

Section 2

STUDIES OF DEPOSITION AND DIFFUSION OF SULFUR ON CATALYST SURFACES BY AUGER ELECTRON SPECTROSCOPY

2.1 Introduction

To interpret our measurements of sulfur poisoning of methanol synthesis catalysts under high pressure reaction conditions (Section 1), we have carried out a series of measurements of the rate of adsorption, distribution, and segregation of sulfur on catalytic surfaces.

An active catalyst possesses a large surface area extended throughout a system of channels, fissures, and pits of submicrometer dimension. During poisoning, a gaseous contaminant in the reactor feedstock can be transported to the active sites on the catalyst surface by various pathways, such as convective flow, gaseous diffusion, bulk diffusion, and surface migration. The objective of our experiments was to identify the adsorption rate, measure the surface diffusion rate, and characterize the state of the surface under specified conditions. We used Auger electron spectroscopy (AES) to measure the relative sulfur concentration on a variety of catalytic surfaces. Sulfur deposition rates were determined by monitoring the increase of surface sulfur with time during exposure of the solid to hydrogen sulfide. Surface diffusion of sulfur on copper was observed, and the rate of migration was evaluated by measuring the lateral redistribution of a sulfur deposit as a function of time and temperature. It was possible to identify and measure surface transport in this way because the bulk diffusivity of sulfur in copper^{1*} in the temperature range of interest is extremely small.

* See list of references, Section 2, on page 2.13.

2.2 Experimental Program

2.2.1 Sulfidation Kinetics

To obtain kinetic data on the rate of sulfur accumulation on a catalyst surface exposed to low concentrations of sulfur-bearing gases, we assembled and calibrated a nozzle-beam dosing device. This device is situated in the AES vacuum chamber so that the concentration of sulfur on a specimen surface can be measured while the surface is being exposed to a calibrated flux of hydrogen sulfide or a mixture of reactant gases. The geometric arrangement of the critical components of the experiment is shown in Figure 2-1. The dosing nozzle is the open end of a stainless steel capillary tube 0.015 cm nominal ID and 70 cm long. The dosing rate is governed by the mass flow rate of gas through the tube, which can be controlled by adjusting the gas pressure at the upstream end of the tube. Total steady-state flow rates in the range 10^{-6} to 10^{-4} torr liter sec^{-1} can be readily attained. Lower values of H_2S flow rates were obtained by diluting the H_2S with H_2 . The flux distribution obtained from the nozzle, determined by scanning the nozzle across the entrance aperture of a quadrupole mass spectrometer, was rather strongly peaked along the extension of the nozzle axis. This flux distribution characteristic and the geometric limitations requiring the nozzle axis to be at a 45° angle to the surface caused the point where the projection of the nozzle axis intersected the surface to receive a greater dosage of gas than the other regions. Surfaces were dosed at room temperature (300 K), and also at an elevated temperatures.

The pumping speed of the vacuum system was high enough to maintain a background pressure of about 10^{-8} torr during dosing. Consequently, gas molecules in the nozzle beam that missed the surface, or were reflected from it without being captured, were pumped out of the chamber with no opportunity for a subsequent collision with the specimen surface.

For these experiments, we prepared samples of the low pressure process catalyst C79-1 by pressing the powdered material into a fine-mesh stainless steel grid to form a thin, flat wafer, 0.5 x 1.5 cm in lateral dimensions. The wafer was crimped to a nickel foil support and heating element (Figure 2-1). Similar specimens of ZnO and Al₂O₃ were also prepared. The copper specimen was a thin foil crimped to the heating element. Each specimen had identical geometry with respect to the dosing nozzle, the Auger electron energy analyzer (CMA), and an argon ion sputtering beam. Each specimen was heated overnight in a stream of hydrogen at 1 atm and 525 K. After cooling in the H₂ atmosphere, the specimen was transferred to the AES vacuum chamber and baked out in vacuum overnight at 475 K. Base pressure in the vacuum chamber was maintained at less than 5 x 10⁻⁹ torr.

The rate of sulfur accumulation on the specimen surface was measured by observing the derivative signal of the CMA in the Auger electron energy range from 0 to 200 eV at 2 min intervals during dosing, with a known and constant average flux of H₂S incident on the surface. The peak-to-peak heights of the AES first derivative sulfur peak (L₃M_{2,3}M_{2,3}, 150eV) were taken to be proportional to the concentrations of surface sulfur. In the case of copper foil, on which measurements were made at multiple points on the surface, the observed sulfur peak intensities were normalized to the intensity of the M_{2,3}M₄M₄ (60 eV) copper peak,² to compensate for otherwise indeterminate variations in surface topography and geometry.

2.2.2 Surface Migration of Sulfur

To investigate transport of sulfur across the copper surface, it is necessary to establish a sulfur deposit with finite dimensional limits from which lateral spreading can be measured. We formed a sulfur adlayer

that terminated in a sharp edge on the specimen by two different procedures. In the first, the entire surface of the specimen was covered with sulfur by dosing with H_2S at 300 K. A portion of the sulfur adlayer was then removed by bombardment with a focussed beam of 600 eV argon ions that intercepted the specimen surface beyond the edge of a stainless steel flag (Figure 2-1). The shadow of the flag created a sharp lateral discontinuity in sulfur distribution on the surface. In the second method, a stainless steel mask was placed over a portion of the specimen surface before H_2S dosing. When dosing was completed, the mask was removed, leaving a sharp-edged adlayer of sulfur on the surface. In the measurement of diffusional surface transport we monitored the concentration profile of the sulfur adlayer at discrete time intervals, after raising the temperature of the specimen to the desired level, by measuring the sulfur AES peak intensity at multiple points spaced approximately 0.25 mm apart along a line on the surface.

In most metals, including copper, sulfur is an indigenous bulk impurity that selectively segregates to the surface at elevated temperatures.³ To prevent bulk sulfur from interfering with our surface migration measurements, we subjected the copper specimen to rigorous cleaning before sulfur dosing. The surface was bombarded for at least 5 min with 600 eV argon ions while maintained at $T > 800$ K. Such a treatment etches the copper surface and also depletes the upper half-dozen atomic layers of bulk impurities that tend to segregate to the surface, such as sulfur and carbon. Carbon was particularly difficult to remove from the specimen, and a number of diffusion experiments were made with carbon impurity present on the surface. There is some indication that the carbon impurity on the surface affects the capture probability and the surface mobility of sulfur on copper.

2.3 Experimental Results

2.3.1 Sulfidation Kinetics

When C79-1 is exposed to a mixture of H_2S (1 vol%) in H_2 , surface sulfur builds up until a steady-state saturation level is reached. These results (Figure 2-2) can be interpreted in terms of a kinetic model with first-order dependence on unoccupied adsorption sites and on H_2S pressure. For such a case, the following rate equation can be applied:

$$d\theta/dt = k(H_2S) (1 - \theta) \quad (1)$$

where θ represents the fraction of available adsorption sites occupied by sulfur ($0 \leq \theta \leq 1$), t is time, k is the adsorption rate constant, and (H_2S) is the concentration of H_2S in the incident gas stream. By integrating Equation (1) between the limits $\theta = 0$ at the onset and $\theta = \theta$ at time t , we obtain:

$$\ln(1 - \theta) = k(H_2S) t \quad (2)$$

Thus, for a specific concentration of H_2S in the incident flux, the slope of a plot of $\ln(1 - \theta)$ against t is proportional to the rate constant, k . Our experimental data was analyzed in this way (Figure 2-3) and the values of k computed from the slopes and the H_2S dosing fluxes (Table 2-1). These values of k differ considerably from those derived from the catalyst activity decay experiments described in Section 1 of this Report. The activity decay results were obtained at high pressures during methanol synthesis in the presence of syngas. By way of contrast, the AES results were obtained with a catalyst surface at very low pressures in the absence of syngas. We would not expect good numerical agreement

between values of a kinetic parameter such as the poisoning rate constant obtained under such divergent conditions.

2.3.2 Surface Migration of Sulfur

The discontinuity in sulfur coverage on the copper surface (produced by selective argon ion bombardment after deposition of H_2S) was manifested as a stable profile shown by the AES line scan in the first panel of Figure 2-4. When the copper foil was heated to successively higher temperature, the shape of the sulfur concentration profile changed in a way that suggested sulfur migration from a region of high concentration to that of low concentration (Figure 2-4). Based on the reported¹ diffusivity of sulfur in copper ($D_{\text{bulk}} \approx 10^{-12} \text{ cm}^2 \text{ sec}^{-1}$ at 800 K), diffusion of sulfur into the bulk of the copper specimen would be negligibly slow relative to the sulfur transport rate observed on the surface. In our experiments, the surface reached a steady state temperature in about 1 min after a step increase in heating current to the copper specimen. The AES line scans (Figure 2-4) were obtained during an interval of 10 to 14 min after the incremental increase in heating current.

To estimate values of the surface diffusion coefficient D from our experimental data, we interpreted the shapes of the concentration profiles in terms of the material diffusing on a plane from a semi-infinite line source of adsorbate⁴. The concentration profile of such a system is described by the equation.

$$c/c_0 = 1/2\{1 - \text{erf}[x/(2\sqrt{Dt})]\} \quad (3)$$

where c_0 is the concentration at the source boundary at time $t = 0$, and x is the distance measured on a line normal to the source boundary. The surface diffusion coefficient, D , was evaluated by Equation (3) and the

data in Figure 2-4 in two ways. First, we measured the distance x , corresponding to a fixed value of $c/c_0 = 0.23$ after 600 ± 60 sec at the specified temperature. Then, we measured the relative concentration, c/c_0 at a fixed distance $x = 1.25$ mm from the original boundary after 840 ± 60 sec at the specified temperature. The values of these parameters in addition to the calculated values of surface diffusion coefficient are shown in Table 2-2 and are plotted as a function of reciprocal temperature in Figure 2-5. The slope of the line on this Arrhenius plot corresponds to an activation energy for surface diffusion, $E = 6.7$ kcal/mole.

At the beginning of this experiment ($T = 300$ K), a small carbon impurity appeared in the AES spectrum (peak height ratio carbon/sulfur = 0.2). The amplitude of the carbon peak increased during the time the specimen was held at 678 K ($C/S = 1$). Hence, this specimen was contaminated significantly with carbon in the region near the surface. Subsequent experiments were carried out after the copper specimen was argon ion bombarded at 800 K for a prolonged period, followed by an interval of vacuum annealing at 800 K, a treatment that reduced the carbon contaminant level below the limit of AES detection. The sulfur adlayer deposited on such a copper surface was found to be immobile up to 800 K. Sulfur deposited on the clean, annealed copper from a gas stream of pure H_2S likewise exhibited no mobility at temperatures up to 800 K. However, surface mobility was measurable from a sulfur adlayer on carbon-free copper that had been argon ion bombarded at 300 K and not subsequently annealed before sulfur deposition. The results of these experiments are summarized in Table 2-3.

2.4 Discussion

2.4.1 Sulfidation Kinetics

The AES measurements demonstrate that the rate of sulfur deposition on the surface of the C79-1 methanol synthesis catalyst at

503 K can be interpreted in terms of a first-order dependency on the concentration of free surface sites and on the H_2S concentration in the incident stream. Similar results were obtained at 300 K (Table 2-1). From the values of the rate constant measured at these two temperatures, we calculate an activation energy of 700 cal/mole.

AES analyzes the elemental composition of a surface to a depth of less than 200 nm. However, the catalyst wafers used in our studies were about 0.1 mm thick and contained considerable pore structure so that only a very small fraction of the total surface was examined by AES.

Under methanol synthesis conditions, gaseous molecules can enter the pores of a catalyst and react by collisional interaction with the interior walls of the pores. (At 500 psi, the average mean free path of an H_2S molecule is about 200 nm, comparable to the mean pore radius of typical oxide-based catalysts.⁵) In contrast, under the conditions of our low-pressure experiments, multiple collisions with the catalyst are unlikely, because the gaseous molecules emanating from the dosing nozzle enter a chamber at a background pressure of about 10^{-7} torr where the average mean free path is about 10^9 nm. Consequently, saturation of the catalyst specimen with a sulfur adsorbate would represent full occupancy of the free sites on the outer surface of the catalyst only.

Mass transport can occur in adlayers by surface migration, and the rate of such a transport process is governed largely by the strength of the adsorption bond and by the availability of free surface sites. In our experiments, the sulfur coverage on the outer surface of the catalyst diminished with time when the incident flux of H_2S was interrupted. In the range 300 to 473 K, the rate data (Table 2-4) yield an activation energy of 2300 cal/mole, a value of reasonable magnitude⁶ for a surface migration process involving a species with a binding energy in the range 20 to 30 kcal/mole. Removal of a large fraction of the

sulfur from the outer surface of a heavily dosed, saturated wafer at 503 K by argon ion bombardment provided further evidence of the sulfur ad-species mobility. When the argon ion beam was interrupted, the sulfur concentration on the surface seen by AES slowly increased, evidently by surface migration of sulfur from within the pore structure.

Neither the chemical structure nor the distribution of the adlayer of sulfur on the C79-1 catalyst can be identified unequivocally from the AES data. In an attempt to determine the location of the adsorbed sulfur species on the catalyst, we observed the rate of sulfur deposition on surfaces of ZnO, Cu, and Al₂O₃, representative of the individual components of the catalyst. That these specific phases existed in the reduced (activated) catalyst was inferred from data supplied by the manufacturer and from x-ray diffraction patterns obtained in our laboratory.

AES examination showed that zinc oxide, in striking contrast to the mixed oxide catalyst, exhibits no detectable sulfur accumulation when exposed to H₂S under our experimental conditions. On the basis of equilibrium data, zinc oxide should be readily converted to the sulfide in a gaseous environment of 1% H₂S in H₂, but kinetic factors appear to play a dominant role in this reaction. Thus, multiple collisions of H₂S molecules on a ZnO surface are required to approach equilibrium conditions within a reasonable period of time.

The rate of sulfur accumulation on a copper surface exhibits a large variation that appears to be related to the cleanliness of the surface. The rate constant values for surfaces lightly and heavily contaminated with carbon bracket those obtained for the C79-1 catalyst (Table 2-1). This observation confirms that the copper phase of the catalyst is particularly susceptible to H₂S chemisorption, as can be inferred from the relatively higher poisoning rate constants obtained

for the copper-rich catalysts in high-pressure measurements (see Section 1 of this report). Carbon and sulfur appear to compete for adsorption sites.

Deposits of sulfur on copper single crystals, exposed to hydrogen sulfide under conditions similar to our experiments, have been examined^{7,8} by low energy electron diffraction (LEED). The precise surface configuration assumed by the sulfur adspecies appears to depend on the magnitude of the incident H_2S flux and on the exposed crystal face. Within the H_2S pressure range of 10^{-9} to 10^{-5} torr, dissociative chemisorption occurs without surface reconstruction, leaving a sulfur adspecies that is free to migrate across the surface. Sulfur saturation corresponding to half a monolayer of adatoms was reported^{7,8} to require an exposure of approximately 10 Langmuir (10^{-5} torr sec⁻¹), which is comparable to our experimental results.

The efficiency with which an H_2S molecule dissociatively adsorbs onto a clean copper surface is measured by the initial sticking probability, S_0 , defined as the ratio of the rate of interaction to the collision frequency:

$$S_0 = N(d\theta/dt)/Z \quad (4)$$

where N is the total density of surface sites and Z , the collision frequency H_2S (molec cm⁻² min⁻¹), is related to the H_2S pressure P :

$$P = Z (4RT/c) \quad (5)$$

In this expression, R is the gas constant, T is the gas temperature (K), and c is the mean velocity of the H_2S molecule (cm min⁻¹). At $\theta = 0$, the first-order rate law [Equation (1)] becomes

$$d\theta/dt = kP = kZ(4RT/c) \quad (6)$$

Therefore, combining Equations (4) and (6) gives

$$S_o = Nk(4RT/c) \quad (7)$$

We observed that the rate of sulfur deposition on copper follows first-order kinetics [Equation (1)]. Hence, for clean copper foil with $N = 1.54 \times 10^{15}$ atoms cm^{-2} , $S_o = 0.4$, that is, nearly every other collision results in adsorption of the H_2S molecule on the copper surface.

Within the limit of AES detectability (approximately 0.05 monolayer), we found that H_2S would not adsorb on either of two types of alumina catalyst support unless the solid material was first heated in vacuum to about 825 K to expel strongly bound water. Others^{9,10} have reported small coverages of weakly bound H_2S on alumina and have suggested that the admolecule is hydrogen-bonded to the OH^- groups on the alumina surface. DeRosset et al.¹¹ noted that the heat of adsorption of H_2S varied with the degree of predrying of the alumina and suggested that the H_2S reacted as a base at Lewis acid sites on dehydrated alumina. With the alumina used in our experiments, the AES spectra showed variations in the fine structure of the LVV lines. These variations accompanied dehydration and subsequent adsorption of H_2S . Specifically, an AES line at 70 eV disappeared when the alumina specimen was heated to 800 K and subsequently cooled to 530 K in hard vacuum (approximately 10^{-8} torr). When the alumina specimen was exposed to H_2S (under the conditions previously described), the line reappeared in the spectrum and grew in intensity as the sulfur concentration on the surface increased. This behavior could indicate that SH^- groups had replaced OH^- groups on the dehydrated alumina surface. Species of this type are strongly bound.¹²

Our measurements indicate that the value of the rate of H_2S adsorption on dehydrated alumina is less than one-third that measured on the reduced mixed oxide catalyst (Table 2-1). However, under typical methanol synthesis conditions, the alumina phase present in the catalyst is likely to be in a hydrated state and thus unable to adsorb H_2S except in a weakly bound state at a very low degree of coverage.

2.4.2 Surface Migration of Sulfur

To a first approximation, surface transport of a chemisorbed species from one site to another involves an activation energy barrier of about 10% of the binding energy of the adspecies.¹⁶ The binding energy of a sulfur atom to a polycrystalline copper surface has been reported¹³ to be 86 kcal/mole. Thus, the observed surface diffusion activation energy of nearly 7 kcal mol⁻¹ (Figure 2-5) leads us to suggest that chemisorbed sulfur is transported by a site-hopping process. The surface diffusion coefficient for sulfur on carbon-contaminated copper at 678 K is similar in magnitude to that reported¹⁴ for the surface migration of sulfur on platinum at 723 K: $D = 3 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$.

Sulfur surface mobility on copper surfaces varies significantly with different pretreatments (Table 2-3). Two factors that might affect the rate of sulfur migration are the presence of carbon on the copper surface and the relative roughness of the surface.

The carbon AES peak shape exhibits the characteristics of graphitic or amorphous carbon, as distinguished from the carbidic form. In the nickel methanation catalysts, such surface carbon has been strongly associated with the formation of catalyst-fouling carbonaceous deposits. In copper, such carbon could preempt high-coordination-number sites, leaving relatively weak binding sites for the sulfur. Such an interpretation is consistent with the observed lower sticking probability,

S_o , of H_2S on heavily carbon-contaminated copper (Table 2-1), and with the higher surface diffusion coefficient found for the carbon-contaminated specimen (Table 2-3).

Argon ion bombardment of a metal surface at moderate temperatures can grossly alter the topography¹⁵ by roughening, producing defects, and selectively exposing crystallites with a particular crystalline orientation. Our results suggest that a clean copper surface modified this way binds a sulfur adlayer less strongly than does a surface on which ion bombardment damage has been repaired by vacuum annealing.

The activation energy for sulfur migration on the carbon-contaminated copper surface (Figure 2-5) is of the same order of magnitude as that estimated for sulfur adlayer diffusion on the C79-1 catalyst surface (Table 2-4). This observation suggests that the mass transport mechanism is identical for the two surfaces and leads us to speculate that the copper phase is the gateway for sulfur poisoning of low-pressure process methanol synthesis catalysts exposed to H_2S -containing feedstocks.

2.5 References

1. F. Moya and F. Cabane-Brouty, *Compt. Rend. (Paris)*, 264 C, 1543 (1967).
2. M. Perdereau, *Surface Sci.*, 24, 239 (1971).
3. R. W. Joyner, C. S. McKee, and M. W. Roberts, *Surface Sci.*, 26, 303 (1971).
4. W. Jost, *Diffusion in Solids, Liquids, Gases*. (Academic Press, New York, 1952), p. 21.
5. S. J. Gregg and K.S.W. Sing, *Adsorption, Surface Area and Porosity*, (Academic Press, New York, 1967), p. 166.
6. J. W. Geus, in *Chemisorption and Reactions on Metallic Films*, J. R. Anderson, ed. (Academic Press, New York, 1971) Chapter 3.

7. J. Benard, *Catalysis Rev.*, 3, 93, (1969).
8. R. W. Joyner, C. S. McKee, and M. W. Roberts, *Surface Sci.*, 27, 279, (1971); H. P. Bonzell, *Surface Sci.*, 27, 387 (1971).
9. A. V. Dec, I. G. Dalla Lana, and H. W. Habgood, *J. Catalysis*, 21, 270, (1971).
10. R. W. Glass and R. A. Ross, *J. Phys. Chem.*, 77, 2576, (1973).
11. A. J. DeRosset, C. G. Finstrom, and C. J. Adams, *J. Catal.*, 1, 235 (1962).
12. J. B. Peri, *J. Phys. Chem.*, 69, 211 (1965).
13. R. P. Elliott, *Constitution of Binary Alloys, First Supplement*, (Mc-Graw Hill, New York, 1965).
14. H. P. Bonzel and R. Ku, *J. Chem. Phys.*, 59, 1641 (1973).
15. D. J. Barber, *Vacuum*, 24, 469 (1974).

Table 2-1

SULFIDATION RATE CONSTANTS FOR CATALYSTS AND CATALYST
COMPONENTS DETERMINED BY AES

Specimen ^a	Carbon Impurity (C/S by AES on S-saturated surface)	Temperature (K)	Rate Constant (Equation 1) ($l \cdot \text{mole}^{-1} \text{ hr}^{-1}$) $\times 10^{-12}$
C79-1	0.75	300	0.75
	0.75	503	1.1 ± 0.03
Al_2O_3^b	0	488	0.24 ± 0.01
Cu (foil)	3.2	300	0.22
	0.2	300	5.6
ZnO	0	300	0
	0	503	0

^aWith the exception of the Cu foil, all specimens were thin wafers pressed from powdered material.

^bGirdler T-372. Dehydration in vacuum at $T \approx 825$ K was required before sulfur uptake was observed.

Table 2-2

SURFACE DIFFUSION COEFFICIENTS DERIVED FROM MEASURED
CONCENTRATION PROFILES OF S ON Cu^a

Temperature	Diffusion Distance, x , at $c/c_0 = 0.23$ After $t = 600 \pm 60$ sec ^b (cm)	Relative Concentration, c/c_0 , at $x = -1.25$ mm After $t = 840 \pm 60$ sec ^b	Surface Diffusion Coefficient (cm ² sec ⁻¹)
393	0.02	-	5×10^{-9}
	-	0.0077	1×10^{-8}
479	0.04	-	2.5×10^{-8}
	-	0.038	3.5×10^{-8}
569	0.05	-	5×10^{-8}
	-	0.11	9×10^{-8}
678	0.14	-	2.5×10^{-7}
	-	0.23	2.5×10^{-7}

^aData from Figure 2-4.

^bTime measured from incremental increase in heating current to raise temperature. Approximately 1 min was required to reach indicated temperature.

Table 2-3

EFFECT OF PRETREATMENT ON SURFACE SULFUR MOBILITY ON COPPER

Surface Treatment Before Sulfur Deposition	Sulfur Concentration Profile by:	AES Peak Ratio C/S	H ₂ S Dose ^a (mol cm ⁻²) x 10 ⁻¹⁵	Diffusion Coefficient (cm ² sec ⁻¹) at T (K)
(1) Ar ⁺ Bombardment at 700 K	Selective Ar ⁺ bombardment	0.2-1	3.7	3 x 10 ⁻⁷ at 678 K
(2) Ar ⁺ Bombardment at 300 K				
(1) Ar ⁺ Bombardment at 800 K	Selective Deposition	0	0.45	< 10 ^{-8c} at 800 K
(2) Vacuum Anneal at 800 K				
(1) Ar ⁺ Bombardment at 800 K	Selective Deposition	0	1.9	< 10 ^{-8c} at 800 K
(2) Vacuum Anneal at 800 K				
(1) Ar ⁺ Bombardment at 700 K	Selective Deposition	0	2.5	10 ⁻⁷ at 800 K
(2) Ar ⁺ Bombardment at 300 K				

^aBased on geometric surface area with a roughness factor of 2. Dosed with a mixture of 1 vol% H₂S in H₂.

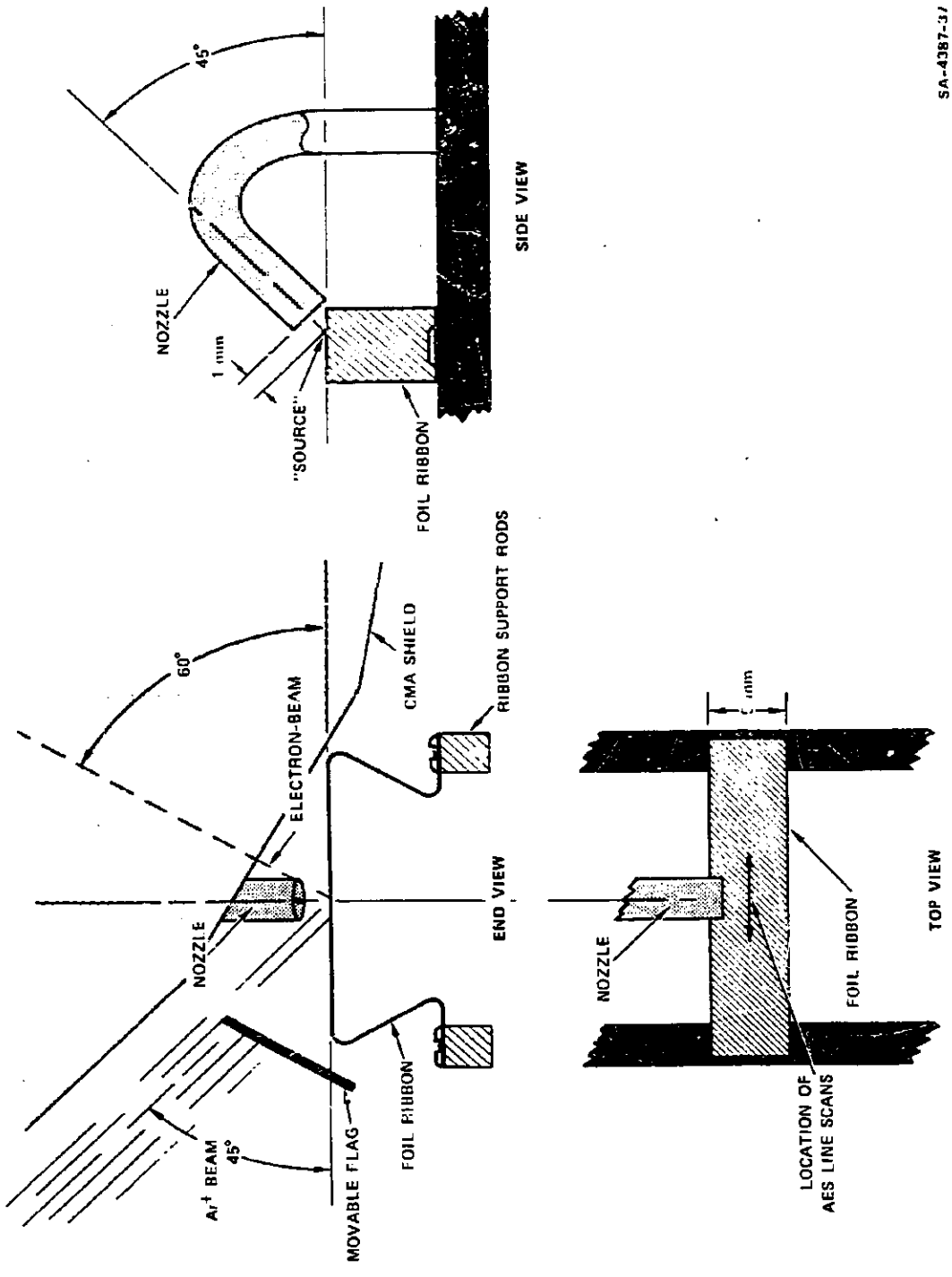
^bDosed with pure H₂S.

^cNo mobility observed at 800 K.

Table 2-4

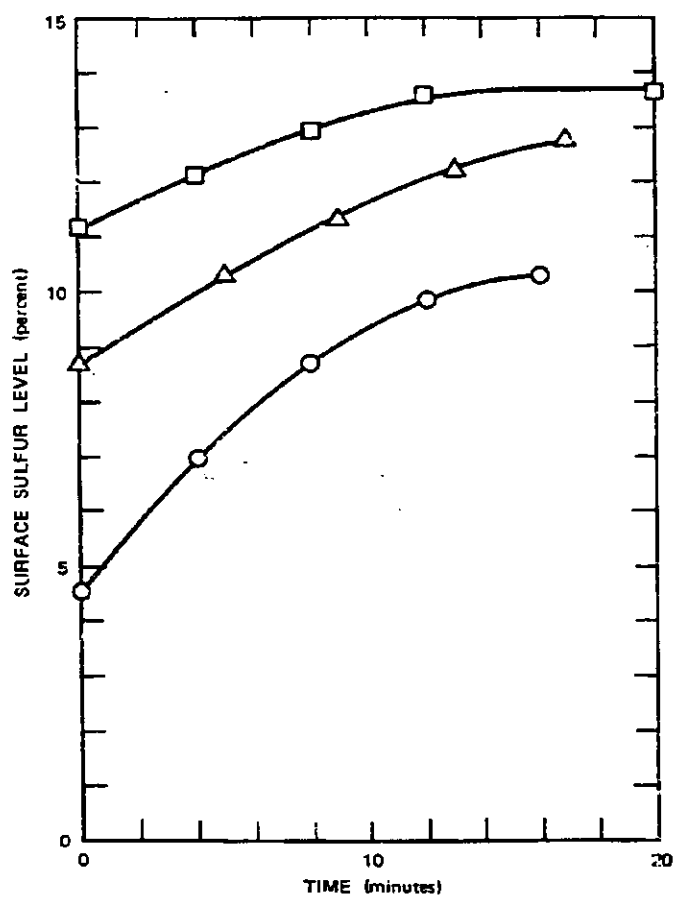
SURFACE MIGRATION RATE OF SULFUR ON C79-1 CATALYST
AS MEASURED BY AES

Temperature	Rate of S Loss from Outer Surface (% min ⁻¹)
300	0.02
373	0.07
473	0.12



SA-4387-37

FIGURE 2-1 EXPERIMENTAL ARRANGEMENT FOR CLEANING, DOSING, AND AES EXAMINATION OF METAL FOILS



SA-4387-23

FIGURE 2-2 SULFUR DEPOSITION ON SURFACE OF C79-1 CATALYST WAFER DURING EXPOSURE TO H₂S
 H₂S flux (molec · min⁻¹ cm⁻²) × 10⁻¹⁵: ○ 1.6; △ 2.3; □ 2.5.
 Temperature: 503 K.

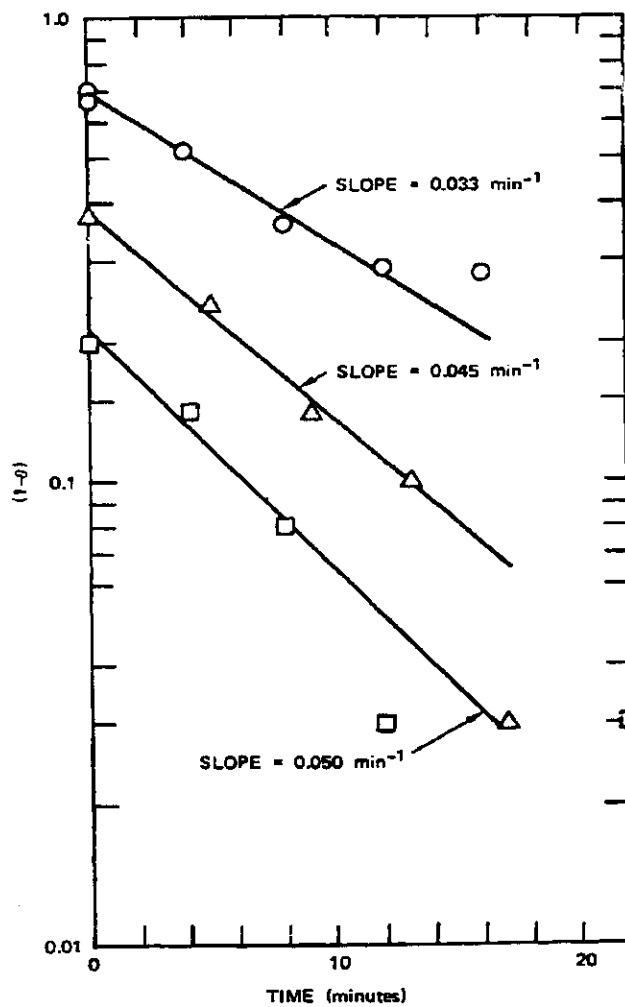


FIGURE 2-3 DIMINUTION IN FRACTION OF AVAILABLE ADSORPTION SITES $(1-\theta)$ ON C79-1 CATALYST WAFER DURING EXPOSURE TO H_2S
 H_2S flux (molec \cdot min $^{-1}$ cm $^{-2}$) $\times 10^{-16}$: \circ 1.6; Δ 2.3; \square 2.5.
 Temperature: 503 K.

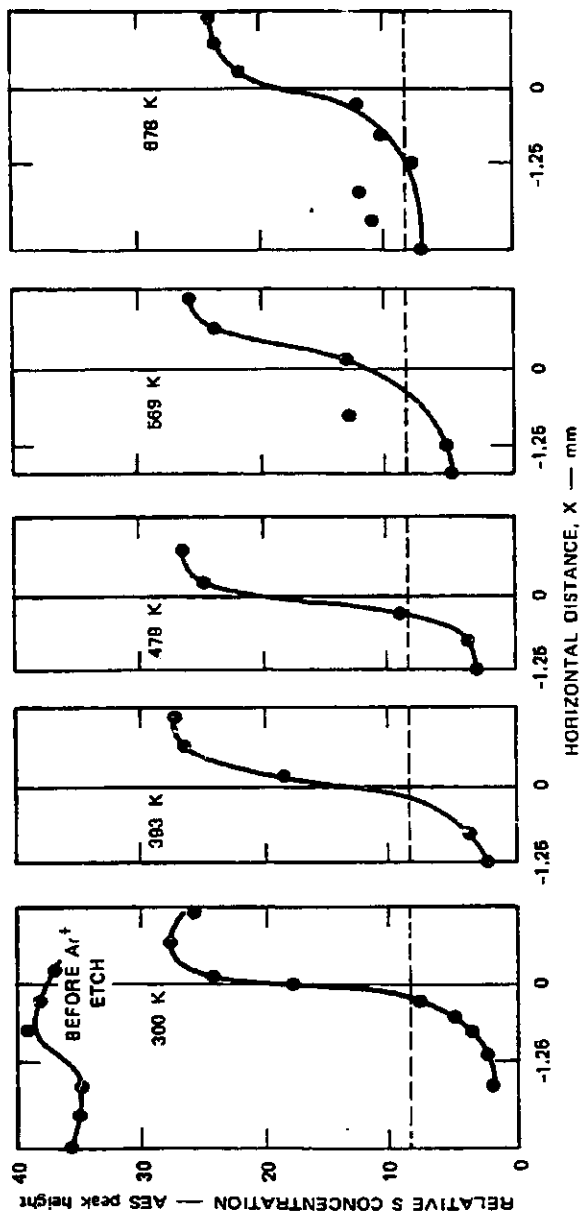


FIGURE 2-4 TRANSPORT OF SURFACE SULFUR ON COPPER AS A FUNCTION OF TEMPERATURE

Dashed line identifies location of $c/c_0 = 0.23$.

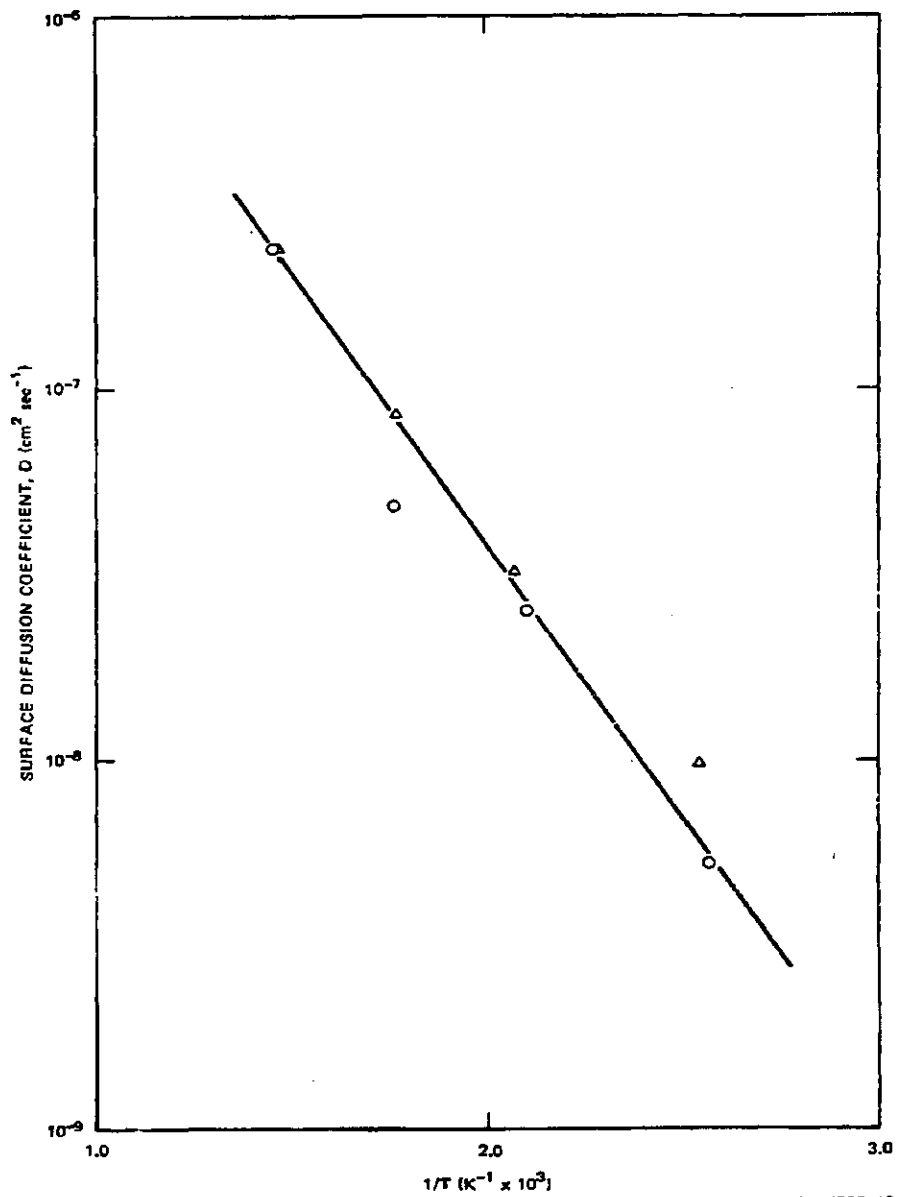


FIGURE 2-5 TEMPERATURE VARIATION OF SURFACE DIFFUSION COEFFICIENT OF SULFUR ON COPPER
 Values of D from measurements of: ○ diffusion distance at fixed concentration; Δ concentration change at fixed distance. Slope corresponds to $E = 6.7 \text{ kcal}\cdot\text{mol}^{-1}$.