Adsorption of Cesium from Alkaline Salt Solutions.—Active cesium was added to a solution containing about 20% by weight of mixed sodium nitrate, sulfate, phosphate and carbonate at about *p*H 13, to give an activity of about 1800 c./m./ml. At equilibrium 0.7 ml. of IR-120 adsorbed about 30% of the original activity, whereas 0.7 ml. of IR-100 adsorbed 97% of the activity.

These experiments were repeated using the sodium form of both resins. Closely comparable results were obtained, IR-120-Na adsorbing 23% and IR-100-Na adsorbing 98% of the original activity.

It is evident that in the strongly alkaline solutions IR-100 has much greater selective adsorptive capacity for cesium ions than IR-120.

This was confirmed in dynamic tests in which an alkaline solution containing 0.4 p.p.m. of inactive cesium to which was added about 7,000 c./m./ml. of active cesium was passed over IR-100 in a column. Cesium was removed quantitatively from the solution until 112 volumes of solution per volume of resin were passed. Under comparable conditions resin IR-120 gave immediate breakthrough.

Tabulation of Results

The performance of resins IR-100 and IR-120 in the adsorption of cesium in trace amounts may be compared as

	IR-100	IR-120
Maximum K_d at *p*H 4 to 4.4	7.8×10^4	18.7×10^4
K_d at *p*H 5.8	18.3×10^4	7.7×10^4
Cs adsorbed from alkaline Na-salt solutions in batch tests	98%	23%
Volume of alkaline Na-salt solution passed per volume resin before breakthrough in dynamic tests	112	0

Acknowledgment.—The authors wish to express their appreciation of the many helpful suggestions made by Dr. Robert Kunin of the Rohm & Haas Company, and the coöperation of Dr. D. S. Ballantine and Dr. F. R. Balcar of the Kellex Corporation Laboratory staff.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Ammonia Decomposition and Related Phenomena on Rhenium Catalysts[1]

BY JAMES PETER MCGEER[2] AND HUGH S. TAYLOR

The kinetics of decomposition of ammonia over metallic rhenium between 380 and 440° at one atmosphere total pressure has been studied with and without added helium, nitrogen and hydrogen. The kinetics conform to those obtained with iron synthetic ammonia catalysts, proportional to $[NH_3]^{0.53}$ and $[H_2]^{-0.89}$ with nitrogen inert and with an observed activation energy of 32 ± 3 kcal. Chemisorption and decomposition of small amounts of ammonia occur on rhenium surfaces at low pressure and temperatures below that at which continuous macro-decomposition occurs. The data indicate strong nitrogen adsorption, weak hydrogen adsorption and surface heterogeneity. Hydrogen adsorption is measurable between −196 and 330°, and parallels similar measurements with iron surfaces. A low temperature interaction between rhenium and nitrogen is indicated by comparison with the behavior of argon on rhenium. Activated adsorption of nitrogen on rhenium has been measured above 250°. Isotopic exchanges occur on rhenium catalysts between ammonia and deuterium, hydrogen and deuterium, and water and deuterium at temperatures between 0 and 100°. Nitrogen isotopes exchange rapidly on rhenium only at 500° and above. Addition of hydrogen accelerates this last exchange. It has been shown that the nitrogen isotope exchange reaction is very sensitive to reduction techniques in catalyst preparation both with iron and rhenium catalysts. The nitrogen exchange increases in rate at a given temperature with increasing thoroughness of reduction. Traces of water vapor are strong poisons for the nitrogen exchange with both iron and rhenium.

The catalytic properties of rhenium have been extensively investigated in relation to dehydrogenation of alcohols. The work was published in a series the last paper of which is given here as a reference.[3] Hydrogenation with rhenium was investigated by Tropsch and Kassler.[4] The catalytic synthesis of ammonia using various forms of rhenium was demonstrated by Greek workers.[5]

The literature on problems related to ammonia decomposition and synthesis has been frequently reviewed. In this country the bulk of the work has been done by Emmett and his collaborators, while other contributions have been made by the Russian school. The latter workers employ the theory of Temkin and Pyzhev[6] to explain all cases of catalytic synthesis and decomposition of ammonia. There are, however, certain well documented cases[7] where the results cannot be fitted to this theory. This investigation was undertaken to determine the course of the ammonia decomposition on a catalyst previously untested in this regard and to relate the results obtained to the other known facts concerning this catalytic reaction.

A. Kinetics of Ammonia Decomposition

Experimental.—The apparatus and technique used were essentially those of Love and Emmett.[7] du Pont anhydrous synthetic ammonia was used, while tank nitrogen, helium and hydrogen were purified using standard procedures.

Two portions of a 25-g. lot of commercial rhenium metal powder were used. These were in the form of a fine, unsupported powder. Catalyst 1 weighed 4.8 g. It was reduced in hydrogen at 490 to 520°. There was no interrup-

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[1] This paper represents a portion of a thesis submitted by J. P. McGeer to the Faculty of Princeton University in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June, 1949.

[2] Ethyl Corporation Fellow 1947–1948; American Cyanamid Company Fellow 1948–1949; now Aluminum Laboratories Limited, Arvida, Quebec, Canada.

[3] M. S. Platanov, *J. Gen. Chem.* (*U. S. S. R.*), **11**, 683 (1941); *C. A.*, **36**, 397 (1942).

[4] H. Tropsch and R. Kassler, *Ber.*, **63B**, 2149 (1930).

[5] C. Zenghelis and C. Stathis, *Compt. rend.*, **209**, 797 (1939).

[6] M. Temkin and V. Pyzhev, *Acta Physicochim.* (*U. R. S. S.*), **12**, 327 (1940).

[7] K. S. Love and P. H. Emmett, THIS JOURNAL, **63**, 3297 (1941).

tion of the gas flow during the experiments, ammonia passing at all times while nitrogen and/or hydrogen were added to it as required. Catalyst 2 weighed 8.3 g. It was first reduced for 45 hours at 450 to 470° in hydrogen flowing at the rate of 3 liters per hour. After each day's experiments a reduction was carried out for 12 to 16 hours, with hydrogen flowing at 9 liters per hour, and the catalyst at 460 to 480°.

Temperatures were measured with a chromel–alumel thermocouple set in a well in the catalyst bed.

For further details of the experimental technique, and for more comprehensive results than are here presented, the reader is referred to the thesis of which this paper is a summary.

Results.—Preliminary experiments showed that nitrogen did not enter the kinetic expression for the decomposition of ammonia over this catalyst. Consequently this gas was generally used as an inert diluent. However, in certain experiments, helium was used for this purpose and the results confirmed those of the preliminary runs.

The results for the activation energy of this reaction are given graphically in Fig. 1. The open circles on the graph indicate an experimental series wherein the gas flow over Catalyst 2 consisted of 175 cc. per minute of ammonia and 50 cc. per minute of hydrogen. The half-filled circles correspond to a run wherein a flow over Catalyst 2 of 150 cc. of ammonia, 50 cc. of hydrogen and 100 cc. of helium, per minute, was employed.

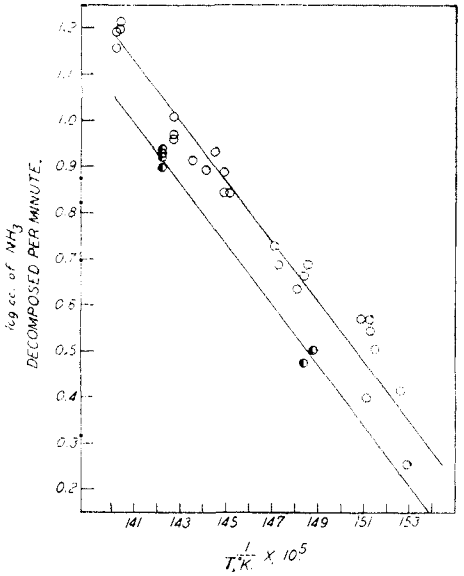

Fig. 1.—Activation energy plot for ammonia decomposition.

The graphically determined values of the activation energy from these two lines are 32.8 ± 2.0 and 33.7 ± 2.0 kcal., respectively.

Figure 2 details the results used in the determination of the order of reaction for hydrogen. The determinations were carried out at a temperature of 430°. The open circles represent determinations carried out on Catalyst 1 with a flow rate of 210 cc. per minute, 80 cc. being ammonia and the balance nitrogen and hydrogen. The half-filled circles correspond to results obtained on Catalyst 2 with a flow of 300 cc. per minute, 150 cc. of this being ammonia and the balance helium and hydrogen.

These two sets of results give, for the order of reaction of hydrogen, −0.93 and −0.85, respectively.

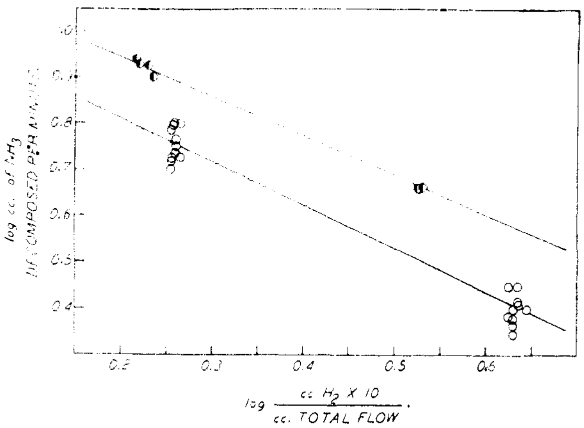

Fig. 2.—Kinetic order for hydrogen in ammonia decomposition.

Collected in Fig. 3 are the data employed for the calculation of the order of reaction for ammonia. The open circles correspond to a flow rate of 143 cc. per minute of a gas mixture of ammonia and nitrogen on Catalyst 1. Half-filled circles represent experiments with Catalyst 2 wherein 275 cc. of gas were flowing per minute, 50 cc. of this being hydrogen, the remainder helium and ammonia. All runs were made at 430°.

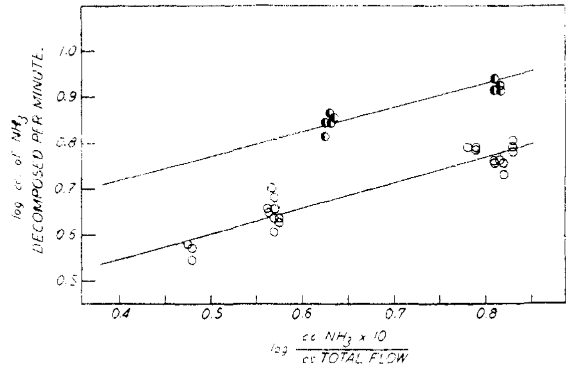

Fig. 3.—Kinetic order for ammonia in ammonia decomposition.

The two sets of data give 0.55 and 0.52, respectively, for the order of reaction of ammonia in the kinetic expression for the decomposition.

Discussion.—The derived kinetic expression for the decomposition of ammonia over rhenium is

$$\frac{-d[NH_3]}{dt} = k\frac{[NH_3]^{0.53}}{[H_2]^{0.89}}$$

Such an expression is valid for the reaction at one atmosphere pressure, and in the temperature range 380 to 440°. The activation energy of the process is 32.2 ± 3.0 kcal. It is similar to the kinetics on iron catalysts with slightly different exponents for the two gases. Also, the ratio of the exponents for ammonia and hydrogen is probably close enough to 0.66 to permit the use of the theory of Temkin and Pyzhev[6] to explain the results as in the case of iron, and our equation may then be written

$$\frac{-d[NH_3]}{dt} = k\left(\frac{[NH_3]^2}{[H_2]^3}\right)^{0.28}$$

B. Adsorption

Experimental.—The apparatus used in this study consisted of a catalyst chamber, a multistage McLeod gage with a bulb volume of 500 cc., a buret, a manometer and pumping and gas purification and storage systems. During the work with ammonia a second, modified, McLeod gage was added for use in micro gas analysis.[8] The multistage McLeod gage served as a pipet in the studies on rate of adsorption and as a gas reservoir during the ammonia experiments.

During the micro gas analysis the ammonia was removed by condensation in a liquid nitrogen trap, and the hydrogen was burned to water over copper oxide wire, the water being condensed in the same liquid nitrogen trap as was used for the ammonia. Residual gas was assumed to be nitrogen. The method was accurate to about 1%.

Dead space measurements were made with helium. Argon adsorption at −195.8° was used to determine the surface area.

Tank gas was used after purification in the case of nitrogen, hydrogen and helium. Oxygen was removed from these with a copper–kieselguhr catalyst.[9] Magnesium perchlorate was used to dry the gas, and, in the case of helium, a charcoal trap immersed in liquid nitrogen was used for further purification. The argon used was an "Airco" product, obtained in a sealed bulb and used directly. Ammonia was prepared by dropping concentrated sodium hydroxide on a sample of ammonium sulfate, in an evacuated bulb. The ammonia was condensed in a liquid nitrogen trap and a middle fraction of this was used. After purification the gases were stored in previously outgassed glass bulbs.

3.71 g. of commercial rhenium powder was used. This was placed in a Pyrex glass chamber 1 cm. in diameter and 3 cm. long. The catalyst was reduced in a hydrogen stream, the schedule being nine hours at 350°, three hours at 460°, two hours at 490° and 0.25 hour at 550°. After cooling in the hydrogen stream the catalyst was sealed off and evacuated for 12 hours at 470°, three hours at 500° and 1.5 hours at 530°. The evacuation technique led in all cases to residual pressures of the order of 10^{-5} mm. During the experiments the catalyst became poisoned on one occasion. It was reduced again by passing 400 liters of hydrogen through it over a period of 21 hours, the chamber being maintained at 420 to 440°. The exit tube was then sealed off again, and the catalyst evacuated for 20 hours at 440 to 480°, and for 20 hours at 500 to 520°. During all of the experiments the catalyst was protected from mercury vapor by gold foil rolled and placed in the tube leading to the catalyst.

Appropriate baths were used for the following temperatures: 0, −78, −126° (melting methylcyclohexane), −153.8° (melting 2-methylpentane), −183 and −195.8°. As vapor baths the following were useful: 100°, boiling water, 184.5° boiling aniline, 281° boiling α-bromonaphthalene. For other elevated temperatures a resistance furnace 25 cm. long and 4 cm. wide was employed. Temperatures were measured both with a chromel–alumel thermocouple and pyrometer and with a thermometer. These agreed within 2°, an accuracy sufficient for our purposes.

Results.—The results for the surface area measurement are plotted in Fig. 4. This standard B.E.T. plot gives a slope and intercept from which the calculated value for the monolayer on the 3.71 g. of catalyst is 0.27 cc. (S.T.P.). Employing the values for the area given by Brunauer and Emmett,[10] areas of 0.24 and 0.28 sq. meter per gram of catalyst, respectively, are obtained.

(a) **Ammonia.**—The adsorption of ammonia was rapid at 22°. At higher temperatures the preliminary experiments indicated irregularities. It was decided to investigate the gas resulting from contact of ammonia with the catalyst at temperatures below that at which macro-decomposition occurred.

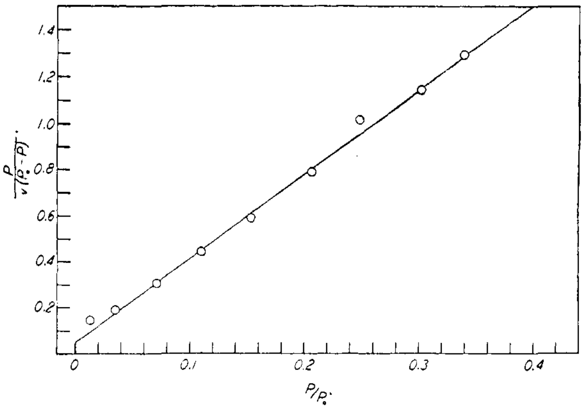

Fig. 4.—B.E.T. surface area plot.

The experiments listed in Table I were carried out as follows. The catalyst was evacuated at 480 to 500° for 16 hours with final gas pressures of the order of 10^{-5} mm., cooled to temperature and maintained at that point. The ammonia pressure in the multistage McLeod gage was then adjusted to the required value before admission to the catalyst. Approximately 0.1 cc. of ammonia was then introduced to the catalyst chamber initially. At the noted times, the stopcock between the catalyst chamber and the McLeod gage was closed and the gas over the catalyst allowed to expand into the analysis system, or into a Toepler pump, from which it could later be transferred to the analytical gage.

Between experiments 2 and 3 and between 3 and 4 nitrogen adsorption measurements at 335° were carried out.

TABLE I

AMMONIA DECOMPOSITION AT LOW PRESSURE AND VARIOUS TEMPERATURES ON A RHENIUM CATALYST

Expt.	Temp., °C.	Initial NH_3 pressure, mm.	Time of sample, min.	Vol. gas removed and analyzed cc. at 1 mm., 25°	Per cent. NH_3	H_2	N_2
1	330	1.46	0.5	18.5	77	22	1
			40	19.5	69	28	3
			150	29.0	10.5	62.5	27
			900	39.0	1	6	93
2	330	1.53	1	25.4	70	28	2
			16	22.1	59	28	13
			120	30.1	25.5	54.5	20
			450	38.8	0	11	89
			1260	19.6	0	37	63
			1380[a]	76.5	0	21	79
3	280	0.79	30	12.3	50.5	47.5	2
			90	10.5	51	47	2
4	210	0.83	150	14.4	45	53	2
			300[b]				
			1260	2.2	0	24	76
5	160	1.32	720[b]	24.2	74	23	3
			1020	14.4	75	22	3
6	110	1.40	420	25.5	78.5	19.5	2
			780[b]				
			1020	24.9	76	23	1

[a] Catalyst opened at the indicated time to Toepler pump and temperature raised to 400°. [b] Catalyst closed off from gas in gage at the time indicated.

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[8] Developed by M. J. Marshall: *cf.* G. Constabaris, Thesis, University of British Columbia, 1948.

[9] F. R. Meyer and G. Ronge, *Angew. Chem.*, **52**, 637 (1939).

[10] S. Brunauer and P. H. Emmett, THIS JOURNAL, **59**, 2682 (1937).

Table II reports a further series of ammonia decomposition studies, carried out after the nitrogen experiments reported below. The first of the series was a control, while in the second and third nitrogen had first been allowed to reach apparent adsorption equilibrium on the surface. At this point, the catalyst chamber was shut off while the McLeod gage was evacuated, and filled to a suitable pressure with ammonia. The catalyst was then evacuated for 30 seconds before the ammonia was admitted. Subsequent procedure was as previously recorded. During the experiment the catalyst chamber was maintained at 330°. Evacuation between runs was carried out at 480 to 500° for 16 or more hours.

TABLE II

AMMONIA DECOMPOSITION AT LOW PRESSURES, BEFORE AND AFTER NITROGEN ADSORPTION

Vol. N_2 ads. cc., 1 mm., 25°	P_{N_2} equilibrium mm.	Initial press. NH_3 mm.	Time, min.	Vol. anal. cc., 1 mm., 25°	Per cent. NH_3	H_2	N_2
0	0	0.69	1.5	10.4	68	29	3
28.6	0.97	0.845	1.5	12.1	72.5	26.5	1
37.9	1.42	1.32	1	14.3	75	23	2
			15	15.4	68	20	12
			120	17.5	24.5	53.5	22

(b) **Hydrogen.**—Figures 5 and 6 record the results for the rate of hydrogen adsorption on the surface at various temperatures. In each case the catalyst was evacuated at 480 to 500° for 16 hours, then cooled to the temperature of the experiment. The initial hydrogen pressure in the McLeod gage varied between 0.22 and 0.229 mm., but for simplicity of comparison the data have been corrected for dead space and to an initial pressure of 0.225 mm. The data in Fig. 5 indicated poisoning of the surface presumably by traces of oxygen, since a preliminary experiment had indicated a minimum of hydrogen adsorption at 100°, and the catalyst was therefore reduced again. The data of Fig. 6 were reproducible.

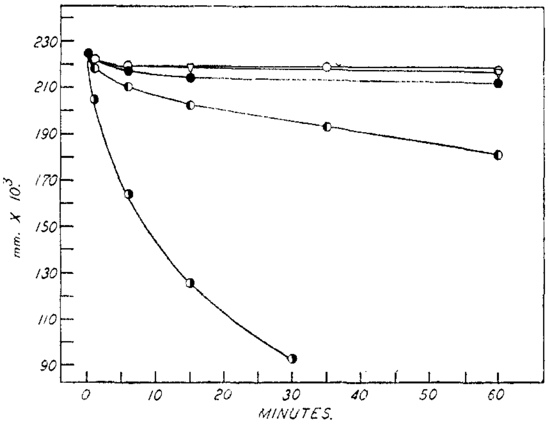

Fig. 5.—Hydrogen adsorption on a poisoned surface: O, −195.8°; ▽, 0°; ●, 100°; ◐, 184.5°; ◑, 281°.

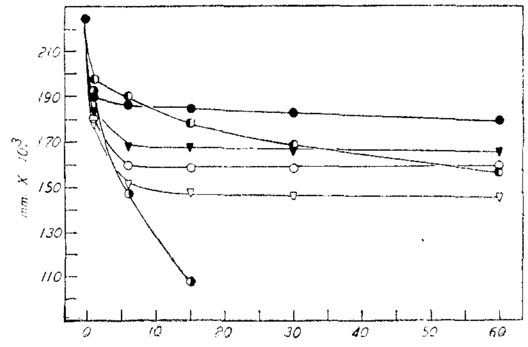

Fig. 6.—Hydrogen adsorption on rhenium catalyst: O, −195.8°; ▽, 78°; ▼, 0°; ●, 100°; ◐, 184.5°; ◑, 281°.

In Fig. 7 the results of a study of adsorption of hydrogen at −78°, as a function of the evacuation technique used, are presented. These results indicated some heterogeneity of the surface, and the experiments recorded in Table III were conducted to check this. The method was to allow apparent adsorption equilibrium to be attained at a given temperature, after which the bath about the catalyst chamber was replaced by one at a lower temperature. When the rate of change of pressure became slow (usually about 20 minutes) the original bath was restored. The pressure values after this last change are not recorded, for in all cases the pressure returned to that value which it had before the first bath was removed.

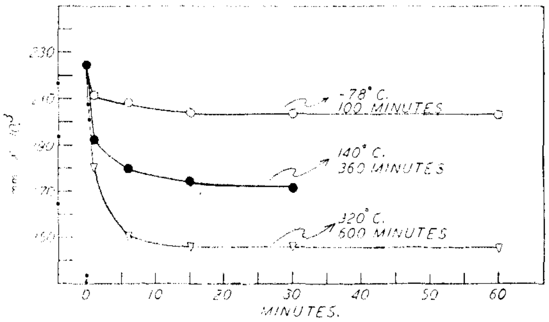

Fig. 7.—Hydrogen adsorption at −78° with varied evacuation techniques.

TABLE III

SURFACE HETEROGENEITY OF A RHENIUM CATALYST AS INDICATED BY HYDROGEN ADSORPTION

Initial bath temp., °C.	Vol. adsorbed cc., 1 mm., 25°	Pressure mm. × 10³	Second bath temp., °C.	Vol. adsorbed cc., 1 mm., 25°	Pressure mm. × 10³
100	28.6	170	0	31.5	165
184.5	81.7	86	0	98.7	55

(c) **Nitrogen.**—Over a period of three hours there was no measurable adsorption of nitrogen at −78, 0, 100 and 184°. Data for gage pressures at temperatures outside this interval are given in Table IV.

The very slow uptake of nitrogen at −195.8° was unusual and the adsorption at this temperature was therefore investigated as a function of catalyst evacuation after a previous adsorption at −195.8°. The results are reported in Fig. 8.

The studies recorded in Table V were undertaken to elucidate further the curious effects apparent with nitrogen. The data in the second column are pressures at various times over a surface which had been evacuated for 150 minutes at

TABLE IV

ADSORPTION OF NITROGEN ON A RHENIUM CATALYST AT VARIOUS TEMPERATURES

Time in minutes	Pressure mm. × 10^3 at Temperature, °C. −195.8	−183	−153.8	281	335
0	211.5	221	225	241.5	159
1	202.5	218.5	208		157
6	145.5	168.5	163.5		
15	80.5	94.5	139.5		152
30	31	59	129.5		148
60	10	54.5	127.5	208	
120		54.5		204.5	
180				202.5	123

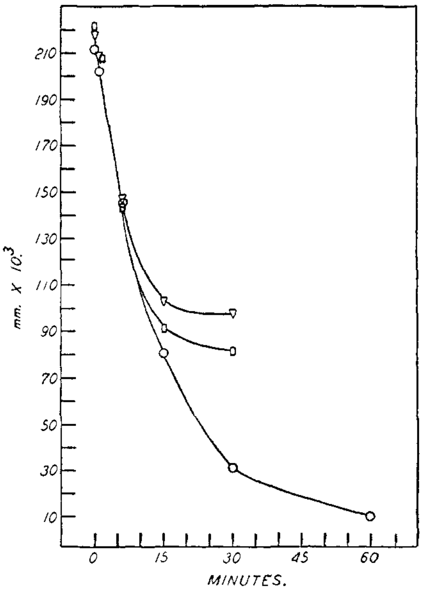

Fig. 8.—Nitrogen adsorption after varied evacuation techniques: O, 120°, 80 min.; ▽, 195.8°, 150 min.; □, −195.8°, 500 min.

−195.8° after an adsorption at the same temperature. It is to be compared with adsorption on a "clean" surface, column 2, Table IV. Evidently some nitrogen is strongly held at −195.8° and is only released by pumping at −120° (*cf.* column 4, Table V). In Fig. 9 the results for argon and nitrogen adsorption on a clean surface at low temperature have been plotted together. For convenience of comparison, initial pressures over the catalyst have been corrected to 0.225 mm.

TABLE V

ADSORPTION OF NITROGEN AS A FUNCTION OF EVACUATION AFTER ADSORPTION AT THE SAME TEMPERATURE

Adsorption temp., °C.	−195.8			−183	
Evacn. Temp., °C.	−195.8	−195.8	−120	−120	−183
Evacn. Time, min.	150	500	80	80	150
Time, min.	Pressure in mm. × 10^3				
0	218.5	221.5	211.5	221	219.5
1	209	208	202.5	218.5	208
6	146	144	145.5	168.5	144
15	103	91	80.5	94.5	91
30	98	81	31	59	81
60			10	54.5	

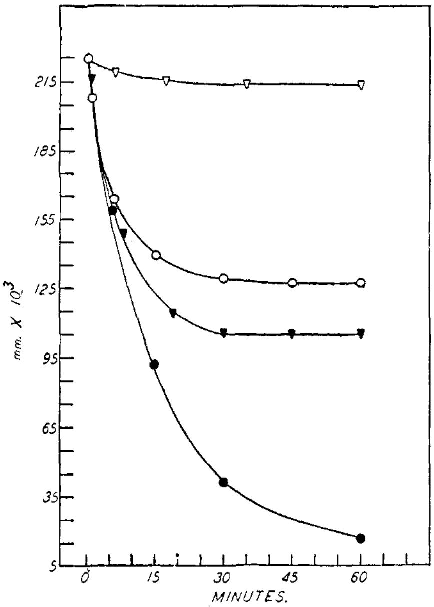

Fig. 9.—Low temperature adsorption of argon and nitrogen: ▽, A at −153.8°; ▼, A at −195.8°; O, N_2 at −153.8°; ●, N_2 at −195.8°.

Discussion.—The data of Table I indicate that the N–H bonds in an ammonia molecule adsorbed on a rhenium surface are easily ruptured, and that the hydrogen atoms so liberated are mobile on the catalyst. Evidently the hydrogen is weakly, though extensively, adsorbed. Such a premise is a ready explanation of the fact that, at all temperatures investigated, hydrogen very quickly appears in the gas phase, while nitrogen is not present in this state until somewhat later, although the amount of the latter liberated in the later stages stoichiometrically far outweighs the hydrogen. These results, following the same line of reasoning, lead to the conclusion that the nitrogen atoms are strongly held, but on a much smaller area of the catalyst.

The results of the adsorption studies and the results with isotope exchange reactions on rhenium as reported in the following section add evidence leading to the same interpretation.

It is to be remembered that macro-decomposition of ammonia on similar catalysts is evident first at about 350°. We may thus conclude that the slow step in the decomposition is the desorption of nitrogen from the surface. This last is one of the fundamental assumptions in the theory of Temkin and Pyzhev,[6] and these results correlate well with those of the kinetic studies presented in the preceding section. The point is particularly emphasized by experiments 5 and 6 of Table I, for the abundance of hydrogen makes it plain that the ammonia molecule has been stripped of hydrogen on the surface, while the failure of nitrogen to appear in the gas over the catalyst indicates why the reaction has failed to continue.

Intercomparison of the experiments reported in Table II and comparison of these with those of Table I indicate that the presence of nitrogen, adsorbed as such from the gas phase on the surface, has no apparent effect on the rate of decomposition of the ammonia. This independence correlates well with the fact that nitrogen does not enter the kinetic expression, and also with the observed difference between the rate of macro-decomposition of ammonia and that of nitrogen isotope exchange.

The experiments with hydrogen, Fig. 6, show both a low and high temperature chemisorption, results which have a parallel in the work of Emmett and Harkness[11] on iron catalysts. That the adsorption at −78° is specific in nature, and involves a high energy bond is indicated by the following facts: (a) although nitrogen has stronger van der Waals forces, it is not at all adsorbed at this temperature; (b) hydrogen adsorbed at −78° is not completely removed by evacuation at temperature; even at 140°, six hours pumping removes only 67% (see Fig. 7); (c) the adsorption at −78° is substantially greater than that at −196° (see Fig. 6).

The minimum in hydrogen adsorption observed at 100°, see Fig. 6, evidently is indicative of a change of type of chemisorption. The higher temperature adsorption, for instance at 184°, is much slower in rate than that occurring at low temperatures, *i.e.*, 0° and less, and hence must involve a higher activation energy.

Since reduction improved the adsorption (compare Figs. 5 and 6) it is to be assumed that oxygen poisoned the surface during the runs reported in the first of these graphs. Since the low temperature adsorption sites were evidently removed more extensively, the poisoning must have been selective in some degree.

The heterogeneity of the surface implicit in the foregoing paragraphs is confirmed by the data of Table III. Although, at apparent equilibrium, much more gas is adsorbed at 184° than at 100°, a lowering of the temperature to 0° produces a greater adsorption in the former case. This excess can only be gas adsorbed at 100°, but not at 184°, and hence, in this range of temperature at least, the desorption–readsorption phenomenon observed by Taylor and Liang[12] must be taking place on this catalyst.

With nitrogen, dissociative adsorption first begins at about 280°. The adsorption is small and slow. Both rate and amount increase with temperature, and certain unreported experiments indicate that, with this gas also, desorption–readsorption is taking place.

The low temperature results are not clear cut. The adsorption at −196, −183 and −154° does not exhibit the characteristics of van der Waals interaction. The adsorption is slow and pumping at temperature will not remove all the gas. The results with argon are more nearly those expected of physical adsorption for, although the rate of uptake is slow, pumping at temperature does remove the gas adsorbed, and at −154° the adsorption is quite small. Although the relative boiling points indicate that it should not be the case, the adsorption of nitrogen is appreciably greater than that of argon.

The adsorption of the nitrogen is apparently not of a dissociative type at these temperatures for no nitrogen isotope exchange was detectable over a period of 72 hours. It may be pointed out, however, that if only van der Waals forces are involved there is an evident danger in calculating from the relative magnitude of these forces as represented by the boiling points of the substances, the relative forces acting in gas–metal adsorption. These facts emphasize that it is the adsorbent–adsorbate complex which is of paramount importance.

A similar effect has been noted by Orr.[13] He draws attention to the observation of Vegard,[14] that the nitrogen molecule in the solid state has a small dipole.

C. Isotope Exchange Reactions in Horizontal Catalyst Chambers

Experimental.—The apparatus consisted of a pumping system, a gas purification and storage system, a Toepler pump for preparation and transfer of samples, and reactor tube disposed horizontally. The latter was of Pyrex, 6.5 cm. long and 3.0 cm. i.d., for all experiments except those with nitrogen isotopes: For these latter, quartz was requisite, and in this case the tube was 8.0 cm. long and 2.4 cm. i.d. In both cases, attachment to the apparatus was through a ground joint, and, from the other end of the reactor, a tube of narrow diameter issued so that reduction in flowing hydrogen could be carried out. Samples were transferred from the chamber to gas sample tubes by means of the Toepler pump. Analyses were carried out in a Nier 60° mass spectrometer. The catalyst chamber was heated by a resistance furnace 25 cm. long and 4.0 cm. i.d. Temperatures were measured with a chromel–alumel thermocouple. Between each set of measurements the catalyst was suitably outgassed.

The gases used were prepared and purified as follows.

Ammonia.—This was prepared as in the work on adsorption.

Hydrogen.—Tank hydrogen was passed through copper turnings at 450°, and dried with calcium chloride and phosphorus pentoxide.

Deuterium.—This was prepared electrolytically and furnished through the kindness of Dr. H. Sadek. It was purified by passage over copper at 450° and dried with phosphorus pentoxide.

Water.—Water of about 1.2% deuterium content was frozen and pumped off.

Nitrogen.—Tank nitrogen was purified in the same train as was the hydrogen.

Heavy Nitrogen.—Initially this was in the form of 35% N^{15} ammonium chloride. Ammonia was liberated, purified and stored as before. To produce the nitrogen as needed small portions of ammonia were burnt over copper oxide at 400°. The water and residual ammonia were then removed by immersion of a tube in liquid nitrogen, and the heavy nitrogen was withdrawn to the Toepler pump. By this method a nitrogen of isotopic content 1000 parts mass 28, 890 parts mass 29 and 210 parts mass 30 was produced.

Several catalysts were used and these were prepared as listed below. (a) The commercial powder catalyst used weighed 2.8 g. disposed along the bottom of the horizontal reactor. It was reduced by heating in hydrogen for 12 hours at 450°. In a static system it decomposed ammonia readily at 360°. This catalyst was the only one tested for the exchanges not involving nitrogen.

(b) Catalyst K2 was prepared by distributing 3 g. of potassium perrhenate along the bottom of the quartz reactor and reducing the compound with flowing hydrogen for six hours at 400°, 14 hours between 400 and 700° and six hours at 700°. It was then evacuated for 15 hours at 800 to 850° before any measurements were made.

(c) Catalyst N was prepared by reduction of ammonium perrhenate. The latter was prepared from 4 g. of potassium perrhenate.[15] The mixture of ammonium nitrate and perrhenate was distributed along the length of the reaction vessel and reduced in flowing hydrogen for 5 hours between 0 and 300°, 17 hours at 300°, 4 hours between 300 and 800°

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[11] P. H. Emmett and R. W. Harkness, This Journal, **56**, 490 (1934).

[12] H. S. Taylor and S. C. Liang, *ibid.*, **69**, 1306 (1947).

[13] R. J. C. Orr, *Proc. Roy. Soc.* (*London*), **A173**, 349 (1939).

[14] L. Vegard, *Z. Physik*, **88**, 235 (1934).

[15] For details see "Inorganic Syntheses," Vol. I, edited by H. S. Booth, McGraw-Hill Book Co., New York, N. Y., 1939, p. 177.

and 16 hours at 800°. Prior to use it was evacuated for 8 hours between 800 and 1000° and for 16 hours at 1000°.

Results.—The results of two experiments on ammonia–deuterium exchange are presented in Table VI. In the first of these the isotope mixture contained 49% deuterium, 5% hydrogen and 46% ammonia, and the pressure over the catalyst was 16 cm. In the second, the mixture was 15.5% deuterium, 1.5% hydrogen and 83% ammonia, the pressure being 15.5 cm.

TABLE VI

THE EXCHANGE REACTION BETWEEN AMMONIA AND DEUTERIUM

Expt.	Time, min.	Temp., °C.	Mass 17 / Mass 18	Mass 17 / Mass 19
1	4	25	13.1	No 19 peak
	240	25	13.1	
	310	110	7.2	
	370	100	4.3	
	1440	100	2.5	19.0
2	10	20	10.9	185
	280	20	10.7	
	340	120	6.8	
	380	120	5.0	
	690	120	5.5	87

Two runs were made to study the reaction between hydrogen and deuterium water and the results of these are presented in Table VII. The first was carried out at 25°, in a mixture originally containing 0.3% deuterium water vapor, 24.7% water and 75% hydrogen. The second took place at 60°, with a mixture of the same composition, at a pressure of 7.0 cm.

TABLE VII

THE EXCHANGE REACTION BETWEEN HYDROGEN AND DEUTERIUM WATER

Expt.	Temp., °C.	Time, min.	Mole % D_2 as D_2 or HD
1	25	0	0.015
		30	.016
		240	.032
		960	.062
2	60	0	.015
		30	.04
		60	.062
		150	.13

The results of an exchange study in a mixture containing 94% hydrogen and 6% deuterium are given in Table VIII. The reactor pressure was 21.9 cm.

TABLE VIII

THE EXCHANGE REACTION BETWEEN HYDROGEN AND DEUTERIUM

Time, min.	Temp., °C.	Mole % HD
5	25	0.41
20	25	0.43
60	25	0.46
390	25	1.65
425	100	2.6

Preliminary attempts to obtain exchange of nitrogen isotopes on the commercial catalyst resulted in no measurable reaction at temperatures up to 520°. It was evident then that quartz was necessary and it was therefore decided that the effect of preparation of the catalyst on its activity would be concurrently investigated.

With catalyst N, a mixture consisting of 88% mass 28, 9.5% mass 29 and 2.5% mass 30, at a pressure of 33 cm., gave no measurable reaction over a period of 36 hours at 900 to 1000° and 12 hours more at 1000°. Addition of approximately 15% by volume of hydrogen after which the temperature was maintained at 900° for one hour also failed to produce exchange.

The results for the other catalysts are given in Table IX. In the Expt. 1 the catalyst was K2 and the isotopic mixture, at a pressure of 27.5 cm. initially consisted of 87.5% mass 28, 10% mass 29 and 2.5% mass 30. Experiment 2 was carried out over the commercial powder. The pressure was 26.2 cm. and the mixture consisted of 88% mass 28, 9.5% mass 29 and 2.5% mass 30.

TABLE IX

NITROGEN ISOTOPE EXCHANGE

Expt.	Time, hours	Temp., °C.	Mass 29 / Mass 30	Remarks
1	0.2	800	4.0	
	0.75	800	5.5	
	15	800	9.1	
	21	850	13.0	
	26	900	16.3	
	38	900–875	20.2	
	43	950	22.5	
	46	1000	23.2	
	47	800	23.3	4% H_2 added
	50	800	27	
2	0	700	3.9	
	11	850	3.9	
	15.5	930	6.5	
	18	900	7.65	10% H_2 added
	18.75	800	12.5	
	19.5	800	18.5	

Discussion.—It is evident from the data in Table VI that the production of deutero-ammonias from ammonia and deuterium takes place in a significantly lower temperature range than does the ammonia decomposition. Taylor and Jungers found the same phenomenon on an iron synthetic ammonia catalyst.[16]

The results presented in Table VII indicate that there is a possibility that the production of the deutero-ammonias does not proceed by a surface reaction. Since the reaction

$$H_2O + D_2 \rightleftarrows HDO + HD$$

proceeds more quickly than

$$NH_3 + D_2 \rightleftarrows NH_2D + HD$$

cf. Tables VI and VII, the production of the heavy ammonias may proceed in the gas phase through a deuterated water intermediate.

$$NH_3 + HDO \rightleftarrows NH_3DOH \rightleftarrows NH_2D + H_2O$$

However, all gases were carefully desiccated before use in the ammonia–deuterium exchange, and previous investigators,[16] working under similar conditions, found that, in the absence of a catalyst, there was no exchange even at temperatures as high as 300°.

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(16) H. S. Taylor and J. C. Jungers, THIS JOURNAL, 57, 660 (1935).

The measurements detailed in Table VIII indicate still another similarity between iron and rhenium catalysts. On the former also there is low temperature hydrogen–deuterium exchange.[17] Although with rhenium no measurements were made at temperatures below 25°, the data of Fig. 6 indicate that such exchange may well proceed measurably at 0° and still lower temperatures.

The nitrogen isotope exchange would seem to indicate that a catalyst capable of decomposing ammonia at 400° or less will not necessarily cause nitrogen isotope exchange in the same temperature range. As on iron catalysts,[18] the addition of hydrogen accelerates the reaction.

The method of preparation seems to have a distinct effect on the catalytic activity. The same order of rate was qualitatively observed with the decomposition of ammonia, *i.e.*, the reaction seemed to be fastest on a catalyst prepared from potassium perrhenate, slowest on that prepared from ammonium perrhenate (proceeding slowly at 600°) and intermediate on the commercial powder. This observed difference in these two related reactions may be due either to difference in extent of sintering during reduction, or to promotional effects of residual potassium oxide. Sufficient data were not accumulated to enable us to make a definite decision as to the cause of the variation.

D. The Nitrogen Isotope Exchange Reactions in Vertical Catalyst Beds

Sometime after the completion of the experiments reported in the preceding section, Dr. P. H. Emmett[17] reported results on nitrogen isotope exchange which were in sharp disagreement with those of Joris and Taylor.[18] A suggestion of his in regard to reduction technique formed the basis of the following experiments. However, the fortuitous placing of the catalyst chamber in a vertical position was done initially for other reasons.

Experimental.—These experiments were essentially similar to those reported in section C. The catalyst chamber was 8 cm. high and 1.5 cm. in diameter. The gases, with the exception of hydrogen, were treated as before. To obtain hydrogen of high purity for the reduction this gas was passed through the following substances, copper at 450°, calcium chloride, phosphorus pentoxide, palladium asbestos at 170°, magnesium perchlorate and a liquid air trap. Tank hydrogen which contained 0.148% oxygen was the raw material. This was used in three ways either without purification (1), or purified with copper, calcium chloride, phosphorus pentoxide and magnesium perchlorate (2), or with the whole train (3).

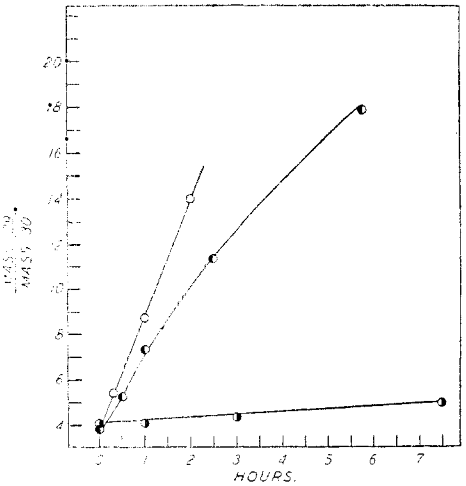

Fig. 10.—Nitrogen isotope exchange on iron catalyst No. 954: O, expt. 4; ◐, expt. 5; ◑, expt. 6.

Two catalysts were used, (a) 7.74 g. of synthetic ammonia singly promoted (10.2% alumina) iron catalyst number 954, occupying 3.5 cc. in the chamber, the grains being approximately 20 mesh, and (b) 6.25 g. of commercial rhenium powder. Each catalyst formed a closely-packed bed in the vertical reaction tube. For each run the iron catalyst was reduced at 450°, evacuated for 2.5 hours at the same temperature and left in vacuum for 10 minutes after which the sample was introduced. The rhenium was reduced at 500 to 520°, evacuated at 450 to 460°, and the temperature was further varied during exchange. In each experiment approximately 1 cc. (S.T.P.) of gas was used, which gave a pressure of about 10 cm. in the reaction chamber.

Results.—The effect of the type of reduction on the rate of nitrogen isotope exchange on the iron catalyst is shown in Fig. 10. The most rapid rate of exchange was obtained by reduction with hydrogen which had been purified in the whole train. This reduction was for ten hours at a space velocity of 9000 and 1.25 hours at a space velocity of 14500. Less rigorous purification gave the intermediate rate of reaction. Reduction was for 13 hours at a space velocity of 5000. The slow rate was obtained by a 12-hour reduction in tank hydrogen at a space velocity of 4500. To eliminate pre-treatment, in each case, before the definitive reduction, tank hydrogen was passed over the heated catalyst for six hours at a space velocity of about 5500.

The results for rhenium are presented in Table X. Some catalyst was lost in the course of the experiments. However, the magnitudes of differ-

TABLE X

THE EFFECT OF METHOD OF REDUCTION OF A RHENIUM CATALYST ON THE RATE OF THE NITROGEN ISOTOPE EXCHANGE REACTION

Method for reduction	Reduction time, hours	No. of liters	Time, hours	Temp., °C.	Mass 29 / Mass 30
1	1	20	0	500	3.8[a]
2	16	242	2	500	4.4
			2.25	560	
			3.25	560	6.4
			6	560	10.3
3	14	462	0	500	3.83[a]
			1	500	4.26
			1.5	560	
			3	560	6.15
			6	560	9.3
1	14	98	24	800	4.14
			27	800	4.61
			32	800	5.88
			44	800	8.4
2	14	320	0	500	4.0
			0.25	560	
			1.5	560	4.3
			5	560	4.9

[a] Initial mass ratio, 29/30.

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[17] P. H. Emmett, Conference on Isotope Exchange Reactions and Chemical Kinetics, Chemistry Conference no. 2, Brookhaven National Laboratory, December, 1948.

[18] G. G. Joris and H. S. Taylor, *J. Chem. Phys.*, 7, 893 (1939).

ence encountered in the rates make exact comparison unnecessary.

Discussion.—The results recorded in Fig. 10 bear a marked similarity to certain observations of Almquist and Black.[19] Following Almquist,[20] we can calculate an excess free energy for the surface iron atoms inactivated toward the isotope exchange by oxygen poisoning. Using 0.3% for the concentration of the water in the hydrogen, we obtain a value of 8 kcal. for this quantity. This value must lie at the lower end of an energy spectrum of surface sites for stepwise removal of the oxygen from the hydrogen produces a stepwise increase in the rate of isotope exchange.

Thus, it seems certain that the surface concerned with nitrogen isotope exchange is heterogeneous. Since it has a free energy some 8 or more kcal. in excess of bulk iron, it would seem reasonable to assume that it is a small portion of the total surface.

It is to be noted that, depending upon the purity of the gas used for reduction, one may reproduce on the same catalyst and in the same system, both the rapid exchange observed by Emmett,[16] or the slow exchange observed by Joris and Taylor.[17]

The results obtained with rhenium show great variation. Rapid reaction at 500° is observed if proper reduction techniques are employed. If, on the other hand, tank hydrogen is used for reduction, rates of the order of magnitude observed in the horizontal chamber are obtained. Since Joris and Taylor used a horizontal reactor in which hydrogen was passed over the catalyst during reduction, while Emmett used vertically disposed beds of material, the conclusion is reasonable that when one reduces a catalyst by passing hydrogen *over* it, the surface is left in a partially oxidized condition. It may very well be that unless reduction is carried out by passing the hydrogen with turbulence *through* the well-packed catalyst bed, the process controlling the escape of oxygen from the surface may be too slow to allow reduction of the highly active sections of the catalyst necessary for nitrogen exchange in any reasonable period of time.

General Discussion

The results described in the previous four sections warrant the conclusion that rhenium catalysts have many properties in common with those of iron. There is a similarity in the kinetics of ammonia decomposition. Both show three distinct, if overlapping, types of interaction with hydrogen and, in both, the addition of hydrogen to the reaction mixture accelerates the nitrogen isotope exchange. Although rhenium is active at a somewhat higher temperature, suitable promotion might reduce this difference.

The non-uniformity of the surface of the metallic rhenium employed has been demonstrated. Both the results with hydrogen adsorption, and those with oxygen poisoning of the surface for nitrogen isotope exchange place such a conclusion beyond reasonable doubt. The negligible effect of nitrogen adsorbed from the gas phase on both macro- and micro-decomposition of ammonia is an indication of the same fact.

It would seem evident that studies of reactions at surfaces by indirect techniques, *i.e.*, adsorption and isotope exchange should be conducted with extreme caution. Unless experimental conditions in the two cases are identical, such subsidiary reactions may occur on parts of the surface which are not operative in the catalysis.

PRINCETON, N. J. RECEIVED JULY 26, 1950

[19] J. A. Almquist and H. L. Black, THIS JOURNAL, **48**, 2814 (1926).

[20] J. A. Almquist, *ibid.*, **48**, 2820 (1926).

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Studies Relating to Boron. III. Some Reactions of the Aliphatic Boranes with Alkali Metals in Liquid Ammonia and Ethylamine[1]

BY J. EDWARD SMITH[2] AND CHARLES A. KRAUS

In this paper are presented the results of a study of reactions of the alkali metals with trimethyl- and tributylboron in liquid ammonia and ethylamine. In ammonia, the metals react quantitatively with both of the boranes according to the equation $Alk_3B \cdot NH_3 + M = MNH_2BAlk_3 + {}^1/_2H_2$. In ethylamine the reactions are more complex; the amount of hydrogen evolved is less than equivalent to the metal required to complete reaction. The solutions of the reaction product of lithium with trimethylborane in ethylamine evolves two moles of methane per mole of borane. In the case of tributylborane, butane is evolved but the reaction is slower and the maximum amount of butane that may be obtained has not been determined. The reaction products of potassium with the boranes are also unstable in ethylamine solution but their rates of decomposition are much slower than those of the corresponding lithium compounds.

I. Introduction

Although the chemistry of boron has received increasing attention in recent years, few investigations have been reported concerning the properties of the alkali metal salts of the alkyl boranes or salts derived from their addition compounds with ammonia and the amines.

Krause and Polack[3] have shown that aromatic boranes in ether solution add an atomic equivalent of alkali metal to form highly colored salts, which correspond to the formula Ph_3BM, where M is an alkali metal[4]; Robinson has shown that a similar reaction occurs in ethylamine. The salt obtained here is associated with one molecule of solvent.

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[1] This paper is based on a portion of a thesis submitted by J. Edward Smith in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, October, 1930.

[2] University Fellow, Brown University, 1928–1929; du Pont Fellow in Chemistry, 1929–1930.

[3] E. Krause and H. Polack, *Ber.*, **59**, 777 (1926).

[4] A somewhat similar affinity for electrons is exhibited by tri-β-naphthylborane, which forms the compound Na_2BAr_3. H. E. Bent and M. Dorfman, THIS JOURNAL, **57**, 1259 (1935). B_2H_6 also adds alkali metal forming $K_2B_2H_6$. A. Stock, W. Sutterlin and F. Kuozen, *Z. anorg. allgem. Chem.*, **225**, 225 (1935).