[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

# The Spin-Isomerization of Hydrogen at Paramagnetic and Diamagnetic Surfaces

BY HUGH S. TAYLOR AND H. DIAMOND

The correspondence existing between the capacity of surfaces to show activated adsorption and their capacity to catalyze chemical reactions between gases so adsorbed indicated that a similar correlation might apply to the ortho–para hydrogen conversion. From a study of various materials, Taylor and Sherman[1] concluded that there is a definite parallelism between the activity of a surface in inducing the spin-isomerization of hydrogen and its ability to adsorb hydrogen in the activated form.

This mechanism has been substantiated by others at high temperatures,[2] but it soon became apparent that, in the lower range of temperature, conversion may be accounted for by another process. Continuing their earlier work on iron synthetic ammonia catalysts Emmett and Harkness[3] reported that they had observed a conversion at liquid air temperatures caused by adsorption presumably of the van der Waals type. In explanation of these results, Taylor suggested, on the same occasion, that the effect might be attributed to the paramagnetic characteristics of the surface in agreement with the observed activity of paramagnetic gases and ions in solution in the same conversion as studied by L. Farkas and Sachsse.[4] Certain data already accumulated in the present work were cited in support of this point of view, a preliminary report[5] of which has already been published as a Communication to the Editor. Some results obtained early in the present investigation showed that on a silver catalyst, presumably diamagnetic, the activity of conversion at liquid air temperatures was greater than at −78°, and rose again at high temperatures, the rise being attributable to the occurrence of activated adsorption. Subsequently, abundant illustrations of this type of behavior were also supplied by Bonhoeffer, Farkas and Rummel,[6] and led them to the suggestion that at low temperatures on charcoal the unimolecular isomerization process may be ascribed to the presence of magnetic dipoles on the charcoal surface. In the following pages are recorded our results for the conversion, in both low and high temperature ranges, on a variety of surfaces paramagnetic in character and on others in which the bulk material is diamagnetic but upon which the isomerization occurs even with gas adsorbed by van der Waals forces.

## Experimental Details

**Apparatus and Procedure.**—The method of following the conversion process was essentially the thermal conductivity method of analysis developed by Bonhoeffer and Harteck.[7] The measurements were made in a Pyrex thermal conductivity vessel provided with about 36 cm. of a platinum wire, 0.025 mm. in diameter and heated by a current of 0.25 ampere from a 12-volt storage battery. The vessel was immersed in a liquid air bath. The hydrogen under study was maintained at 40 mm. pressure during the measurements, and the wire temperature was maintained in the neighborhood of 170°K., where the two forms of hydrogen show a maximum difference in thermal conductivity. The wire temperature was measured in terms of its resistance by a Wheatstone bridge arrangement. The apparatus was calibrated with normal hydrogen (wire resistance = 40.85 ohms) and with 1:1 ortho–para hydrogen (wire resistance = 40.00 ohms). The composition of unknown mixtures was determined by linear interpolation.

**Gases.**—Electrolytic hydrogen, freed from oxygen by platinized asbestos and from water vapor and carbon dioxide by calcium chloride, ascarite and a liquid air trap, was always employed. The 1:1 mixture was obtained by allowing electrolytic hydrogen to equilibrate on charcoal in a tube immersed in a liquid air bath.

**Catalyst Preparations.** (1) **Gadolinium Oxide.**—This catalyst was prepared from a sample (G.D.10) obtained from Dr. P. W. Selwood through the courtesy of Professor B. S. Hopkins of the University of Illinois. The oxalate was precipitated from a hot solution of the nitrate, filtered, washed and ignited at 900° for ten hours. The oxide had a faint cream tinge, the estimated impurities being a trace of terbium and of bismuth.[8]

(2) **Neodymium Oxide.**—This was a pale blue oxide obtained from the same source and prepared as in the case of gadolinium oxide. The estimated impurities were less than 0.02%.[9]

(3) **Lanthanum Oxide.**—A sample containing less than 0.2% of praseodymium and neodymium combined[10] was prepared by ignition of a pure white oxalate.

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[1] H. S. Taylor and A. Sherman, THIS JOURNAL, **53**, 1614 (1931); *Trans. Faraday Soc.*, **28**, 247 (1932).

[2] K. F. Bonhoeffer and A. Farkas, *Z. physik. Chem.*, **12B**, 231 (1931); A. Farkas, *ibid.*, **14B**, 371 (1931).

[3] Emmett and Harkness, THIS JOURNAL, **54**, 403 (1932); Washington Meeting, A. C. S., March, 1933.

[4] L. Farkas and Sachsse, *Z. physik. Chem.*, **23B**, 1 (1933).

[5] Taylor and Diamond, THIS JOURNAL, **55**, 2613 (1933).

[6] Bonhoeffer, Farkas and Rummel, *Z. physik. Chem.*, **21B**, 225 (1933).

[7] Bonhoeffer and Harteck, *Z. physik. Chem.*, **4B**, 113 (1929).

[8] Selwood, THIS JOURNAL, **55**, 4869 (1933).

[9] Selwood, *ibid.*, **52**, 3112 (1930).

[10] Selwood, *ibid.*, **55**, 3161 (1933).

(4) **Lanthanum–Neodymium Oxides.**—The oxalates were coprecipitated and ignited to a mixed oxide, found by a magnetic susceptibility measurement to contain 1.9% of the latter oxide.

(5) **Ceric Oxide I.**—A crude cerium oxalate (U. S. P. Merck) was ignited at 900° to give a distinctly brown oxide, containing as much as 10% of foreign oxides.

(6) **Ceric Oxide II.**—This was prepared from a much purer sample of cerium salts loaned by Professor N. H. Furman. The product of ignition was a light peach-colored oxide. The impurities in this preparation were about 1% lanthanum oxide and 0.2% of the praseodymium and neodymium oxides. This sample was also examined in the partially reduced condition, gray in color, due probably to the lower oxide $Ce_4O_7$.

(7) **Vanadium Pentoxide.**—A brownish-yellow oxide was prepared by ignition of reprecipitated ammonium metavanadate at 460°. It was subsequently ignited *in situ* and cooled in oxygen to avoid decomposition to the lower oxide and finally evacuated at room temperature.

(8) **Vanadium Trioxide.**—The previous sample was heated in a stream of hydrogen at 460° for ten hours and thus converted to black vanadium trioxide.

(9) **Chromium Oxide.**—This was a dark green gel prepared by the method of Lazier and Vaughen,[11] the dried gel being treated in hydrogen at 375° for twelve hours. A more extensive study of this type of gel has already been reported by Howard.[12]

(10) **Zinc Oxide.**—The preparation of this oxide was from the oxalate as described by Taylor and Strother.[13]

(11) **Zinc Chromite.**—This was part of the actual sample used by Taylor and Strother in their hydrogen adsorption measurements.

(12) **Magnetic Iron Oxide.**—Powdered iron was ignited to red heat in a stream of oxygen. The shining black mass obtained was powdered in an agate mortar and evacuated *in situ* at 400°.

(13) **Manganous Chloride.**—The anhydrous salt was prepared by heating the tetrahydrate in a stream of nitrogen and hydrogen chloride at the fusion point. It was evacuated *in situ* at 150°.

(14) **Silver.**—This was prepared from silver oxide, made by precipitation from pure silver nitrate and potassium hydroxide solutions, by ignition in a slow stream of hydrogen at 100°. It was specially tested for paramagnetic impurities such as nickel and iron and also for copper with negative results.

(15) **Copper.**—The sample was prepared by reduction with hydrogen of granular cupric oxide *in situ* at temperatures not exceeding 180°. It was finally evacuated at 195°.

(16) **Alumina.**—The hydroxide was prepared from the nitrate and ammonia. The gel was dried at 125° and evacuated at temperatures rising to 200°.

In general the catalysts were evacuated at high temperatures and cooled to liquid air temperatures *in vacuo*. Exceptions have been noted above. Between experiments at −187° the samples were evacuated first at this temperature for five minutes, then allowed to warm up to room temperatures with continued evacuation. The mass was then cooled to liquid air temperatures *in vacuo* and hydrogen admitted.

## Experimental Results

The first column of Table I lists the various catalysts studied, together with the weight of each sample taken. The second, third and fourth give the temperature of the surface, the pressure of the gas phase over it (before the first sample was withdrawn for analysis), and the time of contact, respectively. The fifth and sixth columns show the extent of conversion from 3 : 1 to 1 : 1 hydrogen at liquid air temperature, and of a 1 : 1 mixture to the 3 : 1 equilibrium at higher temperatures. For the streaming experiments (atmospheric pressure) the velocities of flow are recorded.

## Discussion of Results

The influence of magnetic properties on the ortho–para conversion at liquid air temperatures is most clearly demonstrated by the series of rare earths gadolinium, neodymium and lanthanum oxides. While these are very similar in chemical and physical properties, the first two gave complete conversion in all the static measurements whereas lanthanum oxide showed an efficiency lower by several orders of magnitude. This latter substance is diamagnetic; the other two are strongly paramagnetic. The gram-susceptibilities at room temperature are $130 \times 10^{-6}$ for $Gd_2O_3$ and $30.9 \times 10^{-6}$ for $Nd_2O_3$; the magnetic moments are 37.5 and 16.97 Weiss magnetons, respectively. In qualitative agreement with these figures is the fact that the gadolinium oxide was more active in the flow experiments. An appreciable quantity of hydrogen was taken up by all three oxides at liquid air temperatures, doubtless due to adsorption of the van der Waals type. That such adsorption alone is not sufficient for a high conversion velocity is demonstrated by the very low results obtained with lanthanum.

The mixed lanthanum–neodymium oxide catalyst is of interest since these oxides form a solid solution. The activity was intermediate to that of the separate oxides but low owing to the low concentration of the paramagnetic oxide. There is no evidence of catalytic promotion of the neodymium on the lanthanum oxide nor does the latter function as an effective support. There is simply a "catalytic dilution" corresponding to the magnetic dilution.

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[11] Lazier and Vaughen, THIS JOURNAL, **54**, 3080 (1932).

[12] Howard, *Trans. Faraday Soc.*, **30**, 278 (1934).

[13] Taylor and Strother, THIS JOURNAL, **56**, 586 (1934).

TABLE I

| Catalyst sample, g. | Temp., °C. | Press., mm. | Time of contact | Conv. % ortho → para | Conv. % para → ortho |
|---|---|---|---|---|---|
| $Gd_2O_3$ | −187 | 600 | 40 min. | 100 | |
| | −187 | 450 | 5 min. | 100 | |
| 20 g. | −187 | 200 | 5 min. | 100 | |
| | −187 | | 76 cc./min. | 57 | |
| | −187 | | 124 cc./min. | 37 | |
| | 0 | 570 | 3 min. | | 100 |
| $Nd_2O_3$ | −187 | 490 | 3 min. | 100 | |
| | −187 | 555 | 3 min. | 100 | |
| 20 g. | −187 | | 75 cc./min. | 40 | |
| | −187 | | 126 cc./min. | 26 | |
| $La_2O_3$, 5 g. | −187 | 700 | 360 min. | 17 | |
| 98.1% $La_2O_3$, 1.9% $Nd_2O_3$, 5 g. | −187 | 700 | 360 min. | 50 | |
| $CeO_2$—I (crude), 16 g. | −187 | 520 | 5 min. | 100 | |
| | −187 | 360 | 5 min. | 100 | |
| $CeO_2$—II, 7.5 g.—gray, partially dec. | −187 | 560 | 25 min. | 57 | |
| | | | 48 min. | 80 | |
| Reoxidized | −187 | 570 | 150 min. | 9 | |
| | | | 430 min. | 19 | |
| $V_2O_5$, 9.5 g. initially | −187 | 550 | 17 min. | 36 | |
| | | | 34 min. | 62 | |
| | −187 | 550 | 147 min. | 100 | |
| After heating in oxygen | −187 | 550 | 15 min. | 37 | |
| | −187 | 550 | 34 min. | 61 | |
| | | | 54 min. | 78 | |
| $V_2O_3$ | −187 | 560 | 5 min. | 100 | |
| | −187 | 630 | 5 min. | 100 | |
| 8 g. | −187 | | 76 cc./min. | 60 | |
| | −187 | | 127 cc./min. | 43 | |
| $Cr_2O_3$, 12.5 g. | −187 | | 175 cc./min. | 100 | |
| ZnO, 10 g. | −187 | 625 | 130 min. | 32 | |
| | | | 270 min. | 47 | |
| | | | 360 min. | 58 | |
| $ZnO \cdot Cr_2O_3$ *ex* 15 g. of chromate | −187 | 470 | 45 min. | 100 | |
| | −187 | 525 | 5 min. | 100 | |
| | −187 | | 126 cc./min. | 60 | |
| | −187 | | 165 cc./min. | 49 | |
| Loaded with hydrogen | −187 | 470 | 5 min. | 100 | |
| $Fe_3O_4$ | −187 | 540 | 38 min. | 100 | |
| 21.5 g. | −187 | 705 | 5 min. | 38 | |
| | | | 38 min. | 100 | |
| Re-evacuated | −187 | 640 | 5 min. | 56 | |
| | | | 27 min. | 100 | |
| $MnCl_2$ | −187 | 540 | 5 min. | 100 | |
| 14 g. | −187 | 530 | 3 min. | 100 | |
| | −187 | | 60 cc./min. | 30 | |
| | −187 | | 125 cc./min. | 17 | |
| Ag | −187 | 760 | 55 min. | 10 | |
| 40 g. | −187 | 760 | 170 min. | 28 | |
| | −187 | 760 | 320 min. | 50 | |
| | −187 | 520 | 150 min. | 33 | |
| | −187 | 260 | 150 min. | 35 | |
| | − 78 | 515 | 150 min. | | 12 |
| | − 78 | 260 | 150 min. | | 13 |
| | − 78 | 260 | 250 min. | | 22 |
| | 0 | 515 | 300 min. | | 30 |

TABLE I (*Concluded*)

| Catalyst sample, g. | Temp., °C. | Press., mm | Time of contact | Conv. % ortho → para | Conv. % para → ortho |
|---|---|---|---|---|---|
| | 0 | 260 | 150 min. | | 15 |
| | 0 | 260 | 300 min. | | 30 |
| | 100 | 340 | 17 min. | | 10 |
| | 100 | 340 | 150 min. | | 53 |
| $Al_2O_3$ | 298 | | 5 min. | | 50 |
| 1.34 g. | 304 | | 6 min. | | 43 |
| | 295 | | 6 min. | | 39 |
| | 298 | | 5 min. | | 35 |
| Admitted water, evacuated for 1 min. at 300° | 301 | | 6 min. | | 85 |
| Cu | −187 | 395 | 5 min. | 70 | |
| *Circa* | | | 15 min. | 100 | |
| 50 g. | −187 | 225 | 5 min. | 75 | |
| | | | 14 min. | 100 | |
| | 132 | 560 | 5 min. | | 95 |
| | 302 | 330 | 5 min. | | 100 |
| | −187 | 310 | 5 min. | 55 | |
| | 345 | 545 | 5 min. | | 99 |
| | −187 | 315 | 5 min. | 54 | |
| | 440 | 335 | 5 min. | | 100 |
| | −187 | 350 | 5 min. | 44 | |
| Heated Cu in stream of $H_2$ for 2 hrs., evacuated for 1 hr. at 500° | −187 | 335 | 5 min. | 43 | |
| Heated Cu in stream of $H_2$ and evacuated for several hrs. at 560° | 22 | 355 | 5 min. | | 90 |
| | −187 | 385 | 5 min. | 43 | |

The purer sample of ceric oxide showed low conversion activity in accord with its low paramagnetism. The gram-susceptibility of the purest preparations is only $0.39 \times 10^{-6}$ at room temperature. The preparation showed a higher conversion efficiency when it contained some lower oxide formed by thermal decomposition, the lower oxide being probably more highly paramagnetic than the completely oxidized sample. The good efficiency of the crude ceric oxide is undoubtedly to be associated with its highly paramagnetic rare earth constituents.

Vanadium pentoxide with a gram-susceptibility of $0.86 \times 10^{-6}$ at room temperatures showed a fair conversion efficiency. The trioxide showed a much greater activity. This is in agreement with the much higher paramagnetism of the trioxide as shown by its gram-susceptibility of $13.9 \times 10^{-6}$. Its magnetic moment is equal to 9.5 Weiss magnetons.

The high conversion efficiency on chromium oxide gel even at high velocities of flow must be attributed not only to its high susceptibility ($25.5 \times 10$ at 18°; $20.1 \times 10^{-6}$ at −187°) but also to the great surface extension of the gel structure as revealed in the high van der Waals adsorption of hydrogen at liquid air temperatures.[14]

Zinc oxide is diamagnetic and similar in its conversion efficiency at −187° to lanthanum oxide. In contrast to the oxide, zinc chromite, with a gram-susceptibility of $15 \times 10^{-6}$ at room temperature for the sample actually studied, is very effective even at high velocities of flow. In this case, as with chromium oxide, the high adsorptive capacity for hydrogen is a contributory factor.

As a consequence of the magnetic character of $Fe_3O_4$ one would anticipate a high conversion efficiency. That only a moderate activity was observed is no doubt the result of low surface extension of, and adsorption by, the sample used. Harkness and Emmett[15] have found rapid conversions with iron surfaces partially oxidized to $Fe_3O_4$.

Anhydrous manganous chloride brings about the rapid conversion expected of a highly paramagnetic substance (27.3 Weiss magnetons). This substance reveals that the spin-isomerization can be secured on other than oxide surfaces. The good conversions also indicate that marked adsorption of the hydrogen must occur.

Metallic silver reveals both the low and high temperature types of conversion with lower conversions at the intermediate temperatures

(14) Howard and Taylor, THIS JOURNAL, **56**, 2259 (1934).

(15) Harkness and Emmett, *ibid.*, **55**, 3496 (1933).

than at the extremes of −187 and 100°. This is in agreement with the findings of others. In all cases the isomerization is relatively slow at −187° due to its diamagnetism and to the low adsorption of hydrogen.[16] To account for this conversion it is necessary to assume that the surface atoms have paramagnetic properties not possessed by the metal in bulk. The increase in activity at 100° reveals the existence of activated adsorption at lower temperatures than was possible in the adsorption measurements of Drake and Benton who found that this type of adsorption is measurable at about 200°.

In the case of metallic copper only a small selection of an extensive set of data is presented. These, however, serve to show a low temperature conversion even with a metal diamagnetic in bulk as in the case of silver. Here again a surface magnetism may be called upon in explanation. On the other hand, as the data of Gould, Bleakney and Taylor[17] on chromium oxide gel show for hydrogen–deuterium exchange, it is not impossible that even at the temperature of liquid air some activated adsorption occurs, not detectable by adsorption measurements in the presence of extensive van der Waals adsorption. The data with copper even after heat treatment at temperatures as high as 560° are in marked contrast to the earlier data of Pease[18] on the effect of heat treatment on the catalysis of the hydrogen–ethylene reaction. This suggests that decreased catalytic activity due to heat treatment in the latter reaction may be associated with the activation of the ethylene rather than with that of the hydrogen.

In the case of alumina we meet a second mechanism for the spin-isomerization of hydrogen in the high temperature range. The surface reaction may be in part the usual exchange of atoms from gas adsorbed in the activated state. If this is so the conversion process becomes a more sensitive detector of activated adsorption than actual adsorption measurements. For, the conversion is occurring freely at 300° whereas the measurements of Taylor[19] showed no measurable activated adsorption of hydrogen on a similar preparation of alumina below 400°. There is, however, another possible explanation suggested by the accelerating influence of water vapor on the isomerization process. This suggests a rapid exchange reaction on the surface involving both hydrogen and water vapor, the latter of which is found to show pronounced activated adsorption at such temperatures.[20] This surface reaction is represented by the equation $H_{2\text{para}} + H_2O = H_2O + H_{2\text{ortho}}$. It is identical in nature with the exchange reaction between deuterium and water vapor which we show in a subsequent article[21] to occur rapidly on alumina, *viz.*, $D_2 + H_2O = HD + HDO$. It is obvious that other hydrogen-containing compounds, adsorbed at surfaces in the activated form, may likewise accelerate the ortho–para interconversion as they have been found to undergo exchange reactions with deuterium. It is interesting to note that a similar mechanism has been postulated for a type of homogeneous catalysis. In a study of the molecular structure of boron hydride, $B_2H_6$, L. Farkas and Sachsse[22] find that the gas does not cause any ortho–para conversion at −78°; they conclude, therefore, that the substance is diamagnetic. A conversion, however, does occur at 20 and 100° and this, they believe, results from an exchange reaction, $H_{2\text{para}} + B_2H_6 = B_2H_6 + H_{2\text{ortho}}$, between the two gases.

## Summary

1. Rapid low temperature ortho–para hydrogen interconversion is obtained on surfaces paramagnetic in nature having large capacities for van der Waals adsorption.

2. Paramagnetic metals, oxides and salts may be used to produce such surfaces.

3. Decrease in either magnetic susceptibility or in adsorptive capacity reduces the velocity of low temperature interconversion.

4. A slow conversion at liquid air temperatures on catalysts diamagnetic in bulk, such as silver and zinc oxide, may be due either to paramagnetism of surface atoms or to a residual low temperature adsorption of the activated type.

5. Rapid high temperature conversion associated with activated adsorption has been confirmed.

6. A new high temperature conversion mechanism involving an exchange reaction with water has been demonstrated, and the possibility of other similar exchange conversions has been indicated.

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(16) Drake and Benton, THIS JOURNAL, **56**, 506 (1934).

(17) Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

(18) Pease, THIS JOURNAL, **45**, 1196, 2235, 2296 (1923).

(19) Taylor, *Z. physik. Chem.*, Bodenstein Festband, 475 (1931).

(20) Taylor and Gould, THIS JOURNAL, **56**, 1685 (1934).

(21) Taylor and Diamond, *ibid.*, **57**, 1256 (1935).

(22) L. Farkas and Sachsse, *Trans. Faraday Soc.*, **30**, 331 (1934).

7. It has been shown that sintering of copper catalysts affects the low temperature activity of copper in the ortho–para conversion by no means so adversely as it affects the rate of hydrogenation of ethylene.

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# The Catalytic Exchange Reaction between Deuterium and Water

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In some experiments using the thermal conductivity method of analysis of deuterium–hydrogen mixtures, it soon became apparent that deuterium, when passed through a purification train containing platinized asbestos, might be contaminated with relatively large quantities of the light isotope. Similar effects were noted with deuterium standing in contact with chromium oxide gel. The phenomenon has been subjected to a detailed study involving also several other catalysts. It has been shown that the heavy isotope may be replaced by hydrogen due to a catalytic exchange reaction between deuterium and water retained by the contact material.

## Experimental Procedure

**Method of Analysis.**—The thermal conductivity micromethod of analysis developed by Farkas and Farkas[1] was employed, with minor modifications of technique with respect to cell construction. The cell employed was of Pyrex glass containing a platinum wire 50 mm. long and 0.01 mm. in diameter. It was doubled around a coiled spring to keep it taut and fastened at both ends to tungsten leads sealed directly into the glass. A jacket surrounding the leads was evacuated to eliminate convection currents and so minimize fluctuations in the heat conduction along the leads. The vessel was immersed well below the surface of a liquid air bath during experiments. We are indebted to Dr. N. R. Trenner for invaluable assistance in the construction of the thermal conductivity cell.

The cell wire was calibrated in terms of resistance, rather than temperature, using a Wheatstone bridge arrangement. To attain the requisite two temperatures $T_1$ and $T_2$, greater than that of the liquid air bath surrounding the conductivity cell, two adjustable external resistances yielded heating currents of 14.4 and 15.3 milliamperes with current from a 6-volt battery. The pressure of gas studied was in the neighborhood of $7 \times 10^{-2}$ mm. accurately adjusted in the case of each sample so as to give, with the lower current, a wire temperature $T_1$ equivalent to a wire resistance of 32.3 ohms. The variation of $T_2$ with each sample when the higher current was used defined the deuterium content of the gas, as already made clear by Farkas and Farkas. Access to the cell of water, mercury vapor, grease and other impurities was prevented by means of traps immersed in liquid air or solid carbon dioxide.

**Materials.**—The preparation and characteristics of the catalyst materials used in this work have already been detailed in an earlier paper.[2] The hydrogen gas too was of similar origin and purity. The deuterium gas was generated by electrolysis from deuterium oxide, $d^{25}_4$ 1.1079, using NaOD as electrolyte, freed from oxygen by contact with a glowing platinum wire and from water vapor by a liquid air trap. In some experiments the gas was diffused through a heated palladium tube but this precaution was subsequently found to be unnecessary.

## Experimental Results

**Chromium Oxide.**—We present in Table I data on the composition of the gas in the dead space of a vessel containing 18.7 g. of chromic oxide gel at 184°, that of the gas desorbed from the gel surface and that from the buret from which deuterium was introduced to the catalyst. Four successive experiments (Nos. 1 to 4) were performed, in each of which 25 cc. (N. T. P.) of pure deuterium was adsorbed on the surface and subsequently completely desorbed between successive runs. There is evidence in these experiments of slow exhaustion of the water in the gel. The adsorbent was then allowed to take up approximately 450 cc. of deuterium at 350° in units of 50 cc., the adsorption of each unit being followed by desorption at the same temperature. Experiment 5 details the several isotopic concentrations for an immediately succeeding experiment analogous to those of the first four. Experiment 6 was next performed introducing the *light* isotope, $H_2$; the exchange reaction now took place in the reverse direction, obviously due to the deuterization of the adsorbent in the previous experiments.

The influence of temperature on the rate of exchange is shown in the data on Table II, using 1.75 g. of gel and deuterium as the gas introduced. In each experiment only a few cc. of gas was used.

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[1] Farkas and Farkas, *Proc. Roy. Soc.* (London), **144A**, 467 (1934).

[2] Taylor and Diamond, THIS JOURNAL, **57**, 1251 (1935).