A similar procedure was used in the preparation of phenyl-*p*-anisyliodonium iodide. It was relatively insoluble in water, from which it had a tendency to crystallize in pale yellow needles. One preparation gave a white product, but this, on standing exposed to light, turned yellow.

Anal. Calcd. for $C_{13}H_{12}OI_2$: I, 28.98. Found: I, 28.92, 28.80.

Decomposition of the Iodonium Salts.—The decomposition was effected by immersing a large Pyrex test-tube containing about 5 g. of the salt in a glycerol-bath heated to the required temperature. The test-tube was provided with an ordinary piece of glass tubing to act as a reflux tube. The iodide decomposed at 175°, the bromide at 180°, and the chloride at 181°. In the case of the bromide and the chloride, the amount of free iodine liberated as a result of the decomposition was negligible, compared with the total amount present. When the iodide underwent decomposition, 4.2% of the total iodine was liberated as such. It is believed that the greater portion of this free iodine is due to the iodide ion acting as a reducing agent. This secondary reaction presumably proceeds as follows

$$2(CH_3OC_6H_4)C_6H_5I_2 \longrightarrow I_2 + C_6H_5{\cdot}C_6H_5 + 2CH_3OC_6H_4I$$

Qualitative Identification of the Reaction Products.—The reaction product from each salt was distilled fractionally and in each case the higher boiling fraction (above 200°) solidified on cooling, and upon a single crystallization from alcohol proved to be pure *p*-iodoanisole, m. p. 51–52°. The lower boiling fraction (below 200°) in each case was refluxed for several hours with acetic anhydride and concentrated hydriodic acid. It was then made alkaline and steam distilled. From the steam distillate there was isolated phenyl iodide, phenyl bromide or phenyl chloride, corresponding originally to the iodonium iodide, bromide or chloride. These compounds were identified by micro boiling points and also, in the case of the phenyl bromide, by analysis.

Quantitative Examination of the Reaction Products.—A quantitative estimation of the *p*-iodoanisole in each of the reaction products was carried out by refluxing for a period of ten hours a definite amount of the reaction product (about 1 g.) with 8 g. of stannous chloride, 15 cc. of 40% hydrobromic acid, 15 cc. of glacial acetic acid and 5 cc. of water. The mixture was then made alkaline with sodium bicarbonate and steam distilled. The residue was made acid with sulfuric acid, and the iodine liberated by the addition of ferric chloride, and a second steam distillation was carried out. The iodine in the distillate was determined by a thiosulfate titration. Pure *p*-iodoanisole under these conditions was found to give up 95% of its total iodine, whereas in the case of phenyl iodide the amount of iodine liberated was negligible. On this basis the reaction product from the iodonium bromide gave evidence that at least 87% of the total iodine was present as *p*-iodoanisole. The iodonium chloride showed at least 88% and the iodonium iodide 96%. In the latter case the free iodine already present was considered as having come from the iodide ion.

In the above procedure, when refluxing with stannous chloride, it is essential that glass beads be used to prevent bumping. It is also essential that the ten-hour period of refluxing be not interrupted.

Summary

Phenyl-*p*-anisyliodonium iodide, bromide, and chloride have been prepared. The latter two salts on thermal decomposition have been shown to decompose mainly in such a way that the more electronegative radical (*p*-anisyl radical), based on Kharasch's table, remains attached to the iodine atom.

EDMONTON, ALBERTA, CANADA RECEIVED MAY 21, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Dissociation Pressures of Potassium Deuteride and Potassium Hydride[1]

BY EDITH FORD SOLLERS[2] AND J. L. CRENSHAW

Introduction

Almost all of the numerous comparative studies of compounds containing ordinary and heavy hydrogen have been made on compounds in which the hydrogen was combined with non-metals. Relatively few comparisons of the salt-like metallic hydrides and deuterides, in which the hydrogen is in the form of anions,[3] have been made. A study of the dissociation pressures of these compounds seemed to be of interest from a theoretical point of view and also the results might lead to a new method for the separation of the two hydrogen isotopes.

The dissociation pressures of the hydrides of the alkali and alkaline earth metals have been measured by many investigators but except for a brief statement by Tronstad[4] about the lithium compounds, no data on the dissociation pressures of the deuterides of these metals have been published. The potassium compounds were chosen

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(1) This article is based on the dissertation presented to the Faculty of the Graduate School of Bryn Mawr College by Edith Ford Sollers in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The complete dissertation is on file in the Bryn Mawr College Library.

(2) Alice Freeman Palmer Fellow of Wellesley College.

(3) See Peters, *Z. anorg. allgem. Chem.*, **131**, 140 (1923), where references to previous work are given.

(4) Tronstad, "Nordiska (19 Skandinaviska) Naturforskarmotd 1 Helsingford Den. 11–15 Augusti 1936," p. 381.

for this study since Keyes[5] had obtained reproducible results with potassium hydride over a convenient temperature range, and with less experimental difficulties than are found with other alkali and alkaline earth metals.

There is some confusion in the literature over what happens when a metallic hydride dissociates. Many authors[3,6,7] state that the free metal and the hydride form a solution and therefore the equilibrium pressure of the hydrogen depends on the relative amounts of metal and hydride present. Keyes'[5] work on sodium and potassium hydride and Remy-Genneté's[8] painstaking investigation of calcium hydride seem to show conclusively that no solution is formed and that the hydrogen pressure depends only on the temperature. Except for the work of Remy-Genneté and similar work by Hurd and co-workers,[9] all measurements have been made under conditions which allow the distillation of the metal and of the hydride into cool parts of the tube and are therefore of doubtful significance at temperatures where the vapor pressure of either of these substances becomes appreciable. The vapor pressure of potassium hydride itself has not been measured but that of potassium is well known[10,11] and if temperatures at which its vapor pressure is not more than a few millimeters are not exceeded, it is possible to obtain reproducible results. It is only necessary to have sufficient hydrogen present to change the potassium into hydride as fast as it distills up the tube. The pressure measured under these conditions is that of the hydrogen in equilibrium with the potassium and potassium hydride in the hottest part of the tube.

Experimental Part

The apparatus was constructed of Pyrex glass and is shown in Fig. 1. Its essential features were modeled after Keyes.[5] The hydride or deuteride was prepared from the elements in the reaction tube J which was immersed in a bath (not shown) of a fused mixture of sodium and potassium nitrates. The nitrates were contained in a two-liter copper beaker electrically heated and provided with a mechanical stirrer. The bath rested on a stand so constructed that it could be raised or lowered, quickly and easily, by a screw.

Temperatures were read by means of a platinum–platinum-rhodium thermocouple which was calibrated, before and after the pressure measurements, at the boiling point of water, the melting point of cadmium and the melting point of zinc. The thermocouple was inserted in a tube which was sealed into the reaction tube as shown at C in Fig. 2. The temperatures are estimated to be correct within 0.1°.

The mercury manometer, M, was connected to the reaction tube by capillary tubing so that a small amount of reaction gave a relatively large change in pressure. Pressures were read on a calibrated glass scale by means of a carefully adjusted horizontal thread. No attempt was made to read the pressures more accurately than 0.1 mm. Pressures are given in millimeters of mercury corrected to 0°.

Hydrogen and Deuterium.—In the preparation of hydrogen freshly boiled distilled water was introduced into the evacuated system at A, Fig. 1. This water rested on mercury which stood in the vertical tube below. By alternate applications of atmospheric and excess pressures at I, the mercury was made to push the water repeatedly around the side tube, B, and over the glass beads in the central tube.[12] The system was again evacuated, to remove liberated air, and the water distilled into reservoir C, which had been cooled with solid carbon dioxide in acetone. After further evacuation to a few tenths of a millimeter, the water was redistilled into D in the same way.

Water vapor from D was allowed to react with sodium in tube E. This sodium previously had been filtered into E *in vacuo* through a fine capillary which was then sealed off. The tube had then been thoroughly evacuated again and carefully heated, so that the sodium was spread over as wide a surface as possible. The liberated hydrogen passed through a condenser, cooled with ice water, over a red-hot platinum coil, through a liquid air trap, over phosphorus pentoxide, which had been sublimed into the apparatus, and finally into reservoir F, where it was stored over mercury.

Deuterium was prepared in an analogous manner; 99.5% deuterium oxide from the Ohio Chemical Company was used. Care was taken to prevent contamination of the heavy water during the transfer from the sealed supply tube to the apparatus. The sample was never exposed to the atmosphere for more than a few seconds and the supply tube was resealed immediately after a sample had been removed.

As a test of purity, density determinations were made on both gaseous forms. A Dumas bulb with a capillary stopcock was connected to the manometer and to reservoir F by a ground glass joint (not shown in Fig. 1). The temperature of the gas in the Dumas bulb was taken as equal to that of a water reservoir surrounding it. This was measured by a calibrated thermometer. The pressure was measured on the same manometer as was used for the vapor pressure measurements. Equilibrium conditions were considered established when there had been no change in pressure or temperature for a half hour.

The usual precautions in accurate weighing were taken. A sealed tare of very nearly the same volume as the Dumas

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(5) Keyes, THIS JOURNAL, **34**, 779 (1912).

(6) Ephraim and Michel, *Helv. Chim. Acta*, **4**, 762 (1921).

(7) Hüttig and Krajewski, *Z. anorg. allgem. Chem.*, **141**, 133 (1924).

(8) Remy-Genneté, *Ann. Chim.*, **19**, 263 (1933).

(9) Hurd and co-workers, THIS JOURNAL, **53**, 1681 (1931); **57**, 332 (1935).

(10) Fiock and Rodebush, *ibid.*, **48**, 2522 (1926).

(11) Weiler, *Ann. Physik*, **5**, 1, 361 (1929).

(12) This churning *in vacuo* is very effective in removing dissolved gases. *Cf.* Taylor, THIS JOURNAL, **50**, 2937 (1928).

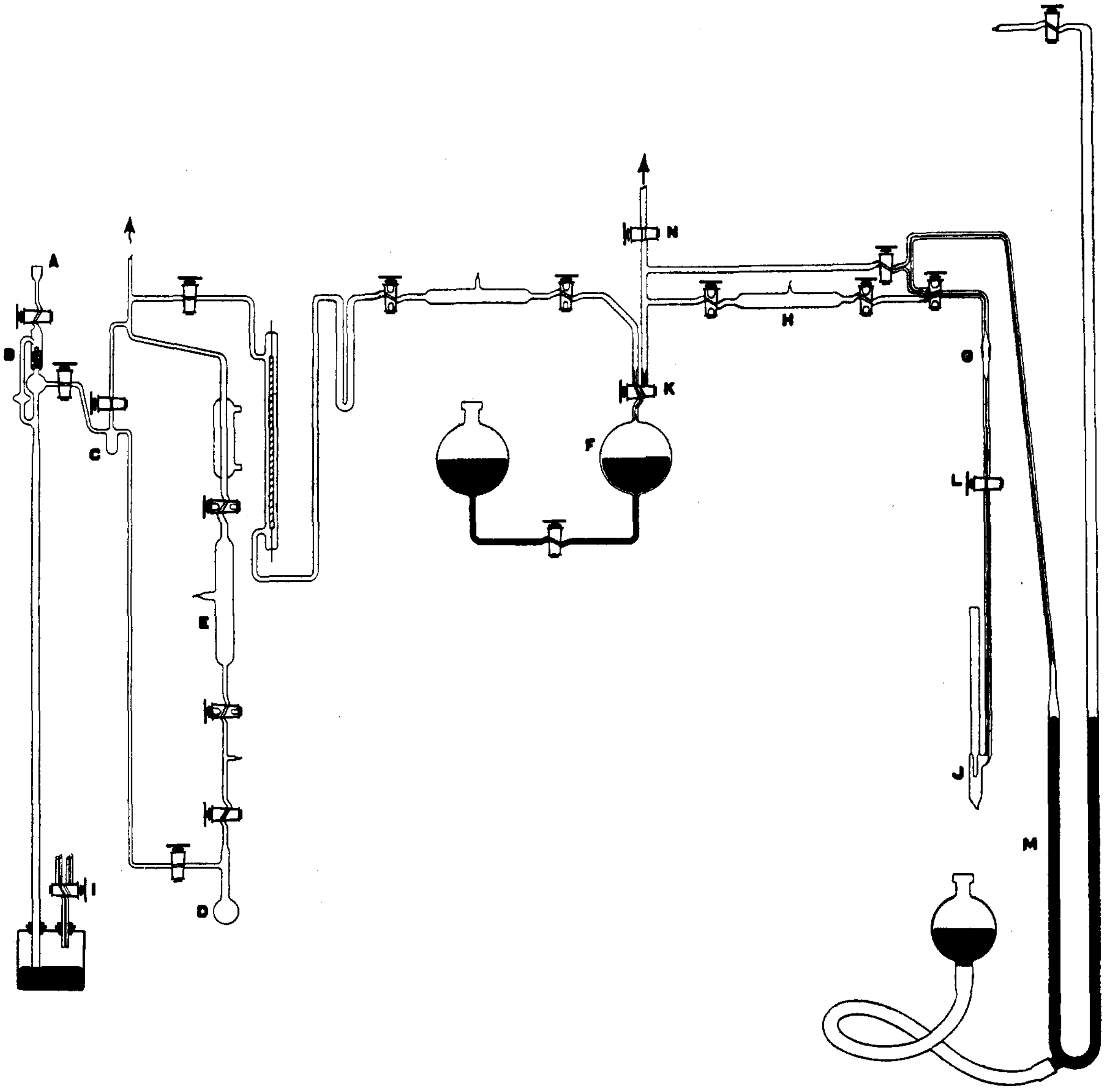

Fig. 1.

bulb was used. The bulb was thoroughly evacuated and weighed before and after each determination. There was never as much as 0.1 mg. difference in the weight of the empty bulb.

The results of the density determinations on samples which were dried by a liquid air trap are given in Table I. The column labelled "weight calculated" contains the values of the weights which the pure isotopic forms would have at the measured temperature and pressure. In every case, calculated and observed weights agree within experimental error.

TABLE I

(Volume of bulb, 284.65 cc.)

Run	Pressure, mm.	Temp., °C.	Weight Calcd.	Weight Obsd.	Error, %
D_2-1	521.5	22.0	0.0323	0.0322	−0.3
D_2-2	517.7	22.0	.0320	.0320	.0
H_2-1	439.5	21.3	.0136	.0137	+ .7
H_2-2	477.6	21.2	.0148	.0149	+ .6

In preparations in which a liquid air trap was not used, the densities were always high, in one run as much as 56% by weight. The high values obtained were probably the result of contamination by water. In the preparation of hydrogen, it is necessary to heat the water, once appreciable gas pressures have been built up. This sometimes results in a small amount of liquid water reacting with the sodium. Hydrogen evolution is then so rapid that water is carried along with it. Part of this water is removed when the gas passes over a second phosphorus pentoxide tube, H. Whatever contamination is left when the gas reaches the reaction tube is of no importance, since the vapor pressure measurements are in agreement whether or not a liquid air trap is used. Apparently, any water present reacts with potassium in the reaction tube to form potassium hydroxide, which has no effect on the system.

Potassium.—Kahlbaum potassium which had been kept under oil was used in most experiments. In a few of the potassium hydride experiments, Baker potassium was used, but there was no discernible difference in the vapor pressure measurements. The potassium was dried with filter paper, put in a test-tube and melted in dioxane which had been distilled over sodium. The melted potassium floated on the dioxane while the crust settled to the bottom of the tube. The liquid potassium was then decanted, freshly cut as soon as solid, and put into a glass boat. The glass boat containing the potassium was inserted in the reaction tube and the tube was sealed off at A, as shown in Fig. 2. This tube was then attached horizontally to the pump by a ground glass joint. A cylindrical, electrically heated furnace was placed around the middle section of the tube up to constriction B. The ends of the furnace were packed carefully with asbestos. The reaction tube was evacuated thoroughly and the middle section baked out at 360 to 400°. The furnace was then moved over the potassium and it was distilled slowly past B. No attempt was made to get a constant amount of potassium into the reaction tube. Amounts varied from thin films to about 1 cc. of solid potassium. During distillation, the pressure never was above 0.002 mm. as measured by a McLeod gage, and became less than 0.0001 mm. before the end. When sufficient potassium had distilled over, the furnace was removed and the reaction tube was sealed off at B.

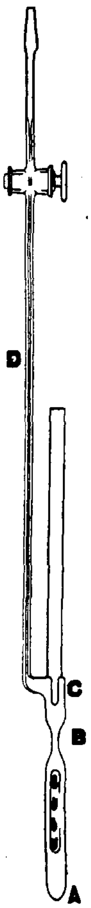

Fig. 2.

Formation of the Hydride and Deuteride.—The reaction tube J, Fig. 1, containing the potassium, was connected to the manometer by a ground glass joint G. The system was evacuated completely. Hydrogen (or deuterium) was then let into the system from reservoir F. It passed over a second phosphorus pentoxide tube H before it reached the reaction tube. Hydrogen pressures between 400 and 500 mm. were used. When the nitrate-bath had been brought to a convenient temperature (300 to 350°), it was raised quickly around the tube. The pressure immediately began to fall. This fall was not so obvious as that described by Keyes[5] because in these experiments the hydrogen reservoir was left open to the tube throughout the hydride formation. In a typical preparation of the deuteride, for example, the pressure fell from 479.2 to 459.0 mm. in twenty-five minutes. In the last eight minutes, there was a drop of only 2.1 mm., so absorption was discontinued. The total volume occupied by the deuterium was about 500 cc. so that the fall in pressure corresponded to about 0.0006 mole of deuterium absorbed.

Pressure Measurements.—Two procedures were used in determining the equilibrium pressures. For temperatures below 300°, the nitrate bath was lowered as soon as sufficient hydride or deuteride had formed, and J allowed to cool to room temperature. The system was then completely evacuated and J connected directly to the manometer. The bath, after adjusting to the desired temperature, was now raised around the reaction tube and the equilibrium pressure allowed to develop from decomposition of the hydride or deuteride. This same procedure was used in one run at higher temperatures but in most cases for temperatures above 300° excessive decomposition of the compound was avoided by leaving a hydrogen or deuterium pressure slightly less than the equilibrium pressure in the reaction vessel. When this method was used, it was not necessary to lower the bath during the evacuation and obviously equilibrium could be attained much more rapidly. The two methods gave results which agreed within the experimental error.

When the readings of the thermocouple (at C in Fig. 2) had become constant to 0.1°, the pressure was read until it remained constant to 0.1 mm. for six or seven minutes. Readings of temperature and pressure were taken in as quick succession as possible, about thirty seconds. The vacuum side of the manometer was pumped continuously to make sure that no pressure developed on that side.

Since the amount of hydride or deuteride formed was always small and since there was always some sublimation, it was possible to make only a few measurements with one preparation. It was found advantageous to determine the pressures over only a short temperature range (10 to 20°) with any one sample, since in this way less time was necessary to regulate the temperature and to bring the system to equilibrium, and excessive sublimation was avoided.

Equilibrium was checked by taking readings with falling and with rising temperatures. In all measurements included, the pressure changed with temperature in the expected manner. However, measurements taken after the temperature had been lowered were considered less exact than those taken after the temperature had been raised, since decomposition occurred more rapidly than combination. Several values were discarded on this basis.

In several cases, equilibrium was also checked by increasing and decreasing the pressure at a given temperature. Except in high temperature measurements, which have been discarded because there was evidence of rapid distillation of potassium, such measurements indicated that equilibrium was established.

The measurements taken in different runs were often in overlapping temperature ranges. Agreement between measurements in different runs was well within experimental error.

Experimental Difficulties.—One of the most serious difficulties was the distillation of potassium onto the cooler part of the apparatus. At high temperatures, potassium distillation is appreciable, as evidenced by a drop in the pressure at constant temperature. In such cases, the pressure does not correspond to an equilibrium condition and measurements are of no significance. The use of capillary tubing (1.0 mm.) above the reaction vessel hinders the distillation of potassium. Small amounts of material and small volumes of reaction vessels also have the advantage of accelerating the acquirement of equilibrium conditions, since less decomposition must occur before the necessary pressure is built up and equilibrium readings can be made before appreciable distillation has occurred.

In some early experiments a larger vessel was used, and a stirrer, operated magnetically, mixed the contents of the reaction tube. The large amounts of material necessary for the size of a container which could include a stirrer required in one instance twelve hours for the preparation of the hydride. There was noticeable potassium distillation, even sufficient to cake around the stirrer and stop its action. Every measurement took at least one or two hours.

Experiments were also made without a stirrer, but with large amounts of potassium. Here again distillation became very evident.

All early experiments were made with an electric tube furnace by which temperature equilibrium was obtained very slowly. The use of the nitrate-bath allows the rapid attainment of a constant temperature, especially if temperature changes are kept small.

In all experiments, the total time during which the potassium is held at a high temperature should be kept as short as possible, not only to prevent appreciable distillation but also to minimize the reaction between potassium and the glass. There seemed to be very little attack if this precaution of short exposures was taken. However, as a further safeguard, tubes were discarded after three runs had been made in them.

Experimental Results

Measurements were made on potassium hydride from 270 to 390° and on potassium deuteride from 270 to 360°. At higher temperatures, it was impossible to obtain constant values for the dissociation pressures. In these cases, there was evidence of considerable distillation into the capillary tube D, Fig. 2. The pressure dropped rapidly while the temperature was held constant. For example, in one experiment with deuteride, the temperature was raised to 366.0° and then held constant. The pressure rose to 165 mm. (as compared to 159 obtained at 361.9°), and then began to fall. It was hoped that addition of excess deuterium would convert any potassium condensed on the walls over to the deuteride. A pressure of 415 mm. of deuterium was put on the system. The pressure was still falling and showed no signs of becoming constant after two hours. This was taken to indicate that the potassium was distilling up the tube faster than the deuterium could combine with it. Obviously equilibrium pressures could not be obtained. Keyes[5] did not observe any such effect. The fact that it was possible to make potassium hydride measurements up to 390°, whereas potassium deuteride measurements could not be made far past 360° seemed to indicate that equilibrium was obtained more quickly in the case of the hydride.

Forty-nine determinations were made on nine different preparations of potassium hydride. For temperatures up to 350°, our results check those of Keyes[5] within the experimental error. Between 350° and 390°, our results are appreciably lower than his but, in this range, the experimental error is larger. The thirty-six determinations made on seven different preparations of deuteride are recorded in Table II.

TABLE II

DISSOCIATION PRESSURES OF POTASSIUM DEUTERIDE

Temp., °C.	Pressure (obsd.), mm.	Temp., °C.	Pressure (obsd.), mm.
270.1	3.1	318.0	34.4
272.8	4.0	320.2	39.5
274.7	5.0	323.7	43.0
282.2	6.7	330.1	56.0
282.6	6.2	331.6	55.3
290.3	8.2	334.4	60.1
292.0	10.0	334.4	60.5
295.0	11.5	336.5	67.0
297.4	14.3	337.2	70.9
297.9	14.5	337.3	67.4
300.9	18.3	340.1	77.3
304.9	21.0	340.8	78.6
307.5	23.6	343.9	86.9
310.9	27.0	349.0	107.2
311.7	24.0	352.5	119.7
313.8	25.5	355.9	135.6
315.0	30.1	360.7	158.6
315.7	26.9	361.9	159.0

The experimental data are plotted in Fig. 3, which contains all the observations except a few at the lower temperatures where there is considerable overlapping. In Fig. 4, $\log_{10} p$ is plotted against $1/T$ and, within experimental error, a

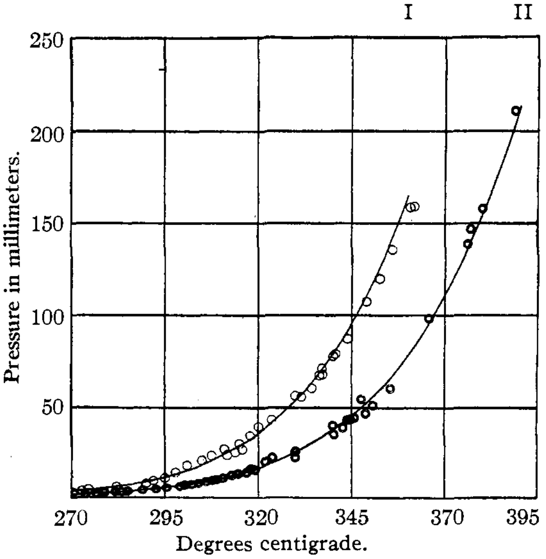

Fig. 3.—I, KD; II, KH.

straight line is obtained. The heavy lines in both plots are the graphs of the following equations which were obtained by the method of least squares.

For potassium deuteride

$$\log_{10} p = -6318.68/T + 12.1977$$

For potassium hydride

$$\log_{10} p = -6185.57/T + 11.6535$$

Keyes gives for potassium hydride

$$\log_{10} p = -5850/T + 2.6 \log_{10} T + 3.895$$

Keyes' equation is derived not from least squares but from his measurements combined with estimated values of specific heats. For our results, the inclusion of a logarithmic term is not justified by the accuracy of the experiments since the points plotted in Fig. 4 do not deviate appreciably from a straight line.

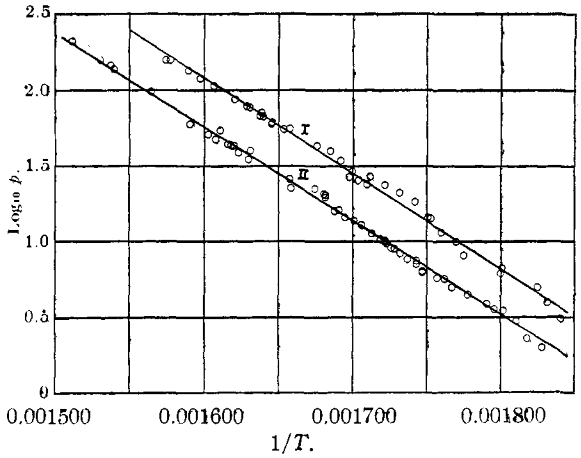

Fig. 4.—I, KD; II, KH.

The equations give for the heats of formation, assumed constant within the range 270 to 390°, for potassium deuteride 14,450 calories, for potassium hydride 14,150 calories. For the hydride, Keyes gives 14,240 calories at ordinary temperatures.

As may be seen from the plots, the experimental error is rather large. The probable errors of the least square equations are: for potassium hydride 0.025, for potassium deuteride 0.024, in $\log_{10} p$. This corresponds to a probable error in pressure of 5–6% in each case. The slight difference in the slope of the two lines in Fig. 4 may not be greater than the experimental error, but since no results were arbitrarily discarded, there is some evidence that the heat of formation of potassium deuteride is slightly greater than that of potassium hydride. There is no question that at a given temperature the dissociation pressure of potassium deuteride is about twice as great as that of potassium hydride.

Table III contains the dissociation pressures of potassium deuteride and potassium hydride as calculated for round temperatures from our equations, as well as Keyes' calculated values for potassium hydride, which are included for comparison.

TABLE III

Temp., °C.	Pressure KD calcd. mm.	Pressure KH calcd. mm.	Pressure KH calcd. mm. (Keyes)
270	3.7	1.8	1.7
280	5.9	3.0	2.8
290	9.5	4.7	4.5
300	14.8	7.2	7.3
310	22.9	11.1	11.3
320	35.0	16.7	17.4
330	52.6	25.0	26.6
340	78.0	36.7	39.6
350	113.8	53.2	58.9
360	164.9	76.5	85.5
370		108.4	125.1
380		152.1	179.9

Discussion

It is of interest to compare the results obtained in this study with the results obtained by other investigators who have compared hydrogen and deuterium compounds.

According to Tronstad,[4] the dissociation pressure of lithium deuteride was found and predicted to be less than that of lithium hydride. However, he does not give any experimental data nor describe his procedure, although the difficulties involved in working with these salts are very great. It might be expected that the difference in pressure would be in the same direction for potassium deuteride and potassium hydride. On the contrary, the present work has shown that the equilibrium pressures of potassium deuteride are about twice as great as those of potassium hydride in the temperature range studied.

Moreover, a combination of the heats of dissociations as determined from band spectra for the reactions

$$\mathrm{LiD} = \mathrm{Li} + \mathrm{D} \quad \text{and} \quad \mathrm{LiH} = \mathrm{Li} + \mathrm{H}^{13}$$

and for

$$\mathrm{D_2} = 2\mathrm{D} \quad \text{and} \quad \mathrm{H_2} = 2\mathrm{H}^{14}$$

would indicate the heat of formation of lithium hydride would be greater than that of lithium

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(13) Crawford and Jorgensen, Jr., *Phys. Rev.*, **49**, 745 (1936).

(14) Farkas, "Ortho Hydrogen, Para Hydrogen and Heavy Hydrogen," The Cambridge University Press, 1935, p. 155.

deuteride. In the case of potassium deuteride and potassium hydride, the reverse has been found, although the difference is scarcely more than the experimental error. Theoretical calculations on the potassium salts would be of considerable interest. Qualitatively, the higher dissociation pressure of potassium deuteride may be explained by the fact that the entropy of deuterium is greater than that of hydrogen. At the temperature of these experiments, this entropy difference probably would be the most important factor in determining the difference in the free energies. At low temperatures, the small difference in the entropies of the hydride and deuteride would become relatively more important and might overbalance the difference between the entropies of the gases. Under these conditions, the hydride would have the higher dissociation pressure, although the pressures of both the hydride and deuteride would be so small that experimental determinations would be difficult. If Tronstad[4] worked at low temperatures, his results on lithium are in aggreement with what we should expect for potassium (see below).

Beebe and his co-workers[15] have compared the adsorption of deuterium and hydrogen by copper, a case somewhat analogous to the formation of the hydrides. In the interval 0 to 125°, the ratio of hydrogen to deuterium adsorbed undergoes an inversion. Hydrogen is more strongly held by copper at lower temperatures and less strongly held at higher temperatures. Although a comparison of compound formation with adsorption may not be significant, our results indicate that, in the case of potassium, the reverse appears to be true. At high temperatures, potassium certainly holds hydrogen more strongly than it does deuterium, and the slight difference in slope of the lines in Fig. 4 suggests the possibility that at low temperatures, the hydride may have the higher dissociation pressure.

It is of interest to compare the effects observed when deuterium is substituted for hydrogen in compounds with the halogens with that found in compounds with the alkali metals. Rittenberg and Urey[16] have determined experimentally the ratio of the equilibrium constants, K_1/K_2, for the reactions: $H_2 + I_2 = 2HI$ and $D_2 + I_2 = 2DI$. The value of about 1.2 in the temperature range 300 to 425° agrees well with that to be expected from theoretical considerations.[17] Although the chlorides have not been investigated experimentally, theory indicates that the substitution of deuterium for hydrogen would have an effect on the ratio of the corresponding equilibrium constants opposite to that found for the iodides. From our data, the ratio of the constants, K_1/K_2, for the reactions $2K + H_2 = 2KH$ and $2K + D_2 = 2KD$ varies from 2.0 at 270° to 2.2 at 360°. Tronstad's[4] work indicates that the corresponding ratio for the lithium compounds is less than unity. It seems that the substitution of deuterium for hydrogen decreases the free energy of formation of the iodine and potassium compounds and causes an increase in this quantity in the case of the lithium compounds and the chlorides.

Work on the sodium compounds is now in progress and preliminary results indicate that (as in the case of potassium) the deuteride has the higher dissociation pressure at temperatures above about 250°.

The results of this investigation suggest a possible method for the separation of the two hydrogen isotopes. If a mixture of hydrogen and deuterium were passed over potassium at 300 to 350°, potassium hydride and deuteride would be formed. The two compounds would, in all probability, form a solid solution. A calculation of the enrichment of the deuterium content of the gas phase from the dissociation pressure which the two compounds have when they exist alone is not justified when so many factors have not been experimentally determined. If the mixture of gases were passed rapidly over an excess of potassium, the relative rates of combination would probably be the determining factors. There is some evidence that hydrogen reacts more rapidly with potassium than does deuterium (p. 11). Potassium hydride is dissociated approximately only one-half as much as potassium deuteride. Therefore, both the relative rates of formation of the hydride and deuteride, and the degrees of dissociation of these compounds would seem to favor separation of the isotopes when a mixture of the two is passed over heated potassium.

Summary

1. The dissociation pressures of potassium hydride have been measured from 270 to 390°. Experimental difficulties and methods to avoid

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[15] Beebe, Low, Wildner and Goldwasser, THIS JOURNAL, **57**, 2527 (1935).

[16] Rittenberg and Urey, *J. Chem. Phys.*, **2**, 106 (1934).

[17] Urey and Rittenberg, *ibid.*, **1**, 137 (1933).

them have been indicated. The pressure values obtained agree with those of Keyes within experimental error.

2. The dissociation pressures of potassium deuteride have been measured by the same method from 270 to 360°. The dissociation pressure of potassium deuteride is approximately twice as great as that of potassium hydride throughout the temperature range studied.

3. From equations connecting the dissociation pressure with the temperature, the following heats of formation per mole have been calculated: for potassium hydride, 14,150 calories; for potassium deuteride, 14,450 calories. The difference is hardly greater than the experimental error.

4. A possible method for the separation of hydrogen and deuterium has been suggested.

BRYN MAWR, PENNA. RECEIVED JULY 6, 1937

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, AND THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Kinetics of the Explosive Reaction between Hydrogen and Oxygen Sensitized by Nitrogen Peroxide[1]

BY GUENTHER VON ELBE[2] AND BERNARD LEWIS[3]

Small traces of nitrogen peroxide exert a remarkable influence on the combination of hydrogen and oxygen, inducing explosions at temperatures where the gases alone are almost completely inert to each other, far below the temperature corresponding to the tip of the hydrogen–oxygen explosion peninsula.[4,5] At any such temperature there exist two sharply defined critical concentrations of nitrogen peroxide between which instantaneous inflammation of the hydrogen and oxygen takes place but above or below which there is only a slow reaction.

Experimental investigation of the phenomenon reveals the following facts.[5] At a given temperature and mixture composition the lower critical concentration (L. C. C.) is raised and the upper critical concentration (U. C. C.) is lowered as the pressure of the hydrogen–oxygen mixture is increased. If the total pressure is kept constant the U. C. C. is lowered on increasing the proportion of oxygen to hydrogen; it is also lowered by the presence of nitrogen. Results on the effect of nitrogen on the L. C. C. are meager; the effect does not seem to be pronounced. Increasing temperature lowers the L. C. C. and raises the U. C. C. As the temperature is decreased the effect of total pressure on the L. C. C. becomes less pronounced. The U. C. C. is much the same in silica as in porcelain vessels. The L. C. C. tends to drift in a rather indefinite way but the difference in the two kinds of vessels is not very great. It will be helpful for the ensuing discussion to reproduce the table[5] of critical concentrations.

TABLE I

CRITICAL CONCENTRATIONS OF NITROGEN PEROXIDE IN A STOICHIOMETRIC MIXTURE OF HYDROGEN AND OXYGEN AT DIFFERENT TEMPERATURES AND PRESSURES

	Pressure of NO_2, mm.							
Temp.,	Lower critical concentration				Upper critical concentration			
°C.	150	300	450	600	150	300	450	600
410	0.053	0.076	0.107	0.144	>9.9	7.9	4.4	3.1
390	.068	.09	.122	.160	4.6	2.7	1.8	1.3
370	.09	.12	...	.15	1.47	0.98	0.59	0.39

Apparently these nitrogen peroxide pressures were not corrected for the equilibrium between nitric oxide and nitrogen peroxide.[4,6] This correction, though affecting the absolute values, does not alter the trend appreciably. The revised values, for example, for 410° are

L. C. C.	0.032	0.053	0.079	0.010
U. C. C.	>6.1	5.5	3.2	2.4

Thus, at this temperature, the L. C. C. and the U. C. C. are roughly proportional and inversely proportional, respectively, to the total pressure. As the temperature is decreased the U. C. C. remain approximately inversely as the pressure, while the L. C. C. tend to become independent of pressure.

The foregoing facts forcibly suggest the occurrence of a branched chain reaction initiated in

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[4] Dixon, Gibson and Hinshelwood, *Trans. Faraday Soc.*, **24**, 559 (1928).

[5] Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **A122**, 610 (1929); *ibid.*, **A124**, 219 (1929).

[6] For this equilibrium consult Zeise, *Z. Elektrochem.*, **42**, 785 (1936).