The InterRelations of Hydrogen and Deuterium Molecules

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Additional information on J. Chem. Phys.

The Inter-Relations of Hydrogen and Deuterium Molecules

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It has been shown that neither stopcock grease nor water in a Pyrex or soft-glass vessel affect the concentration of hydrogen-deuterium mixtures. Diffusion through palladium gives a concentration of the isotopes which is about that to be expected from an atomic diffusion process. Desorption from charcoal at liquid air temperatures gives the concentration effect to be expected from a diffusion as molecules. Mercury, Pyrex and soft-glass surfaces at room temperature and charcoal at liquid air temperatures do not promote the reaction between hydrogen and deuterium.

Chromium oxide and nickel-kieselguhr surfaces promote the reaction between hydrogen and deuterium in the temperature range between $-190°$ and $110°C$. A palladium surface catalyzes the reaction at $270°C$. Experimental values have been obtained for the equilibrium constant of the reaction between hydrogen and deuterium from the temperature of liquid air upwards, in accord with theoretical calculations by Urey and Rittenberg based on statistical mechanics.

WITH the discovery of the heavy isotope of hydrogen, the chemist had available a powerful tool for the investigation of fundamental problems in chemistry. For the purpose of exploring the possibilities of the use of this tool, the following investigations were undertaken. Methods had to be devised for the storage of the gas such that the concentration of hydrogen-deuterium mixtures would remain constant over long periods of time. Before any extensive investigation could be conducted, it was essential that a method be developed for the accurate analysis of gas mixtures containing the three possible molecular species, H_2, D_2 and HD. After the completion of these preliminary experiments and others which eliminated possible sources of error, an investigation was undertaken of the interaction of hydrogen and deuterium at catalytic surfaces the characteristics of which were already known. The quantitative aspects of this reaction permit important conclusions to be drawn as to the type of adsorption processes operative under these conditions. Although various methods had already been discovered for the separation of these two isotopes of hydrogen, interest attached to the investigation of alternative methods of concentration which would be informative as to the nature and mechanism of the processes involved. In the following pages a record of these will be found.

I. Method of Analysis

The method of analysis chosen must be capable of distinguishing the three molecular species possible in a mixture of hydrogen and deuterium, namely, H_2, D_2 and HD. Moreover, the instrument must not cause reaction among these molecules. The mass-spectrograph described by Bleakney[1] fulfills these requirements very well. Bleakney[2] has also given methods by which the mass-spectrograph may be applied to the study of hydrogen isotopes. Briefly, the method is to bombard the sample of gas with electrons of controlled potential and to measure the intensity of the positive ions of different masses which are so produced. A mixture of hydrogen and deuterium may form monatomic, diatomic and triatomic ions of masses varying from one to six. The different ions are given in Table I.

TABLE I. *Types of positive ions.*

Mass	1	2	3	4	5	6
Ion	H^+	$(HH)^+$	$(HHH)^+$	$(DD)^+$	$(DDH)^+$	$(DDD)^+$
		D^+	$(HD)^+$	$(DHH)^+$		

Bleakney[3] and Smyth[4] have discussed the theory of the hydrogen molecule and the probabilities of ionization. The problem is to separate ions of the same mass. The velocity of the electrons producing ionization may be so adjusted that monatomic ions are not produced as primary products and, consequently, are present only to a small extent. Diatomic ions

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[1] W. Bleakney, Phys. Rev. **40**, 496 (1932).
[2] W. Bleakney, Phys. Rev. **41**, 32 (1932).
[3] W. Bleakney, Phys. Rev. **35**, 1180 (1930).
[4] H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931).

may be distinguished from triatomic ions by studying the intensity of the ions as a function of pressure. For example, if we consider the ions of mass 3, the intensity of the $(HD)^+$ ions is proportional to the first power of the pressure while the intensity of the $(HHH)^+$ ions is proportional to the second power of the pressure. If I is the ionic intensity and p the pressure, a plot of I/p *versus* p should give a straight line whose intercept on the I/p axis represents the intensity due to the diatomic ion $(HD)^+$. In this way the various ions may be identified and their relative concentrations determined.

The hydrogen was admitted to the positive ray apparatus through a fine capillary leak while a rapid diffusion pump exhausted this chamber at such a rate that the pressure maintained there was of the order of 10^{-5} mm Hg. This pressure could be regulated by adjusting the pressure of the source or the pumping speed. The lighter molecules will diffuse through the capillary leak faster than the heavier ones but they will also diffuse out through the pumps faster and the assumption is made that these two effects balance each other. The rate of flow through the spectrograph was so rapid that the tungsten filament was not appreciably effective in causing reaction among the molecules.

II. STORAGE OF GAS

Effect of water

Before any kind of comprehensive investigation could be carried out, it was necessary to devise a method for storing quantities of hydrogen-deuterium mixtures under conditions such that the concentration of the mixture would remain constant over long periods of time. Water at once suggested itself for use as a containing fluid, but there arose the possibility of an interchange between the deuterium in the gas phase and the hydrogen atoms in water. Such a process would decrease the concentration of deuterium in the gas phase. The following experiment was performed for the purpose of ascertaining if such an interchange did occur.

A 425 cc Pyrex bulb was fitted with a three-way stopcock at the top and a stopcock at the bottom connecting with a levelling bulb. The bulb was filled with distilled water and then all

but 35 cc of the water displaced by adding, through one arm of the upper stopcock, a deuterium-hydrogen mixture obtained by the electrolysis of heavy water. Both stopcocks were closed and the apparatus shaken for several minutes to saturate the water in the bulb with gas. The pressure in the bulb was about 1.1 atm. A sample of gas was then removed through the second arm of the upper stopcock, leaving the gas in the bulb at atmospheric pressure. The bulb was kept at room temperature and shaken occasionally for 19 days. At the end of this time, a second sample of gas was removed by displacement with water. Analyses of the two samples gave the results found in Table II. The first three

TABLE II. *Storage over water in a Pyrex vessel.*

	H_2	HD	D_2	% D
Initial sample	100	4.68	0.060	2.29
Final sample	100	4.70	0.061	2.30

columns of the table give the relative concentrations of the three molecular species based on the concentration of H_2 as 100. The last column gives the atomic percent of deuterium present in the samples.

Since these results are in disagreement with those reported by Oliphant[5] which indicate that such interchange does take place, it occurred to us that Oliphant's apparatus might have been constructed of soft glass and that possibly such an interchange might occur on a surface of soft glass but not on one of Pyrex. In order to make the test of this possibility as rigid as possible, an experiment similar to the one recorded was carried out with a bulb made of a special glass manufactured by the Corning Glass Company of Corning, N. Y., expressly for use in the construction of glass electrodes and designated by them as "Number 015." This bulb was connected with the two Pyrex stopcocks by ground joints sealed with "Picien." The total volume of the bulb and connecting tubes was 208 cc. Eighteen cc of water were left in contact with a hydrogen-deuterium mixture for 20 days. The analyses of the two samples are given in Table III. The three sets of analyses given for the first sample and the two for the last sample represent check analyses on each sample and are given to show the

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[5] M. L. Oliphant, Nature **132**, 675 (1933).

TABLE III. *Storage over water in a soft-glass vessel.*

	H$_2$	HD	D$_2$	% D
Initial sample	100	43.2	7.73	19.5
	100	44.4	8.05	19.9
	100	43.5	7.82	19.5
Final sample	100	42.8	8.14	19.6
	100	44.6	8.23	20.0

experimental accuracy of the analytical method employed.

These results show definitely that the concentration of deuterium-hydrogen mixtures in contact with water remains constant if precautions are taken to avoid preferential solubility, diffusion, and the presence of metallic surfaces,[6] and that the result reported by Oliphant cannot be interpreted as being an interchange between the deuterium in the gas phase and the hydrogen atoms in the water without the aid of a catalytic surface other than the glass wall of the containing vessel.

Effect of stopcock grease

In using apparatus containing stopcocks, there was the possibility of interchange between the deuterium in the gas phase and hydrogen in the hydrocarbons contained in the stopcock grease. This possible source of error was investigated by the following experiment. Two Pyrex bulbs of approximately 50 cc capacity were evacuated and filled simultaneously from a reservoir containing a deuterium-hydrogen mixture. The first bulb was fitted with a magnetic break at the lower end and, after filling, was sealed off at the upper end. The second bulb was equipped with a stopcock and was coated on the inside with a layer of "Lubriseal." At the end of 22 days the gas in each bulb was analyzed with the results of Table IV.

TABLE IV. *Effect of stopcock grease.*

	H$_2$	HD	D$_2$	% D
Bulb I	100	4.18	0.061	2.07
Bulb II	100	4.25	0.056	2.09

It is evident, therefore, that an apparatus containing stopcocks may be used in the study of deuterium-hydrogen mixtures without fear of the occurrence of interchange between deuterium in the gas and hydrogen in the stopcock grease.

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[6] J. Horiuti and Polanyi, Nature **132**, 819 (1933).

III. METHODS OF CONCENTRATION

After the discovery of the heavy isotope of hydrogen, chemists and physicists began to search for methods of concentration. It soon became evident that the two isotopes differed so greatly in properties that almost any method which was tried would give some separation but that none approached either in efficiency or in capacity that of electrolysis of water. The next, most obvious step was to study these various methods in a more quantitative way in order to elucidate the mechanisms of the processes which were operative. The purpose of this section is to treat in some detail the results obtained in the study of two such methods.

1. Diffusion through palladium

The method of diffusion through clay pipes which was used by Hertz[7] with such success in the separation of the neon isotopes has been applied by him in the preparation of spectroscopically pure deuterium in small quantities.[8] The numberless papers which have appeared on the diffusion of hydrogen through palladium at once suggested the use of a thin sheet of this metal as a diffusion membrane. While the present work was under way, a paper appeared by Harris, Jost and Pearse,[9] but, as will later be shown, their results are perhaps to be questioned.

Experimental. The first results were obtained by use of a system which had no provision for circulation of the gases. Fig. 1 is a diagram of the apparatus. The hydrogen-deuterium mixture used was obtained by electrolysis of approximately 10 percent heavy water to which sodium hydroxide had been added. B is a bulb of 500 cc capacity with a levelling bulb containing mercury. Oxygen was removed from the gas by passage over the platinized asbestos in C. The system may be evacuated through E which leads to a mercury diffusion pump backed by an oil pump. F and M are traps which were kept surrounded by liquid air to prevent any mercury from reaching the palladium tube, K, which is 5 cm long and 6 mm in diameter. A 2 cm length of

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[7] G. Hertz, Naturwiss. **20**, 493 (1932).

[8] G. Hertz, Naturwiss. **21**, 884 (1933).

[9] L. Harris, W. Jost and R. W. B. Pearse, Proc. Nat. Acad. Sci. **19**, 991 (1933).
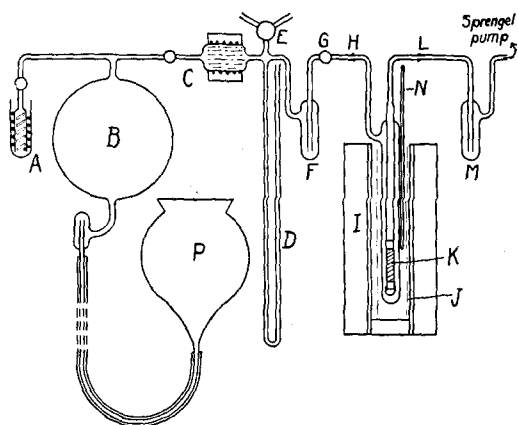
FIG. 1. Apparatus for diffusion through palladium
(no circulating pump)

platinum tube of the same diameter was welded to each end of the palladium tube, and a lead glass cap fused over the lower end. Since the section of the apparatus containing the palladium tube was of soft glass, it was connected to the rest of the apparatus by the ground glass joints, H and L. In order to reduce the temperature gradient up and down the tube, the glass tube outside the palladium was wound with alternate layers of copper foil and asbestos paper, J. The palladium tube was maintained at the desired temperature by means of the resistance furnace I, the temperature being read on two calibrated thermometers (N) placed close to the glass tube surrounding the palladium. By raising the levelling bulb P, the pressure as read on manometer D could be kept at atmospheric until the run was nearly completed at which time the pressure was allowed to drop.

Results without circulation. Two experiments were made, three samples of gas being collected in each experiment: a sample of the original gas, the first gas that diffused through the palladium, and the residual gas remaining after nearly all of the gas had diffused through the palladium. The analyses of these samples are given in Table V.

Circulating system. With the same palladium tube, a new apparatus was built which included a pump for circulating the gas past the palladium. The gas mixture to be diffused was introduced into the apparatus and a sample removed after the circulating pump had been allowed to operate for some time before heating up the palladium tube. As the diffusion process proceeded, the pressure in the system decreased. The final sample which was removed in each case was the residual gas left in the system and, consequently, had not diffused through the palladium.

Experimental results. Two separate runs were made using a total volume of 1350 cc of gas in each case. The analyses of the samples are given in Table VI. Operating temperature: 265°C.

TABLE VI. *Diffusion through palladium with circulation.*

		H_2	HD	D_2	% D
Exp. I	Initial gas	100	5.58	0.096	3.43
	First 52 cc	100	4.20	0.065	2.03
	Residual 69 cc	100	14.3	0.52	6.68
Exp. II	Initial gas	100	7.41	0.127	3.50
	First 35 cc	100	5.62	0.074	2.74
	Residual 65 cc	100	20.0	1.01	9.08

A third run was made using as the starting material a mixture of gas part of which was obtained by electrolysis of ordinary water and the remainder by the electrolysis of nearly pure deuterium oxide. The analyses of the samples are given in Table VII. Operating temperature: 270°C. Total volume of gas: 1350 cc. Sample A indicates the concentration of a sample of gas which diffused through the palladium when the pressure had dropped from 800 mm to 645 mm. Sample B is a similar one removed when the pressure was 136 mm. The fourth column contains the concentration of deuterium calculated as atomic percent. Column five contains the

TABLE V. *Diffusion through palladium without circulation.*

Experiment I	% D	Experiment II	% D
Initial gas	1.83	Initial gas	2.00
First 75 cc	1.56	First 62 cc	1.86
Residual 58 cc	1.81	Residual 80 cc	2.20
Total volume: 511 cc		Total volume: 519 cc	
Operating temperature: 230°C			

TABLE VII. *Diffusion through palladium.*

	H_2	HD	D_2	% D	K'
Initial gas	100	32.4	43.8	34.0	0.24
First 32 cc	100	53.3	7.34	21.1	3.9
Sample A	100	66.2	11.5	25.1	3.8
Sample B	100	140.0	51.4	41.7	3.8
Final 55 cc	100	335.0	280.0	62.2	4.0

values of the concentration ratio of the reaction

$$H_2 + D_2 = 2HD$$
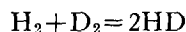
as calculated by

$$K' = [HD]^2 / ([H_2][D_2]).$$

Discussion. The concentrations effected in the system without circulation are quite small and are of no value for any comparisons with theoretical calculations. Since the concentration effects are greatly increased by circulation of the gas, it is at once evident that a concentration gradient is rapidly set up at the surface of the palladium when no provision is made for circulating the gases, and that this gradient prevents the separation from being very efficient. These data with the static system are of practical importance in that they indicate that the frequently used method of admitting hydrogen to a hydrogen discharge tube or spectrograph through a heated palladium tube will cause no great change in the hydrogen-deuterium ratio.

The data obtained with the circulating system may be used for comparison with calculated concentration factors. As is well known, the effect of a diffusion process may be expressed by the equation

$$(Y_0/Y) = (X_0/X)^{(M_x/M_y)^{\frac{1}{2}}},$$

where X_0 and Y_0 indicate the initial and X and Y the final concentrations of the diffusing species. M_x and M_y are the corresponding molecular weights. This expression infers perfect mixing so that there is no accumulation of the less diffusible gas at the surface of the membrane. If the hydrogen and deuterium diffuse as atoms, the exponential factor in the above expression will be $2^{\frac{1}{2}}$.

The values of K' in Table VII show at once that the gas which diffuses through the palladium contains the three molecular species in about equilibrium amounts although the initial gas was not at equilibrium. The value of K' at 270°C is 3.7.[10] The value of K' for the final sample shows that equilibrium can be established on the surface of palladium without the necessity of the gas diffusing through the metal. Since this is so,

no comparison can be made as to the relative rates of diffusion of HD and D_2. The only valid basis on which concentration factors can be calculated is one of atomic percent of deuterium.

The concentration factors in Table VIII are expressed as the ratio of the concentration in the

TABLE VIII. *Concentration factors for palladium diffusion.*

	A	B	C
Experimental	1.95	2.59	1.8[4]
Calculated	2.38	2.44	2.54

final sample to the concentration in the initial gas, the concentration being expressed in atomic percent deuterium. Columns A, B and C refer, respectively, to the three experiments the data for which are given in Tables VI and VII. The calculated factors were obtained by the assumption that the diffusion was atomic. They are different for each experiment because of the difference in the volumes of the last samples.

The experimental factors are about those to be expected from the diffusion of two species whose respective masses differ by a factor of two. Certainly the work function[11] does not have the importance assigned it by Harris, Jost and Pearse who based their conclusions on one experiment the analyses for which were obtained by the use of a Wood's discharge tube.

2. Desorption from charcoal

If hydrogen which has been adsorbed on charcoal is removed from the charcoal by evacuation, it is to be expected that the hydrogen will be desorbed more rapidly than is the deuterium. The magnitude of this difference in rates of desorption will depend upon the type of binding forces which are operative in holding the adsorbed gas to the surface. Eyring and Sherman[12] have shown that for molecules held to the surface by van der Waals forces at 90°A, the ratio of the specific desorption rates for H_2 and HD is 1.13 which is less than that due to a difference in rates of effusion. Since the porous surface of charcoal should also function as a diffusion membrane, the concentration factor might be expected to be increased by means of an effusion

[10] H. C. Urey and R. Rittenberg, J. Chem. Phys. 1, 137 (1933).

[11] W. Jost, J. Chem. Phys. 1, 466 (1933).

[12] H. Eyring and A. Sherman, J. Chem. Phys. 1, 345 (1933).

process. If the gas is atomically bound to the surface of charcoal, the ratio of the specific rates of desorption of H and D will be given by the factor, $s = e^{\Delta E/RT}$, in which ΔE is the difference in the half quanta of zero point energy for an oscillator composed of a surface atom and H, and for a second oscillator composed of a surface atom and D.[12] For such a process at 90A, $s = 5 \times 10^2$.

There are two reasons why such a process should be conducted at a low temperature. First, the amount of hydrogen adsorbed by a charcoal surface increases greatly with decreasing temperature and, since the volume of the last sample of gas removed must be of sufficient size to permit accurate analysis and, consequently, a practical limit is placed on the minimum size of this sample, the ratio of the total volume of gas used to the volume of the final sample desorbed may be increased by increasing the amount of gas initially adsorbed on the charcoal. Second, if atomic binding is operative, the factor s will be increased greatly by decrease in temperature. Whatever the type of adsorption operative in the case of hydrogen on charcoal, a selective desorption of hydrogen and deuterium is to be expected. The following experiments were carried out for the purpose of investigating this separation process experimentally.

Experimental procedure. The apparatus used is shown in Fig. 2. B is a liquid air trap for the purpose of precooling the gas admitted to the catalyst and also of preventing mercury from entering the catalyst bulb, A, in which the active charcoal was packed. The gas was admitted to the 200 cc burette C, measured, and then admitted to the catalyst. Before any runs were made, the charcoal was evacuated 15 hours at 400°C. All runs were made with the charcoal cooled in liquid air. After the gas had been adsorbed on the charcoal, it was desorbed by evacuation either by the Sprengel pump through F or by the diffusion pump through K. For the removal of the last portion of adsorbed gas, the charcoal was allowed to warm up to room temperature. The gas removed by the Sprengel to burette J could either be stored in the 500 cc bulb, I, or run into the sample bulb, G, for analysis.
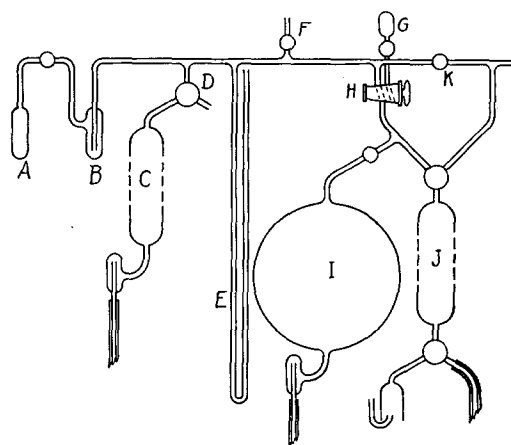

Fig. 2. Apparatus for desorption from charcoal.

Experimental results. In order to determine if concentration of the deuterium were possible by this process, two preliminary runs were made using ordinary, commercial tank hydrogen which had been purified by passage over hot platinized asbestos, calcium chloride, and phosphorus pentoxide. In the first experiment, 10.5 g of "Nuchar" No. 3, manufactured by the Industrial Chemical Company were placed in the catalyst bulb. To obtain as large a concentration as possible, the residual gas from a series of desorptions was collected in I until a quantity of gas was collected which was sufficient to use in a final adsorption-desorption process. Table IX

TABLE IX. *Desorption from charcoal.*

Run	1	2	3	4	5	6	7	8	9	10	Total
Gas adsorbed (cc)	534	560	501	515	511	522	505	516	509	513	5715
Final sample (cc)	54	39	59	54	42	46	35	27	24	22	438

gives the volume of gas adsorbed in each separate run and the volume of the last sample of gas desorbed. A period of one hour was allowed to elapse between the addition of the last hydrogen to the charcoal and the beginning of the desorption process. The pressure at the beginning of the desorption process was about 55 mm in each case. About 12 hours was required to desorb all but the last sample of gas.

This 438 cc of gas collected in I was then readsorbed on the charcoal and, during the desorption process, all but the last 89 cc was discarded. Analysis of this 89 cc sample showed it to be five times as concentrated in deuterium as was the original hydrogen used.

The "Nuchar" used in the above experiment was replaced by 56.7 g of a more active cocoanut charcoal. 5085 cc of purified tank hydrogen were adsorbed on the charcoal and allowed to remain $2\frac{1}{2}$ hours before the desorption was started. The pressure was 42 mm. After 30 hours the charcoal was allowed to warm to room temperature and the last 35 cc of gas collected. Analysis of this sample showed a three-fold increase in deuterium content over that of the initial hydrogen adsorbed.[13]

For the purpose of obtaining more quantitative data on this desorption process, an experiment similar to the one above was conducted using hydrogen which had been obtained by the electrolysis of a sample of water which had been somewhat concentrated in deuterium. The data from this experiment are tabulated in Table X and plotted in Fig. 3.
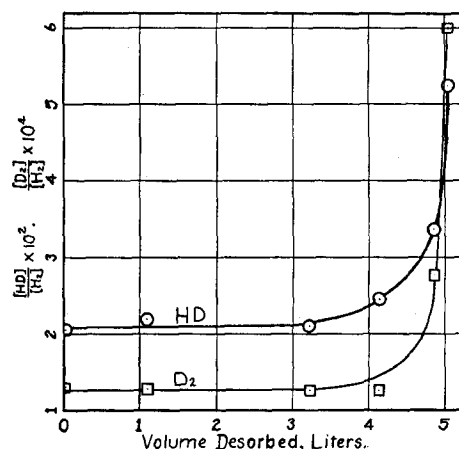
TABLE X. *Desorption from charcoal.*

cc desorbed	$[HD]/[H_2] \times 10^4$	$[D_2]/[H_2] \times 10^4$
Initial gas	235	1.38
0–60	205	1.31
1060–1150	220	1.29
3150–3300	210	1.28
4000–4250	245	1.25
4850–4900	335	2.78
5016–5066	525	6.00

Total volume of gas : 5066 cc.
Total time of desorption : 50 hours.

Discussion. A comparison of the composition of the last sample desorbed with that of the initial gas shows the relative increase in HD concentration to be 2.23-fold and that in D_2 to be 4.35-fold. The corresponding values to be expected for a perfect diffusion process are 2.28 and 3.86, respectively. The concentration factors found experimentally are entirely too small to be ascribed to an activated adsorption and a difference in zero-point energy, but can be explained by a diffusion process combined with a van der Waals adsorption. This point will be considered at greater length in the section of this paper on the interaction of hydrogen and deuterium at surfaces.
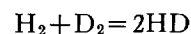
[13] These preliminary results have been published: H. S. Taylor, A. J. Gould and W. Bleakney, Phys. Rev. **43**, 496 (1933).

FIG. 3. Concentration of D_2 and HD by desorption from charcoal at liquid air temperatures.

IV. REACTION BETWEEN HYDROGEN AND DEUTERIUM AT SURFACES

The reaction between hydrogen and deuterium

$$H_2 + D_2 = 2HD$$

is quite analogous in many respects to the ortho-para hydrogen conversion. A. Farkas and L. Farkas[14] report that equilibrium is established in the homogeneous gas phase above 600° which is the same sort of behavior as that found for the ortho-para conversion.[15] Urey and Rittenberg[10] have calculated the equilibrium constant

$$K = [HD]^2 / ([H_2][D_2])$$

for various temperatures and have checked their calculated values experimentally for higher temperatures.[16]

Until the discovery that paramagnetic surfaces which do not exhibit activated adsorption could promote the ortho-para-hydrogen conversion,[17] it

[14] A. Farkas and L. Farkas, Nature **132**, 894 (1933).

[15] A. Farkas, Zeits. f. Elektrochemie **36**, 782 (1930).

[16] H. C. Urey, R. Rittenberg and W. Bleakney, J. Chem. Phys. **2**, 48 (1934).

[17] H. S. Taylor and H. Diamond, J. Am. Chem. Soc. **55**, 2613 (1933). Emmett and Harkness, ibid. **54**, 403 (1932).

was thought[18] that a parallelism existed between the capacity of surfaces to show activated adsorption of hydrogen and their capacity to induce the spin-isomerism of hydrogen, but now that it is realized that this conversion may occur on paramagnetic surfaces on which the adsorption is exclusively of the van der Waals type, it is recognized that this conversion does not offer an unequivocal criterion of activated adsorption. If, for the case of hydrogen, activated adsorption is defined as that type of adsorption which involves linkage of the hydrogen to the surface as individual atoms, the reaction between hydrogen and deuterium does offer itself as such a criterion. Whereas the spin-isomerism of hydrogen may be effected by the presence of a magnetic field such as occurs at the surface of a paramagnetic substance or at a surface on which some paramagnetic substance such as molecular oxygen has previously been adsorbed, the reaction between hydrogen and deuterium is uninfluenced by such magnetic effects. Consequently, the reaction between hydrogen and deuterium adsorbed on a surface can result only in case the molecules lose their identity and the adsorbed hydrogen and deuterium are linked to the surface by chemical bonds. In such a case, the gas which is desorbed from the surface should be an equilibrium mixture of H_2, D_2, and HD. Accordingly, a number of surfaces have been tested as to their ability to induce this reaction.

Experimental method

The apparatus used is shown in Fig. 4. Hydrogen was prepared by electrolysis of a solution of sodium hydroxide in ordinary water and purified by passage over platinized asbestos, calcium chloride and phosphorus pentoxide. Such a preparation would contain a small quantity of HD. Deuterium was prepared by the electrolysis of deuterium oxide made conducting by allowing it to react with a little metallic sodium. The deuterium was purified by passage over platinized asbestos and through a trap cooled to −78°C. A given amount of each gas was admitted to the 300 cc burette, A, and mixed by raising and lowering the leveling bulb, which held mercury as the containing fluid. This gas mixture was
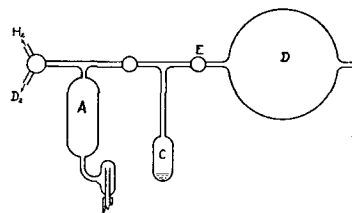
18 H. S. Taylor and A. Sherman, Trans. Faraday Soc. **28**, 247 (1931).

FIG. 4. Apparatus for study of reaction, $H_2 + D_2 = 2HD$, on surfaces.

admitted to the catalyst bulb, C, which was 50 cc in capacity and contained in the bottom a small quantity of catalyst. After a given length of time, stopcock E was opened momentarily thus removing most of the gas in the gas phase from C into the 500 cc bulb D from which it was removed to the sample bulbs by means of a Sprengel pump. The catalyst bulb C is made with a large amount of gas space in order that the sample of gas which is removed shall not be that desorbed from the catalyst but rather that present in the gas phase. The work on charcoal has shown that such a desorption leads to separation of the isotopes.

Mercury and Pyrex surfaces

Before any trustworthy results could be obtained, it was necessary to ascertain whether any HD formation which might be detected was caused only by the catalyst under study and not at some other point in the experimental procedure.

Bradley[19] has recently found evidence of a slow activated adsorption of hydrogen on a mercury surface, and there is no a priori reason why the mercury present in the apparatus might not catalyze the reaction of hydrogen with deuterium. For this reason, a gas mixture was placed in the storage burette and allowed to stand for several days, samples being withdrawn at intervals and analyzed. The results are given in Table XI. This table is also of value in showing the accuracy of the analytical data. From the constancy of the values of K', the concentration ratio $[HD]^2/([H_2][D_2])$, it is apparent that neither a mercury nor a glass surface at room temperature can catalyze the reaction and that any increase in the value of K' which may be observed in subsequent experiments is attri-

19 R. S. Bradley, J. Phys. Chem. **38**, 231 (1934).

TABLE XI. *Hydrogen and deuterium on mercury.*

Time (Days)	H_2	HD	D_2	K'
1	100	39.2	478	0.032
	100	40.5	503	0.033
2	19.3	7.4	100	0.028
	19.3	7.5	100	0.029
5	18.8	7.55	100	0.030
	19.9	7.64	100	0.029

butable in its entirety to the effect of the catalyst in C.

Chromium oxide

The chromium oxide was prepared by the method of Howard.[20] 2.58 grams were placed in the catalyst bulb and reduced for 32 hours at 340°C with tank hydrogen which had been purified by passage over platinized asbestos and through a trap cooled to -78°C. Samples of the initial gas mixture were analyzed at intervals and the concentration ratio K' found always to lie between 0.01 and 0.03. The following experimental results of Table XII are listed in the order

TABLE XII. *Reaction on chromium oxide.*

Expt.	Temp. °C	Time (hours)	H_2	HD	D_2	K'	K
1	-78	20	100	103.2	57.7	1.85	2.88
2	0	6	100	85.8	24.9	2.96	3.19
3	110	2	100	17.7	0.88	3.53	3.46
4	110	4	100	25.8	1.81	3.67	3.46
5	-78	1	100	100.5	33.8	2.99	2.88
6	-78	3	100	99.2	33.9	2.89	2.88
7	-78	15	100	99.5	32.9	3.01	2.88
8	0	1	100	95.6	28.7	3.16	3.19
9	0	3	100	102	32.2	3.23	3.19
10	-190	2	100	41.2	33.2	0.50	2.2
11	-190	26	100	73.1	22.6	2.3	2.2

in which the experiments were performed. In the last column are given the calculated equilibrium constants for the temperatures in question. From experiment 5 onwards the catalyst was evacuated for two hours at 350°C between each run. For the first four experiments the evacuation temperature was usually not so high, but no

[20] J. Howard, Princeton Thesis, 1933. Trans. Faraday Soc. **30**, 278 (1934). See also, Lazier and Vaughen, J. Am. Chem. Soc. **54**, 3080 (1932).

standard procedure of evacuation had been adopted.

In order to make sure that the value determined for K' at liquid air temperature is the true equilibrium value, an experiment was performed to attain equilibrium from the HD side. Since pure HD was not available a mixture with a high K' was obtained by electrolysis of a sample of heavy water. A sample of this mixture was withdrawn for analysis and the remainder admitted to the Cr_2O_3 catalyst and allowed to remain for 25 hours. The analyses are given in Table XIII.

TABLE XIII. *Equilibrium at liquid air temperature.*

Sample	H_2	HD	D_2	K'	K
Initial	100	55.7	8.67	3.57	
Final	100	40.2	7.39	2.18	2.2

Nickel

Approximately 1.8 g of a NiO-kieselguhr preparation was placed in the catalyst bulb. With purified tank hydrogen flowing through the apparatus, the catalyst was warmed slowly to 500°C and kept at that temperature for 90 minutes. After evacuation overnight at 430°C, experiments similar to those for Cr_2O_3 were performed. The experimental results in Table XIV were obtained. A different catalyst was

TABLE XIV. *Reaction on nickel.*

Expt.	Temp. °C	Time (hours)	H_2	HD	D_2	K'	K
1	-190	2	100	80.2	543	0.12	2.2
2	-190	4	100	58.5	529	0.07	2.2
3	-190	48	100	65.5	553	0.08	2.2
4	-78	19	100	83.0	24.6	2.80	2.88
5	0	6	100	64.4	12.3	3.37	3.19
6	110	2	100	67.1	17.4	2.58	3.46
7	-190	21	100	77.5	44.5	1.34	2.2
8	0	15	100	108.1	36.5	3.19	3.19
9	110	2	100	114.5	37.7	3.47	3.46
10	110	4	100	114.8	38	3.45	3.46

used in the first six experiments than was used in the last four. A standard evacuation technique of 2 hours at 430°C was adopted.

In order to approach equilibrium at -78°C from the other side, a mixture showing a high K' was placed on the catalyst for 19 hours and the data of Table XV was obtained.

TABLE XV. *Equilibrium at* $-78°C$.

Sample	H_2	HD	D_2	K'	K
Initial	100	63.0	11.2	3.57	
Final	100	54.5	10.2	2.89	2.88

Wet soft-glass surface

The data given in Table III may be used to show that the value of the equilibrium constant remains unchanged after the gas has been in contact with a moist, soft-glass surface for a period of 20 days. The values of K' calculated from these data are given in Table XVI.

TABLE XVI. *Hydrogen and deuterium on moist soft-glass.*

	K'		
	1	2	3
Initial sample	2.40	2.43	2.41
Final sample	2.25	2.40	

Columns 1, 2, and 3 represent check analyses on the same sample of gas. The calculated value of K at room temperature is 3.25. If, therefore, a moist, soft-glass surface were efficacious in promoting this reaction, the values of K' determined for the final sample should be higher than those for the initial sample. Such is not the case.

Charcoal at liquid air temperature

Bonhoeffer and Harteck[21] showed that charcoal at liquid air temperatures is very efficient in converting ortho- to para-hydrogen. Taylor and Sherman[18] and, later, Bonhoeffer, Farkas and Rummel[22] showed that the conversion efficiency decreased with increasing temperature until the efficiency dropped to zero at room temperature, but that at higher temperatures the efficiency began to increase with increasing temperature. The latter authors interpreted the high temperature conversion as being due to an activated adsorption and the low temperature conversion as being due to a van der Waals adsorption plus a magnetic effect either of the charcoal surface itself or of impurities in the charcoal. In view of the previously quoted work on paramagnetic surfaces,[17] such an interpretation of the low temperature work seemed logical, but direct proof was lacking.

[21] Bonhoeffer and Harteck, Zeits. f. physik. Chemie B4, 113 (1929).

[22] Bonhoeffer, Farkas and Rummel, Zeits. f. physik. Chemie 21B, 225 (1933).

The data of Table X offer two arguments in favor of such a conclusion. If these data are used in the calculation of K', the values in Table XVII are obtained. If the hydrogen were held to

TABLE XVII. *Equilibrium constants on charcoal.*

cc desorbed:	Initial gas	0–60	1060–1150	3150–3300
K':	4.0	3.2	3.8	3.5
cc desorbed:	Initial gas	4000–4250	4850–4900	5016–5066
K':	4.0	4.8	4.0	4.6

the surface atomically, equilibrium between the molecular species (H_2, D_2 and HD) should be attained and the values of K' in the above table should approach the calculated value for K of 2.2 for this temperature. Instead, they remain high. Moreover, if activated adsorption were present but the establishment of equilibrium were a slow process, the last values of K' should be lower than the first since these last samples had been on the charcoal some two days. On the contrary, they become larger due to the more rapid desorption of H_2. It should be added that Farkas and Farkas[14] report no HD formation on charcoal at $-195°C$.

The concentration factors obtained are also explicable only in terms of a van der Waals adsorption. Whereas an activated adsorption would necessitate a ratio of rate of desorption of hydrogen to rate of desorption of deuterium of $s = 500$,[12] the concentration observed corresponds almost exactly to that attainable from a diffusion process for which the ratio of specific rates is given by the expression

$$s = (M_2/M_1)^{\frac{1}{2}},$$

M_1 and M_2 being the molecular weights of the diffusing species. For H_2 and HD, $s = 1.15$. For H_2 and D_2, $s = 1.41$.

The results show decisively that the adsorption of hydrogen on charcoal at the temperature of liquid air is of the van der Waals type and that the ortho-para conversion observed under these conditions is due solely to the paramagnetism of the surface.

Palladium

The data given in Table VII may be used for an investigation into the effect of palladium in

promoting the reaction between hydrogen and deuterium. The values of K' are obtained. (Table XVIII.) The calculated value of K at 270°C is 3.67.

TABLE XVIII.

Sample.	Initial gas	First 32 cc	A	B	Final
K':	0.24	3.87	3.85	3.81	4.00

Discussion

If the first four experiments on Cr_2O_3 are considered only as preliminary work, the data show that reaction between hydrogen and deuterium occurs on the surface of Cr_2O_3 in the temperature range between −190 and 110°C and that the rate of this reaction is rapid. At −190° the value of K' rises from 0.03 or less initially to 0.5 in two hours and equilibrium is attained in 26 hours. At −78° the rate has become so rapid that equilibrium is attained in one hour. On the assumption that activated adsorption is a necessary prelude to chemical reaction at surfaces, the adsorption of hydrogen on Cr_2O_3 even at these low temperatures must be partly of the activated type. In view of the work of Howard,[20] who measured both van der Waals and activated adsorption on chromium oxide, the existence of an activated adsorption below 0°C was very surprising.

Since equilibrium is established in the gas phase, the rate of adsorption and desorption must be rapid and, since this process proceeds rapidly at low temperatures, the desorption process must have a low activation energy of the order of a few kg cal. and, consequently, the heat of adsorption must be yet smaller. Howard found the high temperature adsorption process to have a heat of adsorption of ∼25 kg cal. and an activation energy of ∼20 kg cal. Since any desorption process requiring an activation energy of 45 kg cal. will proceed at an immeasurably slow rate at low temperatures, it is obvious that the activated adsorption which is operative at low temperatures has entirely different characteristics from that measured by adsorption measurements at high temperatures.

That the adsorption is of the activated type may be easily seen. Any acceleration in rate of reaction caused by a van der Waals adsorption

can only be due to an increase in the concentration of the reactants at the surface, and such a concentration cannot cause the rapid reaction of hydrogen and deuterium. Experimentally, this fact is known from the work on charcoal which shows that at −190°C where the adsorption is large, there is no reaction.

With nickel, the results are almost the same as with Cr_2O_3 except that the catalyst is not so active and reaction at −190°C is slower than it is with Cr_2O_3. With Cr_2O_3 at that temperature equilibrium is attained in 26 hours, but with nickel the value rises only to 1.34 in 21 hours. Analogous energy considerations hold in the two cases; the activated adsorption which is observed at low temperatures must have different characteristics from that measured by Benton and White.[23]

No claim is made that all of the low temperature adsorption on Cr_2O_3 and Ni is of the activated type. Any surface which will promote the reaction of hydrogen and deuterium will also promote the ortho-para hydrogen conversion, but, because of magnetic effects, the converse is not true. In a flow system at liquid air temperatures Cr_2O_3 gives 100 percent conversion of
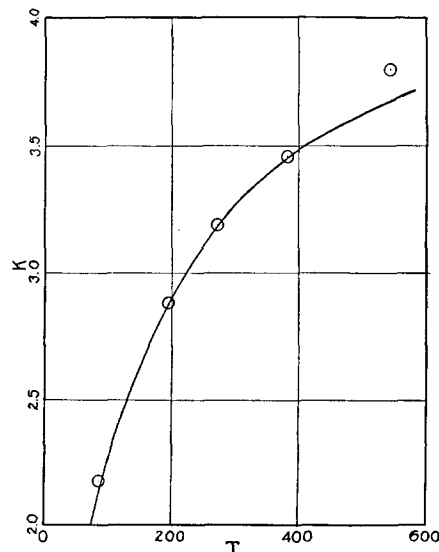

FIG. 5. Variation with temperature of the equilibrium constant for the reaction between hydrogen and deuterium.

[23] A. F. Benton and T. A. White, J. Am. Chem. Soc. **52**, 2325 (1930).

ortho- to para-hydrogen at a space velocity of 60, while the results here recorded show that the hydrogen-deuterium reaction is comparatively much slower. It is evident, therefore, that the effect of the activated adsorption at this temperature on the ortho-para conversion is negligible as compared with the combined effect of van der Waals adsorption plus the paramagnetism of the surface. The reaction between hydrogen and deuterium does offer a method for the detection of activated adsorption in temperature regions in which it would be indistinguishable from van der Waals adsorption by the experimental methods customarily employed.

These results show that some of the hydrogen adsorbed on Cr_2O_3, Ni and undoubtedly other catalytic surfaces is in a chemically very reactive form even at liquid air temperatures and that, consequently, the reaction kinetics of a catalytic hydrogenation process is determined rather by the behavior of the substance hydrogenated than by the hydrogen.

Finally, the data give an experimental determination of the variation of the equilibrium constant, K, as a function of temperature from -190 to $270°C$. The data are plotted in Fig. 5. The curve is that calculated from statistical mechanics by Urey and Rittenberg and the points represent values obtained in this investigation.

The Mercury Photosensitized Decomposition of the Deuteroammonias

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A method of preparation of ammonias in which one, two and three hydrogens are replaced by deuterium has been devised. It reveals that the preparation of magnesium nitride from magnesium and ammonia yields amido- or imido-compounds as intermediate stages of great stability. The physical properties of deuteroammonia preparations have been studied. Ultraviolet absorption spectra reveal the presence of all three substituted deuteroammonias in the preparations studied. The mercury photosensitized decomposition of trideuteroammonia is more than ten times slower than the corresponding reaction of ammonia. It is also inhibited much more strongly by deuterium than is ammonia decomposition by hydrogen. Increasing deuterium content of ammonia decreases the rate of sensitized decomposition. The kinetics of decomposition are qualitatively similar but quantitatively different. The quantitative results are compared with data on quenching of fluorescence of mercury resonance radiation by the several gases in question and lead to important conclusions concerning the nature of the collisions involved in the decomposition process.

THE isolation of deuterium oxide from water by processes of electrolytic separation offers the experimental chemist a large field of investigation into compounds in which deuterium has displaced hydrogen. It is evident that the choice of compounds to be studied is very large and choice will at first be best dictated by the use to which the products may be put in testing various physico-chemical theories. It is for reasons of this kind that we have prepared derivatives of ammonia and obtained products which contain ammonias in which one, two and three atoms of hydrogen have been replaced by deuterium. We shall show that this work has led to interesting conclusions concerning the preparation of magnesium nitride, to important observations concerning the physical properties of the ammonias, to measurements of the absorption spectra of the ammonias for ultraviolet light and to a determination of the relative stabilities of the several ammonias towards collisions with excited mercury.

PREPARATION OF THE DEUTEROAMMONIAS

Three different preparations of the deuteroammonias have been made by allowing the vapor of deuterium oxide $(D_4^{20} = 1.1052)$ to interact with three different preparations of magnesium nitride. The vapor was allowed to diffuse into an evacuated tube containing the

[1] C. R. B. Fellow from Louvain University, 1933–1934.