

Chemisorption of Hydrogen Sulfide and Carbon Disulfide on Sulfided Nickel Oxide and Vanadium Pentoxide

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The adsorption of both H_2S and CS_2 on sulfided nickel oxide and vanadium pentoxide was studied, using a volumetric technique. Equilibrium measurements (for H_2S at 500–650°C and for CS_2 at 55–200°C) indicate that a Langmuir model is adequate for interpreting the adsorption and desorption characteristics of both systems. Much larger quantities of H_2S are adsorbed than either CS_2 or S_2 and this is explained in terms of the geometry of the adsorbent and the disposition of molecular orbitals of the adsorbate. Semiempirical calculations based on the absolute rate theory show that a model in which the adsorbed complex is completely mobile is most satisfactory.

The sulfur exchanging properties of sulfided nickel oxide and vanadium pentoxide are shown to bear a relation to the efficacy with which these materials can be used as catalysts for the formation of CS_2 from methane and sulfur. Rate measurements of the adsorption of sulfur and the desorption of CS_2 give further support to the hypothesis that surface reaction between adsorbed sulfur and either gaseous or physically adsorbed methane is the rate-determining process during CS_2 synthesis.

In a previous paper (1) the adsorption of sulfur on sulfided nickel oxide and vanadium pentoxide was examined and it was concluded that sulfur is adsorbed strongly but reversibly on both of these adsorbents which are active catalysts for the synthesis of carbon disulfide from hydrocarbons and sulfur (2). In the present study the adsorption of H_2S and CS_2 , both of which are products of the catalyzed reaction between methane and sulfur, was investigated. The detailed study of the adsorption of H_2S and CS_2 enables a picture of the sulfur exchanging properties of nickel sulfide and vanadium pentoxide to be formulated.

It was already established (2) that both H_2S and CS_2 retard the rate of forma-

tion of CS_2 when vanadium pentoxide supported on γ -alumina is used to catalyze the reaction between methane and sulfur. Some preliminary work also indicated that both products are adsorbed on the supported V_2O_5 catalyst. Two alternative models were proposed to explain the kinetic results. One of these purports the rate of CS_2 formation to be controlled by a surface chemical reaction between chemisorbed sulfur and gaseous or physically adsorbed methane. The second model rests on the hypothesis that desorption of CS_2 controls the rate. Both models yielded kinetic equations in qualitative agreement with the experimental results. Quantitative measurements of initial rates of CS_2 formation also provided sufficient evidence to indicate that the surface chemical reaction is likely to be the rate controlling process in the sequence of mass transfer, adsorption, chemical reaction and desorption steps comprising the overall reaction. Experimental data on the rates of CS_2 desorption

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and S₂ adsorption provide further evidence to support this earlier contention.

EXPERIMENTAL METHODS

Apparatus

The adsorption of both H₂S and CS₂ were studied using a volumetric technique. Details of the general arrangement of apparatus was given previously (1). Electromagnetically operated high-temperature stopcocks were employed as before since it was desirable to maintain the whole of the apparatus, excepting the McLeod gauges, at a uniform temperature sufficient to prevent condensation or adsorption of any condensable vapors (such as sulfur or carbon disulfide) on the glass walls of the connecting tubing.

Pressures were measured with a Pirani gauge which was calibrated with H₂S or CS₂ against a standard McLeod gauge prior to each adsorption experiment. Although CS₂ is a condensable vapor, the pressure of the vapor in the capillary of the McLeod gauge under maximum compression was ca. 250 torr. Since this is less than the saturated vapor pressure (355 torr) of CS₂ at 25°C (3) it may be assumed that the McLeod gauge is capable of measuring the pressure of the CS₂ vapor. Corrections for non ideality were less than the estimated accuracy (ca. ± 5%) of pressure readings and were therefore not applied. It was necessary, however, to apply corrections for thermomolecular flow (4) since there was a considerable temperature difference between the Pirani gauge (operated at 250°C) and the McLeod gauge (maintained at 25°C).

Since sulfur vapor could arise as a product of the interaction of either H₂S or CS₂ with the adsorbent, provision was made for an appendix which could be maintained at 0°C and which would therefore condense sulfur vapor. Any sulfur removed in this way could then be estimated by oxidation with excess oxygen as previously described (1).

The amount of gas adsorbed was calculated by first observing the initial pressure of the dose of gas to be admitted and finally the steady Pirani reading after

sharing with the volume containing the adsorbent and allowing the system to attain equilibrium. The separate volumes of the apparatus comprising the dosing volume and reaction vessel were estimated by sharing helium from a standard McLeod gauge. Kinetic data could be recorded by noting the Pirani reading as a function of time.

Materials

The adsorbents used were 10% (w/w) NiO supported on porous alumina and 10% (w/w) V₂O₅ supported on the same material. Nickel sulfide (NiS) was obtained by passing H₂S or sulfur over the solid at 400°C for 8 hr. This was subsequently outgassed at 750°C *in vacuo* for 36 hr and then cooled to the temperature chosen for the experiment. Quantitative gravimetric analyses indicated that nickel and sulfur were present in non-stoichiometric proportions, NiS₁₋₁ representing the average atomic ratio after the sulfiding and outgassing treatment. The vanadium pentoxide was unaffected by this treatment.

Hydrogen sulfide was obtained from Matheson Co. Inc. in cylinders, its purity being 99.5%. This was subsequently distilled *in vacuo* using liquid air as refrigerant and finally stored. 'Analar' grade CS₂ was fractionated at a pressure of 74 torr prior to storing as a liquid in a blackened reservoir. Portions of the purified CS₂ were withdrawn as desired and air was removed from the liquid by repeated freezing in liquid air and melting *in vacuo*.

Surface areas were determined by application of the BET technique using N₂ at -196°C. The specific surface area of the supported nickel sulfide was 180 m²/g and that of supported vanadium pentoxide 139 m²/g. For details of other materials used, a previous paper (1) should be consulted.

RESULTS

Adsorption-Desorption Isotherms

The H₂S was adsorbed in the temperature range 500-650°C on both supported

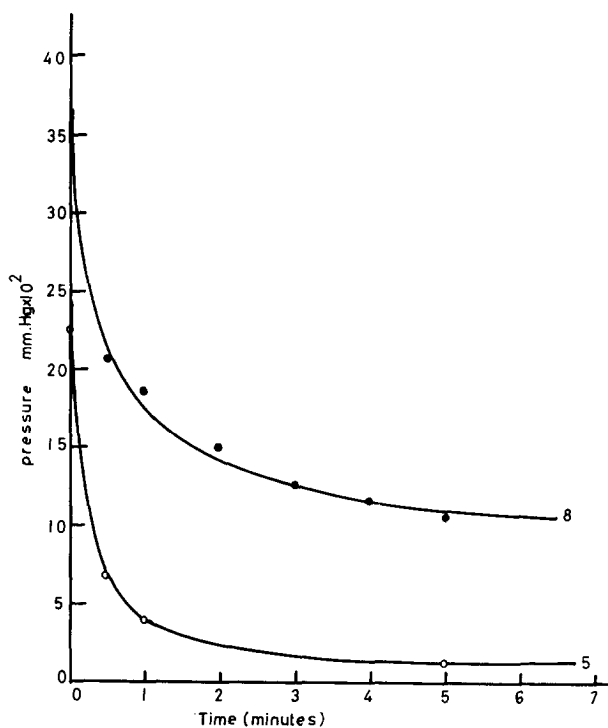


FIG. 1. Adsorption of H_2S : adsorbent—sulfided nickel oxide on alumina, $T = 600^\circ C$; values on curves indicate dose number.

nickel sulfide and vanadium pentoxide. No net adsorption was observed for CS_2 on either adsorbent at such temperatures, but adsorption was measured at temperatures between 100 and $200^\circ C$. Measured doses of the gas under observation were admitted to the outgassed adsorbent at various fixed temperatures. Although the first few doses of gas were adsorbed rapidly, subsequent doses were adsorbed more slowly and left a residual gas pressure. Figure 1 shows a record of the uptake of H_2S on supported nickel sulfide at $600^\circ C$ and is typical of results obtained. That a reversible type of adsorption occurs is demonstrated by experiments in which the adsorbent is evacuated for 0.5 min, without change in temperature, during the course of adsorption. As Fig. 2 illustrates, the steady pressure which is attained following evacuation and isolation from pumps is somewhat less than the pressure at which the adsorption was interrupted. Analysis of the gas desorbed showed that neither H_2S nor CS_2 decom-

posed. It is probable therefore that both H_2S and CS_2 are adsorbed nondissociatively or, if dissociative adsorption does occur, surface reassociation occurs prior to desorption.

Isotherms were constructed by noting, after each measured dose of adsorbate had been admitted to the reaction vessel, the steady equilibrium pressure above the adsorbent. On completion of the adsorption experiment, the dosing section was completely evacuated and the rate at which the gas was desorbed was found by noting the rate of increase in pressure in a large fixed volume. Successive decrements were desorbed in this way so that some desorption points on the isotherm could be included. The results did not conform to either Freundlich or Temkin type isotherms. Although reasonable straight lines were obtained when the Freundlich isotherm equation was tested by double logarithmic plots of volume adsorbed versus pressure, values for the saturation volume v_m deduced from such plots

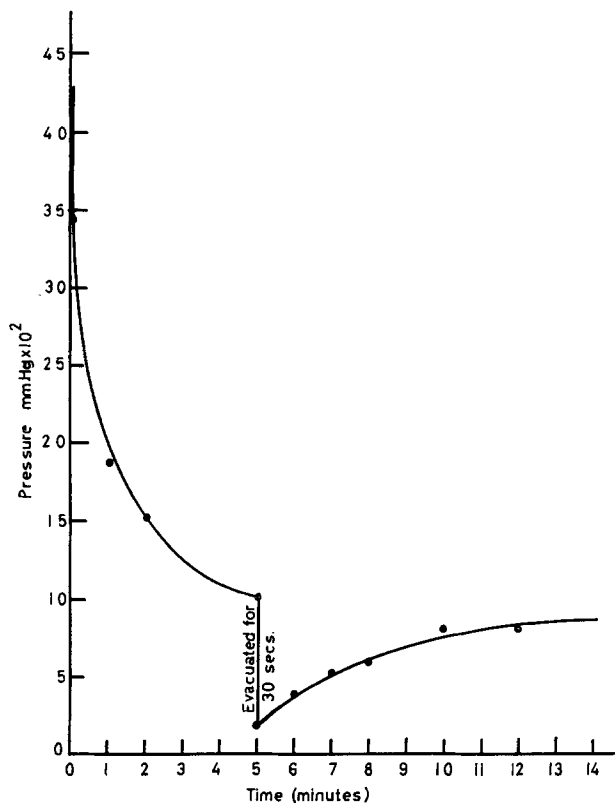


FIG. 2. Desorption of H₂S: adsorbent—sulfided nickel oxide on alumina, $T = 600^{\circ}\text{C}$.

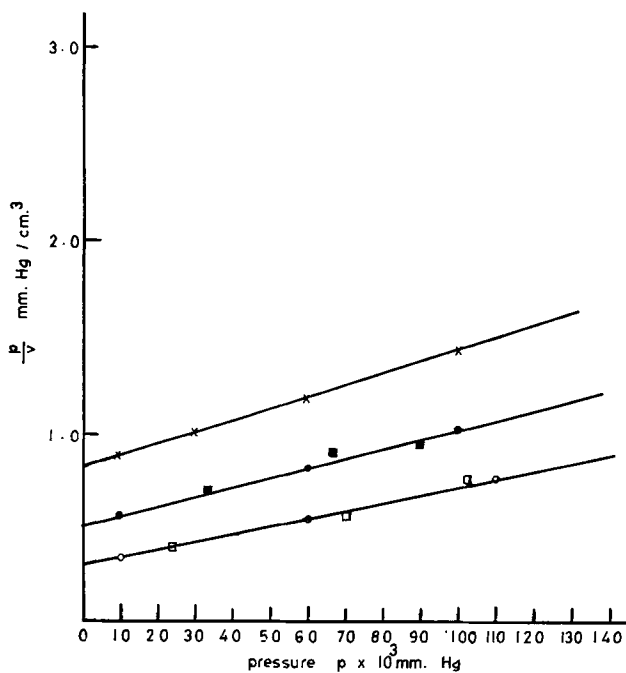


FIG. 3. Langmuir isotherm plots for CS₂: adsorbent—sulfided V₂O₅ on alumina; ○, 55°C; ●, 100°C; ×, 128°C; □, desorption at 55°C; ■, desorption at 100°C.

TABLE 1
EXPERIMENTAL PARAMETERS FOR THE LANGMUIR ISOTHERM EQUATION

System	T (°C)	Slope (= S) (cm^{-3})	Intercept (= i) (mm Hg cm^{-3})	Max. vol. adsorbed $\left(\frac{1}{S}\right)$ v_m (cm^3 NTP)	$b \left(= \frac{S}{i}\right)$ (mm Hg)
H ₂ S on	600	1.75	0.02	0.57	87.5
sulfided	650	1.75	0.04	0.57	43.8
nickel oxide	750	1.75	0.045	0.57	39.0
H ₂ S on	500	2.10	0.035	0.48	60.0
vanadium	600	1.83	0.056	0.55	32.7
pentoxide	650	1.80	0.080	0.55	22.5
CS ₂ on	100	3.50	0.045	0.28	77.8
sulfided	150	4.6	0.11	0.22	41.8
nickel oxide	200	6.3	0.41	0.16	15.3
CS ₂ on	55	4.20	0.30	0.24	14.0
vanadium	160	4.20	0.50	0.24	8.4
pentoxide	128	4.20	0.81	0.24	5.2

were quite inconsistent and the slopes did not increase regularly with absolute temperature. The results did, however, conform to the Langmuir isotherm equation and typical of the results are the hyperbolic plots portrayed in Fig. 3, of p/v versus p obtained for CS₂ on supported vanadium pentoxide, where p represents the equilibrium pressure and v the volume of gas adsorbed. These plots give good straight lines for the temperatures studied and are in accord with the previous implication that nondissociative adsorption is occurring. The isotherms are parallel and the values of v_m deduced from the slopes and intercepts of the plots are given in Table I. The monolayer coverages

represent just over 1% of the BET monolayer volume determined using N₂ as adsorbate at -196°C . Except for regions of low coverage, isosteric heats of adsorption (Table 2) estimated using the Clausius-Clapeyron relation appear to be essentially independent of coverage as demanded by the assumptions implicit in the Langmuir theory.

Adsorption Kinetics

Adsorption kinetics were examined by following the change of gas pressure with time for each dose of gas admitted to the adsorbent. The rate of uptake of adsorbate for a given gas pressure was then estimated by drawing tangents to these

TABLE 2
ISOSTERIC HEATS OF ADSORPTION

Sulfided nickel oxide on alumina				Vanadium pentoxide on alumina			
H ₂ S		CS ₂		H ₂ S		CS ₂	
θ	ΔH (kcal/mole)	θ	ΔH (kcal/mole)	θ	ΔH (kcal/mole)	θ	ΔH (kcal/mole)
.201	27.4	.105	35.3	.190	12.2	.223	37.4
.305	20.7	.158	35.0	.288	8.05	.348	31.1
.411	18.1	.236	31.6	.380	6.76	.450	25.6
.600	18.8			.475	6.55	.500	26.6

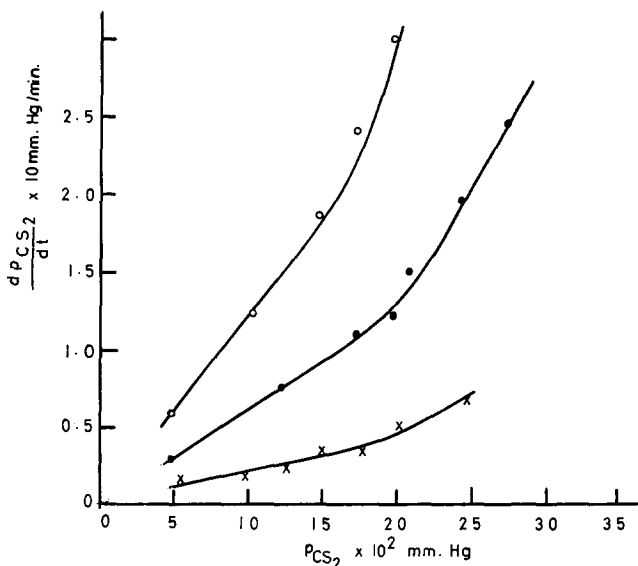


FIG. 4. Rate of adsorption of CS₂ as a function of p_{CS_2} : adsorbent—sulfided nickel oxide on alumina; X, 100°C; ●, 150°C; ○, 200°C.

curves (e.g., Fig. 1). For H₂S on both adsorbents it was found that the adsorption process was first order over the pressure and temperature range investigated since good straight lines were obtained by plotting the rate of uptake as a function of the pressure of H₂S. This also implies that the fraction of active surface available for adsorption remains sensibly constant over the range of conditions studied during each set of rate measurements. Tables 3 and 4 give the first-order rate constants derived from the slopes of the rate curves and the corresponding activation energies. The activation energies were found to vary approximately linearly with coverage.

The rate of adsorption of CS₂ was linearly dependent on the pressure of CS₂ provided that the active surface covered did not change by more than a factor of about 10%. For a short period after the commencement of adsorption the rate appears to be greater than first order (Fig. 4). The departure of the rate curve from first-order behavior may be accounted for by the amount of free surface varying during adsorption. In the initial stages of adsorption this term varies appreciably if the surface becomes blocked by the ad-

sorbate overlapping other potential adsorption sites but becomes sensibly constant as the fraction of surface covered becomes greater. Such an explanation was offered previously to account for the kinetics of N₂O adsorption (5) and CS₂ adsorption (6) at a charcoal surface and also the adsorption of SO₂ on nickel oxide (1); it may well be applicable in this particular case especially if the CS₂ molecule is adsorbed in such a manner as to offer steric hindrance to any other adsorbate molecule approaching the surface. Values for the first-order rate constants and the corresponding activation energies for the adsorption of CS₂ are given in Table 3. The activation energies deduced are linearly dependent on coverage.

Desorption of CS₂

The kinetics of CS₂ desorption from the supported vanadium pentoxide catalyst at 100°C was also examined by noting Pirani readings as the vapor was allowed to desorb into a previously evacuated fixed volume. The experimental curve of θ versus $\ln t$ (Fig. 5) is linear and this implies that the Elovich equation (7) is a fairly good representation of the kinetics of desorption. Adopting a simple model for the

TABLE 3
 FIRST-ORDER KINETIC CONSTANTS

Sulfided nickel oxide on alumina				Vanadium pentoxide on alumina			
H ₂ S ($\theta = 0.6$)		CS ₂ ($\theta = 0.2$)		H ₂ S ($\theta = 0.4$)		CS ₂ ($\theta = 0.5$)	
<i>T</i> (°C)	<i>k</i> (min ⁻¹)	<i>T</i> (°C)	<i>k</i> (min ⁻¹)	<i>T</i> (°C)	<i>k</i> (min ⁻¹)	<i>T</i> (°C)	<i>k</i> (min ⁻¹)
600	0.19	100	0.20	500	1.68	55	.0028
650	0.33	150	0.63	600	2.46	100	.0176
		200	1.25	650	2.70	128	.0245

desorption of CS₂, we assume that the activation energy of desorption decreases linearly with the amount adsorbed and write

$$-d\theta/dt = K\theta \exp\{-[E_a(0) - \beta\theta]/RT\}, \quad (1)$$

where $E_a(0)$ is the activation energy for desorption corresponding to a coverage $\theta = 0$, and K and β are constants. Assuming that we can ignore the variation in θ in comparison with the much larger variation in $\exp(-\beta\theta/RT)$, Eq. (1), when integrated from θ_0 (the coverage at $t = 0$) to θ gives

$$\theta = \frac{RT}{\beta} \ln \left\{ \frac{1}{\alpha\beta t/kT + \exp(-\beta\theta_0/RT)} \right\} \quad (2)$$

where the constant α represents the term $K\theta \exp\{-E_a(0)/RT\}$. If $t \gg RT \exp(-\beta\theta_0/$

$RT)/\alpha\beta$, which is true except in the region of $\theta = 0$ and $\theta = 1$, then Eq. (2) reduces to the Elovich equation and concurs with the experimental results. The constant β may therefore be evaluated from the slope of the plot shown in Fig. 5. Since E_a is a linear function of θ , $E_a(0)$ may be estimated by adding $\beta\theta$ to $E_a(\theta)$. For a given coverage the activation energy of desorption is the sum of the heat of adsorption and the activation energy of adsorption both of which may be found from the data in Tables 1 and 2. By this procedure we estimate $\beta = 34$ kcal/mole and $E_a(0) = 53$ kcal/mole. Extrapolation of the data in Table 1 gives $\Delta H(0) \approx 49$ kcal/mole so the activation energy of adsorption on a clean surface should be about 4 kcal/mole. This is quite consistent

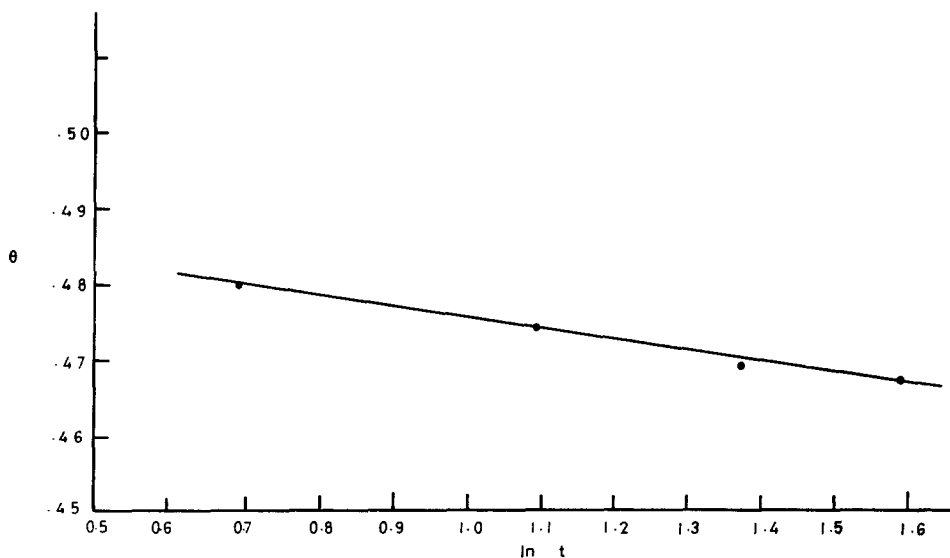


Fig. 5. Elovich plot for the desorption of CS₂: adsorbent—sulfided V₂O₅ on alumina, $T = 100^\circ\text{C}$.

with the experimental value (ca. 9.7 kcal/mole) found for the activation energy of adsorption at $\theta = 0.5$. The constant K was determined from Eq. (1) by evaluating $(-d\theta/dt)$ at a given coverage. The computed value of K is $6 \times 10^{18} \text{ min}^{-1}$.

DISCUSSION

General Features Relating to the Adsorption of H₂S and CS₂

Each of the adsorption isotherms measured conforms to the generalized Langmuir adsorption equation over the range of pressures studied. It is notable that, for the prevailing experimental conditions, the volume of H₂S or CS₂ occupying a monolayer on either supported nickel sulfide or vanadium pentoxide is only about 1% of the BET capacity estimated by the adsorption of N₂ at -196°C . The work of DeRosset *et al.* (8) on the adsorption of H₂S on alumina at low coverages indicates that, in the temperature range $260\text{--}560^\circ\text{C}$, H₂S occupies only 2% of the anionic surface sites. They found that isosteric heats of adsorption derived from the experimental isotherms ranged from 25 to 38 kcal/mole. The small number and strength of the adsorption sites suggest that surface Al-S bonds are formed and that it is these adsorption sites which have an important bearing on catalytic activity. Thus, the adsorption of H₂S at NiS supported on alumina is similar insofar as only a small proportion of cationic surface sites are utilized during chemisorption and isosteric heats of adsorption range from about 19 to 27 kcal/mole. This merely implies that chemisorption is occurring at a limited number of sites and does not infer any particular model for the formation of surface chemical bonds. Indeed we shall see later that the manner in which H₂S is adsorbed on alumina differs in several respects from the adsorption of H₂S and CS₂ on the catalysts employed in the present study. Supporting this contention is the different nature of the isotherms found for the adsorption of H₂S on alumina which clearly display non-linear Langmuir plots of p/v versus p and

which can be resolved into two distinct linear regions implying a bimodal distribution of energy amongst sites. No such behavior was detected for the adsorption of H₂S and CS₂ on supported NiS and V₂O₅ which gave linear plots of p/v versus p . Obedience to a Langmuir equation usually means that the surface is energetically homogeneous and there is no interaction between neighboring adsorbed species. Since only a small number of surface sites are occupied by the adsorbed H₂S or CS₂ little mutual interaction would occur. Furthermore, at low surface coverage the most energetic sites will be occupied first (9) and it would not be unreasonable to suppose that the energy of these particular sites are sufficiently close for the experimental data not to reveal any departure from linearity.

The maximum quantities of H₂S and CS₂ adsorbed by the supported NiS and V₂O₅ were calculated from slopes of p/v versus p plots. Transposing the units, these amounts become (i) 25×10^{-6} moles of H₂S/g of supported NiS at 600°C and 24×10^{-6} moles of H₂S/g of supported V₂O₅ at 600°C , and (ii) approximately 8×10^{-6} moles of CS₂/g for both supported NiS and V₂O₅ at $150\text{--}200^\circ\text{C}$. We may recall that it is possible for S₂ to be adsorbed dissociatively at these surfaces and that the corresponding maximum amount of S₂ adsorbed on supported NiS at $600\text{--}700^\circ\text{C}$ is 5×10^{-6} moles of S₂/g and on supported V₂O₅ is 4×10^{-6} moles of S₂/g (1). We therefore have to account for the fact that far more H₂S may be accommodated by the adsorbate than either CS₂ or S₂. This may be explained qualitatively by supposing H₂S to occupy one active surface Ni atom per molecule (which clearly need not necessarily imply associative adsorption on a catalyst containing both anionic and cationic sites) whereas both S₂ and CS₂ require at least two active Ni atoms per molecule. The isotherms and kinetics for the adsorption of CS₂ suggest that dissociation does not occur. However, the kinetic data do show that there is a possibility of adsorbed CS₂ creating hindrance to adsorption at neighboring sites. Thus,

if the linear molecule of CS_2 can be considered to be chemisorbed in a plane parallel to the NiS surface and bonded to it through a sulfur atom the experimental facts become interpretable. Since the distance between two nearest neighbor Ni atoms in the principal $\{1100\}$, $\{0110\}$, and $\{1010\}$ planes of the NiS lattice is approximately 2.6 Å (10, 11), a CS_2 molecule, whose overall length is 3.1 Å (10), would span a greater distance than two nickel atom sites and thus would overlap other potential adsorption sites. With the possibility of free rotation of the adsorbate in a plane parallel to the surface an even greater number of adsorption sites would become inaccessible. Because the disposition of the antibonding π -molecular orbitals (which differ little from the original nonbonding lone pair of electrons) on each of the S atoms of CS_2 are such that two lie in the plane of the S-C-S axis while the other two are at right angles to it, the molecule will have the greatest chance of becoming adsorbed when the potential energy is a minimum with the S-C-S axis parallel to the surface. The distance between neighbor nickel atoms in the $\{0001\}$ planes, on the other hand, is ≤ 3.5 Å (11) and there is a distinct possibility of dual site attachment through the two S atoms of CS_2 , especially if there is excess sulfur incorporated in the NiS lattice which causes shrinkage of the cell dimensions. Thus it is quite feasible for CS_2 to require a larger number of active adsorption sites per molecule than either H_2S or S_2 when adsorbed at NiS. A similar argument is applicable for the adsorption of CS_2 at supported V_2O_5 .

Rates of Adsorption of H_2S and CS_2

Semiempirical calculations of the rates of adsorption of H_2S and CS_2 for the supported NiS and V_2O_5 surfaces were performed by application of the absolute rate theory. It was found that the best correlation between theoretical and experimentally measured rates of adsorption was obtained if it were assumed that, for each gas, the adsorption complex possesses two degrees of freedom of translation. For a

mobile complex the rate of adsorption is given by

$$r_a = \frac{\sigma q_0 p \exp\{-E_a/RT\}}{(2\pi mkT)^{1/2}}, \quad (3)$$

where σ is the site area occupied by the adsorbed species, the maximum quantity of gas adsorbed at the temperature T and prevailing gas pressure p ; m represents the mass of the adsorbate, k the Boltzmann constant and E_a the experimentally measured activation energy. The values of q_0 and E_a are available from the experimental data, while a value of 10 \AA^2 is assumed for σ . Table 4 compares the calculated rates of adsorption of H_2S and CS_2 at NiS and V_2O_5 with the corresponding experimental values which could be estimated in the same units by knowing the combined volume of the dosing section and reaction vessel. The values agree tolerably well considering the assumptions inherent in the absolute rate theory and compare with one another to within an order of magnitude. Calculations on the basis of the adsorbed complex having no degrees of freedom of translation or rotation gave values for the theoretical rate of adsorption ranging from, in the same units, 1.87×10^{-14} for H_2S on NiS to 5.55×10^{-13} for CS_2 on NiS. It is evident, therefore, that a model in which the adsorbed complex is completely mobile is the most satisfactory.

The experimental data obtained for the rate of desorption of CS_2 from a V_2O_5 surface was also compared with the value predicted from the absolute rate theory. If the model selected for adsorption is correct then the CS_2 should be desorbed from a mobile complex and the rate would be given by

$$r_a = \sigma q \theta \frac{16\pi^3 m I (kT)^3}{h^5} \exp\{-E_d/RT\}, \quad (4)$$

where θ is the extent of coverage and E_d the experimental activation energy for adsorption. The value of E_d is, in accordance with the expression for the rate of desorption given by Eq. (2), assumed to decrease linearly with coverage

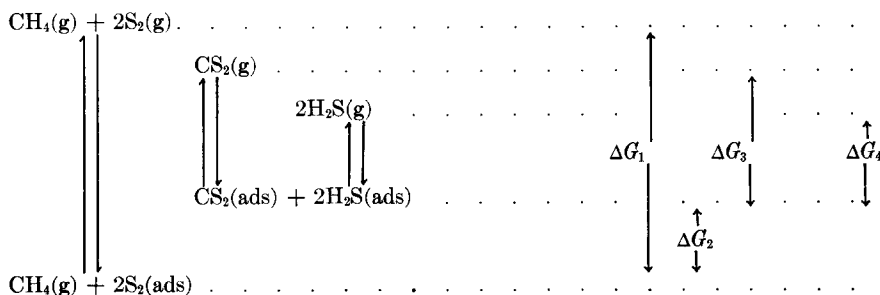
TABLE 4
 CALCULATED AND EXPERIMENTAL RATES OF ADSORPTION

System	H ₂ S on V ₂ O ₅	H ₂ S on NiS	CS ₂ on V ₂ O ₅	CS ₂ on NiS
Temp. of adsorption <i>T</i> (°C)	600	600	100	100
Exptl. mean activation energy <i>E</i> (kcal/mole)	4.0	12.8	9.7	7.6
Max. quantity adsorbed <i>q</i> ₀ (moles/g)	24 × 10 ⁻⁶	25 × 10 ⁻⁶	8 × 10 ⁻⁶	8 × 10 ⁻⁶
Calc. rate (moles/g min; mm Hg)	2.98 × 10 ⁻⁶	9.28 × 10 ⁻⁸	1.94 × 10 ⁻⁹	8.14 × 10 ⁻¹⁰
Exptl. rate (moles/g min; mm Hg)	3.78 × 10 ⁻⁶	3.62 × 10 ⁻⁷	6.24 × 10 ⁻⁸	7.07 × 10 ⁻⁷

$$E_a(\theta) = E_a(0) - \beta\theta. \quad (5)$$

At half coverage the value of E_a is, according to the experimental data, equal to 38.6 kcal/mole. Substituting this value in Eq. (4) and assuming $\sigma = 10 \text{ \AA}^2$, the absolute rate theory predicts a value of 1.51×10^{-9} moles/g min for r_a , the rate of desorption of CS₂ from V₂O₅ at 100°C. In

confirmed by independent experiments in which the adsorption of methane (2) and of sulfur (1) on supported sulfided V₂O₅ and NiO was examined. In view of the results in this paper relating to the adsorption of H₂S and CS₂, the following scheme is considered to represent the general overall catalytic chemical reaction between methane and sulfur.



the same units the experimental rate of desorption is 7.15×10^{-8} moles/g min which agrees with the predicted rate to within an order of magnitude.

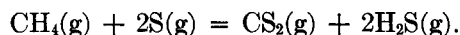
Formation of CS₂ from Sulfur and Methane

Energetics. The formation of CS₂ from natural gas and sulfur is of considerable commercial interest. The catalytic reaction between methane and sulfur over a variety of catalysts has been studied at both high temperatures (viz. $\approx 1000^\circ\text{C}$) (12) and at lower temperatures in the region of 600°C (2, 13, 14). The kinetics of reaction in the low temperature region suggest that sulfur is adsorbed by the catalyst while methane is not adsorbed (2). This was

The conservation of energy demands that

$$\Delta G^0 = 2\Delta G_1^0 + \Delta G_2^0 - \Delta G_3^0 + 2\Delta G_4^0, \quad (6)$$

where ΔG^0 is the standard free energy change for the reaction



The standard free energies of adsorption ΔG_1 will be related to the ratio of the rate constants for adsorption and desorption according to the type of adsorption isotherm obeyed. Since, for the adsorption of S₂(1) and of H₂S and CS₂, the Langmuir adsorption isotherm fits the data reasonably well, we may write

$$\Delta G_1^0 = -RT \ln b_1, \quad (7)$$

where b_1 is the constant in the Langmuir equation (equivalent to an equilibrium constant for adsorption) and may be estimated from the ratio of the slope to the intercept of plots of p/v versus p (see Table 1). Values of b_1 were readily obtained for H_2S on the two adsorbents studied. Since it was impracticable to measure the adsorption of CS_2 at the same temperature as that for H_2S , as a first approximation it was assumed that the isosteric heat of adsorption λ_3 for CS_2 was independent of temperature and the constant b_3 estimated from the relation

$$\ln\left(\frac{b_3}{b'_3}\right) = \frac{\lambda_3}{R}\left(\frac{1}{T} - \frac{1}{T'}\right), \quad (8)$$

where b'_3 is the Langmuir constant as determined at the experimental temperature T' . By invoking the interdependence of energies for the system the free energy change associated with the surface reaction may be estimated. A value for ΔG^0 was obtained from the free energies of formation of CH_4 (16) and of H_2S and CS_2 (17). It was therefore possible to calculate, from Eq. (6), ΔG_2^0 the standard free energy for the reaction between gaseous methane and adsorbed sulphur to produce adsorbed H_2S and CS_2 .

For the V_2O_5 catalyst ΔG_2^0 amounts to +5 kcal/mole and for the NiS catalyst -4 kcal/mole. The sulfur exchanging properties of a sulfided nickel oxide surface thus appear to be superior to those of a V_2O_5 surface. Provided CS_2 does not require a much larger amount of energy to desorb from NiS than V_2O_5 , a sulfided nickel oxide catalyst should act as efficiently as a vanadium pentoxide catalyst for the sulfur-methane reaction. Table 5

shows that the free energy of desorption of CS_2 from V_2O_5 exceeds that for CS_2 from NiS by only 4 kcal/mole. We conclude that sulfided nickel oxide should be equally as effective as vanadium pentoxide when catalyzing the formation of CS_2 from methane and sulfur, and this is borne out in practice (2).

Kinetics. The kinetics of CS_2 formation over a supported V_2O_5 catalyst was studied by Thomas and John (2) who demonstrated that in the region of 600-700°C the overall reaction between methane and sulfur was not limited by either external mass transfer or in-pore diffusion effects. Earlier work (12) showed that such effects were absent at even higher temperatures. Either of two rate-controlling processes were shown to conform to the experimental results. These were (i) surface reaction between adsorbed sulfur and gaseous methane, and (ii) the desorption of CS_2 . The latter mechanism was rejected on the grounds that the reciprocal of the initial rate of CS_2 formation was found to be inversely proportional to the reciprocal of the initial partial pressure of S_2 (for constant initial partial pressure of CH_4) whereas the desorption rate controlled mechanism demands that the initial rate should be constant and independent of either partial pressures or total pressure. However, the conclusions were somewhat tentative due to the inaccuracy of chemical analyses at low conversions.

Ignoring changes in θ in comparison with changes in $\exp\{\beta\theta/RT\}$ the intercept of a plot of $\ln(d\theta/dt)$ versus θ gives a value of $\sim 10^{19}$ min⁻¹ for K in Eq. (1). The rate of desorption of CS_2 may thus be expressed

TABLE 5
THERMODYNAMIC CONSTANTS FOR THE CH_4/S_2 SYSTEM FOR TWO ADSORBENTS AT 600°C

System	1	2	3	1	2	3
subscript	S_2 on V_2O_5	H_2S on V_2O_5	CS_2 on V_2O_5	S_2 on NiS	H_2S on NiS	CS_2 on NiS
b atm ⁻¹	3.65×10^5	2.48×10^4	1.06×10^{-6a}	2.13×10^6	6.65×10^4	1.32×10^{-7a}
ΔG^0 kcal/mole	-22	-17	+25 ^a	-21	-19	+28 ^a

^a Denotes value estimated from Eq. (8) utilizing the experimental value of b'_3 at 100°C.

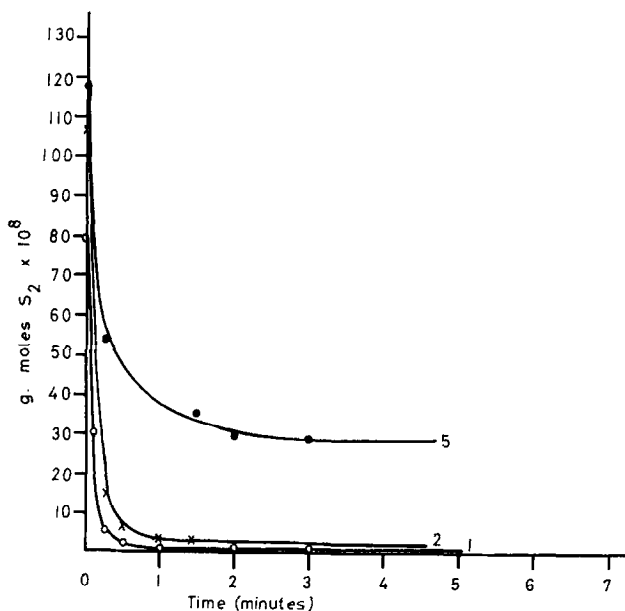


FIG. 6. Adsorption of S₂: adsorbent—sulfided V₂O₅ on alumina, $T = 600^{\circ}\text{C}$; values on curves indicate dose number.

$$-d\theta/dt = 10^{19}[\exp\{- (55 - 34\theta)/RT\}] \text{ min}^{-1}$$

Assuming this equation to be applicable at 600°C one may calculate, knowing θ , the rate of desorption under the conditions of synthesis. Since the amount of CS₂ which could be adsorbed at 600°C is immeasurably small, one can assume that the catalyst is not covered to more than about 1% during synthesis. Thus, substituting $\theta = 0.01$ in the desorption rate expression and transposing the units to g mole/hr g ($\theta = 0.01$ corresponds to 1% of the maximum measured coverage of 8×10^{-6} g mole/g) one finds the rate of desorption of CS₂ to be 4 g mole/hr g. The rate of formation of CS₂ over a V₂O₅ catalyst at 600°C is approximately 0.4×10^{-2} g mole/hr g for a partial pressure of S₂ equal to 0.1 atm and CH₄ equal to 0.15 atm. Under these conditions at least, the rate of desorption of CS₂ in a closed system is faster than the rate of synthesis by a factor of 10^3 . Unless the coverage during synthesis is appreciably smaller than 1% it may therefore be assumed that the desorption controlled mechanism is not rate limiting.

In order to test further the hypothesis

that surface reaction is rate determining, some data on the rate of adsorption of S₂ on sulfided V₂O₅ at 600°C is required. Some experiments, using the apparatus described previously (1) were therefore conducted to measure the rate of adsorption of S₂ under these conditions. Figure 6 shows the results of such experiments; and the rate of S₂ adsorption was approximately 10^{-5} g moles/min g when a dose (doses 1 and 2) was admitted resulting in an equilibrium pressure of 10^{-4} mm Hg and about 5×10^{-5} g moles/min g when a dose (dose 5) was admitted resulting in an equilibrium pressure of 10^{-2} mm Hg. We thus conclude that the rate of adsorption of S₂ on a sulfided V₂O₅ catalyst at 600°C is of the order of 10^{-1} g moles/hr g. It is therefore clear that the rate of adsorption of S₂ is not rate limiting. The present results therefore provide further evidence in favor of the surface reaction between adsorbed sulfur and gaseous methane controlling the overall rate of CS₂ synthesis.

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