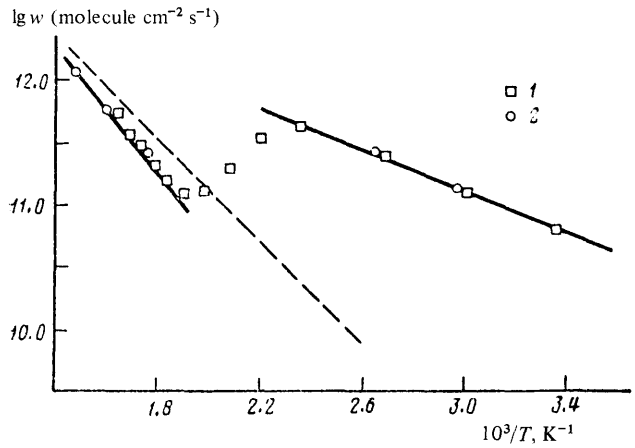


Figure 5. Temperature dependence of the rates of the desorption (*1*), hetero-exchange (*2*), and homo-exchange (broken straight line) of nitrogen on barium nitride.[62]

Fig.5 gives the temperature dependence of the rate of the desorption of nitrogen from the surface of $BaN_{0.62}$. The rate of desorption corresponds to the equilibrium degree of covering of the surface at the temperature of the experiment and a

nitrogen pressure of 52 Pa, that is it was measured for the same state of the surface as the rate of exchange. It is possible to distinguish three ranges in which this dependence has different forms: the high-temperature range (525–608 K), where the rate of desorption coincides with the rate of hetero-exchange; the low-temperature range (300–425 K), where the rate of desorption is 10–100 times the rate of homo-exchange; and the intermediate range, in which the rate increases with decrease in temperature. The explanation for this form of the dependence is that in addition to the atomic form of nitrogen, which is involved in the exchange in the high-temperature range, a weakly bound form of N_2 appears on the surface with decrease in temperature, and determines the nature of the desorption and exchange in this range.

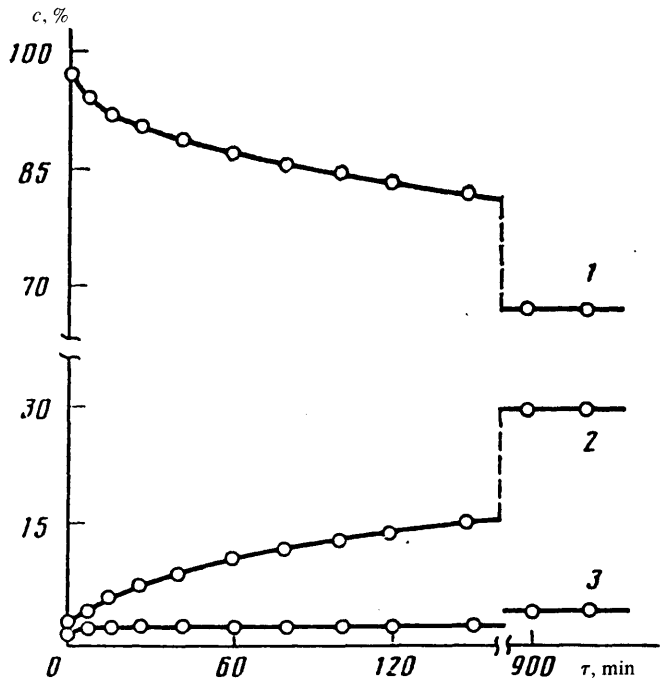


Figure 6. Dependence of the concentration c of the isotopic forms of the nitrogen molecules in the gas phase on the duration of exchange on $BaN_{0.62}$ (333 K, 52 Pa): *1*) $^{15}N^{15}N$, *2*) $^{14}N^{14}N$, *3*) $^{14}N^{15}N$.

To investigate the nature of the weakly bound form, the hetero-exchange of nitrogen on barium nitride was studied at 373 K and 333 K.[62] The kinetics of the process at 333 K are shown in Fig.6. Only a change in the concentration of the molecules $^{14}N^{14}N$ and $^{15}N^{15}N$ is observed, and there is practically no formation of mixed molecules $^{14}N^{15}N$. Thus only the reversible transfer of molecules between the surface and the gas phase takes place in the system, leading to hetero-exchange, and there is no redistribution of the atoms between the nitrogen molecules. This indicates that the low-temperature form of nitrogen is molecular in character, and also that it is inert with respect to homo-exchange.

A similar picture is observed for strontium nitride, where molecular nitrogen may be present in unexpectedly large quantities. Fig.7 gives the temperature dependence of the concentration of nitrogen in an Sr_2N specimen.[72] It can be seen that in the range 623–423 K, the concentration of nitrogen changes comparatively little, but with subsequent decrease in temperature, an abrupt change takes place, and N_2 is adsorbed in quantities corresponding to 20 surface monolayers, or ~13% of the initial concentration of nitrogen in the specimen. Experiments on the adsorption of a mixture of $^{14}N^{14}N$ and $^{15}N^{15}N$ molecules showed that all the nitrogen absorbed at a temperature below 423 K is in the molecular form and can be desorbed into the gas phase without change in the isotopic composition.

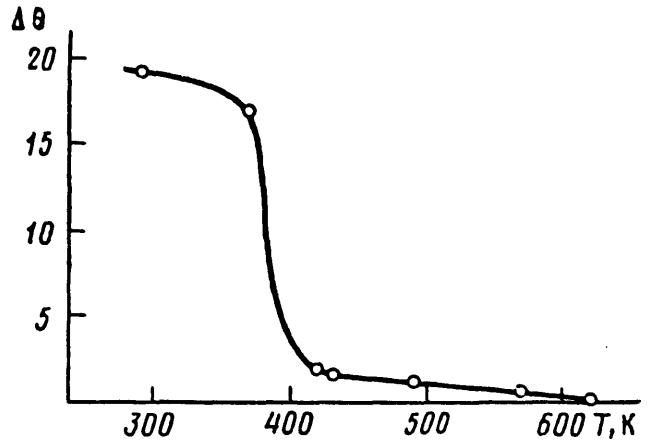


Figure 7. Change in the nitrogen concentration ($\Delta\theta$, number of monolayers) in Sr_2N with change in temperature at a pressure of 52 Pa.

This raises the question of the state of the bound nitrogen molecules. In this case it is clearly impossible to speak of physical adsorption, which is observed on many metals close to 100 K.[73] In this case there is evidently a more extensive chemical interaction. It may be assumed that in the general case, nitrogen passes through all oxidation states from 0 to −3 in the course of the reaction. If it is assumed that two-electron transitions takes place, intermediate compounds corresponding to the formal valence states N_2^0, N_2^{2-}, N_2^{4-}, and N^{3-} should be formed.[72] The nitrogen molecule shows an important feature which distinguishes it from other unsaturated compounds: in the rupture of the triple bond N ≡ N, the greater part of the energy is used up in the rupture of the first bond (527 kJ mole^{-1}); 260 kJ mole^{-1} is used up in the rupture of the second bond, and only 159 kJ mole^{-1} in the rupture of the third. This makes preferable the many-electron reduction of N_2 with the transfer of four or six electrons to the nitrogen molecule.[75] Thus the reaction with metals usually finishes with the complete rupture of the N ≡ N bond and the formation of nitrides, which can be regarded as derivatives of ammonia.

In some cases, however, mainly for alkaline earth metal nitrides, the reaction with nitrogen may lead to the formation of pernitrides.[76] The unusual features of these compounds is that a certain proportion of the nitrogen present preserves a nitrogen–nitrogen bond, so that hydrolysis gives not only NH_3 but also hydrazine, indicating according to the authors of Ref.74, that pernitrides contain nitrogen as the ion N_2^{4-}.

Interesting results have been obtained in extensive studies to find methods for the low-temperature activation of nitrogen in metal complexes in solution.[75,77] Contrary to existing ideas, it was found that complexes containing N_2 as ligand in the coordination sphere of the metal are encountered extremely widely. Moreover, it was possible to obtain catalytic systems based on Ti[77] and Mo,[75] capable of bringing about the catalytic fixation of nitrogen.

In many cases, however, the molecular nitrogen in the coordination compounds is in the inactive state, and attempts to involve it in any chemical reaction lead to the liberation of free N_2. It was of interest to determine whether the nitrogen absorbed in molecular form by strontium and barium nitrides is reactive. It was noted above that this form is not active in homomolecular exchange. It is also incapable of reacting with hydrogen. The introduction of H_2 into the system leads to the absorption of hydrogen and the displacement of nitrogen in the molecular form into the gas phase without the formation of even traces of NH_3.

Hydrolysis is widely used to study the reactivity of nitrogen in coordination compounds. This reaction has been used to test two series of strontium nitride specimens: the specimens of series *A*, containing molecular nitrogen in quantities corresponding to ~20 monolayers, and the specimens of series *B*, obtained from series *A* after desorption of the molecular form.[72] The hydrolysis was carried out using an oxidising agent (ammonium vanadate), which is incapable of reacting with NH_3 but which readily reacts with stronger reducing agents, for example hydrazine.

Table 4. Hydrolysis of strontium nitride.

Specimens	10^6 [N_2], mole g^{-1}	10^6 W_O, mole g^{-1}	10^6 W_B, mole g^{-1}	
			N_2H_4	N_2H_2
Series *A*	330	680	170	340
Series *B*	~0	20	6	12

Symbols: [N_2] is the concentration of the molecular form of nitrogen in the specimen; W_O the consumption of the oxidising agent; and W_B the concentration of the reducing agent in the hydrogenolysis products, calculated as hydrazine and di-imide.

The averaged results of the experiments are given in Table 4, and show that the consumption of the oxidising agent is determined practically completely by the presence of molecular nitrogen in the specimens. If it is assumed that the direct product of the hydrolysis is hydrazine, the calculations show that the quantity of N_2H_4 liberated corresponds to only half of the nitrogen combined in the molecular form. This gives grounds for assuming that the hydrogenolysis is undergone by a derivative of not hydrazine but di-imide, in which a double bond N=N is preserved. The protonation of this compound should give N_2H_2, whose reducing equivalent is half that of N_2H_4. With this assumption, the observed consumption of the oxidising agent corresponds satisfactorily to the concentration of molecular nitrogen in the specimens.

Thus the molecular form of nitrogen detected on strontium and barium nitrides, although insufficiently activated to react with H_2 or to take part in homomolecular exchange, is capable of being converted into the combined state as a result of the hydrolysis of the nitrides. It may be assumed that the nitrogen in this form is present as the N_2^{2-} group, analogous to the peroxide group O_2^{2-} in oxygen-containing compounds. Some of these oxygen-containing compounds also decompose with the liberation of molecular oxygen without rupture of the peroxide bond.[78]

The possible formation of derivatives of di-imide in the reaction of metal complexes with nitrogen was discussed in Ref. 75.

VI. THE HEAT OF ADSORPTION OF NITROGEN AND THE ACTIVATION ENERGY OF THE ISOTOPIC EXCHANGE OF N_2

In the isotopic exchange of oxygen on oxides, taking place by the third type of mechanism, the magnitude of the activation energy coincides satisfactorily with the heat of adsorption of oxygen.[28] Since the isotopic exchange of nitrogen also takes place by the third type of mechanism, it was of interest to determine whether the same regular feature applies to nitrogen.

The heats of adsorption of nitrogen on nitrides have been measured by two methods:[79] the calorimetric method and the kinetic isotopic method proposed in Ref. 63. The essential features of the last method are as follows. In the measurement of the rates of adsorption w_{ads} and desorption w_{des}, the observed change in pressure in the gas phase is determined by the difference between w_{ads} and w_{des}. Thus the rates are usually measured either under conditions of adsorption equilibrium, when $w_{ads} = w_{des}$ (the isotopic exchange method), or, on the contrary, at a distance from equilibrium, when one of these quantities is negligible compared with the other. In a system in which exchange is taking place by the third type of mechanism, these two processes can be distinguished using isotopes, by arranging the experiment in such a way that at the initial moment of time the adsorption flux is represented by one isotope, and the desorption flux by the other. In this case the adsorption and desorption can be measured independently while they take place simultaneously both under equilibrium conditions and at a certain distance from equilibrium. By changing the temperature for a fixed degree of covering of the surface, it is possible to determine the activation energy of adsorption and desorption, and hence the heat, which is denoted q_{kin} to distinguish it from the quantity q_{cal} determined calorimetrically. Table 5 shows that the two methods give similar results.[79]

Table 5. The heat of adsorption and the activation energy of the isotopic exchange of nitrogen.[79]

Nitride	Sr_2N	$BaN_{0.62}$	CeN	$UN_{1.70}$	α-U_2N_3
q_{cal}, kJ $mole^{-1}$	60	115	125	170	240
q_{kin}, kJ $mole^{-1}$	60	90—140	—	—	225
$E(N_2)$, kJ $mole^{-1}$	55	50	130	105	225

Comparison of the activation energy of isotopic exchange $E(N_2)$ with the heat of adsorption of nitrogen (Table 5) showed that the values agree satisfactorily for strontium and cerium nitrides and α-U_2N_3. $BaN_{0.62}$ and $UN_{1.70}$, however, show an appreciable discrepancy, which was attributed[79] to the partial binding of nitrogen by bulk layers of the nitride.

Barium nitride and the uranium nitride $UN_{1.70}$ can readily undergo a change in chemical composition with change in the conditions. Since in the measurement of the heat of adsorption, a pressure higher than the equilibrium pressure is established at the initial moment, it is natural to expect that this may lead not only to the adsorption of nitrogen on the surface but also to its transfer from the surface into the bulk, which corresponds to two processes:

$$N_2 + 2[\ ]_s \rightarrow 2[N]_s + q_s \quad (8)$$

$$N_2 + 2[\ ]_v \rightarrow 2[N]_v + q_v \quad (9)$$

Here, $[\ ]_S$ and $[\ ]_V$ represent unoccupied positions on the surface and in the volume respectively. In this case the measured heat is

$$q_{meas} = \frac{n_s}{n} q_s + \frac{n_v}{n} q_v$$

where n_S and n_V are the numbers of molecules transferred from the gas phase to the surface and to the volume respectively; $n = n_S + n_V$. When $q_V > q_S$, this leads to a value of q_{meas} which is higher than the heat of adsorption q_S. Similarly, the redistribution of nitrogen between the surface and the volume also leads to distortion of the true value of the heat of adsorption when the kinetic method is used.

In some cases, the process of volume binding according to Eqn.(9) may predominate, as is probably the case for $BaN_{0.62}$ and $UN_{1.70}$. In the equilibrium diagram, uranium nitride $UN_{1.70}$ lies in the range of compounds of variable composition bounded by the phases U_2N_3 and UN_2. The heat of adsorption of nitrogen on this specimen (170 kJ mole^{-1}) is close to the heat of the reaction

$$UN_{1.51} + 0.09\,N_2 \rightarrow UN_{1.69}$$

which amounts to 185 kJ mole^{-1}.[80] The heat of adsorption of nitrogen on barium nitride (115 kJ mole^{-1}) also does not differ greatly from the heat of the process

$$6Ba_3N + N_2 \rightarrow 4Ba_3N_2$$

which equals 140 kJ mole^{-1}.[55]

The influence of bulk processes has also been noted in the measurement of the heats of adsorption of oxygen on various oxides.[81] Since oxides have an extremely stable chemical composition and a comparatively low oxygen mobility, however, this does not lead to significant discrepancies between the values of $E(O_2)$ and $q(O_2)$. Distortion of the values obtained for the heat of adsorption may also take place in the case of metallic catalysts, because of solution processes in the layers of metal next to the surface. It must therefore be borne in mind that the measured value of the heat of adsorption may not always characterise the bond energy of the surface species taking part in the catalytic process.

Unlike the heat of adsorption, the activation energy of isotopic exchange is measured under conditions of adsorption equilibrium. In this case, therefore, there are no secondary processes leading to the values of q which are too high. Thus Table 5 shows that the discrepancy (where it exists) is observed only in the direction of an increase in q above E. The activation energy of isotopic exchange apparently corresponds to the true value of the heat of adsorption. For systems with a labile chemical composition, isotopic exchange probably provides the most reliable method for determining it.

VII. THE DEPENDENCE OF THE CATALYTIC ACTIVITY IN ISOTOPIC EXCHANGE REACTIONS ON THE HEATS OF ADSORPTION OF NITROGEN AND OXYGEN

Table 3 shows that the rate of the isotopic exchange of nitrogen on different catalysts differs by many powers of ten. It cannot be related to any physicochemical characteristics of the catalysts. As in the case of oxides, it may be assumed that the bond energy of the surface nitrogen should be of the greatest interest from this viewpoint. Thus Fig.8, constructed from the data in Table 3, shows a distinct relationship between the catalytic activity and the heat of adsorption $q(N_2)$, for which the value of $E(N_2)$ was used.

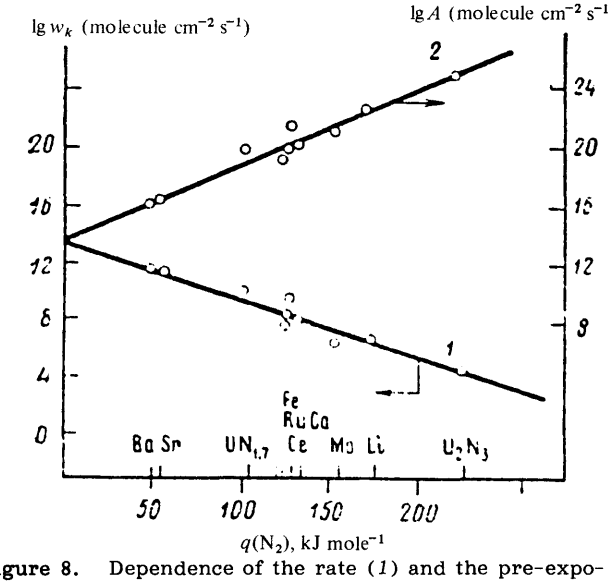


Figure 8. Dependence of the rate (*1*) and the pre-exponential factor (*2*) of the isotopic exchange of N_2 on nitrides and metallic iron and ruthenium (573 K, 52 Pa) on the heat of adsorption.

The highest activity in the isotopic exchange of nitrogen is shown by strontium and barium nitrides, which have the minimum heat of adsorption, equal to ~50 kJ mole^{-1}. The rate of exchange of nitrogen on these catalysts is one hundred times the rate of exchange on Fe. The lowest activity is shown by α-U_2N_3, on which the heat of adsorption of nitrogen is 225 kJ mole^{-1}. Overall, an increase in the heat of adsorption by 175 kJ mole^{-1} in the series of nitrides and metals examined leads to a decrease in the rate of exchange by a factor of 10^7. There is a simultaneous increase in the pre-exponential factor, corresponding to the existence of a compensation effect.

The heat of adsorption of nitrogen on magnesium nitride is probably even higher than that on α-U_2N_3, and this specimen does not show appreciable activity up to 973 K.[25]

A similar relationship is observed for the isotopic exchange of oxygen on oxides, as can be seen by comparing Fig.8 and Fig.3. Moreover, this similarity is not only qualitative, but also quantitative, as can be clearly seen from Fig.9, which gives simultaneously the dependence of the isotopic exchange of nitrogen and the isotopic exchange of oxygen, carried out

under identical conditions, on the corresponding values of the heats of adsorption. The fact that the relationships coincide is extremely unexpected, and indicates that the chemical nature of the reacting molecules and the chemical nature of the catalysts are important primarily in the way in which they influence the heat of reaction. If the heats are equal, the rates of exchange are approximately the same, irrespective of whether the system contains molecular nitrogen or oxygen.

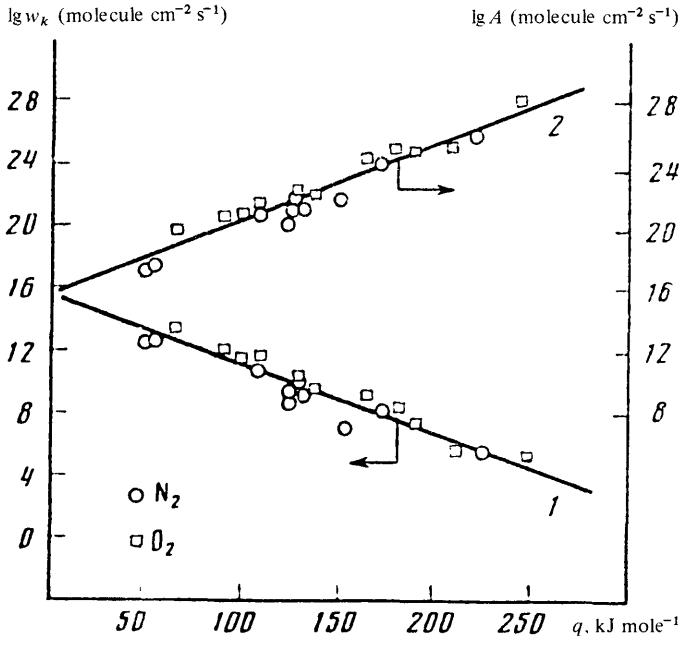


Figure 9. Dependence of the rate (*1*) and the pre-exponential factor (*2*) of the isotopic exchange of nitrogen and oxygen (573 K, 1.33 kPa) on the heat of adsorption.

The similarity in the entropy factors is probably because the entropies of the free molecules of nitrogen and oxygen are similar and the exchange mechanisms are the same. It is more difficult to understand why the values of the activation energy of isotopic exchange of nitrogen and oxygen are equal with identical values of q, since in the case of N_2 the reaction at each stage involves bonds whose energy is 450 kJ mole^{-1} greater than for O_2. The only explanation for this fact is probably that in the dissociative adsorption of both N_2 and O_2 there is almost complete compensation of the energy required for rupture of the bonds in these molecules, by the energy of the reaction of the resulting atoms with the surface. In other words, the heat of adsorption makes the principal contribution to the energy barrier of the equilibrium adsorption–desorption process.[82]

There are a number of facts which show an analogy between the observed regularity and the energy characteristics of more complex catalytic reactions. Thus in Ref. 83 it is the heat of the process that is used to characterise the reactivity of the substances being oxidised, and its use makes it possible to describe satisfactorily the regular features of the complete oxidation.

Of considerable interest is the numerical value of the coefficient α in Eqn. (3), which shows the fraction of the heat of adsorption of oxygen $q(O_2)$ appearing in the activation energy of the oxidative reaction. Since in different reactions the removal of oxygen takes place in different activated complexes, the coefficient α should apparently change with variation of the chemical character of the reacting molecules. Analysis of a large number of oxidative reactions has shown, however, that the value of α remains approximately constant and equal to ~0.5 in all cases.[83] This coefficient is also equal to ~0.5 for a number of other reactions, including the reaction of ammonia synthesis.[85] The coefficient α has also been found to be constant in the isotopic exchange of nitrogen and oxygen, in spite of the difference in the chemical character of the O_2 and N_2 molecules, the only difference being that the coefficient α in both cases is equal to 1, since the quantities E and q are equal.

Finally, to return to the fact that the relationships for nitrogen and oxygen in Fig. 9 are identical, it should be noted that the rate of exchange, in addition to the heat of adsorption, is also determined by the proportion of the active surface. Thus if the surfaces of the catalysts being studied are biographically non-uniform, the non-uniformity cannot be strongly defined. Otherwise, it would be necessary to assume the existence of some universal law of distribution of the active centres of the surface with respect to energy for all the catalysts which have been compared.

VIII. ESTIMATION OF THE RATE OF THE SYNTHESIS OF AMMONIA FROM DATA ON THE ISOTOPIC EXCHANGE OF N_2

The present section considers first those predictions about the synthesis of ammonia that can be made using data on the exchange of nitrogen. It has been noted that in the limiting stages of oxidation reactions, the removal of oxygen from a catalyst surface takes place via different activated complexes, which, in addition to oxygen, also contain various fragments of the substance being oxidised. Naturally, these complexes are not formed in isotopic exchange. Thus from the rate of exchange of O_2 it is possible to predict only the relative change in the rates of oxidation in a given series of catalysts. The synthesis of ammonia under conditions not too far removed from equilibrium, however, takes place by the Temkin–Pyzhov mechanism, whose limiting stage is the adsorption of nitrogen, that is a stage which is present in "pure form" in isotopic exchange. In this case, exchange data make it possible to calculate not only the relative values but also the absolute values of the rates of synthesis.[22,86]

The equation for calculating the rate of the synthesis of ammonia has the following form:[22]

$$w_c = w_k(p/p^* - 1) \qquad (10)$$

where w_C is the rate of the synthesis of ammonia, measured at a partial pressure of nitrogen in the reaction mixture p; p^* is the volatility of the nitrogen adsorbed on the catalyst under the conditions of the synthesis reaction; and w_k the rate of the isotopic exchange of N_2 at a nitrogen pressure equal to p^*. The value of p^* is calculated from the equation

$$p^* = \frac{1}{K_p}\frac{p^2(NH_3)}{p^3(H_2)}$$

where $p(NH_3)$ and $p(H_2)$ are the partial pressures of ammonia and hydrogen respectively in the reaction mixture, and K_p the equilibrium constant of the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Thus Eqn. (10) shows that the activity of the catalysts in the

synthesis of ammonia should be proportional to their activity in isotopic exchange, measured under identical conditions.

Some data on the activity of nitrides in the synthesis of NH_3 [25,53,61,66] are given in Table 6, which also gives for comparison the data for the promoted iron catalyst SA-1.[61] It can be seen that Mg nitride, which is inert in the isotopic exchange of nitrogen, is also inactive in the synthesis of ammonia. The lanthanides, except for cerium, have a low activity in exchange, and show appreciable activity in the synthesis only in the temperature range close to 800 K, whereas CeN and $UN_{1.70}$ are active in both reactions. Even a qualitative examination shows, however, that in most cases, particularly on the nitrides of Sr and Ba, which are of greatest interest (the expected rate of synthesis should be 100–1000 times that on Fe), the experimentally measured rate is found to be much lower than that calculated from data on the isotopic exchange of nitrogen using Eqn.(10), or even close to zero.

Table 6. The activity of nitrides in the synthesis of ammonia at a pressure of 98 kPa.

Nitride	T, K	$[NH_3]$, mole %	lg w (molecule $cm^{-2}s^{-1}$)		Phase composition after the synthesis
			expt	calc	
Cu_3N	423	2.2	13.0	0.0	metal
Li_3N	673	0.03	11.3	12.0	hydride
$MgN_{0.6}$*	873	—	—	—	nitride
$CaN_{0.9}$	773	0.08	12.3	13.3	mixed phase
$SrN_{0.5}$*	873	—	—	—	mixed phase
$BaN_{0.62}$	573	0.32	13.8	14.5	hydride
LaN	773	0.054	11.2	—	nitride
CeN	673	0.26	11.4	11.5	nitride
PrN	773	0.075	10.8	—	nitride
NdN	773	0.054	10.3	—	nitride
TbN	823	0.025	10.3	—	nitride
HoN	773	0.030	10.8	—	nitride
$UN_{1.70}$	623	0.24	11.6	12.9	nitride
CA-1	673	0.27	11.8	—	

*Inactive

The discrepancy may be due to two factors: either the reaction does not take place by the Temkin–Pyzhov mechanism, so that the assumptions on which the calculation is based are incorrect, or side reactions take place under the synthesis conditions, leading to a decrease in the rate of the catalytic reaction. Subsequent studies have shown[66] that the factor responsible lies not in a change in the mechanism but in the physicochemical characteristics of the nitrides, which are examined below.

IX. THE STABILITY OF NITRIDES. THERMODYNAMIC ESTIMATIONS

The study of the synthesis of ammonia has revealed extremely significant differences in the behaviour of nitrides. Some nitrides, including those of the lanthanides and uranium, have been found to be stable in a nitrogen–hydrogen mixture;[66] in this case the formation of ammonia is the result of a catalytic process. X-Ray diffraction data have shown that the phase composition of the original catalysts remains unchanged after the reaction (Table 6). The nitrides of another group, namely those of lithium and the alkaline earth metals, are unstable and undergo phase transformations during testing. In this case, the formation of ammonia is also observed under the conditions of the experiment, but this results not from a catalytic process but from a chemical reaction between the nitride and the hydrogen of the gas phase. The formation of ammonia stops completely after the nitride has been converted into the hydride.

The ability to form hydrides is well known for the electropositive metals of groups I, II, and III of the periodic system.[87] To understand the characteristic features of the behaviour of nitrides and to determine the possible range of their stable operation, it is appropriate to examine the thermodynamic properties from the viewpoint of the stability of the nitrides in a nitrogen–hydrogen mixture.

It will be assumed that the original system contains either a nitride phase, for example M_3N, or the corresponding hydride phase MH. It will be assumed that the nitrogen pressure is 25 kPa, and the hydrogen pressure 75 kPa. To estimate the stability of a given phase, it is necessary to determine the free energy of the reaction:

$$6MH + N_2 \rightarrow 2M_3N + 3H_2 \qquad (11)$$

Since the change in the heat capacity in this reaction is slight, it will be assumed that

$$\Delta G^0_T = \Delta H^0_{298} - T\Delta S^0_{298}$$

In addition to reaction (11), the formation of NH_3 is also possible in the system being considered. Since the free energy of formation of ammonia is extremely small, however, this possibility will not be taken into account, since the calculations are only approximate.

Table 7. Stability of nitrides in a nitrogen–hydrogen mixture.

Compound	$-\Delta H^0_{f,298}$, kJ $mole^{-1}$	$-\Delta S^0_f$, J $mole^{-1}$ K^{-1}	Stability range
Li_3N	197	79	>600 K
LiH	91	69	—
Mg_3N_2	462	202	unlimited
MgH_2	75	127	—
Ca_3N_2	440	210	>700 K
CaH_2	189	131	—
Sr_3N_2	391	225	>600 K
SrH_2	177	158	—
Ba_3N_2	364	243	>800 K
BaH_2	179	156	—
CeN	327	107	unlimited
CeH_2	253	181	—
U_2N_3	374	334	unlimited
UH_3	117	186	—

Table 7 gives the original thermodynamic data, taken from Ref.87–91, and the results of an estimation by the present authors of the temperature range of stability of the nitrides. In agreement with experimental observations of the phase composition of the specimens after the experiments (Table 6), the calculation showed that the nitrides of the lanthanides and uranium are stable throughout the entire temperature range. According to the calculation, the nitrides of lithium and the alkaline earth metals should be stable only at temperatures above 600–800 K, and that their hydrides are stable at lower temperatures. In fact, the situation for the nitrides of lithium and the alkaline earth metals is found to be even less favourable. Thus in the presence of H_2 these systems can also form mixed compounds containing nitrogen and hydrogen (amides and imides), whose existence cannot be taken into account, since their thermodynamic properties are unknown. As a result of the existence of these compounds, the range of stability of the nitrides of the metals of groups I and II is displaced to much higher temperatures, which are of no interest for catalysis, because of the low equilibrium yields of NH_3.

The catalytic activity of the actual mixed phases is low. Thus in the presence of the mixed phase formed by strontium, the formation of ammonia is not observed up to 873 K.[92]

In the case of the unstable nitrides, hydrogen also has a strong and irreversible deactivating influence on the isotopic exchange of N_2.[25]

An interesting representative of the group of unstable nitrides is barium nitride, for which the conversion into the hydride takes place particularly readily, leading to a high rate of formation of ammonia in the low-temperature range (470–570 K). The reaction of barium nitride with H_2 takes place in two stages.[92] In the first stage, after the introduction of the nitrogen–hydrogen mixture, vigorous absorption of H_2 takes place without the liberation of ammonia, and is complete with the formation of the compound $BaN_{0.6}H_{1.8}$. This overall composition probably corresponds not to any individual substance but to a mixture of nitrogen- and hydrogen-containing compounds.

In the second stage, hydrogenation takes place with the liberation of NH_3. The total quantity of ammonia formed corresponds closely to the initial concentration of nitrogen in the nitride, and is independent of whether the nitrogen–hydrogen mixture of pure H_2 is passed over the specimen. This indicates that the nitrogen of the gas phase is not involved in the catalysis process, and that NH_3 is formed only as a result of the hydrogenation of the nitride.

Barium hydride can be reconverted into the nitride by heating in an atmosphere of nitrogen, to give a cyclic process for preparing ammonia.[92]

Unlike other metals, copper cannot form hydrides. The nitride Cu_3N is thermodynamically unstable ($\Delta H^0_{f\,298} = 75$ kJ mole^{-1}), which, like the nitrides of Fe[45] and Ge,[43] readily decomposes in the presence of hydrogen to give metallic copper and an equivalent quantity of ammonia.

X. COMPARISON OF THE EXPERIMENTAL AND CALCULATED RATES OF SYNTHESIS OF AMMONIA

The calculation of the rate of synthesis of NH_3 from isotopic exchange data is obviously meaningful only for stable nitrides. Table 6 shows that the highest activity corresponds to uranium nitride, on which the rate of ammonia synthesis is close to the rate of the same process on an iron catalyst. A high activity is also shown by cerium nitride, and this has stimulated the examination of a fairly large number of lanthanides in order to find in this series other catalysts capable of bringing about the synthesis of ammonia at a high rate. However, in this reaction as in isotopic exchange, the activity of all the other nitrides was found to be lower by several powers of ten than that of CeN.

This result is extremely unexpected, since the lanthanide nitrides have the same crystal structure and similar thermodynamic and chemical properties. The difference must be attributed to differences in the electrical characteristics, since CeN has the highest electrical conductivity of nitrides in this series.[54] An interesting feature is that a similar regularity is also observed in the series of lanthanide oxides, where the maximum electrical conductivity and the maximum activity in the oxidation of hydrogen correspond to the element next to cerium, namely praseodymium.[30]

The calculated and experimental rates of ammonia synthesis are compared in Fig.10, taken from Ref.53. The broken straight line corresponds to the equality $w_{calc} = w_{expt}$. (It should be noted that Fig.10 cannot be used to reach conclusions about the relative activity of catalysts, since the data for different catalysts relate to different conditions.) It can be seen that for the nitrides of cerium and molybdenum and for metallic iron, there is satisfactory agreement between the calculated and measured rates, whereas for uranium nitride a considerable discrepancy is observed, and w_{expt} is smaller than w_{calc} by a factor of more than 10.

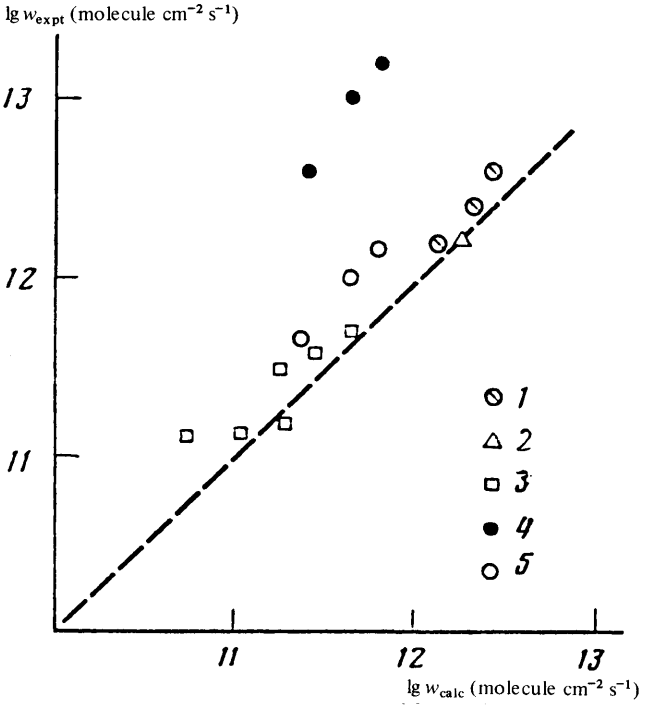


Figure 10. Comparison of the experimental and calculated rates of ammonia synthesis on Fe (*1*), Mo_2N (*2*), CeN (*3*) and on $UN_{1.70}$ without allowance (*4*) and with allowance (*5*) for the influence of H_2.

It is natural to assume that the fact that the rate of ammonia synthesis is lower than the calculated value in this case may be due to the deactivating influence of hydrogen, although the presence of hydrogen cannot bring about phase transformations in uranium nitride. This was confirmed in a study of the influence of H_2 on the isotopic exchange of nitrogen.[53] The introduction of hydrogen into the system leads to its appreciable absorption and is accompanied by a decrease in the rate of the isotopic exchange of N_2. The retardation by hydrogen in this case is reversible, and when the exchange is subsequently carried out in pure nitrogen, the activity is completely restored. The theoretical calculation of the rate of ammonia synthesis on uranium nitride with allowance for the influence of hydrogen on the activation of N_2 [53] leads to satisfactory agreement with experiment (Fig.10).

Hydrogen has no deactivating action and has no influence on the isotopic exchange of nitrogen on a cerium nitride catalyst.[24]

Thus for nitrides, as for metallic catalysts, where the deactivating action of hydrogen has no significant influence or can be taken into account, the isotopic exchange of N_2

provides an adequate characteristic of the activation of molecular nitrogen and its ability to take part in the ammonia synthesis reaction.

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The results examined in the present review show the general character of the mechanism and regular features of the catalytic action of oxides in the activation of molecular oxygen and extensive oxidation reactions on the one hand, and the catalytic action of metals and nitrides in the activation of molecular nitrogen and the synthesis of ammonia on the other. This makes it possible to approach from a single viewpoint the problem of selecting catalysts for the range of reactions being considered.

It is not excluded that this general character may be even wider and may be observed in other systems, where the activation of a diatomic molecule takes place by dissociative adsorption on a catalyst surface. It is therefore of interest to carry out comparative studies of a number of analogous systems, and in particular to compare the catalytic action of hydrides in the isotopic exchange of H_2 and hydrogenation, and of chlorides in the isotopic exchange of Cl_2 and chlorination.

It may also be noted that the activation of nitrogen, that is a molecule which is often placed in a unique position because of its inertness, is in fact not an exceptional phenomenon. It obeys the same regular features as the activation of molecular oxygen.

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