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Kinetics of Isotope Exchange between Hydrogen and Liquid Ammonia on Heterogeneous Catalysts

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The isotope exchange between hydrogen and liquid ammonia has been studied in the temperature range between −60° and +25°C at pressures up to 150 atm in the presence of various catalysts, in particular supported platinum catalysts. Comparative exchange experiments were carried out with gaseous ammonia at pressures from 25 Torr up to the saturation pressure (8.7 atm at 20°C).

(1) Group eight metals catalyze the H/D exchange with liquid ammonia even at temperatures below −60°C. The activity decreases in the order: Pt, Pd, Ni, and Fe. (2) For a platinum-carbon catalyst suspended in liquid ammonia the rate of exchange increases proportionally to the amount of catalyst in the range from 10 to 100 g/liter. (3) Platinum catalysts supported on carbon and on silica gave the same exchange constants per unit weight and resulted in the same activation energy irrespective of the widely different surface areas. (4) The following apparent activation energies were obtained: Pt/C, 10.0 ± 0.5; Pt/SiO_2, 9.6 ± 0.6; Pd/C, 11.3 ± 0.7; Raney-Ni, 11.5 ± 0.8 kcal/mole. (5) Comparative measurements with potassium amide indicated that this homogeneous catalyst has a considerably higher activity and a lower activation energy (5.4 ± 0.6 kcal/mole) than the heterogeneous catalysts. Contrary to exchange on these catalysts transport processes are rate determining in the potassium amide system under the conditions investigated. (6) While the rate of exchange in liquid ammonia increases proportionally to the hydrogen pressure in the case of potassium amide a dependence on the square root of the hydrogen pressure has been found for the platinum/carbon catalyst. (7) The experimental results support the following mechanism: Isotope exchange occurs between chemisorbed hydrogen atoms and a chemisorbed ammonia molecule, i.e. according to a Langmuir-Bonhoeffer-Hinshelwood mechanism. In principle the mechanism is the same in the gas as well as in the liquid phase. The number of atoms exchanged per unit time is, however, considerably smaller in the liquid, since a large portion of the surface is blocked up for hydrogen chemisorption by adsorbed ammonia molecules. If any, there is only a very small contribution from an ionic mechanism to the total exchange in liquid ammonia.

While isotope exchange between ammonia and water proceeds with great rapidity due to an ionic mechanism, no exchange occurs between ammonia, either gaseous or liquid, and hydrogen at ordinary temperatures. Only above 600°C is exchange of hydrogen atoms noticeable in the thermal interaction, as has been found by A. Farkas (*1*). The exchange in the gas phase can, however, be effectively catalyzed, e.g. by metal catalysts. In connection with the technically so important ammonia synthesis reaction, a great number of investigations have been carried out on the deuterium exchange between gaseous ammonia and hydrogen in the presence of heterogeneous catalysts. Recent work on the ammonia catalysis has been reviewed by Mars, Scholten, and Zwietering, as well as by H. Taylor (*2*).

A further incentive to study this catalytic isotope exchange reaction has been the large equilibrium separation factor which presented a promising possibility for the production of heavy water. After Claeys, Dayton, and Wilmarth (*3*) had observed that the exchange can be most effectively catalyzed even at temperatures as low as —70°C by solutions of potassium amide in liquid ammonia, several authors (*4, 5, 6*) have studied this reaction with a view to deuterium enrichment. In connection with such an investigation recently carried out in this Laboratory (*7*) the behavior of heterogeneous catalysts in liquid ammonia is of interest. No conclusive study has as yet been carried out apart from preliminary experiments by Mitani (*8*) who found a slow deuterium exchange between hydrogen and liquid ammonia in the presence of platinum black. On the other hand Becker and co-workers (*9*) observed a favorable activity of a platinum suspension catalyst in the deuterium exchange reaction between hydrogen and liquid water. It is, therefore, of interest to study the analogous reaction in the liquid ammonia system. Furthermore the H_2/NH_3 exchange offers a possibility of following a catalytic reaction from the gas phase into the region of the liquid phase by steadily increasing the ammonia partial pressure. The present work is mainly devoted to a study of the kinetics of the exchange reaction on platinum catalysts. Some others are merely dealt with to indicate the types of heterogeneous catalysts which could also be considered active in the liquid ammonia/hydrogen system.

METHODS

In principle the same experimental procedure has been used for both sets of experiments with gaseous and liquid ammonia:

The reaction mixture of ammonia and deuterium-enriched hydrogen was brought into intimate contact with the catalyst. This could be achieved either by strong agitation of the catalyst suspended in liquid ammonia or by intensive stirring of the gas phase. Gas samples taken at known intervals were separated into their constituents and then analyzed mass spectrometrically. From the decrease of deuterium content in the hydrogen and increase in the ammonia, rates of reaction could be evaluated.

Substances

Pure ammonia was available from "Union Rheinische Braunkohlen-Kraftstoff-A. G., Wesseling." Traces of impurities ($<0.1\%$) were removed by reaction with potassium amide and subsequent degassing of the liquid ammonia in high vacuum.

HD was prepared by reacting water enriched in deuterium with aluminum foil in the presence of KOH and a few drops of mercury in a stainless steel container under rigid high vacuum conditions. After a pressure of about 15 atm had been reached, the container was cooled in liquid nitrogen and the gas expanded into a 5 liter gas cylinder. This gas containing 2–3% deuterium was used to enrich hydrogen up to 1500 ppm, corresponding to a ten-fold natural D-content. HD-gas for the runs at high pressures could be diluted with tank hydrogen using an active copper catalyst to remove traces of oxygen.

For the runs at low pressure the deuterium-enriched hydrogen was purified by means of finely divided uranium metal which is able to take up hydrogen at room temperature. Foreign gases can be removed by degassing and pure hydrogen released at elevated temperatures (*10*). Thus uranium can be conveniently used not only for purification but also for the storage and transportation of hydrogen within the vacuum system.

The following catalysts were obtained from "Degussa, Deutsche Gold- und Silber-Scheideanstalt, Frankfurt": (1) activated carbon with 10% platinum; (2) activated carbon with 10% palladium; (3) activated silica with 10% platinum; (4) Raney-iron; (5) Raney-nickel.

Aluminum was extracted from the Raney catalysts with KOH (*11*). Before use all heterogeneous catalysts were flushed with hydrogen and finally degassed at 120°C in high vacuum. Potassium amide used as homogeneous catalyst was prepared *in situ* from potassium and liquid ammonia.

D_2O, 99.78%, was obtained from Norsk Hydro-Elektrisk Kvaelstofaktieselskab, Oslo, Norway. All other reagents were "pro analysi" grade.

Apparatus

Purification, storage, handling of gases, etc., was carried out in a conventional high vacuum system ($<10^{-5}$ mm Hg) which also contained a section for the preparation of the samples for mass spectrometric analysis.

For high pressure work up to 200 atm a 150 cm^3 stainless steel autoclave obtained from Messrs. Andreas Hofer, Mülheim/Ruhr was used, while for experiments up to 15 atm two additional reactors of similar design were constructed in our own workshop (Fig. 1). Intensive mixing of gas and liquid could be achieved by means of a stirrer with two perforated plates. The piston was operated magnetically at frequencies between 15 to 240 strokes/min. The autoclave could be kept at constant temperatures in the range —75 to +100°C by circulating thermostated methanol or water through a copper coil soldered on to the autoclave wall. The system was well insolated by sponge rubber. The reactors for experiments up to 15 atm were simply immersed in the thermostat. Unless a calibrated mercury thermometer was used tem-

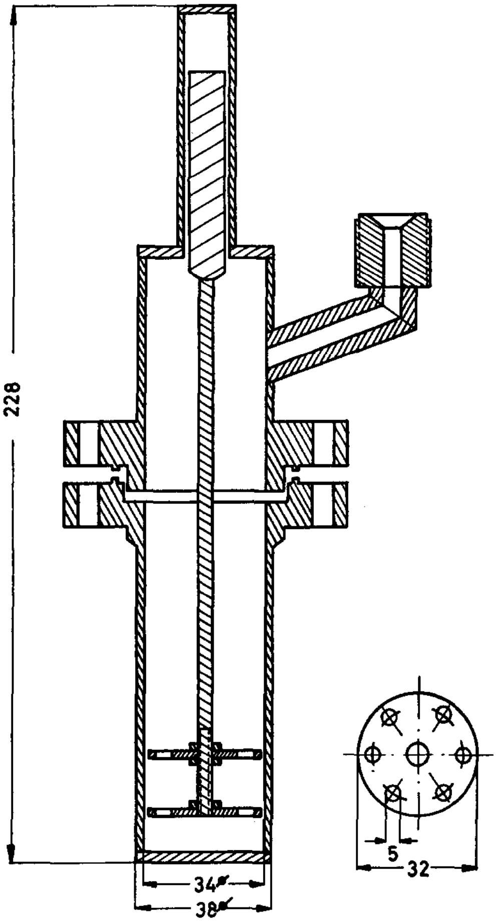

FIG. 1. Pressure reactor, scale in mm.

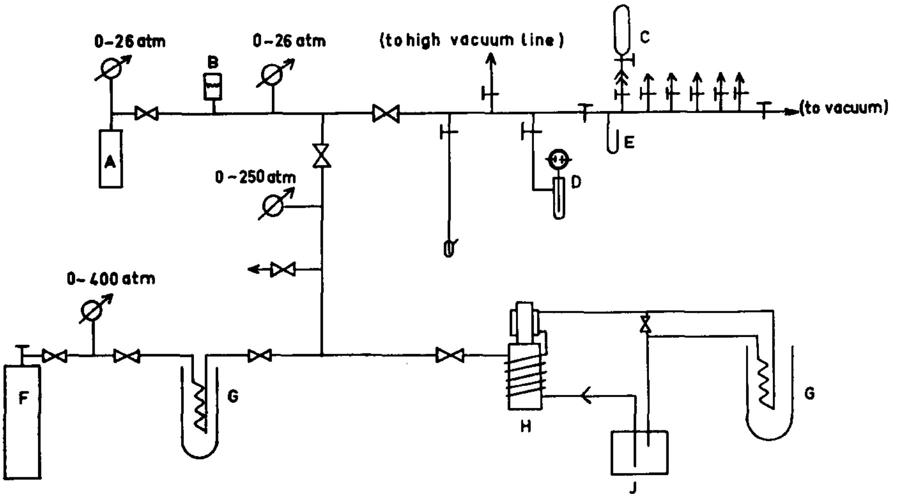

FIG. 2. High pressure apparatus. A, ammonia container; B, blow-off valve; C, sample bulb; D, Penning gauge; E, mercury manometer; F, hydrogen tank; G, cooling trap; H, reactor; J, thermostat.

peratures were measured with an ammonia vapor pressure manometer. The high pressure set-up is schematically drawn in Fig. 2.

Procedure

Ammonia, the amount of which had been determined from pressure–volume measurements, was condensed into the previously evacuated reactor. Hydrogen enriched with deuterium generated from uranium hydride was admitted until the desired pressure was reached and the reactor then brought to the temperature of the particular experiment. In the high pressure runs the autoclave was first thermostated after the ammonia had been introduced and then the hydrogen pressure was adjusted by means of the controlling valve of the 200 atm gas cylinder containing the H_2/HD mixture. In both cases the starting points of the reaction were subsequently determined by extrapolation of the time versus exchange efficiency graphs.

For comparative studies of the gas phase reaction a 2 liter glass vessel was charged with the catalyst and a known amount of ammonia added after the system had been properly degassed and adjusted to the desired temperature of the experiment. The ammonia was then condensed in a tiny side tube attached to the reaction vessel and the H_2/HD mixture introduced. After warming up the ammonia the gas was thoroughly mixed within a few seconds by means of a fan operated magnetically inside the reaction vessel. In this way the amounts of the components and zero time of the reaction could be exactly determined. At suitable intervals gas samples were taken small enough to avoid any appreciable changes in the reaction conditions. In the high pressure experiments a sensitive controlling valve fitted to the autoclave was used to expand the gas samples into test bulbs. In these the gas mixture can be kept without danger of further isotope exchange. The gas samples were drawn through an effective cooling trap by means of a Toepler pump in order to completely condense the ammonia. This was subsequently decomposed on a tungsten wire at 1400°C. The hydrogen freed from ammonia as well as the hydrogen obtained in the ammonia decomposition were analyzed for deuterium with a 180° special H/D mass spectrometer, Atlas-Werke, Bremen, Type HD 57. For calibration purposes water with a deuterium content of 153 ± 0.5 ppm was available, from which further standards could be prepared by mixing with pure D_2O. The water samples were completely decomposed to hydrogen on zinc in the usual way (*12*). The accuracy of a single determination was $\pm 1\%$.

Evaluation of Experiments

For small deuterium contents the isotope exchange

$$NH_3 + HD \underset{K_B}{\overset{K}{\rightleftharpoons}} NH_2D + H_2$$

can be treated as a first-order reaction:

$$dx/dt = -K[x - (y/\alpha)] \qquad (1)$$

where x and y denote the mole fraction of deuterium in hydrogen and ammonia respectively. α is the equilibrium separation factor:

$$\alpha = y_\infty/x_\infty = K/K_B \qquad (2)$$

which is given by the ratio of the rate constants for the forward (K) and backward (K_B) reaction.
From a material balance it follows:

$$y = \alpha x_\infty - r(x - x_\infty) \qquad (3)$$

with

$$r = 2n_H/3n_A$$

n_H and n_A being the number of moles of hydrogen and ammonia, respectively. Hence integration of the differential equation:

$$dx/dt = -K\left(1 + \frac{r}{\alpha}\right)(x - x_\infty) \qquad (4)$$

results in:

$$\ln\frac{x - x_\infty}{x_0 - x_\infty} = -K\left(1 + \frac{r}{\alpha}\right)t \qquad (5)$$

with the boundary condition $x = x_0$ at time $t = 0$.

The equilibrium separation factor between hydrogen and liquid ammonia can be represented in a wide range of temperatures by the following equation (4)

$$\log \alpha_{\mathrm{liq/gas}} = -0.2428 + 237/T$$

The deuterium content x_∞ of the hydrogen can be obtained by means of Eq. (3) if x and y are determined on the same gas sample taken at any time. Since the mass-spectrometric analyses are carried out on gas samples, the results for ammonia have to be corrected using the vapor pressure ratio recently determined in this Laboratory (*13*) for the relevant temperature range.

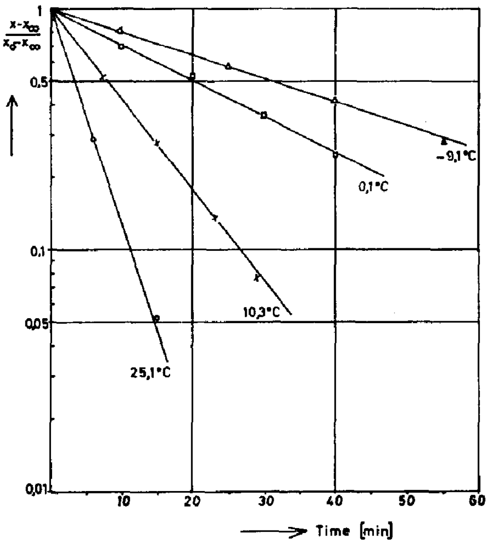

FIG. 3. Degree of exchange versus time. Platinum-carbon catalyst; liquid ammonia: 0.38 mole; H_2; 0.011 mole; stirring frequency; 240 strokes/min.

In all experiments a plot of ln $(x - x_\infty)/(x_0 - x_\infty)$ versus time t according to Eq. 5 resulted in straight lines from which the half value time τ can be read off. Typical examples are shown in Fig. 3; τ is related to the reaction velocity constant K:

$$K = \frac{\ln 2}{[1 + (r/\alpha)]\tau} \tag{6}$$

The efficiency of catalysts can be expediently demonstrated by the number of moles reacting per unit time under the prevailing experimental conditions. With respect to isotope reactions an exchange constant can be defined giving the number of atoms of the particular element which pass from one component to the other in a certain time. For the reaction in question the sum of H and D atoms changing over from hydrogen into ammonia has to be considered. This is equal to the number of atoms travelling in the opposite direction due to the conservation of mass. Since the forward and backward reaction show different rate constants (Eq. 2) this number depends on the particular deuterium concentration. Thus the exchange constant

$$\lambda = 2n_{\mathrm{H}}K \tag{7}$$

is defined as the total number of D and H atoms which pass from hydrogen into ammonia or vice versa on the assumption that the deuterium content in the hydrogen equals $x = 1$ and in the ammonia $y = 0$.

RESULTS

a. Comparison of Various Metal Catalysts

Comparative experiments on the rate of H/D exchange with different metal catalysts were carried out in the 150 cm^3-reactor at a stirring frequency of 120 strokes/min. The autoclave was charged with 1 g of catalyst suspended in 10 ml of liquid ammonia and deuterium-enriched hydrogen at a pressure of 1.5 atm. In the case of KNH_2 saturated solutions were used. Half

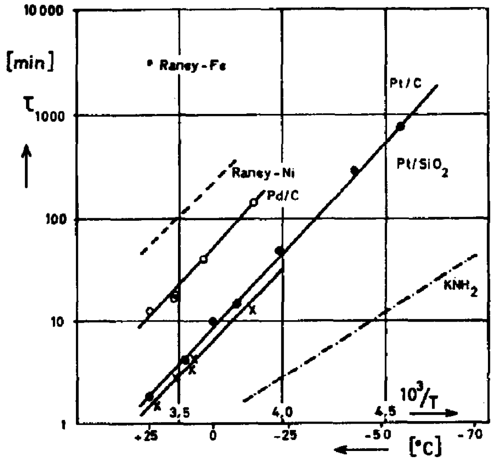

FIG. 4. Comparison of the activity of various catalysts.

value times τ are plotted as a function of temperature in Fig. 4. It can be seen that the activity of the metals for the exchange reaction between hydrogen and liquid ammonia increases in the order: Raney-Fe, Raney-Ni, Pd/C, Pt/C. From the Arrhenius plot an apparent activation energy of 10–12 kcal/mole is obtained for the heterogeneous catalysts, which is considerably greater than the 5.4 kcal/mole found for the homogeneous catalyst potassium amide.

b. Exchange Kinetics on Platinum Catalysts

Experiments with liquid ammonia. Previous comparative experiments with dissolved potassium amide had shown that the rate of exchange increases proportionally with the frequency of stirring without reaching a limiting value under the experimental conditions. In significant contrast with these results no influence of the intensity of *phase mixing* has been found for the platinum catalysts. From a frequency of 17 up to 240 strokes/min practically no change of the reaction rate was observed.

The influence of the *catalyst concentration* has been studied in the range 10 to 100 g/liter. A typical example is shown in Fig. 5 which refers to experiments with a platinum/carbon catalyst. The experimental conditions were as follows: 150 cm^3 reactor, stirring frequency 240 strokes/min, 10 ml liquid ammonia, 1.5 atm hydrogen, temperature 10.4°C. A strictly linear relation exists between the rate of exchange and the catalyst concentration.

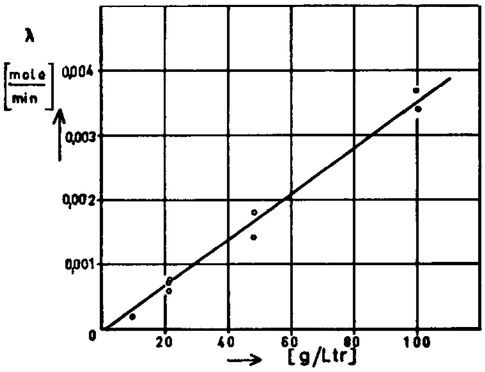

FIG. 5. Influence of catalyst concentration.

The *temperature dependence* has been studied on two supported platinum catalysts. From the Arrhenius plots activation energies of 10.0 ± 0.5 and 9.6 ± 0.6 kcal/mole were obtained for the platinum/carbon and platinum/silica catalyst, respectively.

In all experiments the amounts of hydrogen and ammonia were kept constant, so that the volume of the liquid as well as the gas pressure changed with temperature. Consequently the above apparent activation energies contain contributions from the temperature dependence of the solubility of hydrogen, from transport processes, etc. It is interesting to note that not only the activation energies but also the actual rates of exchange per unit weight of catalyst agree within the accuracy of the measurements between the two types of catalysts although the *surface areas* (*18*) are widely different: 950 and 410 m^2/g for Pt/carbon and Pt/silica, respectively. Obviously the catalytic activity is solely related to the amount of platinum and for the catalysts studied here the carrier seems to have no influence. Further discussion of this result would require more detailed information on these two different catalysts, e.g. pore size, metal surface area, etc.

The influence of the *hydrogen pressure* has been studied up to 135 atm. The exchange constant λ versus the square root of hydrogen pressure is plotted in Fig. 6 for a platinum/carbon catalyst. The experimental conditions were as follows: high pressure autoclave, stirring frequency 125 strokes/min, 1.28 g catalyst suspended in 70 ml liquid ammonia, temperature 20.0°C. The λ values given refer to one gram of catalyst.

Experiments with gaseous ammonia. For comparison with the results in liquid ammonia the exchange has also been studied in the gas phase on the same platinum/carbon catalyst. In one series of experiments the ammonia pressure was kept constant at 149 Torr when the hydrogen pressure varied from 50 to 600 Torr. As in the case of liquid ammonia the exchange con-

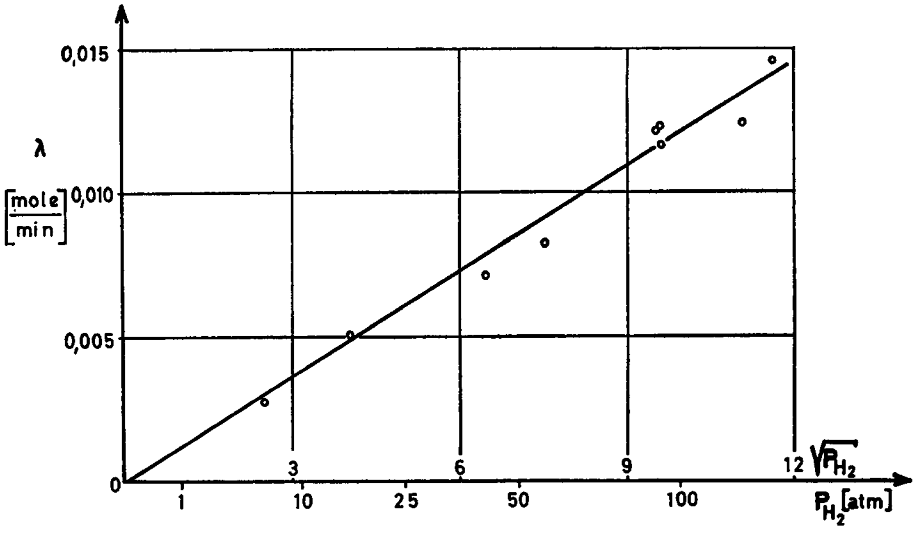

Fig. 6. Influence of hydrogen pressure, exchange with liquid ammonia.

stant λ is a function of the square root of the hydrogen pressure (Fig. 7). In another set of experiments the hydrogen pressure was kept constant while the ammonia pressure varied from 25 Torr up to the saturation pressure of 8.7 atm at 20.0°C. The results are illustrated in Fig. 8 which refers to a hydrogen pressure of 1 atm. Above the saturation pressure the exchange constant λ as obtained from experiments in liquid ammonia is indicated.

Various kinetic equations have been suggested for gas phase reactions (*19*) of which the following represents the results remarkably well over the whole range of ammonia pressures.

$$\lambda = \frac{a \cdot p_{\mathrm{NH_3}}}{(b + p_{\mathrm{NH_3}})^2} \cdot p_{\mathrm{HD}}^{1/2} \qquad (8)$$

By means of the method of least squares the best values are $a = 120$ and $b = 0.1$ if λ is expressed in millimole/min and the pressures in atm. These constants have

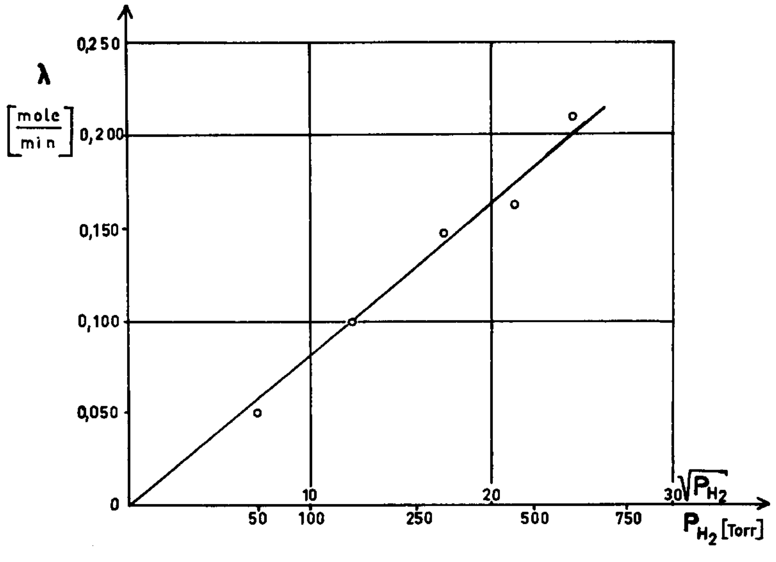

Fig. 7. Influence of hydrogen pressure, exchange with gaseous ammonia.

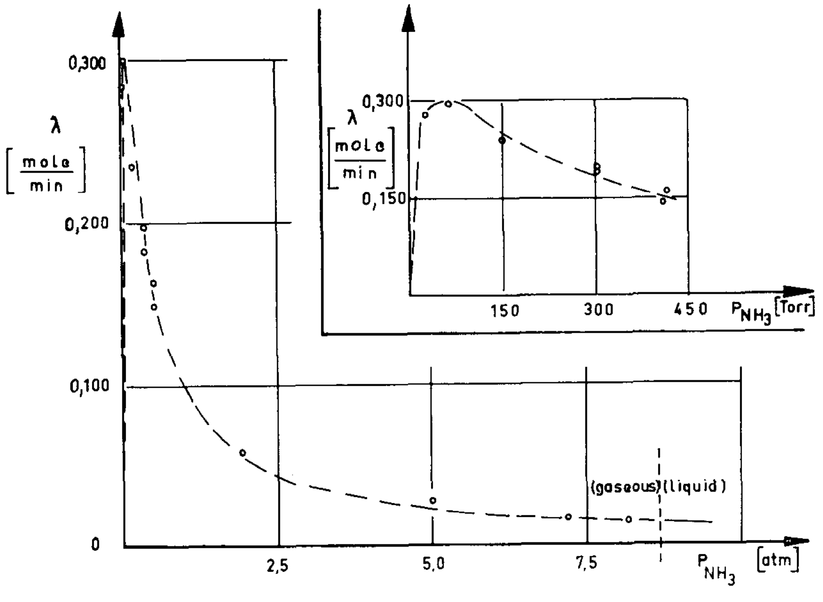

FIG. 8. Influence of the ammonia pressure.

been used to draw the dashed curve in Fig. 8.

DISCUSSION

a. Comparison of Various Catalysts

Homogeneous catalysts. According to well-known concepts the following two groups of catalysts are conceivably active in liquid ammonia. On the one hand an increase in NH_4^+ or NH_2^- concentration could accelerate the exchange rate in analogy to acid-base catalysis. From studies by Roth and co-workers (*5*) as well as from our own experiments it is, however, evident, that all substances tested on this basis are inactive except the alkali amides. On the other hand it has been found that in aqueous systems some salts with cations (e.g. Cu^+, Ag^+, Au^+) having the same number of electrons as the neutral atoms of usual hydrogenation catalysts (e.g. Ni, Pd, Pt) are capable of activating molecular hydrogen. So far no positive effect has been found, e.g. in our own experiments with monovalent gold and silver compounds. It may be, however, that, according to a discussion by Halpern (*14*), an optimal stability of the complexes formed in liquid ammonia is required.

Summarizing, it would appear that the alkali amides, in particular potassium amide, are the only homogeneous catalysts of any practical significance studied thus far.

Metal hydrides. Some metals react even at low temperatures with molecular hydrogen and are capable of forming hydrides up to a limiting composition, e.g. UH_3 and TiH_2. Wicke, Küssner, and Otto (*15*) suggested the use of this property for what these authors have called "Hydride-formation-catalysis." For instance, palladium coated with a layer of uranium can spontaneously take up hydrogen even at $-100°C$, although, e.g. at $+30°C$ palladium does not react with hydrogen directly. Furthermore Bigeleisen (*16*) noticed that UH_3 exchanges rapidly with gaseous D_2 at room temperature. Equilibrium is, however, obtained only slowly since the reaction rate is limited by the diffusion of hydrogen into the interior of larger particles.

At first sight one, therefore, might expect catalytic activity for certain hydride-forming metals or hydrides. Our experiments indicated that neither titanium and uranium nor titanium hydride and uranium hydride did show a catalytic effect in the H_2/NH_3 isotope exchange. Most probably ammonia reacts with the catalysts, forming a layer of metal nitride which blocks up the surface for further reaction. Wicke and co-workers have similarly argued to explain the inefficiency of UH_3 as a hydrogenation catalyst for ethylene as a consequence of formation of uranium carbide.

Metal catalysts. As is well known metals of the eighth group of the periodic table are particularly effective hydrogenation catalysts. Kemball (*17*) has systematically studied these metals as catalysts in the isotope exchange between hydrogen and gaseous ammonia and has shown that only small activation energies are exhibited. In our experiments (Fig. 4) we have found a catalytic effect also in liquid ammonia. The increase in the rate of exchange is, however, considerably smaller than in the gas phase. This significant finding will be discussed in detail on the basis of kinetic studies in the next section.

b. Exchange Kinetics on Platinum Catalysts

In the wide range of pressures from 50 Torr up to 150 atm the rate of H/D-exchange on platinum catalysts is a function of the square root of hydrogen pressure both for gaseous and liquid ammonia. On the other hand the rate of the gas phase reaction at a constant hydrogen pressure at first increases with rising ammonia pressure and after reaching a maximum continuously decreases. Extrapolation of the gas phase results above the saturation pressure leads exactly to the reaction rate directly obtained in experiments with liquid ammonia. These findings suggest that the isotope exchange reaction on a platinum catalyst follows an analogous mechanism both in the gas and liquid phase experiments, which can therefore be discussed along the same lines.

This result is not self-evident since on liquefaction ammonia exhibits a certain degree of electrolytic dissociation. Thus the presence of ions might lead to a principally different mechanism in the liquid phase. On the basis of this reasoning an increase in the NH_4^+ concentration could effect the reaction rate in the following way:

$$NH_4^+ + e^-(Pt) \rightleftharpoons NH_3 + H_{ad}$$

The adsorbed hydrogen atoms could undergo isotope exchange with molecular hydrogen.

"Acidification" of the liquid ammonia by addition of hydrogen chloride up to a concentration of $5M$, however, resulted only in a slight increase in the exchange constant. One therefore has to conclude that an "electrochemical" mechanism, if at all, will be operative only to a minor extent even at high NH_4^+ concentrations.

A study of the "base-analogous" medium is practically not possible since NH_2^- ions, if present even at very small concentrations, are catalytically so active that they would completely mask the effect due to the platinum catalyst. In the analogous hydrogen/water system the electrochemical mechanism may play a more important role. This would appear reasonable in view of the larger ion product of water ($p_m = 10^{-14}$ at 25°C) as compared to that of ammonia ($p_m = 10^{-22}$ at −33°C).

In order to further elucidate the exchange mechanism it has to be demonstrated that the experimental results refer to the reaction proper on the catalyst and are not influenced by transport processes. In contrast to the homogeneous catalysis this is true in the experiments with platinum catalysts for the following reasons: (1) the intensity of phase mixing has no influence on the reaction rate; (2) the exchange constant increases with the square root of the hydrogen pressure; (3) the observed activation energy of 10 kcal/mole would be excessive for transport processes.

In principle the catalytic exchange reaction could proceed in either of the two ways:

(1) Both reactants are chemisorbed and exchange occurs between these species (Langmuir-Bonhoeffer-Hinshelwood-mechanism).
(2) Either hydrogen or ammonia is chemisorbed and exchange takes place with the other component not chemisorbed (Rideal-Eley-mechanism).

Chemisorption of hydrogen on Group VIII metals leads to dissociation into atoms with relatively small activation energies. Dissociative chemisorption can not only occur on the metal/gas interface but also on the phase boundary metal/liquid (*20*). Chemisorption of ammonia on metals has been repeatedly studied. Thus Wahba and Kemball (*21*) concluded from their extensive experiments that dissociation of the ammonia into smaller fragments like NH_2, NH, or even N atoms has to be considered. No conclusive arguments can be advanced to discriminate between these possibilities on the basis of our present experiments with liquid ammonia.

For the case of an exchange reaction between ammonia and deuterium according to a Langmuir-Bonhoeffer-Hinshelwood-mechanism a rate law as given in Eq. 8 should hold (*19*). In fact Weber and Laidler (*22*) have found this to be true for the gas-phase exchange on an activated iron surface. The present experiments with ammonia and a platinum/carbon catalyst show that the dependence of the exchange rate on ammonia as well as hydrogen pressure can be remarkably well represented by this equation over a wide range of pressures, not only in the gas phase reaction but also in the liquid ammonia up to 150 atm hydrogen.

The influence of the pressure of the reactants can thus be visualized in the following way: Since exchange occurs between hydrogen atoms and chemisorbed ammonia the observed dependence on the square root of hydrogen is to be expected. Starting from very small ammonia pressures the rate at first increases with rising ammonia concentration, simply since more NH_3 molecules are available for the exchange to occur. Simultaneously fewer surface sites are accessible to the hydrogen with the consequence that the rate passes through a maximum and then decreases. This process comes to an end when multilayer adsorption sets in. Extrapolation of the steep slope in Fig. 8 leads to a pressure which is in the order of 1/10 of the saturation pressure of ammonia. Above this pressure certainly multilayer formation has to be considered. On further increase of the ammonia pressure the exchange rate changes only little and remains constant on transition to the liquid phase.

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