# Catalytic Exchange of Hydrogen Sulphide and of Hydrogen with Deuterium on Disulphides of Molybdenum and Tungsten

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The exchange reaction between hydrogen sulphide and deuterium has been followed in the temperature range 150-200°C on a molybdenum disulphide catalyst and in the range 40-100°C on a sample of tungsten disulphide, the latter having a substantially greater surface area than the former. Studies have also been made on the exchange reaction between hydrogen and deuterium on both catalysts. Rates for both reactions are comparable on molybdenum disulphide whereas tungsten disulphide is a more effective catalyst for the exchange of hydrogen than for hydrogen sulphide.

The kinetics of the hydrogen sulphide+deuterium exchange and the poisoning effect of hydrogen sulphide on the hydrogen+deuterium reaction show that the sulphide is much more strongly adsorbed than the hydrogen on both catalysts. The "hydrogen "\* formed initially from the exchange of the sulphide contains  $H_2$  as well as HD and possible mechanisms for this reaction are discussed.

A marked compensation effect exists for all the reactions studied and there is a linear relationship between the logarithm of the frequency factors and the corresponding activation energies.

Several sulphides of transition metals are used as catalysts for reactions involving sulphur-containing compounds in industrial processes such as the vapour-phase hydrogenation of coal and the dehydrosulphurization of petroleum fractions, reviewed respectively by Donath<sup>1</sup> and McKinley.<sup>2</sup> However, there have been comparatively few fundamental investigations of these catalysts and much of the published information refers to reactions at relatively high temperatures which often yield a complex mixture of products resulting from hydrogenation, isomerization and hydrocracking.

It seemed worthwhile to obtain detailed information about the activity of some sulphides for the simple exchange reactions between hydrogen sulphide and deuterium, and between hydrogen and deuterium. In this way, we hoped to establish the temperature ranges in which the sulphides activate the H—S bond and the H—H bond and to learn something of the mechanism of these reactions which often play an important role in the more complex processes carried out at higher temperatures on these catalysts.

Molybdenum disulphide and tungsten disulphide were selected for investigation. Both are typical sulphide catalysts and the adsorption of hydrogen on the former has been examined by Badger, Griffith and Newling<sup>3</sup> and on the latter by Schuster (see ref. (1)) and by Friz.<sup>4</sup> The only previous work involving exchange reactions on these sulphides was carried out by Rittenberg<sup>5</sup> and the publication is not readily accessible. He showed that hydrogen deuteride was the initial product of the exchange reaction between hydrogen and heavy water and suggested that a heterolytic splitting of the hydrogen molecule occurs.

\* Terms such as "hydrogen" and "hydrogen sulphide" are used in the generic sense, irrespective of isotopic content.

## EXPERIMENTAL

The apparatus is shown in fig. 1; it consisted of a reaction vessel A connected through a U-tube to a Toepler pump B which was used for mixing gases and displacing them either into the reaction vessel or into the thermal conductivity cell C. The reaction vessel was connected at D to a calibrated dosing volume and storage bulbs for the gases and at E to a conventional pumping system giving pressures of the order of  $10^{-6}$  mm. The ground-glass joint F was used to attach an evacuated bulb in order to transfer samples of gas to a Metropolitan Vickers MS2 mass spectrometer.



FIG. 1.—Diagram of apparatus;

- A, reaction vessel;
- B, Toepler pump;
- C, thermal conductivity cell;
- D, connection to calibrated dosing volume and storage bulbs;
- E, connection to pumping system;
- F, ground-glass joint for removal of samples; and
- G, connection for mercury reservoir.

The construction and operation of the thermal conductivity cell which was used to analyze mixtures of hydrogen and deuterium have been described,<sup>6</sup> except that the operating voltage for the Wheatstone bridge circuit was raised to  $5.4\pm0.0005$  V. The gauge was calibrated with mixtures of hydrogen and deuterium, and the resistance of the cell varied linearly with composition permitting the hydrogen in mixtures to be determined to  $\pm 1$  %. No change of resistance was observed when a mixture of hydrogen and deuterium was equilibrated over a heated nickel wire. Small variations in the resistance were detected from day to day using pure deuterium and the value was checked before each run following a procedure recommended by Eley and Tuck.<sup>7</sup>

#### MATERIALS

Hydrogen and deuterium (obtained by electrolysis of 99.95 % heavy water) were purified by diffusion through palladium.

Hydrogen sulphide was prepared <sup>8</sup> by dropping 10 % sulphuric acid on to sodium sulphide, both A.R. reagents, and purified by passage through water and sodium sulphide solution, dried over calcium chloride and phosphorus pentoxide and by passage through a trap at  $-78^{\circ}$ C, and collected in a trap cooled in liquid nitrogen. The product was thoroughly degassed to remove permanent gases and subjected to three trap-to-trap distillations before it was stored for use.

The samples of catalyst were obtained from the Billingham Division of I.C.I. Ltd. The molybdenum disulphide had been prepared by the action of hydrogen sulphide on ammonium molybdate solution and the resulting thiomolybdate was dried in nitrogen and reduced at  $350^{\circ}$ C with a 1:1 mixture of hydrogen+hydrogen sulphide. The tungsten disulphide had been prepared in a similar manner except that the final reduction was carried

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out with hydrogen at 450°C. Both catalysts were dispersed on glass wool in the reaction vessel; the tungsten disulphide which was supplied in pellet form was crushed before use.

The pretreatment of the two catalysts was slightly different. The molybdenum disulphide was evacuated for 12 h at 175 to 200°C and then treated with a 2:1 mixture of deuterium+hydrogen sulphide for the same period at 200°C. The cycle of treatment was repeated several times and reproducible results obtained for the exchange reaction. In subsequent work, the reaction mixture was left in contact with the catalyst overnight at reaction temperature and then it was evacuated for 3 to 4 h at the temperature to be used for the next experiment. The tungsten disulphide as supplied contained excess sulphur and a more vigorous pretreatment was necessary to remove the sulphur. The tungsten disulphide was evacuated initially for 4 days at about  $425^{\circ}$ C and then subjected to the same treatment as molybdenum disulphide and finally heated at  $320^{\circ}$ C for 1 week in a gas mixture. Between experiments, the catalyst was left overnight at reaction temperature (about  $100^{\circ}$ C) and evacuated for 4 h at  $320^{\circ}$ C.

#### EXPERIMENTAL PROCEDURE FOR $H_2S+D_2$ EXCHANGE

The required pressure of hydrogen sulphide was admitted to the reaction vessel and then condensed in trap X. The appropriate pressure of deuterium was admitted to the reaction vessel and some of this was transferred to the thermal conductivity cell to determine the initial resistance corresponding to pure deuterium. Reaction was started by removing the liquid-air trap from X and simultaneously transferring the deuterium into the reaction vessel by means of the Toepler pump. Measurements of the progress of the reaction were made by freezing-out the hydrogen sulphide with liquid air around trap X at known times, and after 3 min, circulating the permanent gas over the catalyst to ensure homogeneity and transferring a sample to the thermal conductivity cell. The reaction was restarted after each analysis in the same way that was used at the beginning of the reaction. Liquid air was maintained around trap Y throughout each experiment to prevent hydrogen sulphide reaching the thermal conductivity cell and a final analysis was made after the gases had been in contact with the catalyst for at least 12 h.

## RESULTS

A blank experiment was carried out on the exchange of hydrogen sulphide and deuterium in the absence of catalyst in order to determine whether there were complications from homogeneous reactions or the catalytic activity of glass. No exchange was observed below  $350^{\circ}$ C and a very slow reaction below  $400^{\circ}$ C probably caused by the dissociation of the hydrogen sulphide into its elements which begins at  $400^{\circ}$ C.<sup>9</sup>

The surface areas of samples of both catalysts, pretreated in the same way as the samples used for reactions, were determined by adsorption of krypton at liquidnitrogen temperature and found to be 2.16 and  $78.2 \text{ m}^2/\text{g}$  for the molybdenum and tungsten disulphides respectively.

Analyses were made of the composition of the molybdenum disulphide catalyst before pretreatment and average values of 59.1 % Mo and 36.7 % S were obtained whereas the expected composition is 60.0 % Mo. The amount of sulphur in a sample after use was 38.2 %.

# $H_2S+D_2$ exchange on $MoS_2$

The same sample of 2.53 g of catalyst was used in all experiments. The usual pressures of hydrogen sulphide and deuterium were 39 and 77 mm respectively and therefore the reaction vessel (114 ml) contained  $1.47 \times 10^{20}$  molecules of hydrogen sulphide. The exchange took place in the temperature range 150-200°C and

followed the usual apparent first-order kinetics  $^{10}$  for an exchange reaction. A typical plot is shown in fig. 2 based on the equation,

$$-\log_{10}\left(\lambda - \lambda_{\infty}\right) = k_1 t / 2 \cdot 303 - \log_{10}\left(\lambda_0 - \lambda_{\infty}\right),\tag{1}$$

where  $\lambda$  is the resistance of the thermal conductivity cell at time t, and  $\lambda_0$  and  $\lambda_{\infty}$  are the corresponding initial and final readings. The rate constants  $k_1$  were converted into absolute initial rates of exchange R in atoms/sec cm<sup>2</sup> of catalyst surface



FIG. 2.—Typical kinetic plots for the H<sub>2</sub>S+D<sub>2</sub> exchange reaction in which  $\lambda$  is the resistance of the cell at time t and  $\lambda_{\infty}$  the final equilibrium value; O, MoS<sub>2</sub> at 200°C;  $\Box$ , WS<sub>2</sub> at 65°C; and  $\bullet$ , WS<sub>2</sub> at 85°C.

using the method described by Harris  $^{10}$  and the Arrhenius plot for R is shown in fig. 3 and the derived activation energy and frequency factor are given in table 1.

Table	1/	ACTIVATION	ENERGIES	AND	FRÉQUENCY	FACTORS
		FOR RI	ACTIONS	on M	loS <sub>2</sub>	

reaction	temp. range (°C)	E (kcal/mole)	$\frac{\log_{10} A}{(A \text{ in atoms/sec cm}^2)}$
$H_2S+D_2$	150-200	19·1 ±0·7	$20.9 \pm 0.3$
$H_2 + D_2$ (mixture B)	140-200	10·2 ±0·3	$16.9 \pm 0.2$
$H_2+D_2$ (mixture C)	140-200	9·4 ±0·4	16·1±0·2

The linearity of the plots according to eqn. (1) is evidence that the experimental technique which involved alternatively stopping and starting the reaction was valid. This is also confirmed by the satisfactory Arrhenius plot; de Ruiter and Jungers <sup>11</sup> have used the linearity of an Arrhenius plot as a criterion of adequate contact between reactants and a solid catalyst. However, the technique did not suffice to follow rapid reactions because the error in timing associated with the interruption of the reaction became appreciable and this was shown by the fact that rates determined above 200°C fell below the expected values corresponding to the Arrhenius plot in fig. 3.

A series of experiments with the normal pressure (39 mm) of hydrogen sulphide and various pressures of deuterium between 39 and 154 mm gave the order of reaction with respect to deuterium as 1.0. An order with respect to hydrogen sulphide of -0.3 was obtained in a corresponding way, using the same range of pressures.

The final percentages of hydrogen in the "hydrogen", as determined by thermal conductivity, were around 33 % with the normal gas mixture and were in good agreement with the calculated percentage of 33.4 % based on the equilibrium data given



FIG. 3.—Arrhenius plots for reactions on MoS<sub>2</sub>, R referring to rates in atoms/sec cm<sup>2</sup>; O, H<sub>2</sub>S+ D<sub>2</sub> exchange on first sample of catalyst. All the remaining results were obtained with the second sample of catalyst which showed slightly greater activity;  $\bullet$ , H<sub>2</sub>S+D<sub>2</sub> exchange;  $\Box$ , H<sub>2</sub>+D<sub>2</sub> exchange with mixture B;  $\blacksquare$ , H<sub>2</sub>+D<sub>2</sub> exchange with mixture C;  $\triangle$ , scattered points for H<sub>2</sub>+D<sub>2</sub> exchange with mixture A.

by Jones and Sherman.<sup>12</sup> Mass-spectrometric analyses of samples withdrawn at the end of the reactions also confirmed that equilibrium corresponding to the reaction

$$H_2 + D_2 \rightleftharpoons 2HD$$
 (2)

had been attained. Analyses of the relative amounts of  $D_2S$ , HDS and  $H_2S$  could not be made because the deutero-compounds exchanged within the mass spectrometer, presumably with water adsorbed on the walls, and were converted into  $H_2S$ . This exchange reaction could be followed by measuring the change of the appropriate peaks in the mass spectrometer with time, but part of the reaction occurred very rapidly because the initial values of the peaks corresponded to a larger percentage of hydrogen in the "hydrogen sulphide" than expected.

Analyses of samples from *partially* completed experiments showed that the properties of the three isotopic "hydrogen" molecules did not correspond to equilibrium for reaction (2) and the departure from equilibrium was slightly greater for reaction at the higher temperatures as shown by the values of  $q = [HD]^2/[H_2][D_2]$  given in table 2.

# $H_2 + D_2$ exchange on $MoS_2$

A new reaction vessel (79.6 ml) containing 3.03 g of catalyst was used; this second sample of molybdenum disulphide was slightly more active than the first

TABLE 2.—VALUES FOR  $q = [HD]^2/[H_2][D_2]$ , and the corresponding values q' after allowing for the influence of  $H_2+D_2$  exchange for partial runs with  $H_2S+D_2$ exchange on MoS<sub>2</sub>

temp. (°Č)	% of $H_2S+D_2$ reaction completed	q	q'	equilibrium const. K for reaction (2)
140	28	1.2	0.97	3.52
160	31	1.1	0.91	3.55
180	46	1.0	0.77	3.58
200	39	0.7	0.55	3.60

sample for hydrogen sulphide + deuterium exchange, as shown in fig. 3. Three gas mixtures were used; A consisted of 72 and 54 mm of hydrogen and deuterium respectively, and B and C contained added hydrogen sulphide at pressures of 13 and 63 mm respectively. Exchange between hydrogen and deuterium occurred in the temperature range 140 to 200°C and was followed by withdrawing samples of gas and determining the amount of HD by means of the mass spectrometer. The reactions followed the first-order equation,

$$\log_{10} \left( 1 - x/x_{\infty} \right) = -k_2 t, \tag{3}$$

where x refers to the percentage of HD at time t, and  $x_{\infty}$  is the calculated equilibrium value. Reliable results were obtained with mixtures B and C and the Arrhenius plots for the absolute rates evaluated from  $k_2$  are shown in fig. 3 and the derived activation energies and frequency factors are given in table 1. The rates for mixture A showed considerable scatter and are plotted in fig. 3 although no reliable activation energy could be obtained. All samples taken after reactions with mixture A contained traces of hydrogen sulphide. The relative rates of reaction with mixtures B and C corresponded to an inhibition of the exchange dependent on the -0.5power of the pressure of hydrogen sulphide.

## $H_2S+D_2$ exchange on $WS_2$

A reaction vessel (76.7 ml) containing 2.90 g of tungsten disulphide was used for all experiments with this catalyst. The normal gas mixture consisted of 63 mm of hydrogen sulphide, corresponding to  $1.60 \times 10^{20}$  molecules in the reaction vessel, and twice as much deuterium. Exchange occurred in the temperature range 40-100°C and eqn. (1) was obeyed except for a sharp change in the resistance at the beginning of each experiment as illustrated in fig. 2. The Arrhenius plot is given in fig. 4 and the derived data in table 3. The order of the reaction was found to be 0.8 with respect to deuterium by using pressures from 63 to 250 mm; a second series of experiments with pressures of hydrogen sulphide from 31 to 125 mm gave an order of -0.1 with respect to the sulphide.

TABLE 3.—Activation energies and frequency factors for reactions on  $WS_2$ 

reaction	temp. range (°C)	E (kcal/mole)	$\frac{\log_{10} A}{A \text{ in atoms/sec cm}^2}$
$H_2S+D_2$	40-100	9·0±0·3	$15.8 \pm 0.2$
$H_2 + D_2$ (mixture D)		$1.1 \pm 0.1$	12·0±0·1
$H_2 + D_2$ (mixture E)	0-100	$3 \cdot 1 \pm 0 \cdot 1$	12·7±0·1
$H_2 + D_2$ (mixture F)	0-100	<b>4</b> ⋅5 ±0·1	$13.2 \pm 0.1$

There was a greater percentage of hydrogen in the "hydrogen" at the end of each experiment than the calculated equilibrium value. The excess percentage

corresponded closely to the amount of hydrogen formed initially as shown by the sharp change of resistance. This indicated that irreversible adsorption of hydrogen sulphide occurred by the reaction

$$H_2S(g) \rightarrow S(a) + H_2(g) \tag{4}$$

to an extent corresponding to 1 molecule for each 300 Å<sup>2</sup> of surface. Confirmation of the amount of reaction (4) was obtained from the experiments with different gas mixtures. The excess percentages of hydrogen varied from  $2 \cdot 2$  to 7 % as the relative amounts of deuterium to hydrogen sulphide decreased while the expected values ranged from 3 to 8%.



FIG. 4.—Arrhenius plots for reactions on WS<sub>2</sub>, R referring to rates in atoms/sec cm<sup>2</sup>; O, H<sub>2</sub>S+D exchange;  $\triangle$ ,  $\Box$  and  $\blacksquare$ , H<sub>2</sub>+D<sub>2</sub> exchange with mixtures D, E and F, respectively.

Mass-spectrometric analyses of samples taken at the end of the reactions indicated that equilibrium for reaction (2) was attained but considerable deviations from equilibrium were observed in *partially* completed experiments as are shown by the values of q in table 4.

TABLE 4.—VALUES FOR  $q = [HD^2]/[H_2][D_2]$ , and the corresponding values q' after allowing for the influence of  $H_2+D_2$  exchange for partial runs with  $H_2S+D_2$  exchange on  $WS_2$ 

temp. (°C)	% of $H_2S + D_2$ reaction completed	q	q'	equilibrium const. K for reaction (2)
45	9	0.37	0.26	3.30
65	10	0.38	0.25	3.35
85	15	0.67	0.43	3.39
105	12	0.37	0.25	3.44

 $H_2 + D_2$  exchange on  $WS_2$ 

Three gas mixtures were used; D consisted of 41 and 83 mm of hydrogen and deuterium respectively, and E and F contained added hydrogen sulphide at pressures of 13 and 63 mm respectively. Reproducible results were obtained with all three

mixtures for the first experiments carried out after each pretreatment of the catalyst but subsequent experiments without further pretreatment gave slower reactions. Rates of exchange determined from the first experiments using eqn. (3) are shown as Arrhenius plots in fig. 4 with the derived data summarized in table 3. A comparison between the results for mixtures E and F indicated that the hydrogen + deuterium exchange reaction was inhibited by hydrogen sulphide by a dependence on the pressure which varied from -1.0 at 0°C to -0.5 at 100°C.

## DISCUSSION

The results with tungsten disulphide will be discussed first because they present a simpler picture than those with molybdenum disulphide. The hydrogen+ deuterium exchange is a more rapid reaction than the hydrogen sulphide + deuterium exchange and this holds even with mixture F which corresponded closely to the gas mixture used in the exchange experiments with the sulphide. It is clear, both from the inhibition of the hydrogen+deuterium exchange by hydrogen sulphide and the accompanying increase in activation energy, that the sulphide is more strongly adsorbed than hydrogen. Donath <sup>1</sup> has shown that the adsorption of hydrogen takes place rapidly on tungsten disulphide at 0°C but some reversible chemisorption must occur at much lower temperatures because we find an appreciable rate of exchange at -78°C provided the tungsten sulphide was thoroughly evacuated at 320°C.

The slower rate and the greater activation energy for the hydrogen sulphide+ deuterium exchange indicate that the rate-determining step of this reaction is different from that of the hydrogen+deuterium exchange. In other words, the processes associated with the dissociative adsorption/desorption of the sulphide are slower than those for the hydrogen. Despite this, the values of q in table 4 indicate that the "hydrogen" formed initially from the exchange of the sulphide contains a substantial proportion of  $H_2$  and comparatively little HD. If HD had been the only initial product, the values of q would have been equal to K the equilibrium constant for the interconversion reaction (2) throughout the course of the exchange reaction of hydrogen sulphide. On the other hand, if  $H_2$  had been the only initial product, the value of q would have been zero initially and risen gradually as reaction The comparatively rapid exchange between hydrogen and deuterium occurred. necessarily makes the observed values of q higher than the true values q' corresponding only to the exchange between hydrogen sulphide and deuterium. The size of this effect was estimated from the average percentages of H<sub>2</sub> and D<sub>2</sub> present during the period before q was measured and from the rate constant  $k_2$  obtained in experiments with mixture F. A simple calculation gave the percentage y of HD formed by the exchange of the isotopic species of hydrogen. This was subtracted from the observed percentage of HD and corresponding additions of y/2 to the observed percentages of  $H_2$  and  $D_2$  were made before the values of q' given in the fourth column of table 4 were derived.

There are two possible explanations to account for the initial formation of  $H_2$ . First, exchange might occur by the following pair of reactions

$$\mathrm{H}_{2}\mathrm{S}(g) \rightarrow \mathrm{S}(a) + \mathrm{H}_{2}(g)$$

and

$$D_2(g) + S(a) \rightarrow D_2S(g). \tag{5}$$

Secondly, the strongly adsorbed hydrogen sulphide may give a high concentration of adsorbed H atoms on the surface so that most of the "hydrogen" returning initially to the gas phase is  $H_2$  and not HD. It is unfortunate that no experimental method was available to determine the isotopic species of "hydrogen sulphide" formed initially because the first of these mechanisms would lead to  $D_2S$  and the second to HDS.

The rate-determining step of the hydrogen sulphide+deuterium exchange reaction may be either the adsorption/desorption reactions (5) or the corresponding reactions (6)

$$H_2S(g) \rightarrow HS(a) + H(a)$$
  
D(a)+HS(a)  $\rightarrow$  HDS(g). (6)

Either scheme fits the observed kinetics which are approximately first order in deuterium and zero order with respect to hydrogen sulphide. Reactions (5) imply kinetics of this type as the hydrogen sulphide is known to be strongly adsorbed. However, similar kinetics will operate for the reactions (6) if certain assumptions are made. These are: (i) the deuterium is weakly adsorbed on sites which are not capable of taking up species containing sulphur atoms, (ii) there is strong adsorption of the species S(a) and HS(a) so that the total concentration of these two species is independent of the pressure of hydrogen sulphide, (iii) the amount of HS(a) is small compared with S(a) and the equilibrium ratio of HS(a)/S(a) which varies with the square root of the "hydrogen" pressure is maintained. It follows that the concentration of both D(a) and HS(a) will depend on the square root of the "hydrogen" pressure, and the desorption stage of reactions (6) will have the observed kinetics which must equally apply to the adsorption stage as this will occur at an identical rate in the exchange process.

In many respects the results with molybdenum disulphide are similar to those with tungsten disulphide and attention will be directed mainly to the differences between the two catalysts. The results in fig. 3 indicate that the two exchange reactions occur at comparable rates on molybdenum disulphide, the hydrogen + deuterium exchange being slightly faster with mixture B at lower temperatures but slower with mixture C over almost the whole of the temperature range studied. Thus, it is possible that some exchange of hydrogen and deuterium occurs via "hydrogen sulphide". It is coincidence that the temperature required to bring about the hydrogen+deuterium exchange corresponds closely to  $150^{\circ}$ C at which Badger, Griffith and Newling <sup>3</sup> found extensive activated adsorption of hydrogen began. If we had used a larger sample of catalyst with a surface area equivalent to that of the tungsten disulphide sample, we would have observed exchange at much lower temperatures in a range similar to that used for mixtures E and F on the latter catalyst.

The scattered results for the hydrogen+deuterium exchange with mixture A and the presence of hydrogen sulphide in the gas mixture at the end of these experiments show that the surface of molybdenum disulphide is not stable but can be reduced by hydrogen in the temperature range 140-200°C. It is possible that a more vigorous pretreatment, identical to that used for the tungsten disulphide, might have given a more stable surface capable of bringing about a more rapid exchange of hydrogen and deuterium, but there would have been a danger of causing some changes in the bulk composition of the catalyst.

The negative order with respect to sulphide pressure of -0.3 for the hydrogen sulphide+deuterium reaction may be a consequence of the rather similar rates for both exchange reactions on molybdenum disulphide. Whereas, on tungsten disulphide the hydrogen+deuterium exchange is sufficiently fast to keep up with the rate of adsorption/desorption of hydrogen sulphide, this may not hold on molybdenum

disulphide and so the rate of sulphide exchange is partially controlled by the rate of hydrogen+deuterium exchange. This negative order is evidence against reactions (5) and implies that reactions (6) are more likely.

The absence of any irreversible adsorption of hydrogen sulphide on molybdenum corresponding to reaction (4) is not significant because it would not have been detectable with the small surface area of the sample used. The larger values of q and q', corrected for the effect of hydrogen+deuterium exchange, in table 2, compared with those in table 4 are mainly a consequence of the greater proportions of the overall reaction which had occurred when the analyses of the partially completed experiments were made with molybdenum disulphide. However, the values of q' indicate that, as with tungsten disulphide, H<sub>2</sub> in addition to HD is formed initially from the exchange of the hydrogen sulphide.

The influence of the difference in surface area has already been noted in relation to the apparently different activities of the two catalysts for both exchange reactions. Although the activation energies for both reactions were higher on molybdenum than on tungsten disulphide the frequency factors were correspondingly greater. In fact, all the data in tables 1 and 3 show an excellent example of the compensation effect and fit closely the relationship

$$\log_{10}A = 11.25 + 0.52E. \tag{7}$$

However, we consider that it would be premature to attempt to discuss the significance or the interpretation of this relationship until it has been established for a wider range of reactions on these catalysts.

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