

# The Chemisorption of Hydrogen Sulfide, Methyl Sulfide, and Cyclohexene on Supported Nickel Catalysts

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Magnetization measurements on supported nickel catalysts have shown that hydrogen sulfide is dissociatively chemisorbed, forming four chemisorptive bonds with the nickel surface. This is confirmed by deuterium exchange results. The mechanism of chemisorption of methyl sulfide is strongly temperature dependent. It is associatively adsorbed at room temperature forming two chemisorptive bonds, but at higher temperatures extensive C—H and C—S bond rupture occurs.

Cyclohexene is dissociatively chemisorbed at 25°C, forming two adsorbed hydrogen atoms and a diadsorbed C<sub>6</sub>H<sub>5</sub> radical. This conclusion is confirmed by deuterium exchange experiments.

## INTRODUCTION

The purpose of this work was to study, by magnetization measurements, the mechanism of chemisorption of several vapors on supported nickel catalysts, and to compare the results obtained by this method with the results of deuterium exchange experiments.

## EXPERIMENTAL METHOD

Magnetization-volume and pressure-volume isotherms were obtained as previously described (1). Temperature control was achieved by surrounding the permeameter secondary coils and sample chamber with an oil bath maintained to within  $\pm 0.1^\circ\text{C}$ , or by an ice-water or Dry-Ice-acetone bath.

The catalyst samples used were Universal Oil Products nickel-kieselguhr containing 52.8% Ni, and Harshaw nickel-silica catalyst Ni-0101, containing 44% Ni. Details concerning the former have been published (2). The adsorption and magnetization data on the Harshaw catalyst were similar to those obtained on the U.O.P. sample, indicating a similar particle size and nickel surface area. The catalyst

samples were reduced in purified hydrogen for 20 hr and evacuated to  $10^{-6}$  mm Hg, both at a temperature of 350° to 370°C.

Deuterium exchange experiments on the hydrogen sulfide treated samples were performed by two methods. A known volume of hydrogen sulfide was chemisorbed and then a known volume of deuterium was admitted. The gas was circulated over the sample, and the sample was evacuated through a Töpler pump for analysis. The second method involved chemisorbing a known volume of hydrogen sulfide. The system was then evacuated through a Töpler pump. A known volume of deuterium was then admitted, after which the gas mixture was evacuated and analyzed. Gas samples were analyzed on a Consolidated Electroynamics Corp. mass spectrometer model 21-611.

Cyclohexene vapor was admitted to the free spaces of the apparatus under its own vapor pressure. Successive doses were admitted to the sample chamber and the volume of cyclohexene adsorbed was calculated, after correction for the volume of gas remaining in the free spaces. For the run at 0°C the maximum pressure over the sample was less than 1 mm, for that at

120°C the pressure reached a maximum of 7 mm. Treatment of the cyclohexene vapor as an ideal gas was therefore believed to be justified.

Matheson hydrogen sulfide was used without further purification—analysis showed only traces of impurities. Deuterium gas was used as supplied by Stuart Oxygen Co. Matheson, Coleman, and Bell cyclohexene was used. This was purified by distillation followed by storage over sodium wire.

### RESULTS

**Hydrogen sulfide.** For the catalyst samples studied there is a linear decrease of relative magnetization,  $M'/M$ , with

are shown in Fig. 1, together with the pressure-volume isotherms obtained simultaneously.

Quantitative desorption of hydrogen and of hydrogen sulfide was attempted with the use of a Töpler pump or a two-stage diffusion pump backed by a Töpler pump. The volume of hydrogen which may be removed from a U.O.P. sample at progressively higher temperatures is shown in Table 1. The  $H_2$  evacuated/ $H_2S$  adsorbed ratio varied from 0.60 to 0.70 for different catalyst samples, the average being about 0.65. Mass spectrometer analyses showed that in every case, after chemisorption of hydrogen sulfide to a pressure of 1.1 atm or less, hydrogen was the only gas in the free

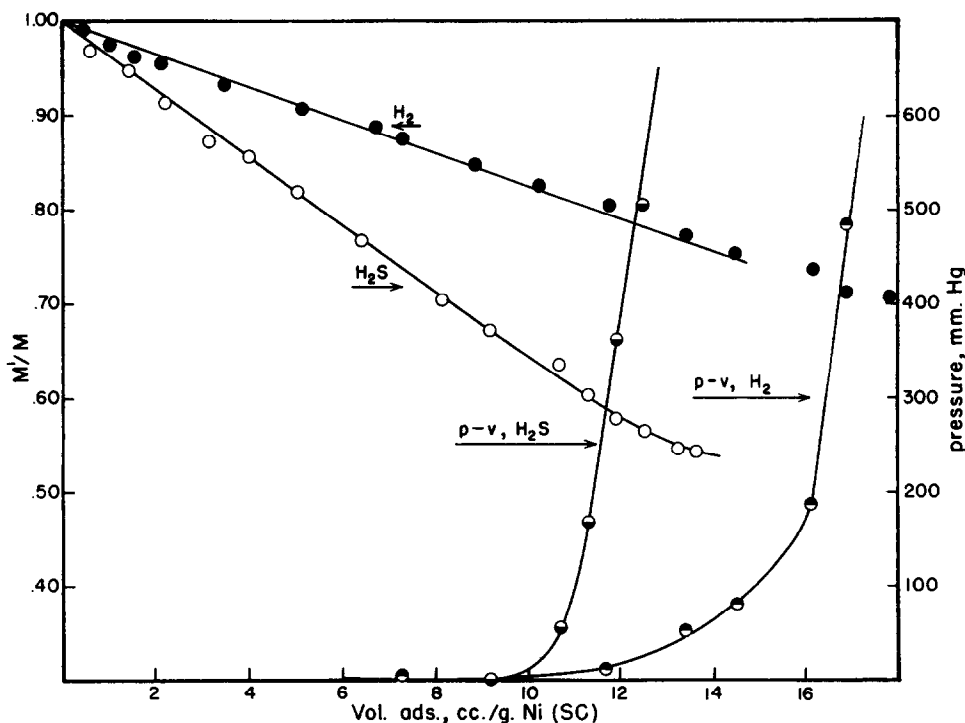


FIG. 1. Magnetization-volume and pressure-volume isotherms for  $H_2$  and  $H_2S$  at 25°C on nickel-kieselguhr.

volume of chemisorbed hydrogen sulfide to a pressure of approximately 1 atm. At temperatures of 0°, 25°, and 115°C the slope of the magnetization-volume isotherms was  $2.0 \pm 0.1$  times the slope of the corresponding hydrogen isotherms. The data obtained at 25°C on a U.O.P. sample

spaces over the samples and, on evacuation of chemisorbed hydrogen sulfide, hydrogen was the only product desorbed.

This failure of hydrogen to desorb quantitatively from a surface on which hydrogen sulfide was adsorbed was found to depend on the extent of surface coverage.

TABLE 1  
 VOLUMES (SC) OF H<sub>2</sub> EVACUATED FROM NICKEL-KIESELGUHR AFTER ADSORPTION  
 OF H<sub>2</sub> AND OF H<sub>2</sub>S, RESPECTIVELY

Wt. of sample	6.627 g	Wt. of sample	7.319 g
Adsorption temp.	0°C	Adsorption temp.	35°C
Maximum press.	210 mm	Maximum press.	640 mm
H <sub>2</sub> adsorbed	55.7 cc	H <sub>2</sub> S adsorbed	65.9 cc
H <sub>2</sub> evac. at 0°C	13.7 cc	H <sub>2</sub> evac. at 25°C	23.0 cc
H <sub>2</sub> evac. at 360°C	36.0 cc	H <sub>2</sub> evac. at 360°C	18.2 cc
H <sub>2</sub> evac. at 400°C	3.4 cc	H <sub>2</sub> evac. at 400°C	0.2 cc
Total H <sub>2</sub> evac.	54.6 cc	Total H <sub>2</sub> evac.	41.4 cc
H <sub>2</sub> evac./H <sub>2</sub> ads.	0.98	H <sub>2</sub> evac./H <sub>2</sub> S ads.	0.63

At low coverages it proved possible to remove a larger fraction of the hydrogen originally admitted in the form of hydrogen sulfide. An example of these results is as follows: after adsorption at 25°C of 5.80 cc H<sub>2</sub>S (amounting to 1.43 cc/g Ni on a U.O.P. sample), it was found possible to remove 5.5 cc H<sub>2</sub> by evacuation at 360°C. This is a H<sub>2</sub> evac./H<sub>2</sub>S ads. ratio of 0.95 as compared with 0.65 for complete or nearly complete coverage with H<sub>2</sub>S.

Since hydrogen (resulting, presumably, from dissociative adsorption of hydrogen sulfide) could not be evacuated quantitatively when the hydrogen sulfide was permitted to approach full surface coverage, an attempt was made to determine if the hydrogen which could not be removed below 400°C could be exchanged with deuterium. An evacuated sample, containing hydrogen as a result of prior chemisorption of hydrogen sulfide, was treated with excess deuterium—the deuterium being circulated over the sample for 2 hr at room temperature and then evacuated. But only traces

of H<sub>2</sub> and HD were found in the gaseous mixture. These results are shown in Table 2.

Hydrogen-deuterium exchange experiments were also carried out by another method. Hydrogen sulfide was adsorbed on a reduced and evacuated nickel-kieselguhr sample to a pressure of 370 mm. Deuterium was then admitted to the sample, and the gas mixture in the free spaces was in contact with the sample for several hours at near 0°C. Mixtures of H<sub>2</sub>, HD, and D<sub>2</sub> were then evacuated and analyzed. The results are shown in Table 3.

Pressure-volume data are given in Table 4 for the chemisorption of hydrogen and of hydrogen sulfide on a nickel-kieselguhr to which increments of hydrogen sulfide were added. Pressures are given as observed immediately after admission of the indicated volume of hydrogen sulfide and after the pressure had increased to a constant value (usually 15–20 min). The gas liberated was hydrogen. From the experimental data it may be seen that the volumes of hy-

TABLE 2  
 HYDROGEN-DEUTERIUM EXCHANGE RESULTS ON H<sub>2</sub>S-TREATED NI-KIESELGUHR AFTER EVACUATION\*

H <sub>2</sub> S admitted	73.1 cc
H <sub>2</sub> evacuated at 25°C	25.5 cc
H <sub>2</sub> evacuated at 360°C	20.2 cc
H <sub>2</sub> evacuated at 450°C	0.3 cc
Residual H <sub>2</sub>	27.1 cc
D <sub>2</sub> admitted	20.1 cc
Gas mixture evac. at 25°C	11.2 cc
(Composition: H <sub>2</sub> , 1%; HD, 5–6%; D <sub>2</sub> , 93–94%)	
Gas mixture evac. at 360°C	7.1 cc
(Composition: H <sub>2</sub> , 3%; HD, 7–8%; D <sub>2</sub> , 89–90%)	

\* All volumes are given as measured at 25°C and 740 mm over 7.752 g U.O.P. catalyst.

TABLE 3  
HYDROGEN-DEUTERIUM EXCHANGE RESULTS ON H<sub>2</sub>S-TREATED Ni-KIESELGUHR<sup>a</sup>

H <sub>2</sub> S admitted at 0°C	70.0 cc
D <sub>2</sub> admitted at 0°C	17.5 cc
Gas mixture evac. at 0°C (Composition: H <sub>2</sub> , 38%; HD, 47%; D <sub>2</sub> , 15%)	33.9 cc
Gas mixture evac. at 140°C (Composition: H <sub>2</sub> , 64%; HD, 29%; D <sub>2</sub> , 7%)	16.0 cc
Gas mixture evac. at 360°C (Composition: H <sub>2</sub> , 84%; HD, 15%; D <sub>2</sub> , 1%)	6.5 cc
Total vol. H <sub>2</sub> S + D <sub>2</sub> admitted	87.5 cc
Total vol. H <sub>2</sub> + HD + D <sub>2</sub> evac. (Total vol. evac.-vol. D <sub>2</sub> admit.)/(vol. H <sub>2</sub> S ads.) = 56%	56.4 cc

<sup>a</sup> All volumes are given as measured at 27°C and 752 mm over 6.91 g U.O.P. catalyst.

drogen which are evolved approached, and finally exceeded, the incremental volumes of hydrogen sulfide which were admitted to the sample (compare columns 1 and 6, Table 4. Chemisorption of hydrogen on nickel at higher coverages results, as is well known, in a continued slow uptake of hydrogen. With hydrogen sulfide the opposite effect occurs—hydrogen is slowly evolved into the gas phase.

In a separate experiment hydrogen was chemisorbed on reduced, evacuated nickel-kieselguhr sample to a pressure of 700 mm. Admission of a known volume of hydrogen

sulfide resulted in a like volume of hydrogen being desorbed—the relative magnetization simultaneously decreasing very slightly. For a volume of 1.9 cc H<sub>2</sub>S admitted, 1.5 cc H<sub>2</sub> was desorbed, and  $M'/M$  decreased from 0.729 to 0.726. When hydrogen sulfide was then passed over the sample at 25°C the magnetization decreased to zero after approximately 1 hr. Evacuation at 360°C did not increase the magnetization but passage of hydrogen over the sample at 360°C raised the relative magnetization (measured at 25°C) to about 0.1.

TABLE 4  
PRESSURES OF H<sub>2</sub> AFTER ADMISSION OF H<sub>2</sub>S<sup>a</sup>

1 Volume H <sub>2</sub> S admitted (cc)	2 Cumulative volume H <sub>2</sub> S (cc)	3 Initial pressure (mm)	4 Final pressure (mm)	5 Volume of gas in free space (cc)	6 Volume H <sub>2</sub> desorbed (cc)	7 $M'/M$ , measured after pressure reached final value
0.00	0.00	—	—	—	—	1.000
2.11 <sup>b</sup>	2.11	—	—	—	—	0.988
6.38	8.49	—	—	—	—	0.952
7.02	15.51	—	—	—	—	0.910
7.06	22.57	—	—	—	—	0.873
7.11	29.68	2	0	—	—	0.831
3.02	32.70	2	2	0.05	0.05	0.817
3.07	35.77	5	7	.17	.12	0.795
3.30	39.07	16	23	.55	.38	0.772
3.37	42.44	50	79	1.89	1.34	0.755
5.03	47.47	171	211	5.03	3.14	0.738
5.45	52.92	210	378	9.02	3.99	0.731
5.27	58.19	445	563	13.43	4.41	0.718
3.58	61.77	571	676	16.13	2.70	0.715
2.46	64.23	716	769	18.84	2.71	0.711

<sup>a</sup> All volumes are given at SC as measured at 25°C over 7.271 g U.O.P. catalyst.

<sup>b</sup> Free space volume, 18.04 cc.

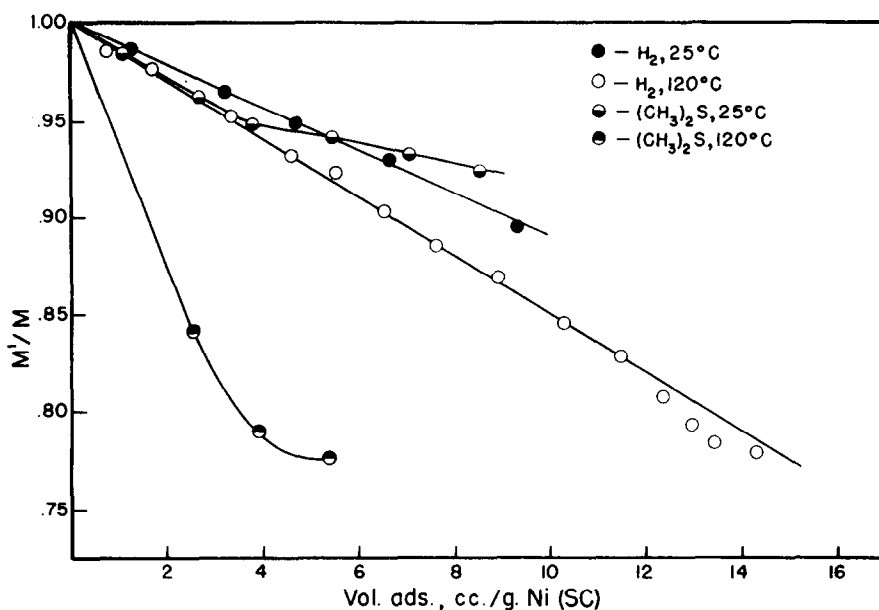


FIG. 2. Magnetization-volume isotherms for  $\text{H}_2$  and  $(\text{CH}_3)_2\text{S}$  at  $25^\circ$  and  $120^\circ\text{C}$  on nickel-kieselguhr.

**Methyl sulfide.** Magnetization-volume isotherms for methyl sulfide were obtained at  $25^\circ$  and  $120^\circ\text{C}$ . These and the corresponding hydrogen isotherms are shown in Fig. 2. The pressure-volume isotherms are shown in Fig. 3. In a separate experiment, methyl sulfide was admitted to the nickel-

kieselguhr sample at  $25^\circ\text{C}$ , and the products of evacuation were collected as the temperature was slowly raised to  $400^\circ\text{C}$ . Evacuation at room temperature for a short time yielded methane. Evacuation up to  $250^\circ\text{C}$  yielded methane and ethane together with small amounts of hydrogen.

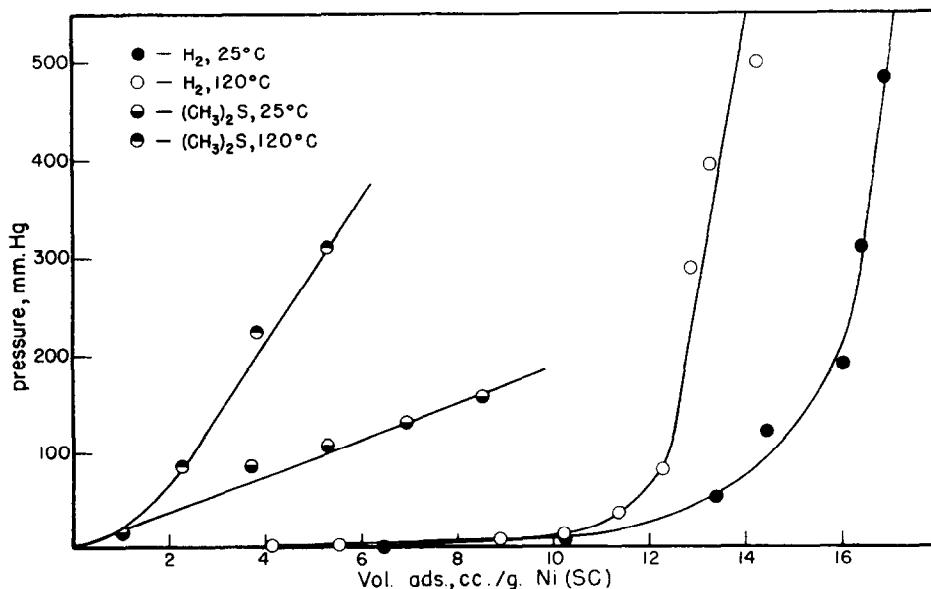


FIG. 3. Pressure-volume isotherms for  $\text{H}_2$  and  $(\text{CH}_3)_2\text{S}$  at  $25^\circ$  and  $120^\circ\text{C}$ .

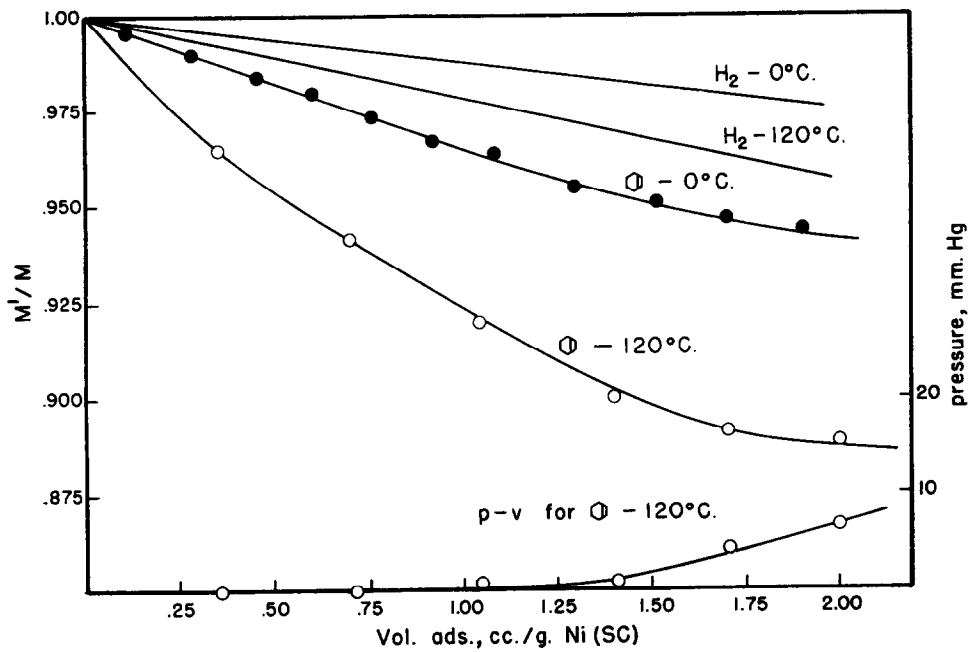


FIG. 4. Magnetization-volume and pressure-volume isotherms for hydrogen and cyclohexene at  $0^\circ$  and  $120^\circ C$  on nickel-kieselguhr.

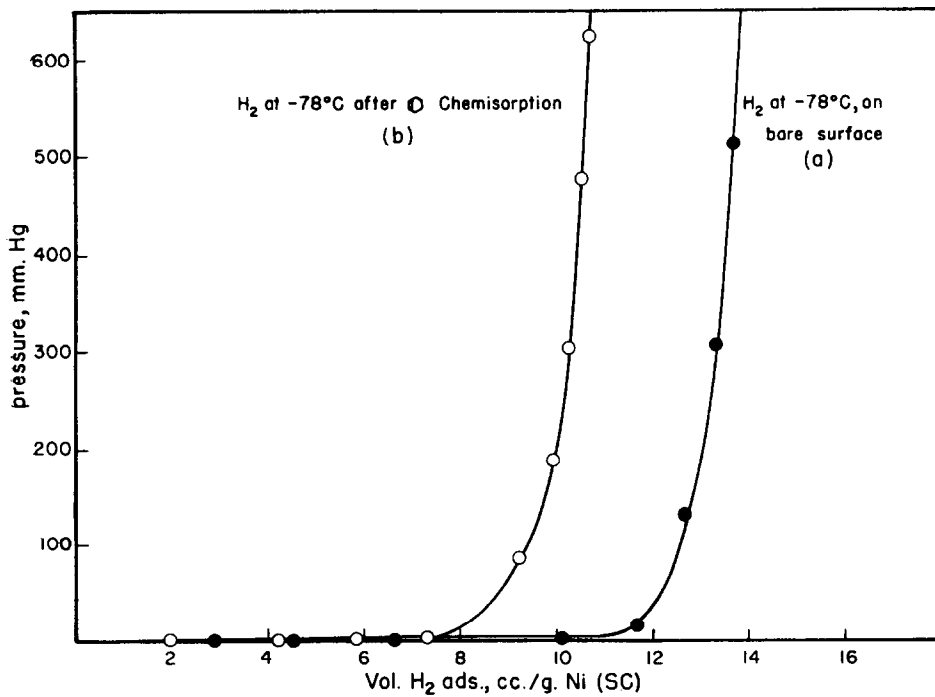


FIG. 5. Pressure-volume isotherms for hydrogen at  $-78^\circ C$ , prior to and after chemisorption of cyclohexene.

Hydrogen was the principal product of evacuation above  $300^\circ\text{C}$ .

**Cyclohexene.** Magnetization-volume isotherms for the chemisorption of cyclohexene at  $0^\circ$  and  $120^\circ\text{C}$  are shown in Fig. 4, which also shows the corresponding isotherms for hydrogen.

Pressure-volume isotherms for the chemisorption of hydrogen at  $-78^\circ\text{C}$  prior to and after chemisorption of cyclohexene (at  $25^\circ\text{C}$ ) were also obtained. Figure 5(a)

## DISCUSSION

**Hydrogen sulfide.** The method for relating the slope of the magnetization-volume isotherm to the number of chemisorptive bonds formed by any molecule on superparamagnetic nickel has been described previously (3). The number of bonds formed (i.e., the number of nickel atoms seriously involved in bond formation) is twice the isotherm slope for the molecule under consideration, divided by

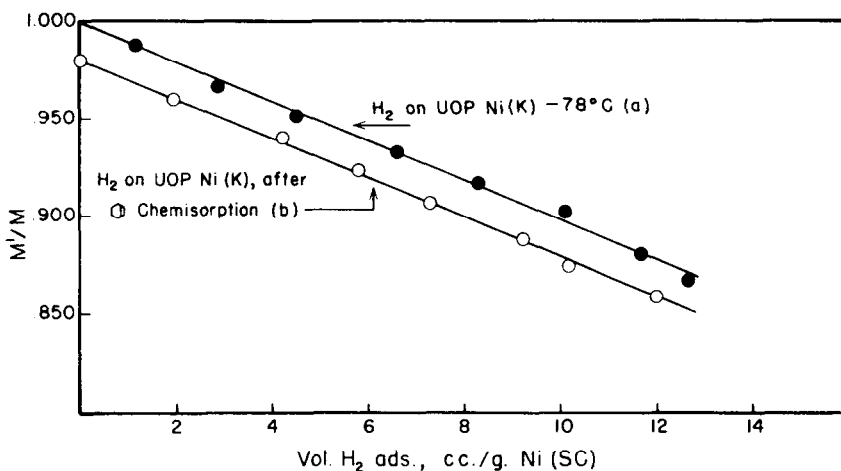


Fig. 6. Magnetization-volume isotherms for chemisorption of hydrogen at  $-78^\circ\text{C}$ , prior to and after chemisorption of cyclohexene.

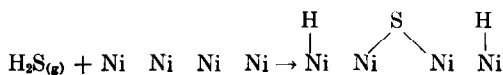
shows the pressure-volume isotherm for hydrogen on reduced, evacuated nickel-kieselguhr at  $-78^\circ\text{C}$ . Figure 5(b) shows a similar isotherm for hydrogen after the preadsorption at  $25^\circ\text{C}$  of  $1.50\text{ cc (SC) C}_6\text{H}_{10}$  vapor/g Ni. It will be observed that the presence of the preadsorbed cyclohexene denied access of  $3.10\text{ cc (SC) H}_2$  to the nickel surface.

Magnetization-volume isotherms for hydrogen, prior to and after chemisorption of a known volume of cyclohexene, were made in connection with the pressure-volume isotherms given in the foregoing. These isotherms are shown in Fig. 6. The slope of the hydrogen isotherm at  $-78^\circ\text{C}$  after chemisorption of  $1.50\text{ cc (SC) C}_6\text{H}_{10}$  as shown in Fig. 6(b) is the same as that for hydrogen on a bare nickel surface at the same temperature as shown in Fig. 6(a).

that of molecular hydrogen, under the same conditions.

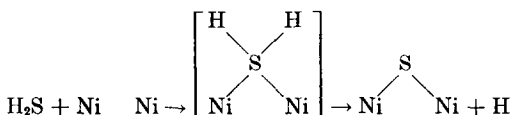
There is little doubt that hydrogen sulfide is dissociatively chemisorbed above  $0^\circ\text{C}$ . This is shown by the fact that hydrogen is found in the free space above the supported nickel catalyst and that only hydrogen is removed by evacuation. Furthermore, after chemisorption of hydrogen sulfide to low surface coverage, a nearly equal volume of hydrogen may be desorbed with a corresponding increase of relative magnetization.

The decrease in relative magnetization caused by chemisorption of hydrogen sulfide is, within experimental error, twice that caused by an equal volume of hydrogen. Chemisorption of hydrogen sulfide must, therefore, involve the formation of four bonds, as follows:



The conclusion appears to be in complete agreement with deuterium exchange experiments directed at determining the number of readily exchangeable hydrogen atoms per molecule of hydrogen sulfide adsorbed (4).

Table 4 shows that even at high surface coverage hydrogen sulfide is rapidly adsorbed. But then hydrogen is slowly desorbed and the volume of hydrogen so desorbed approaches and then exceeds the incremental volumes of hydrogen sulfide. As the magnetization falls after each admission of hydrogen sulfide, it may be assumed that the initial step throughout is one of molecular hydrogen sulfide being chemisorbed on bare nickel, but that such molecules dissociate *in situ*. If the coverage is low the dissociated hydrogen is quickly adsorbed on bare sites, but at high coverage the dissociated hydrogen is forced out to the gas phase, thus,

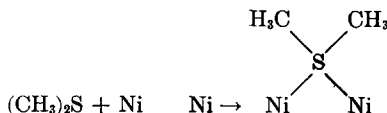


If the two foregoing mechanisms occurred without further complication, it would be expected that all the hydrogen brought to the surface in the form of hydrogen sulfide could be removed as molecular hydrogen. But such is not the case. As surface coverage with hydrogen sulfide becomes complete it is found that only about two-thirds of the total hydrogen may be removed by evacuation, even though the temperature is raised to 400°C. The conclusion that under these conditions some of the hydrogen is "locked-in" is confirmed by the deuterium exchange experiments reported in Tables 2 and 3. From Table 3, it is clear that virtually all the deuterium which was admitted to the sample could be evacuated at 360°C or below, and that this deuterium exchanged with 56% of the total hydrogen admitted to the sample as hydrogen sulfide. This situation is in sharp contrast to the ex-

change of adsorbed hydrogen with gaseous deuterium where the entire adsorbed layer comes rapidly to equilibrium (5) with the gas phase at 20°C.

From these results it is apparent that there are two chemically different types of hydrogen resulting from the chemisorption of hydrogen sulfide on nickel catalysts. It appears likely that the hydrogen which is neither evacuable nor exchangeable with deuterium, is held below the sulfide layer which acts as a barrier preventing diffusion of hydrogen to and from the surface. In view of the very limited solubility (6) of hydrogen in nickel at 25°C, and the results of Gundry and Tompkins (7), it is doubtful if this large volume of hydrogen could be dissolved in the nickel.

**Methyl sulfide.** The initial slope of the magnetization-volume isotherm for methyl sulfide at 25°C is very near that of the corresponding hydrogen isotherm, as shown in Fig. 2. This shows that, at this temperature, methyl sulfide is adsorbed associatively, i.e.,



The dissociation of methyl sulfide, which occurs when the temperature is raised, is very temperature dependent, and at 120°C dissociation is extensive. Since some methane may be evacuated at 25°C, it is clear that dissociation, at least to a slight extent, must take place at room temperature.

At 120°C, the ratio of isotherm slopes for methyl sulfide and hydrogen shows that extensive dissociation both of C—S and C—H bonds has taken place, and this is confirmed by the nature of the products obtained by evacuation. Roughly eight to ten bonds are formed at this temperature for each methyl sulfide molecule adsorbed.

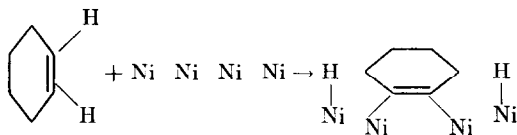
**Cyclohexene.** Galwey and Kemball (8) have shown that after chemisorption of cyclohexene at any temperature between 0° and 180°C approximately two hydrogen atoms, per cyclohexene molecule adsorbed, will rapidly exchange with excess deuterium. Above 100°C an additional four hy-



drogen atoms per cyclohexene molecule were exchanged. These results suggest that a stable, adsorbed C<sub>6</sub>H<sub>5</sub> radical is formed together with two dissociated, adsorbed hydrogen atoms in the 0°–100°C region, and that further dissociation takes place at higher temperatures. The precision claimed by Galwey and Kemball is  $\pm 0.5n$ , where  $n$  is the number of H atoms exchanged per molecule adsorbed.

The magnetic data are in agreement with the conclusions of Galwey and Kemball. Figure 4 shows that admission of a molecule of cyclohexene to nickel at 25°C yields between five and six bonds. The apparent total number of bonds formed per adsorbed molecule is  $5.3 \pm 0.5$  as derived from the magnetic data and  $4.0 \pm 1.0$  as obtained by Galwey and Kemball. The magnetic data also confirm the view that further dissociation takes place at elevated temperature, as many as eight bonds being formed per molecule at 120°C.

The principal mode of adsorption in the room temperature region seems quite probably to be that suggested by Galwey and Kemball,



Several reasons may be advanced to explain why the observed magnetization isotherm slope is a little greater than that predicted by the preceding mechanism. The most plausible reason is that some additional C—H (or even C—C) bond rupture may occur. This occurs readily above 100°C and must probably occur for a few molecules even at room temperature. As few as 10% of cyclohexene molecules reacting in this way would be enough to raise the slope of the magnetization-volume isotherm to the observed value.

Additional evidence that chemisorption of cyclohexene in the room temperature region occurs primarily by dissociation forming a C<sub>6</sub>H<sub>5</sub> radical is given by the pressure-volume isotherms for hydrogen at -78°C. prior to and after admission of

a known volume of cyclohexene as shown in Fig. 5. Adsorption of a definite volume (SC) of cyclohexene vapor at room temperature results in slightly more than twice this volume of hydrogen being denied access to the surface. This suggests that each dissociated cyclohexene molecule occupies four sites which would otherwise be available for four atoms of hydrogen.

The conclusion just stated depends on the assumption that hydrogenation of cyclohexene, or of the adsorbed C<sub>6</sub>H<sub>5</sub> radical, does not occur during the chemisorption of hydrogen at -78°C. Previous results have established this point for preadsorbed benzene (9). Furthermore, hydrogenation would be indicated by the sorption of *more* rather than *less* hydrogen in the presence of the preadsorbed cyclohexene. In this connection direct evidence that hydrogenation of the adsorbed C<sub>6</sub>H<sub>5</sub> radical does not occur at -78°C is provided by the slope of the magnetization-volume isotherms for hydrogen prior to and after chemisorption of the cyclohexene at 25°C, as shown in Fig. 6. The slope of the hydrogen isotherm after chemisorption of cyclohexene [Fig. 6(b)] is the same as that obtained for hydrogen on a bare nickel surface [Fig. 6(a)]. If some hydrogen were being used to hydrogenate the adsorbed hydrocarbon species the initial slope in Fig. 6(b) would be less than that in Fig. 6(a), as actually occurs when hydrogen is admitted to preadsorbed ethylene at room temperature (10).

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