

ous wave lengths, in the order indicated, with results as follows: 5209 Å., 0.038°; 5461 Å., 0.028°; 5890 Å., 0.000°; 6101 Å., 0.004°; 6438 Å., -0.002°. The measurements were made in the reverse order on the material from another forty-five minute run, with results: 6438 Å., 0.018°; 6104 Å., 0.024°; 5890 Å., 0.028°; 5461 Å., 0.029°; 5209 Å., 0.024°.

**Preparation of Trinitrostilbene Dichloride.**—Three grams of trinitrostilbene was dissolved in a solution of chlorine in benzene and exposed to the radiation from a 250-watt lamp for two days. The residue from the evaporation of the benzene solution, recrystallized from glacial acetic acid, yielded 1.5 g. of the pure dichloride, white crystals, m. p. 185.5–186.5° (corr.) with slight decomposition. The material was analyzed by refluxing a sample with an alcohol solution of sodium iodide, and titrating the liberated iodine. Calcd. for  $C_{14}H_9O_6N_3Cl_2$ , 18.4%. Found: Cl, 18.5, 18.6%. The precipitate which remained after the titration, recrystallized from glacial acetic acid, yielded pure trinitrostilbene, m. p. 156.5–158°, identified by mixed melting point with a known sample.

### Summary

In circularly polarized sodium light of wave length 5890–5896 Å., trinitrostilbene does not combine with bromine to yield an optically active product. Trinitrostilbene does not absorb light of this wave length.

Trinitrostilbene combines with chlorine in circularly polarized light of wave length 3600–4500 Å. to yield optically active trinitrostilbene dichloride. The reaction with chlorine is more rapid than with bromine, the maximum rotatory power being attained in about forty-five minutes. On longer irradiation, the optical activity decreases and finally disappears.

The absorption spectra of trinitrostilbene and its dichloride and dibromide have been measured.

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## The Catalytic Interconversion of Ortho-Para Hydrogen over Iron, Platinum and Nickel Catalysts

BY P. H. EMMETT AND R. W. HARKNESS

In previous communications<sup>1,2,3</sup> a few of the results that have been obtained in a study of the catalytic interconversion of ortho to para hydrogen over iron synthetic ammonia catalysts have been presented. The present paper gives the detailed experimental results together with a discussion of their relation to other published catalytic ortho-para interconversion measurements. The conversion over nickel and platinum catalysts has been studied only in so far as it is poisoned by the activated adsorption of hydrogen.

### Experimental

The ortho-para hydrogen conversion apparatus was similar to that described by Bonhoeffer and Harteck.<sup>4</sup> Tank hydrogen containing 0.2% or less nitrogen as an impurity was freed from oxygen by passage over hot finely divided copper, and passed through a flowmeter, a phosphoric anhydride drying tube and a well baked out charcoal trap of 100-cc. capacity immersed in liquid air. This charcoal tube served the double purpose of removing the small amount of nitrogen that was in the hydrogen and of

acting as a catalyst for bringing the initial ortho-para ratio to that corresponding to the temperature of liquid air. The hydrogen could then be passed either directly from the charcoal bulb through a U-tube immersed in liquid air and into the catalyst tube, or through a tube of platinized asbestos heated to 200°, a U-tube immersed in liquid air, and into the catalyst tube. Samples of the gas could be taken from the exit of the catalyst tube into a conductivity gage of the type already described.<sup>4</sup> Readings were taken with a pressure of 40 mm. in the gage; the latter was operated in such a way as to keep the current through the platinum filament constant. The temperature of the liquid air bath surrounding the gage and of that around the charcoal tube were taken with a 10-junction copper-constantan couple in conjunction with a Leeds and Northrup type K potentiometer. Corrections were applied to the gage reading for any temperature changes in the temperature of the liquid air bath. The maximum combined uncertainties of each analysis of the ortho-para mixture corresponded to about 2% of the difference in the gage resistance for normal 3:1 ortho-para compared to 1:1 ortho-para hydrogen.

The doubly promoted iron synthetic ammonia catalyst (931) contained 1.59% potassium oxide and 1.3% aluminum oxide as promoters. The preparation, reduction, and properties of this type of catalyst have been described many times previously.<sup>5</sup> The pure iron catalyst (973) contained 0.15% aluminum oxide as impurity. The nickel catalyst was made by reducing a fused oxide in

(1) Emmett and Harkness, *THIS JOURNAL*, **54**, 403 (1932).

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

(3) Harkness and Emmett, *ibid.*, **56**, 490 (1934). The principal results of adsorption measurements made in conjunction with the ortho-para conversion studies were also reported in this communication. The detailed account of these adsorption studies is, for convenience, being published separately from the ortho-para work.

(4) Bonhoeffer and Harteck, *Z. physik. Chem.*, **B4**, 113 (1929).

(5) Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925); Almqvist and Crittenden, *ibid.*, **18**, 1307 (1926).

hydrogen at about 300°. The platinum catalyst was in the form of platinized asbestos.

### Results

The various experiments on the ortho-para hydrogen interconversion may be conveniently grouped under the dependence of conversion on the time of contact, pressure, temperature and the presence of poisons. Each of these four factors was separately investigated.

As pointed out by Farkas,<sup>6</sup> if the rate of conversion of para to ortho hydrogen is truly first order with respect to para and ortho hydrogen then a plot of  $\log (p_0 - p_\infty)/(p - p_\infty)$  against  $t$  should be linear at a given temperature and total pressure, where  $p_0$ ,  $p$ , and  $p_\infty$  represent, respectively, the fraction of the hydrogen in the para form initially, after time of contact  $t$ , and at equilibrium at the temperature of the catalyst. For some undetermined reason the experimental conversion *vs.* time of contact curves showed a sharp departure from linearity above certain percentage conversions, the conversion failing to increase sufficiently with time of contact. The limiting conversion at which this "break" usually occurred was a function of temperature, pressure and the percentage poisoning but was usually equivalent to 80% or more of the possible conversion. In all experiments relative to the effect of pressure, temperature and poison on the rate of conversion care was taken to work with such rates of flow as would be included on the linear portion of the conversion *vs.* time of contact curve.

The dependence of the time of half conversion,  $\tau$ , upon the total pressure of hydrogen was determined at a number of different pressures. The results of typical experiments for iron catalysts together with the results of similar experiments carried out by Bonhoeffer and Farkas<sup>7</sup> for platinum are shown in Fig. 1. As is evident from the curves of Fig. 1,  $\tau$  increases with pressure, being proportional to  $(P^{1/n} + \text{constant})$  where  $n$  has some value equal to or greater than unity. The curves shown in Fig. 1 for the iron catalyst were taken on a sample of catalyst (973) that had been cooled from 450° in hydrogen. On a sample of promoted catalyst (931) that had been cooled in helium,  $\tau$  increased about 6-fold in going from 88 to 750 mm., both at -190 and -125°.

Early in the present work it was discovered that

an iron catalyst after being pumped out at 450° and then cooled to -190° in helium was 10 to 20 times as active for the para-ortho conversion at -190° as a catalyst cooled in hydrogen. Later, adsorption evidence was obtained to indicate the existence of two types of activated adsorption of hydrogen on the iron, both of which appeared<sup>2</sup> to poison the catalyst for the low temperature para-ortho conversion. To obtain quantitative data on the poisoning effect of these two known<sup>3</sup> types of activated adsorption of hydrogen on the ortho-para interconversion, small quantities of hydrogen

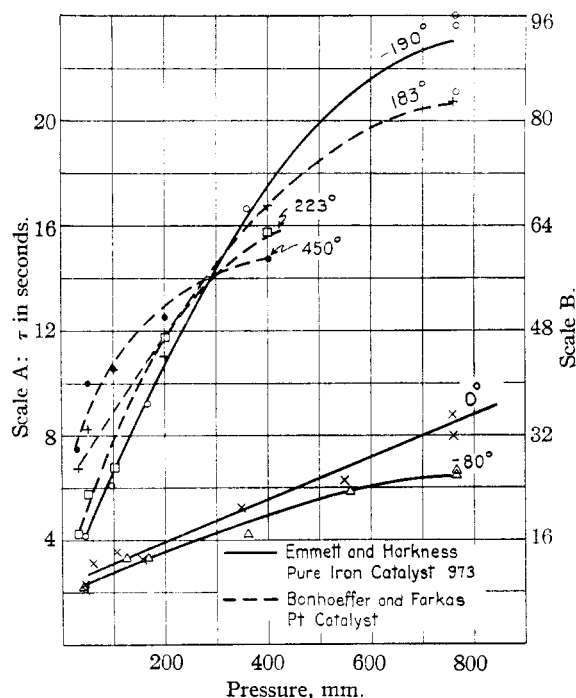


Fig. 1.—Effect of pressure on the time of half conversion in the catalytic ortho-para hydrogen interconversion on pure iron catalyst 973. All of these runs were made on a catalyst sample that had been cooled in hydrogen after reduction at 450°.

were added with the help of a McLeod gage (used as a gas buret) to the 0.25-cc. sample of iron catalyst 931, the activity of the latter being determined at -190° both before and after the addition of the poison. Fortunately both at -78 and 100° it was found possible to adsorb considerable gas on the catalyst by several hours of exposure of the catalyst to hydrogen pressure of 1 mm. or less. The results of these experiments are shown by the curves in Fig. 2. The poisoning effect at -190° caused by adsorption at -78° (type A activated adsorption) was comparatively small, increasing gradually to about 20%

(6) A. Farkas, *Z. physik. Chem.*, **B10**, 419 (1930).

(7) Bonhoeffer and Farkas, *ibid.*, **B12**, 231 (1931).

poisoning of the surface by 0.16 cc. of adsorbed hydrogen.<sup>8</sup> The hydrogen adsorbed at 100° (type B activated adsorption) was much more poisoning per unit volume adsorbed. Thus as shown by curve 1, only 0.06 cc. of hydrogen decreased the activity of the 0.25 cc. of catalyst by about 85%.

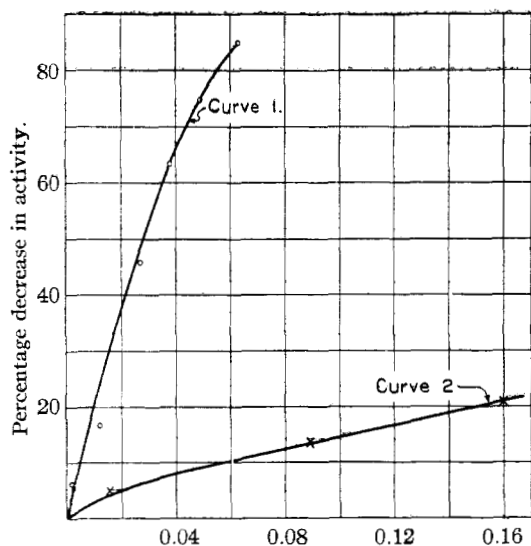


Fig. 2.—Poisoning effect of activated adsorption of hydrogen on the ortho-para conversion rate at  $-190^{\circ}$  on catalyst 931. Space velocity of 38,000 used.

Curve 1 is for type B activated adsorption of hydrogen ( $100^{\circ}$ ); curve 2, type A activated adsorption ( $-78^{\circ}$ ). The ordinate is percentage decrease in the expression  $\log(p_0 - p_{\infty})/(p - p_{\infty})$ .

The poisoning effect of hydrogen for the ortho-para hydrogen conversion at  $-190^{\circ}$  was also determined for both nickel and platinum catalysts. The results on nickel are summarized in Table I. At  $-190^{\circ}$  in the same apparatus in which iron catalysts could be run indefinitely with no poisoning effect, the nickel catalyst gradually lost activity. Apparently activated adsorption of hydrogen is capable of occurring slowly at  $-190^{\circ}$  on an active nickel catalyst.<sup>9</sup> At higher temperatures, the poisoning was much more marked. The results on platinum are also included in Table I. In this case a sample of platinized asbestos was used as catalyst. It was degassed at only  $345^{\circ}$  and therefore may have been already partially covered with adsorbed hydrogen at the

(8) This 20% poisoning was definitely due to type A adsorption and not to traces of type B adsorption because a check run at  $0^{\circ}$  and pressures such as used in the  $-78^{\circ}$  poisoning showed only 0.005 cc. of type B adsorption in half an hour. At  $-78^{\circ}$ , the rate of type B adsorption was therefore negligibly small.

(9) Benton and White, *This Journal*, **52**, 2325 (1930).

beginning of the experiment. Nevertheless, it decreased about 50% in activity on being exposed to 1 atmosphere pressure of hydrogen at  $130^{\circ}$ .

TABLE I  
POISONING ACTION OF HYDROGEN FOR THE ORTHO-PARA  
HYDROGEN CONVERSION AT  $-190^{\circ}$

	Flow cc./min.	Possible conversion, %	Reaction velocity constant, <sup>a</sup> <i>k</i>
On 1 cc. of a nickel catalyst			
Cooled in helium	159	77	30.4
12 min. H <sub>2</sub> at $-190^{\circ}$	159	75	28.5
40 min. H <sub>2</sub> at $-190^{\circ}$	159	70	24.7
125 min. H <sub>2</sub> at $-190^{\circ}$	159	66.6	22.4
150 min. H <sub>2</sub> at $-190^{\circ}$	159	65	21.9
37 min. H <sub>2</sub> at $-78^{\circ}$	37	18.1	0.95
32 min. H <sub>2</sub> at $-78^{\circ}$	37	17.4	.91
165 min. H <sub>2</sub> at $300^{\circ}$	37	2.0	.16
On 15 cc. of platinized asbestos			
Cooled in helium after degassing at $340^{\circ}$	16.4	32	0.176
Exposed <sup>b</sup> to H <sub>2</sub> at $25^{\circ}$	16.4	22	.117
Exposed <sup>b</sup> to H <sub>2</sub> at $130^{\circ}$	16.4	16	.082
Exposed <sup>b</sup> to H <sub>2</sub> at $345^{\circ}$	16.4	20	.103

<sup>a</sup>  $k = \frac{1}{t} \log \frac{p_0 - p_{\infty}}{p - p_{\infty}}$ , where  $t$  is the time of contact in minutes. <sup>b</sup> Time of exposure to hydrogen at each temperature was about one-half hour.

The poisoning influence of nitrogen and of oxygen on the activity of the iron catalysts was also investigated to some extent. The effects of adding nitrogen to the catalyst at  $450^{\circ}$  and at  $100^{\circ}$  were uncertain owing to the possible complicating effect of small amounts of hydrogen that were known to be evolving from the catalyst slowly at  $450^{\circ}$  during the time that nitrogen was being allowed to stand in contact with the catalyst. However, at 100 and  $450^{\circ}$  after exposure of about fifteen minutes to 1 atm. pressure of nitrogen the catalyst 931 decreased in activity by 15 and 50%, respectively. This amount of poisoning therefore constitutes a maximum value for the effect due to nitrogen. Adding nitrogen at  $-190^{\circ}$  to a catalyst cooled in hydrogen from  $450^{\circ}$  produces about a 70% decrease in activity, the value of the reaction velocity constant  $k$  dropping from 5.48 for the hydrogen cooled sample to 1.56 after adding nitrogen; adding nitrogen at  $-190^{\circ}$  to a helium cooled catalyst sample, on the other hand, produced only a 29% decrease in activity,  $k$  dropping from 68.8 to 49.2. The 70% poisoning effect of adsorbed nitrogen could be removed for the most part by warming the catalyst to room

temperature for a few minutes in a stream of hydrogen. From the oxygen poisoning experiments several conclusions can be drawn. Adsorption of 0.08, 0.18 and 0.28 cc. of oxygen at  $-190^\circ$  on a 5-cc. sample of catalyst 973 that had been cooled in hydrogen from  $450^\circ$  resulted in 200, 245 and 310% increases, respectively, in the activity of the catalyst for the ortho-para conversion at  $-190^\circ$ . Furthermore, oxygen added at about  $64^\circ$  to a hydrogen cooled catalyst decreases the para-ortho conversion rate at  $0^\circ$  very materially without decreasing to any large extent the activity at  $-190^\circ$ .

In some experiments the activity at  $-190^\circ$  actually increased as a result of oxygen addition at  $64^\circ$  on a hydrogen cooled catalyst. Thus in one run the addition of 1.75 cc. of oxygen to 5 cc. of pure iron catalyst 973 in successive stages increased the activity of the catalyst for the conversion at  $-190^\circ$  from 0.04 to 0.172 while at the same time decreasing the activity at  $0^\circ$  from 0.400 to 0.008. Additions of oxygen at  $-190^\circ$  to a helium cooled sample resulted in a slight loss of activity.

A number of runs were made to determine the temperature coefficient of the rate of interconversion of ortho-para hydrogen. A typical run is shown in Fig. 3 for the temperature range  $-190$  to  $30^\circ$  on a catalyst cooled in hydrogen. The observed energy of activation increased from about 160 calories at  $-190^\circ$  to about 4800 calories at  $30^\circ$  in this run. Other runs in the range  $-40$  to  $+40^\circ$  have shown observed  $E$  values as high as 6600 calories. Finally in Fig. 4 there is shown one of several curves obtained on a sample of catalyst 931 that had been reduced in hydrogen at  $450^\circ$  and then cooled to  $-190^\circ$  in helium. The plots of  $\log k$  against  $1/T$  are not linear; the apparent energy of activation decreases with rising temperature from about 730 calories at  $-190^\circ$  to 230 calories at  $-125^\circ$ .

### Discussion

The dependence of the rate of the ortho-para conversion on temperature and pressure represented by curves in Figs. 1, 3 and 4 can perhaps best be understood by formulating a general kinetic equation for the catalytic conversion. The

total net rate of conversion of para to ortho hydrogen will always be equal to the difference between the rate of condensation of para molecules on the base catalyst and the rate of their desorption from the catalyst. Hence, per unit catalyst surface

$$-dN/dt = k_1(1 - S)P\bar{p} - k_2S\bar{p} \quad (1)$$

where  $N$  is the number of para hydrogen molecules in the gas phase in the reaction vessel;  $\bar{p}$ , the fraction of the gaseous hydrogen in the para form at any time  $t$ ;  $S$ , the fraction of the surface covered by adsorbed hydrogen;  $k_1$ , the number of

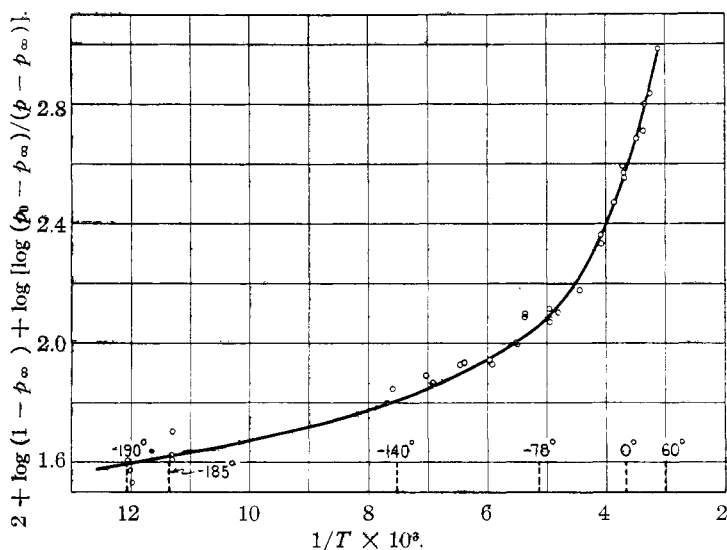


Fig. 3.—Temperature coefficient of the ortho-para hydrogen conversion on iron catalyst 973 cooled from  $450^\circ$  in hydrogen. Space velocity of 550 was used. The ordinate is the logarithm of the reaction velocity constant (see equation 11).

molecules of hydrogen hitting one square cm. of bare catalyst per second per unit pressure of hydrogen with sufficient energy of activation to become adsorbed;  $k_2$ , the rate of desorption per unit surface covered with adsorbed para hydrogen and  $\bar{p}$ , the portion of the desorbing molecules that are in the para form.  $\bar{p}$  is also assumed to represent the fraction of the adsorbed molecules that are in the para form. Furthermore, for a surface reaction that is truly monomolecular with respect to the adsorbed para and ortho molecules, one may write

$$-dN/dt = k_5S\bar{p} - k_6S(1 - \bar{p}) + d\bar{N}/dt \quad (2)$$

where  $k_5$  and  $k_6$  are the rates of conversion per sq. cm. of surface covered with adsorbed para and ortho hydrogen molecules, respectively, and  $\bar{N}$  is the number of para hydrogen molecules on the

surface of the catalyst at any time  $t$ . Since at equilibrium, from equations 1 and 2

$$k_1(1 - S)P = k_2S \quad (3)$$

and

$$k_0 = k_3 p_\infty / (1 - p_\infty) \quad (4)$$

and since with a small amount of catalyst present  $\bar{N}$  will be very small compared with  $N$  and there-

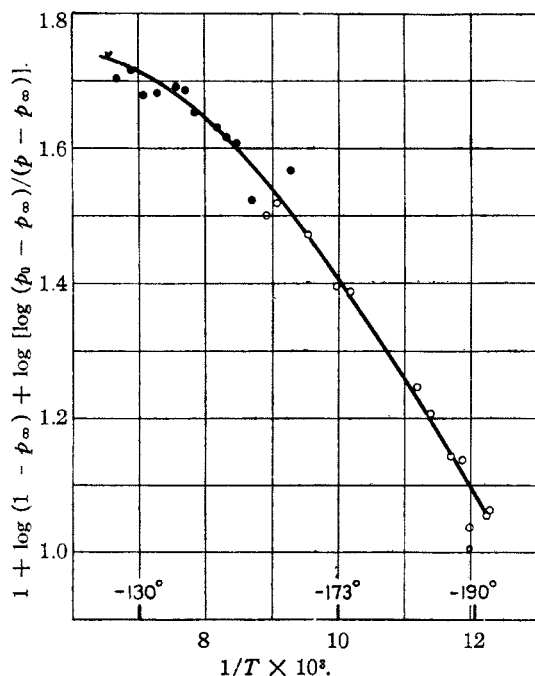


Fig. 4.—Temperature coefficient of the ortho-para hydrogen conversion on iron catalyst 931 cooled in helium from 450 to  $-190^\circ$ . Space velocity of 16,000 was used. The ordinate is the logarithm of the reaction velocity constant (see equation 11).

fore  $d\bar{N}/dt$  may be neglected in comparison with  $dN/dt$ , equations 1, 2, 3 and 4 may be combined to obtain the equation<sup>10</sup>

$$-dN/dt = \frac{k_1(1 - S)k_3(1 - p_\infty)Pp}{k_2(1 - p_\infty) + k_3} - \frac{k_1(p_\infty)(1 - S)k_3P(1 - p)}{k_2(1 - p_\infty) + k_3} = k_7p - k_8(1 - p) \quad (5)$$

where

$$k_7 = \frac{k_1(1 - S)Pk_3(1 - p_\infty)}{k_2(1 - p_\infty) + k_3} = \frac{k_3S(1 - p_\infty)}{[(1 - p_\infty) + k_3/k_2]} \quad (6)$$

In order to integrate equation 5 it is convenient to substitute  $PVpA/RT$  for  $N$ , where  $A$  is Avogadro's number. The integrated form of equation 5 then becomes

$$k_7t = \frac{b(1 - p_\infty)P}{T} \ln \frac{p_0 - p_\infty}{p - p_\infty} \quad (7)$$

(10) The expression  $k_3(1 - p_\infty)/(k_2(1 - p_\infty) + k_3)$  included in  $k_7$  can be shown to represent the fraction of the para molecules which after becoming adsorbed undergo conversion to ortho molecules on the surface rather than desorb again as para molecules.

where the constant  $b$  is  $VA/R$ . From equations 6 and 7, furthermore, it becomes apparent that  $\tau$ , the time of half conversion, is given by

$$\tau = \frac{b(1 - p_\infty)P[(1 - p_\infty) + k_3/k_2] \ln 2}{Tk_3S(1 - p_\infty)} = \frac{k_9P}{S} \quad (8)$$

the constant  $k_9$  being a function of  $T$  but not of  $P$ .

The dependence of the time of half conversion  $\tau$  on the pressure now becomes understandable. In the low temperature region the amount of van der Waals adsorption increases as  $P^{1/2}$ . This agrees with the curve in Fig. 1 for the conversion over iron at  $-190^\circ$ . No isotherms have been obtained for the adsorption of hydrogen on iron at  $-78$  and at  $0^\circ$ . However, for molecular adsorption if one evaluates  $S$  in terms of  $P$  from equation 3 the time of half conversion will be given by the equation

$$\tau = k_9[(k_1P + k_2)/k_1] \quad (9)$$

This represents approximately the curves of Fig. 1 for the conversion over iron at  $-78$  and  $0^\circ$ . If it be postulated that the conversion takes place as a result of the hydrogen molecules dissociating on adsorption into adsorbed atoms and then recombining and evaporating from the surface in the equilibrium ortho-para ratio for the temperature of the catalyst, it can be shown that the usual type of Langmuir isotherm equation for atomic adsorption will lead to the equation

$$\tau = \left( \frac{k_1P}{k_2} + 2 \sqrt{\frac{k_1P}{k_2}} + 1 \right) k_{10} \quad (10)$$

This equation at least qualitatively conforms to the results obtained by Bonhoeffer and Farkas<sup>7</sup> for the conversion over platinum as well as to our own results for the conversion over iron at  $-78$  and  $0^\circ$ .

The above equations have all been derived for a static system. However, for the reaction being considered, they are equally applicable to a flow system,  $t$  being in this case the time of contact which is defined as the ratio of the apparent volume of the catalyst to the volume of gas (at the temperature and pressure of the catalyst system) passing the catalyst per unit time.

The temperature coefficient of the catalytic para-ortho conversion may be obtained with the help of equations 6 and 7. In measuring the variation of reaction rate with temperature in the flow system employed in the present experiments it was found convenient to keep the flow of gas  $F$ , as measured at room temperature and pres-

sure, constant. Since the time of contact  $t^{11}$  is given by the equation  $t = V_c P 273 / FT (760)$  equation 7 for the temperature coefficient measurements at constant  $F$  becomes

$$k_7 = b_1(1 - p_\infty) \log(p_0 - p_\infty) / (p - p_\infty) \quad (11)$$

where constant  $b_1$  is independent of temperature. The apparent or observed energy of activation  $E_{\text{obs.}}$  may then be calculated from the variation of  $k_7$  with temperature since by the usual definitions

$$\frac{d \log k_7}{dT} = \frac{E_{\text{obs.}}}{RT^2}, \text{ and} \quad (12)$$

$$\log k_7 = (-E_{\text{obs.}}/RT) + C \quad (13)$$

From equations 11 and 13 it follows that a plot of  $\log(1 - p_\infty) + \log [\log(p_0 - p_\infty) / (p - p_\infty)]$  against  $1/T$  gives  $E_{\text{obs.}}/R$ . Such plots are shown in Figs. 3 and 4.

With the help of equation 6 the observed temperature coefficients may now be interpreted in terms of the temperature dependence of the various constants included in  $k_7$ . At the higher temperatures,  $-78$  and  $0^\circ$ , where the conversion appears to be dependent upon an activated adsorption of hydrogen, it is probable that  $k_s$ , the rate of conversion on the surface, is large compared to the rate of evaporation  $k_2$  for molecules held by activated adsorption. For this case equation 6 will simplify to

$$k_7 = k_2 S (1 - p_\infty) \quad (14)$$

Hence

$$\frac{d \log k_7}{dT} = \frac{d \log k_2}{dT} + \frac{d \log S}{dT} + \frac{d \log (1 - p_\infty)}{dT} \quad (15)$$

The value of  $(1 - p_\infty)$  is practically constant above  $-78^\circ$ ; hence the last term in equation 15 may be neglected. By making the usual<sup>12</sup> assumptions that  $k_2$  is proportional to  $e^{-E_2/RT}$  and  $k_1 = C_1 e^{-E_1/RT} / (T)^{1/2}$  where  $E_2$  and  $E_1$  are the energies of activation of desorption and adsorption, respectively, then one obtains from equation 3 the relation

(11) It seems probable that the time of contact in those cases in which adsorption and desorption is fast should be equal to  $(1/F) [(273 V_c P / 760 T) + V_{\text{ads.}}]$ . Use of the simple equation adopted in this paper might cause an appreciable error in those cases in which  $V_{\text{ads.}}$  is about as large as  $273 V_c P / 760 T$ . In the temperature coefficient runs of Figs. 3 and 4 and the  $-190^\circ$  pressure coefficient run of Fig. 1, this would not be serious for the volume of gas adsorbed is equal to or less than one-tenth the volume of gas in the space between the catalyst particles. For the  $-78$  and  $0^\circ$  pressure coefficient runs, however, the ratio of the volume of gas adsorbed on the catalyst to the volume in the catalyst "dead space" varies from about one-tenth at  $760$  mm. to about 1 at  $30$  mm.; use of the simplified time of contact equation has therefore probably resulted in a steeper slope for these two curves than one would obtain by including the  $V_{\text{ads.}}$  term in the calculations of time of contact. Since in these two cases, however,  $dN/dt$  cannot in general be neglected with respect to  $dN/dt$ , an exact treatment becomes very complicated and has not as yet been worked out.

(12) Taylor, *THIS JOURNAL*, **63**, 578 (1931).

$$S = \frac{1}{1 + \sqrt{T} C_3 e^{-\frac{(E_2 - E_1)}{RT}}} = \frac{1}{1 + \sqrt{T} C_3 e^{-\lambda/RT}} \quad (16)$$

where  $\lambda$  is the heat of adsorption of hydrogen on iron and equals  $E_2 - E_1$ .

Hence

$$\frac{d \log S}{dT} = \frac{-(\lambda + RT/2)(1 - S)}{RT^2} \quad (17)$$

and

$$E_{\text{obs.}} = E_2 S + (1 - S)E_1 - RT/2 (1 - S) \quad (18)$$

It can be shown that this last equation should represent the case of atomic adsorption of hydrogen on the surface as well as that of molecular adsorption.

According to equation 18 the apparent energy of activation for the higher temperature region will be intermediate between the energy of activation of the adsorption process and that of the desorption process. The sudden rise in  $E_{\text{obs.}}$  at about  $-90^\circ$  as the temperature was being raised makes it probable that the conversion between  $-90$  and  $40^\circ$  is to be associated with Type A activated adsorption. However, unfortunately sufficient data were not obtained to ascertain whether or not equation 18 could represent the energy of activation for the conversion in this higher temperature region. The only values (about 10,000 calories) obtained for the energy of activation for Type A adsorption were for a catalyst sample that had been cooled from  $450^\circ$  in helium and was not contaminated with any Type B activated adsorption. On the other hand, the temperature coefficients of the ortho-para hydrogen conversion covering the range  $-78$  to  $40^\circ$  (1500 to 6600 calories) were determined only on samples that had been cooled in hydrogen and were therefore pretty well covered with Type B adsorption.

At the lower temperature, if, as is probable, the rate of reaction on the surface of the catalyst ( $k_s$ ) is much smaller than the rate of desorption  $k_2$  it is apparent that equation 6 will simplify to  $k_s S$ . Then for the low temperature conversion

$$\frac{d \log k_7}{dT} = \frac{E_{\text{obs.}}}{RT^2} = \frac{d \log k_s}{dT} + \frac{d \log S}{dT} = \frac{E_m}{RT^2} - \frac{\left(\lambda + \frac{RT}{2}\right)(1 - S)}{RT^2} \quad (19)$$

where  $\lambda$  is the heat of van der Waals adsorption of hydrogen on iron and  $E_m$ , the true energy of activation for the conversion of adsorbed para hydrogen to adsorbed ortho hydrogen, is defined by the equation

$$k_s = C_4 e^{-E_m/RT} \quad (20)$$

the constant  $C_s$  being independent of temperature. Then from equation (19)

$$E_{\text{obs.}} = E_m - (\lambda + (RT/2)(1 - S)) \quad (21)$$

The positive temperature coefficient even in the region in which only van der Waals adsorption occurs is then to be accounted for by the fact that a considerable energy of activation  $E_m$  is involved in the low temperature transformation, this quantity being slightly larger than the heat of adsorption  $\lambda$ . Furthermore, as  $T$  increases and  $S$  therefore decreases  $E_{\text{obs.}}$  would decrease according to this equation. In fact, the change in  $E_{\text{obs.}}$  from about 730 cal. per mole of hydrogen to about 230 calories in going from 80 to 143°K. is consistent with a change of 0.28 in  $S$  between these two temperatures,  $\lambda$  being about 2100 calories per mole of hydrogen adsorbed. This is in good agreement with the adsorption data.<sup>3</sup>

This assumption of a reaction on the surface that is slow compared with the rate of adsorption and desorption will also account for the negative temperature coefficients that have been reported for the low temperature ortho-para conversion over nickel, copper and sodium chloride<sup>13</sup>  $E_m$  of equation (19) being in such cases presumably smaller than  $\lambda$ , the slowness of the surface reaction being due to small values of  $C_s$ .

Mention should be made<sup>14</sup> of one possible way of avoiding the conclusion that the observed positive temperature coefficient of the low temperature catalytic ortho-para conversion over iron corresponds to a positive value for the true energy of activation  $E_m$ . If the conversion ( $k_s$ ) on the surface is very fast compared with the rate of van der Waals desorption, the observed energy of activation will be given substantially by equation 18, the  $E_2$  and  $E_1$  now referring to the energies of activation of van der Waals desorption and adsorption processes. In this case  $E_m$  might have any value from about that of  $\lambda$ , the heat of adsorption, down to zero. Although this interpretation is improbable if one accepts the generally assumed very high rates for van der Waals adsorption, it cannot be ruled out with certainty until more is known in regard to the absolute rate of adsorption and desorption of hydrogen on iron catalysts at -183°.

The poisoning effect of nitrogen adsorbed at

(13) Bonhoeffer, Farkas and Rummel, *Z. physik. Chem.*, **B21**, 225 (1933).

(14) Experimental work by Farkas and Sachsse [*Z. physik. Chem.*, **B23**, 1 (1933)], in agreement with the theory developed by E. Wigner [*ibid.*, **B23**, 28 (1933)] has shown that the homogeneous catalysis of the para-ortho hydrogen conversion by paramagnetic oxygen molecules involves little if any energy of activation.

100 and 450° was no greater than 15 and 50%, respectively. At both of these temperatures some activated adsorption of nitrogen<sup>15</sup> would be expected, the amount adsorbed in a given time being much greater at 450° than at 100°. It is not unreasonable to believe that the observed poisoning may have been caused by the activated adsorption of nitrogen. The poisoning effect of nitrogen at -190° on a catalyst cooled in hydrogen might indicate some type of complex formation at -190° between nitrogen molecules and adsorbed (type B) hydrogen. The possibility of such a complex formation has been indicated in other previous work.<sup>16</sup>

The increase in activity of the hydrogen cooled iron catalysts on exposure to oxygen at -190° may be due to the catalytic activity of the paramagnetic oxygen<sup>17</sup> molecules adsorbed as such upon the hydrogen covered iron catalyst. On the other hand, it might result from oxygen displacing or combining with the poisonous type B hydrogen adsorption, or modifying the poisonous nature of the latter. The poisoning experiments in which oxygen was added to a hydrogen cooled sample at 64° increased the -190° activity, probably by removing some of the adsorbed hydrogen. The decrease in the activity at 0° caused by adding oxygen at 64° is merely another indication that the higher temperature conversion is occurring through quite a different mechanism than the conversion at -190°. The oxygen addition at -190° decreased rather than increased the -190° activity if the sample was cooled in helium from 450°. It thus appears that oxygen adsorbed at -190° is a poorer catalyst than the iron itself, but much better than iron covered with a layer of type B activated adsorption.

The poisoning effect of the activated adsorption of hydrogen on the low temperature catalytic para-ortho conversion over nickel, platinum and iron constitutes very strong evidence that the phenomenon of activated adsorption on these metals is to some extent at least a surface phenomenon since such poisoning could probably not result from mere solution within the lattice of the metal. The implications of the poisoning experiments on iron will be further elaborated in connection with the detailed adsorption results that will be presented in a separate paper.<sup>3</sup>

(15) Emmett and Brunauer, *THIS JOURNAL*, **56**, 35 (1934).

(16) Müller and Schwabe, *Z. Elektrochem.*, **38**, 861 (1932); Rupp, *Z. angew. Chem.*, **42**, 709 (1929).

(17) Rummel, *Z. physik. Chem.*, **A167**, 225 (1933).

### Summary

1. The ortho-para conversion of hydrogen over the iron catalysts has been studied as a function of the temperature, pressure, time of contact and presence of various poisons. Kinetic expressions consistent with the observed data have been obtained.

2. The poisoning effects of activated adsorption of hydrogen on the  $-190^\circ$  para-ortho hydrogen conversion over platinum and nickel have also been noted. This poisoning effect constitutes very strong evidence that the activated adsorption of hydrogen by nickel, platinum and iron is in part at least a surface phenomenon.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

## The Adsorption of Hydrogen by Iron Synthetic Ammonia Catalysts

BY P. H. EMMETT AND R. W. HARKNESS

Some of the experimental results obtained in the course of a study<sup>1</sup> of the ortho-para interconversion of hydrogen over iron synthetic ammonia catalysts required for their interpretation more detailed information than was available relative to the adsorption of hydrogen by the iron catalysts. The rates and amounts of adsorption as a function of pressure between 25 and 760 mm. and of temperature between  $-195$  and  $450^\circ$  have therefore been determined and are reported in the present paper. The results combined with the ortho-para interconversion studies already described establish definitely the existence of two types of activated adsorption<sup>2</sup> (type A and type B) of hydrogen on iron in addition to the usual physical adsorption.

### Experimental

The adsorption apparatus was the one used by Emmett and Brunauer.<sup>3</sup> By means of a trap cooled in liquid air and placed in the line leading to the catalyst, all hydrogen used for reduction purposes was kept free of traces of stopcock grease, water vapor, etc. The dead space in the catalyst system was determined in the usual manner with purified helium. Ten cc. of catalyst was used in the adsorption measurements. The system with the catalyst at  $450^\circ$  could be pumped down to  $2 \times 10^{-4}$  mm. in about an hour. After each adsorption run the catalyst was reduced for about an hour at  $450^\circ$  and was then evacuated for from one to three hours.

The doubly promoted iron synthetic ammonia catalyst (931) contained 1.59% potassium oxide and 1.3% aluminum oxide as promoters. The

preparation, reduction and properties of this type of catalyst have been described many times previously.<sup>4</sup> The pure iron catalyst was No. 973, another sample of this same catalyst having been used by Benton and White<sup>5</sup> in their adsorption experiments.

### Results

Typical adsorption isotherms for hydrogen on catalyst 931 at  $-195$  and  $-183^\circ$  are shown in Fig. 1. Equilibration occurred practically instantaneously both in adsorption and in desorption

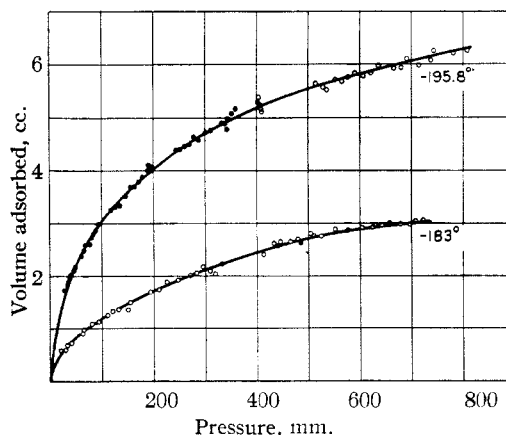


Fig. 1.

runs. The adsorption decreased quite rapidly with increasing temperature, as is evident from the 760 mm. isobar of Fig. 4, the calculated heat of adsorption being about 2000 calories per mole of hydrogen. This value is typical of physical adsorption; Benton and White obtained 1600 calories for the heat of adsorption on pure iron catalyst 973.

(1) Emmett and Harkness, *THIS JOURNAL*, **57**, 1624 (1935).

(2) Harkness and Emmett, *ibid.*, **56**, 490 (1934).

(3) Emmett and Brunauer, *ibid.*, **56**, 35 (1934).

(4) Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925); Almquist and Crittenden, *ibid.*, **18**, 1307 (1926).

(5) Benton and White, *THIS JOURNAL*, **54**, 1820 (1932).