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THE MECHANISM OF THE EXCHANGE OF HYDROGEN GAS
WITH SOLUTIONS OF POTASSIUM AMIDE IN LIQUID AMMONIA **

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 - + Based on a dissertation submitted by June C. Dayton, in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Southern California.
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ABSTRACT

It has been shown that the rate of conversion of parahydrogen by liquid ammonia solutions of potassium amide is proportional to the concentrations of amide ion and parahydrogen. The specific rate constant at -50° C. was found to be $7740 \text{ l. mole}^{-1} \text{ min}^{-1}$. Deuterium gas exchanges with these solutions at approximately the same rate, and HD has been established as the initial product.

INTRODUCTION

The exchange of deuterium gas with solutions containing the strong bases amide and hydroxide ion has been reported in a previous note in this Journal.¹ Much more detailed experiments involving the exchange and parahydrogen conversion in solutions of aqueous alkali have elucidated the principal details of the exchange process in this medium. The following is an account of similar experiments performed with solutions of potassium amide in liquid ammonia. The difficulties involved in preparing and handling the air-sensitive potassium amide and the extreme rapidity of this exchange process limit the accuracy of the present data. However, in view of the rather extensive effort that will be required for a detailed analysis of the amide exchange mechanism, it seems desirable to present this portion of the work at this time. Most of these experiments, as in the hydroxide catalyzed exchange, involve the study of the parahydrogen conversion, since a mass spectrometer was not available in the early stages of the research. However, two experiments reported below again indicate that the parahydrogen conversion is effected principally through an exchange mechanism.

EXPERIMENTAL

The experimental procedures reported previously² were used with the following modifications and additions.

Reaction Cell. - The rate measurements of the parahydrogen conversions

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- (1) Y. M. Claeys, J. C. Dayton, and W. K. Wilmarth, J. Chem. Phys., **18**, 759 (1950).
 - (2) W. K. Wilmarth and C. F. Baes, Jr., ibid., **20**, 116 (1952).

by solutions of potassium amide in liquid ammonia were made in a cell of the type shown in Fig. 1. For this study a sidearm with a ground glass joint was added below the stopcock to facilitate the attachment of the cell to the vessel used for the amide preparation.

Preparation of Potassium Amide. - The apparatus was designed for the preparation and transfer of potassium amide to the reaction cell in vacuo because the amide decomposes with explosive violence in contact with air. Several vessel designs were tested, and the final design is shown in Fig. 12. This apparatus was connected to the reaction cell by the ground glass joint at A.

The amide was prepared by decomposition of a potassium-ammonia solution using Raney nickel as a catalyst. (Spongy platinum³ was also tried but its use was discontinued because of the longer time required for the decomposition.) The Raney nickel was prepared in the usual manner, by the action of sodium hydroxide on a powdered nickel-aluminum alloy, and was stored under alcohol. In a given experiment a small quantity of the alcohol-nickel slurry was put into a small thin-walled bulb from which the alcohol could be removed in vacuo. The bulb was sealed off and introduced into the amide preparation vessel. Potassium in a glass tube of the appropriate length was placed at point C, and a seal was made at D. The metal was pinholed under vacuum into bulb E and the residue removed by a seal at F. The catalyst fell into the bulb E when the thin wall of its container was broken with a magnetically operated hammer G consisting of an iron rod sealed in glass. Anhydrous ammonia was then distilled onto the catalyst and the potassium. The liquid ammonia level was kept below the sintered glass filter H until the

(3) R. Feulgen, Ber., 54B, 360 (1921).

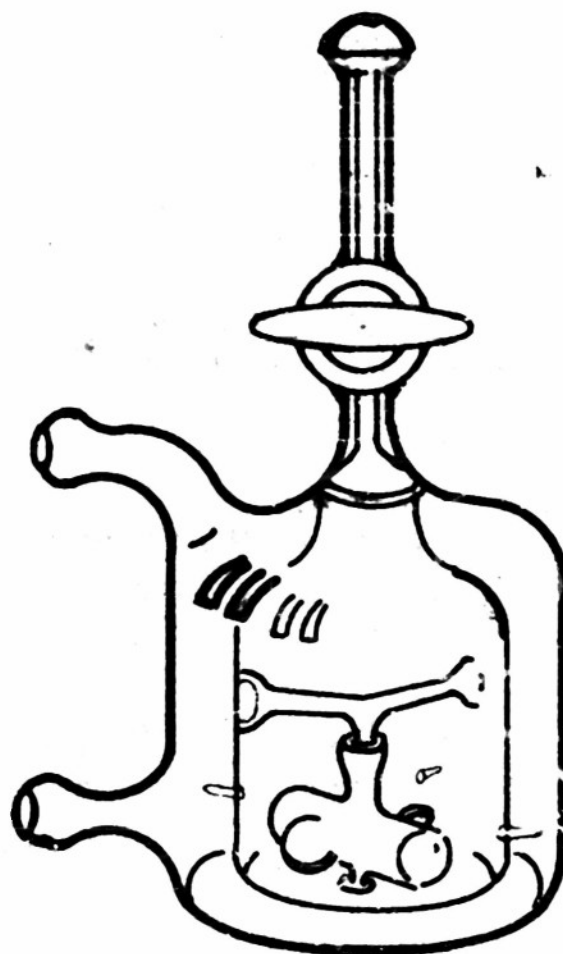
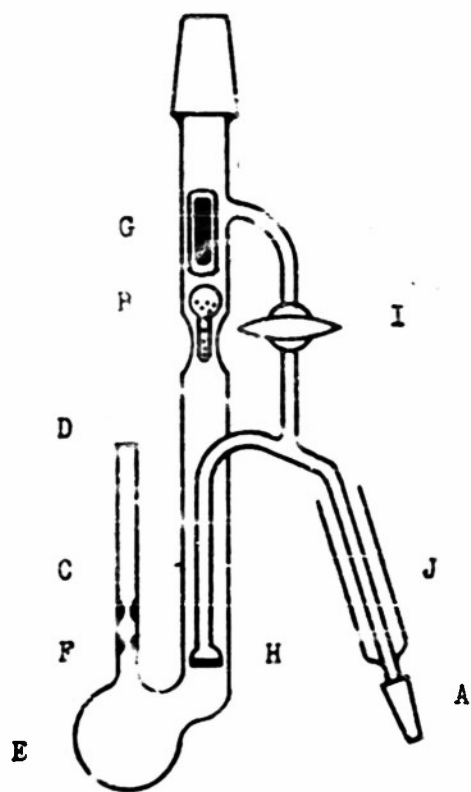


FIGURE 1 - Magnetically stirred reaction vessel



*Vessel for
Amide Preparation*

Figure 1a

blue color of the metal-ammonia solution faded to colorless or pale yellow. This color change was usually accomplished within twenty minutes of the ammonia addition at a temperature of -45°C . (With one preparation of Raney nickel it was noticed that the amide solutions were a light green color. Such solutions were discarded, due to the presence of the divalent nickel ions.) The amide solution was then diluted with ammonia to the desired level above the sintered glass filter. Stirring was effected by allowing the ammonia solution to boil. A quantity of solution containing the desired amount of amide was forced into the reaction cell. This quantity could be roughly estimated from the amount of potassium introduced, the total volume of ammonia, and a rough calibration of the vessel volume above the sintered glass filter. The transfer was accomplished by closing stopcock I and raising the temperature of bulb E until the internal pressure was about one atmosphere. At the same time, the reaction cell was cooled by pouring liquid nitrogen into the jacket. To ensure transfer of the solution and not just distillation of ammonia, additional cooling of the connection tube to the cell was accomplished by inserting a dry ice-ether solution in the jacket J. By opening stopcock I and cooling bulb E the ammonia in the cell was distilled back, leaving pure potassium amide and ammonia vapor in the reaction cell. The tube connecting the cell to the apparatus in which the amide was prepared was then sealed off.

Rate Measurements. - The cell containing ammonia vapor and amide was evacuated. A known volume of anhydrous ammonia was distilled into the cell. It was necessary to surround the sidearm area with a temporary aluminum foil jacket containing dry ice-ether mixture to condense ammonia which could then wash down traces of solid amide into the solution. Parahydrogen was introduced at

50 to 60 cm. pressure. The timer and stirrer were started simultaneously. The stirrer revolved at 1200 RPM, a speed which was fast enough to ensure that the hydrogen in solution was in equilibrium with that in the gas phase so that the rate of solution was not the rate-determining step of the process for amide concentrations below 0.005 N. Samples of hydrogen could be removed during the run by opening the reaction cell to a short section of capillary tubing which in turn could be opened to the 20 ml. sample tubes. The stopcock was always flushed before each sampling to ensure that the sample obtained was representative at the time of removal. At least four gas samples were removed over a period of time covering the half-life of the conversion whenever possible. After the run the ammonia was distilled off and water from which dissolved gases had been removed was distilled in vacuo onto the amide. When the amide was completely destroyed, the sidearm of the cell was opened. The hydroxide-ammonia solution was washed from the cell, boiled 10 minutes to remove the ammonia, and titrated with 0.01 N HCl to a phenolphthalein endpoint. Precautions to destroy the amide before letting air into the cell were not taken with the initial amide runs (Nos. 19, 21, 23, 25, 26), and there exists the possibility that a fraction of the amide was converted to nitrite.⁴ However, the rate data on these points in comparison with the later ones indicate that no unusually large error occurred in these analyses.

The rate constants, k , k' and k^0 are defined in the previous paper.² k is evaluated directly from the measured resistance of the pirani gauge:

$$k = -\frac{1}{t} \ln \frac{P_t - P_\infty}{P_0 - P_\infty} = -\frac{1}{t} \ln \frac{R_t - R_\infty}{R_0 - R_\infty}$$

(4) F. W. Bergstrom and W. C. Fernelius, Chem. Rev., 12, 43 (1933).

where P_t , P_0 and P_∞ denote the concentration of parahydrogen expressed in per cent and R_t , R_0 and R_∞ denote the resistance values for hydrogen samples at time t , 0, and ∞ , respectively. k' is defined to correct for the presence of undissolved gas above the solution:

$$k' = k \frac{\text{total moles of gas}}{\text{moles of gas in solution}}$$

and k^0 , the specific reaction rate constant, permits one to correct for the conversion due to the solvent and to introduce the functional dependence of the rate upon the catalyzing ion or molecule.

With the use of these equations the rate data for the conversion of parahydrogen by potassium amide at -50°C . were calculated and are listed in Table I. A graph of molar rate constant k^0 versus potassium amide concentration is illustrated in Fig. 2.

The value used for hydrogen solubility in the amide solutions at -50°C . was that for pure ammonia extrapolated from the data of Larsen and Black:⁵ 0.011 ml. H_2 (STP) / ml. ammonia. Since the volume of liquid ammonia was measured at dry ice-ether temperatures and the runs were made at -50°C ., a correction for volume increase was made using the density data of Cragoe and Harper.⁶ The correction for parahydrogen conversion by the solvent was within the limit of error of the experiment and can be ignored.

(5) A. T. Larsen and C. A. Black, Ind. Eng. Chem., **17**, 715 (1925).

(6) C. S. Cragoe and D. R. Harper, III, Bur. Stand. Sci. Papers, **420**, 313 (1921).

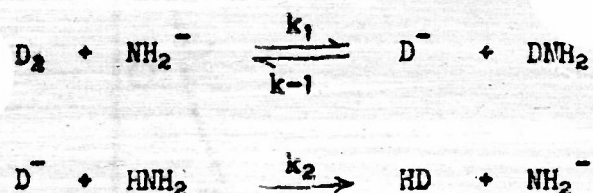
Table I
Rates of Parahydrogen Conversion by Potassium Amide
in Liquid Ammonia Solution at -50°C .

Run No.	Concentration mol/l.	k min. ⁻¹	k' min. ⁻¹	k ⁰ l. mol. ⁻¹ min. ⁻¹
48	0.000354	0.01480	1.274	3640
26	0.000386	0.00544	0.5917	1530
47	0.000547	0.01710	1.472	2680
50	0.001106	0.02080	1.790	1610
25	0.001158	0.00845	2.330	2010
23	0.001223	0.007610	1.456	1190
45	0.00609	0.04259	3.665	602
21	0.00902	0.03935	6.989	775
19	0.02634	0.09500	18.364	697

DISCUSSION

The plot of the specific rate constant against total potassium amide concentration in Fig. 2 shows that k^0 increases rapidly with dilution. The dissociation constant of potassium amide in liquid ammonia is not available at -50°C. , but an attempt to correlate the rate with the actual concentration of amide ion can be made by using the known dissociation constant at -33°C. , $K = 7.3 \times 10^{-5}$.⁽⁷⁾ Amide ion concentrations calculated from this equilibrium constant are plotted against the rate constant k' in Fig. 3. Although the points scatter considerably, this plot is more satisfactory than that of Fig. 2. The slope of the least-mean-squares line represents a specific rate constant for amide ion, $k^0 = 7740 \text{ l. mole}^{-1} \text{ min.}^{-1}$.

In a general sense, the mechanism of the amide ion catalysis seems to be analogous to that for hydroxide ion in water. It can perhaps best be formulated as:



The appearance of HD as an intermediate rules out any appreciable one-step change of D_2 to H_2 , a process which would occur if the two hydrogen atoms on the amide ion were displaced in a single step. The formulation of D^- may be an oversimplification in that D^- may react with a solvent proton before solvation equilibrium is established. Since the activation energy for the amide exchange is not known, attempts to distinguish between the two possibilities are even less fruitful than in the hydroxide system.

(7) W. W. Hawes, J. Am. Chem. Soc. 55, 4422 (1933).

Figure 1

Rate of Reaction of Parahydrogen
with H_2O_2 at -90°C .

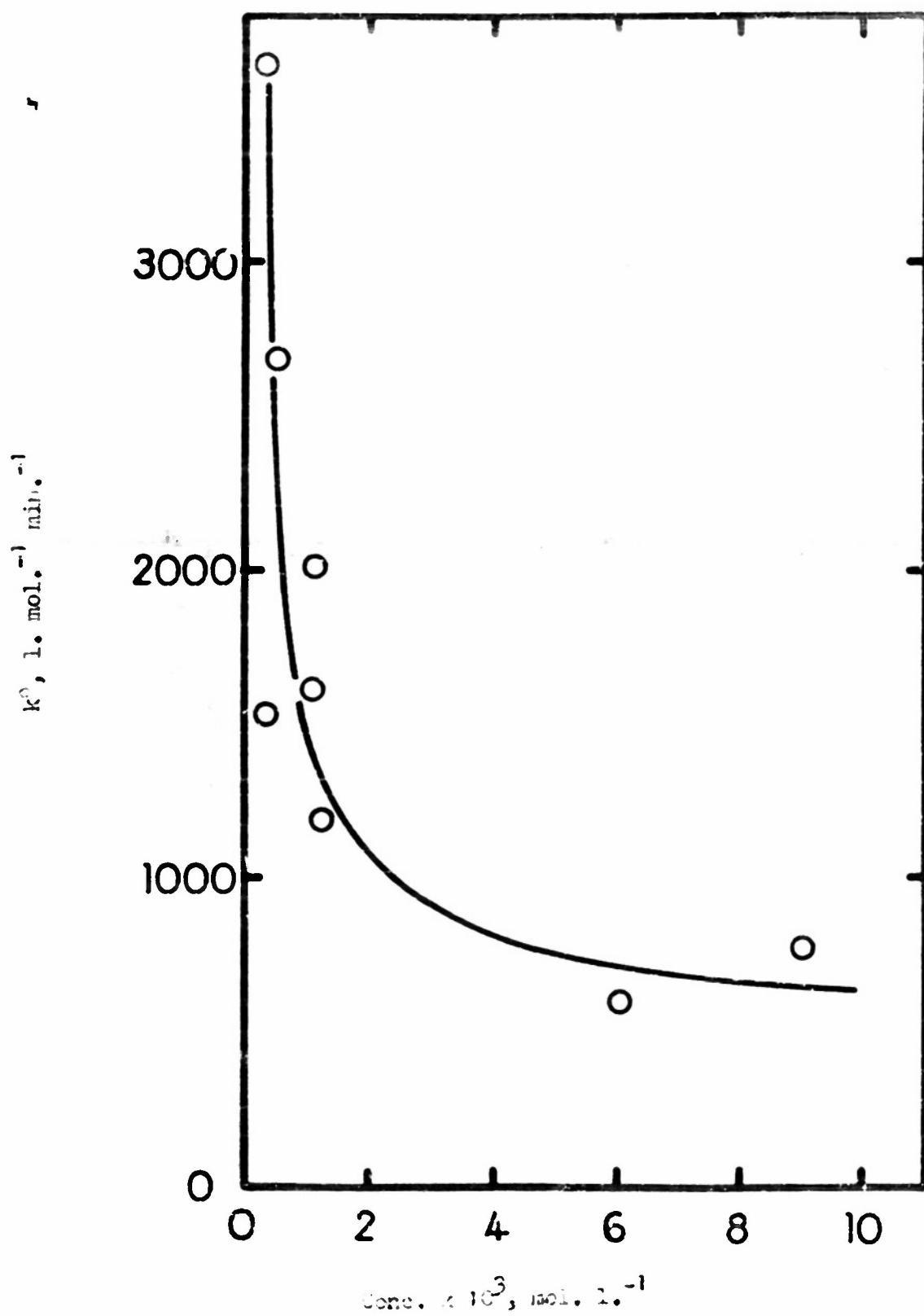
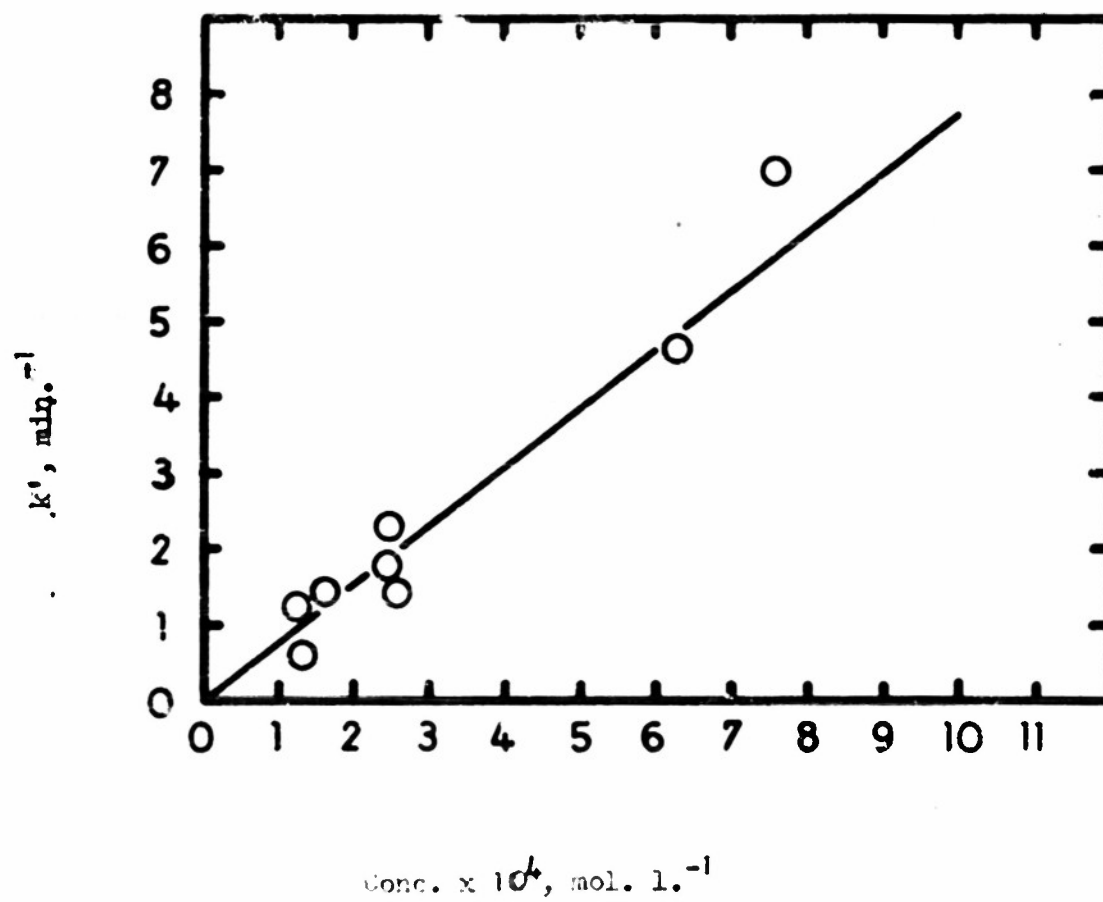


Figure 3

RATE OF PARAHYDROGEN CONVERSION IN SOLUTION BY AMIDE ION
IN LIQUID AMMONIA AT -50°C .



The exchange of deuterium gas was studied in only two experiments. The data is listed in Table II in terms of the mole percentages of D_2 and HD as a function of time. A plot of run No. 109, in which the exchange was followed almost to completion, is shown in Figure 5.

The rate constants for the exchange of D_2 and HD are listed in Table III.

Table II

DEUTERIUM EXCHANGE WITH POTASSIUM AMIDE IN LIQUID
AMMONIA AT $-52.6 \pm .2^\circ\text{C}$.

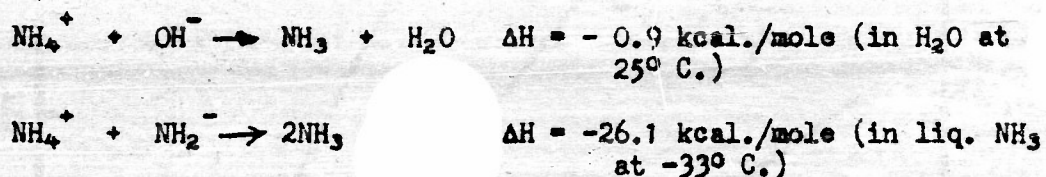
Run No.	Conc. KNH_2 (moles/l.)	Time (min.)	Mole % D_2	Mole % HD
107	0.000149	0	98.9	2.4
		15	87.9	14.3
		60	66.6	35.1
		135	43.3	54.4
		214	30.3	58.5
		314	18.3	54.0
		400	12.2	46.2
109	0.00268	0	100.0	0.9
		15	72.1	28.5
		31	49.8	43.3
		50	30.5	48.2
		101	10.5	37.2
		162	3.3	19.5
		210	0.9	10.1
		261	0.9	5.3
		310	0.7	2.1

Table III

RATES OF EXCHANGE WITH POTASSIUM AMIDE IN
LIQUID AMMONIA AT -53°C .

Run No.	107	109
Conc. KNH_2 mol. $\text{l.}^{-1} \times 10^4$	1.49	26.8
Conc. NH_2 mol. $\text{l.}^{-1} \times 10^4$	0.805	4.58
$k^1 \text{ D}_2$ min. $^{-1}$	0.565	2.08
$k^1 \text{ HD}$ min. $^{-1}$	0.235	1.31
$k^0 \text{ D}_2$ l. mol. $^{-1}\text{min.}^{-1}$	4.9×10^3	(from Fig. 4)
$k^0 \text{ HD}$ l. mol. $^{-1}\text{min.}^{-1}$	2.8×10^3	(from Fig. 4)

The most striking feature of the amide catalysis is the remarkable rapidity with which exchange occurs. At -50° C. the rate constant is approximately 10^4 times that for hydroxide at 100° C. and, assuming a constant activation energy and pre-exponential factor in the latter case, 10^{14} larger than the hypothetical constant for hydroxide in water at -50° C. If one now assumes the same pre-exponential factor for the amide and hydroxide processes and ignores the difference in solvent, one can calculate an activation energy of 10 kcal./mole for the parahydrogen conversion. The decrease from the 23.8 kcal./mole observed for hydroxide should be related to the difference in base strengths of the two ions. This information is not available at comparable temperatures or in a single solvent, but an approximation can be obtained from the heats of the two processes:



Since both equilibria involve the formation of uncharged molecules from charged ions, the medium effects are undoubtedly large, but even an error of 50% would not invalidate the mechanism. It is interesting to note that metal salts of the isoelectronic base methide ion, when exposed to hydrogen, form metal hydrides and methane as the stable products.⁽⁸⁾ The similarity between this reaction and the mechanism we have proposed is obvious, but formation of a stable hydride in a solvent of low dielectric constant would support only the gross features of a hydride mechanism for the exchange.

A comparison between the rates of reaction for the various isotopic hydrogen species is shown in Fig. 4. Isotope effects are undoubtedly

(8) H. Gilman, A. L. Jacoby and H. Ludman, J. Am. Chem. Soc. 60, 2336 (1938).

Figure 4

RATE OF EXCHANGE IN SOLUTION BY AMIDE ION IN LIQUID
AMMONIA AT -53°C .

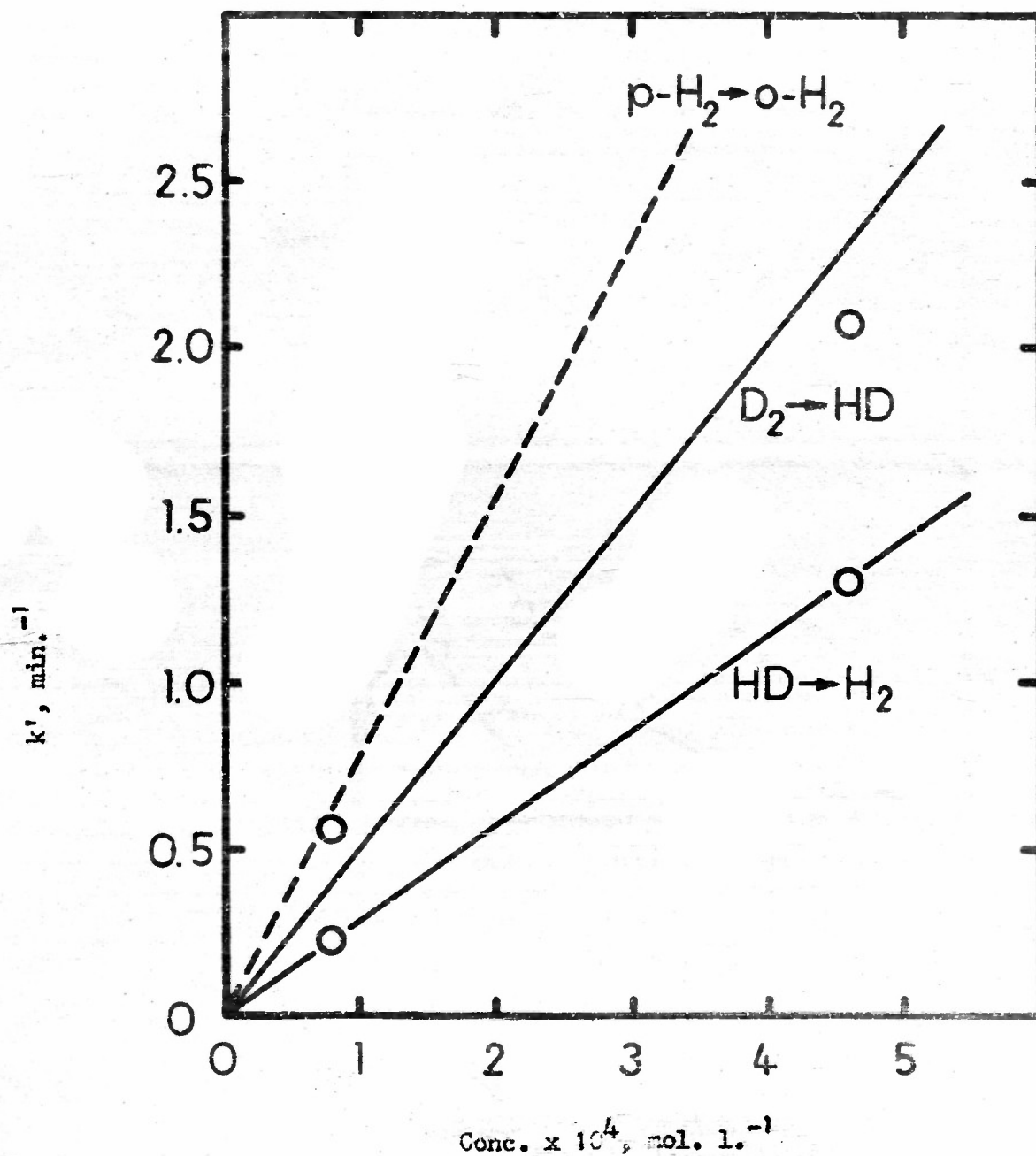
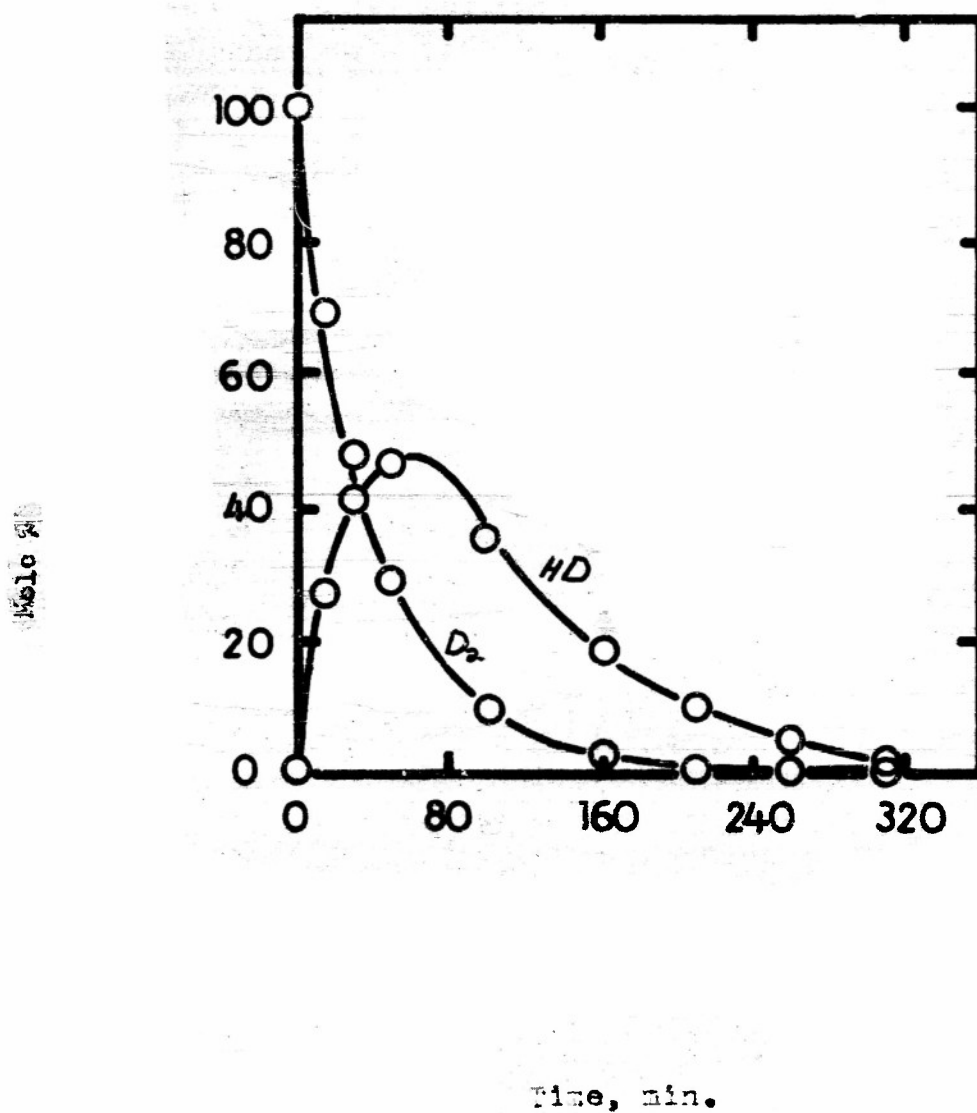


Figure 5

VARIATION IN PERCENT OF D_2 AND HD WITH
TIME DURING EXCHANGE WITH POTASSIUM
ASIDE IN LIQUID AMMONIA AT $-55^\circ C$.

Run 109



partly responsible for the different slopes, but other factors are also present. The exchange of HD may produce either H₂ or HD by reaction with a solvent proton, so the disappearance of HD represents only about half the rate at which it reacts. The higher rate for parahydrogen as compared with deuterium may be due to some conversion by perturbations too low in energy to produce exchange. Thus the positive identification of the isotope effect will be complicated, and we are able to say at present only that it is probably not very large.