Section 4

SULFIDATION AND REGENERATION OF CATALYSTS

4.1   Introduction

        A procedure for restoring the activity of a sulfur-poisoned
catalyst by chemical treatment would be most valuable to industrial
catalyst technology. On particularly attractive approach to this problem
is the removal of surface and bulk sulfur from the catalyst by exposure
to a stream of pure hydrogen and formation of H_2S at a suitable pressure,
temperature, and space velocity. By this technique, the catalyst would
be in a reduced state during regeneration, and could be restored to
synthesis service without going through an activation procedure. Before
attempting extensive experimental measurements, we examined the thermo-
dynamics of the sulfur-copper-hydrogen system, and, because of its
relevance to Fischer-Tropsch synthesis, the sulfur-iron-hydrogen system.
Specifically, we address the thermodynamic and kinetic aspects of ad-
sorption/desorption of chemisorbed sulfur, the surface structure of
bound sulfur, and the growth rates and thermodynamics of bulk metal
sulfides.

        An alternative to catalyst regeneration is to allow the chemi-
sorbed sulfur to react with oxygen to form a volatile sulfur oxide. In
industrial practice, such a process would involve at least two steps:
regeneration (oxidative sulfur removal) and activation (catalyst reduction).
Although less attractive than hydrogen treatment, this technique may be
an economically viable alternative. Chemisorbed sulfur on Cu(110) single
crystal surfaces reacts with oxygen to form SO_2 at measurable rates in

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the temperature range 900 to 1100 K.[1*] In this temperature range, the
problem of catalyst sintering and loss of active surface area may be
severe particularly for copper catalysts.

4.2   Bulk Metal Sulfides

The thermodynamics and phase diagrams of bulk Fe and Cu sulfides
are relatively well documented.[2] Iron forms a number of sulfide phases,
as shown in Figure 4-1. FeS is the most stable phase at 573 K, with
$\Delta H_f^o = -22$ kcal mol^{-1}. For the Fe-S system, the thermodynamic data[3]
shown in Figure 4-2 predict at equilibrium $P_{H_2S}/P_{H_2} = 6$ ppm at 573 K.
For the Cu-S system, Cu_2S is the most stable phase with $P_{H_2S}/P_{H_2} = 4$ ppm
at 500 K ($\Delta H_f^o = -20$ kcal mol^{-1}),[3] as shown in Figure 4-3.

Hydrogen sulfide dissociatively chemisorbs on iron surfaces at
low temperatures,[4] and bulk incorporation proceeds at temperatures as
low as 193 K. Diffusional transport appears to control the growth of
bulk sulfide layers in many transition metals, but not in iron, in which
dissociation at the surface is reported as the slow step.[4] Rates of
sulfur incorporation follow the order[4-6] Fe > Ni > Pd > Ag > Pt.

4.3   H₂S Adsorption/Desorption

Chemisorption of sulfur may involve a number of steps, e.g.,
reversible molecular adsorption, dissociation or association, recon-
struction of adsorbed sulfur into a two-dimensional compound, and in-
corporation of adsorbed sulfur into a two-dimensional compound, and
incorporation into the bulk as a dissolved atom or ion or as a precipi-
tated sulfide phase. Such process steps are illustrated by Figure 4-4
for H₂S adsorption on a transition metal (Me).

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[*]References in Section 4 are listed on page 4.8.

The rates of adsorption of H_2S on metals are very rapid. In Figure 4-5(a,b) we show the coverage of adsorbed sulfur on Cu(110)[1] and Cu(001),[7] respectively, as a function of H_2S exposure. The probability of adsorption per incident H_2S molecule was constant (and approximately unity) for both surfaces until a fractional coverage with sulfur atoms corresponding to $\theta = 1/2$ was reached, presumably saturation coverage. Further slow adsorption was observed at 295 K accompanied by reconstruction of the adsorbed layer. This process is discussed further below.

The high, surface coverage-independent sticking probability for H_2S adsorption on these copper crystal planes suggests that there is no barrier to adsorption and dissociation until saturation coverage is attained. The constant probability of adsorption implies that a weakly bound adsorbed precursor is involved in the adsorption/dissociation sequence. A most likely precursor would be molecularly adsorbed H_2S, as indicated in Figure 4-4. Weakly chemisorbed or physisorbed H_2S would have time to move over the surface and find a dissociation site before desorbing. Some weakly bound H_2S was observed[4] on Fe films at 193 K so we might expect a similar H_2S adsorption behavior for Fe as for Cu.

The rapid rates of adsorption and dissociation of H_2S on Fe and Cu suggest that the rate of sulfur poisoning of these clean or hydrogen-covered metal surfaces is not limited by reaction at the surface. In other words, the energy barriers to adsorption, surface diffusion, and dissociation are so low that they allow rapid reaction even at room temperature. As a result, the coverage of adsorbed sulfur on these metal surfaces will be controlled in practical terms by equilibrium thermodynamics.

4.4   Surface Structures

Recent advances in surface-sensitive techniques, especially low energy electron diffraction (LEED), allow detailed analysis of the

geometric structure of crystal surfaces and adsorbed atoms. On Fe(001) at low coverage, the C(2x2) pattern appears; it is stable up to 773 K.[8] At high sulfur coverage, the surface slowly transforms through a series of coincidence lattice structures with little net increase in coverage. These structures have been interpreted[9,10] as narrowing regions of C(2x2) phases with dense close-packed boundaries and S atoms located at sites with a coordination number of four. On Cu(001), the low coverage pattern is C(2x2),[11] although P(2x1)[12] has been reported at high coverage. On Cu(111), the stable structure[11] is $\sqrt{3} \times \sqrt{3}$ R 30°. On Cu(110),[1,11] the C(2x2) pattern is favored at low coverage. With approximately 30% additional coverage (to 0.65 monolayer), a P(3x2) sulfide layer is slowly reconstructed.

The LEED results are summarized in Table 4-1. In general, the (111) (110) and (001) faces of Fe and Cu form high-coordination structures at sulfur surface coverage of 1/4 to 1/2 monolayer. Additional H_2S exposure often causes a slow reconstruction into a surface compound with little additional S uptake.

An unsuccessful attempt to remove sulfur adsorbed on an iron based ammonia synthesis catalyst[13] by reaction with hydrogen enabled us to estimate an upper limit for sorption on iron. The catalyst could not be regenerated in 1 atm H_2 at 893 K for 1000 hr. This result suggests that $P_{H_2S}/P_{H_2} \leq 10^{-9} \pm 10^{-1}$. This upper limit is plotted (as +) in Figure 4-2.

Indirect data concerning sulfur chemisorption on iron at elevated temperatures were obtained by measuring the effect of sulfur activity on the carburization/decarburization and nitrogenation of iron. The initial carburization rate of (100) oriented iron foils by CH_4 decreased by 50% in 0.26 ppm H_2S/H_2 at 1073 K.[16] The initial nitrogenation rate of the same foils by NH_3 at 1123 K decreased by 50% in 0.46 ppm H_2S/H_2.[16] The

initial decarburization rates in 1 atm H_2 at 1413 K[17] decreased a factor of 8 in the presence of 28 ppm H_2S. By assuming that the initial rates decreased in proportion to the fractional sulfur coverage and by applying the Langmuir adsorption isotherm, we find half coverage of sulfur on iron for 0.26, 0.46, and 4.0 ppm H_2S in H_2 at 1073, 1123, and 1413 X, respectively. These data points are included in Figure 4—4 and show the upper limit point at 893 K to be more accurate than expected.

We can assume that the entropy change for sulfur chemisorption is approximately the same as the entropy change for bulk sulfidation, since the vibrational entropy contributions of the solid phases are small. The dashed line in Figure 4-2 represents the best fit to the three equilibrium points, with ΔS_{ads} taken to be equal to ΔS for FeS at 1000 K. From the slope of the line, we determine ΔH_{ads} = -33 kcal mol^{-1} s for chemisorption of sulfur on iron by H_2S.

The literature reports only a single data point for reversible chemisorption of sulfur on copper.[8] Based on the same entropy value for chemisorbed sulfur as for Cu_2S, we obtain $\Delta H_{ads} \cong -16$ kcal mol^{-1}.

The results of the sparse thermodynamic data for sulfur chemisorption on Fe and Cu indicate that chemisorbed sulfur is far more stable than the bulk sulfides, as is the case for Ag silver, for which some equilibrium measurements are available.[3,11] In Table 4-2, in which these results are summarized, E_b is the binding energy of a sulfur atom at 1000 K at the surface or in the most stable bulk sulfide. These data were obtained assuming that ΔS for chemisorption and of the most stable sulfide are the same, except for the silver system for which published data were used. For silver, the two-dimensional (reconstructed) layer apparently has a lower heat of formation that chemisrobed sulfur except on the (110) plane. This same trend probably exists for Fe and Cu, except that the transition may occur at a different sulfur coverage.

4.5   Regeneration

A measure of the degree of regeneration of sulfur-poisoned Cu catalysts by reaction with H_2 may be obtained from thermodynamic considerations. For Cu at 500 K, the equilibrium pressure ratio of H_2S to H_2 is less than $< 10^{-8}$ (Figure 4-3), so that a considerable amount of H_2 would be required to remove the sulfur contaminant from the catalyst surface. Temperatures in excess of 1000 K would be required to attain a higher equilibrium partial pressure of H_2S (> 100 ppm). As a result, we did not pursue this approach of catalyst reactivation.

Oxidative removal of surface sulfur on Cu by conversion to SO_2 appears more promising. On the (110)Cu surface, the removal of surface sulfur by reaction with oxygen has been studied[1] at elevated temperatures ($\sim$ 900 K). From these results, a time interval of about 30 min would be required to remove 1/2 monolayer of sulfur at an oxygen pressure of 1 atm and 500 K. At these temperatures and exposure times, sulfur removal would entail conversion to copper oxide.

To assess this oxidative regeneration process, we measured by N_2O-titration the surface area of the copper component of reduced catalyst C79-1 (see Section 3) before sulfidation, after sulfidation, and after exposure to oxygen and rereduction in hydrogen. The catalyst was sulfidized by exposing it to pulses of H_2S (1000 ppm) in H_2 at room temperature. The catalyst was reactivated by raising the temperature of the sample to 473 K in a stream of oxygen (20 vol% in He) over a period of 30 min at a total pressure of 1 atm. Subsequently the catalyst was reduced in H_2 at 473 K, and then cooled in He to 300 K before being exposed to pulses of N_2O. All these measurements were done at atmospheric pressure.

Significant changes in copper surface area resulted from sulfidation-oxidation-reduction (Table 4-3). The surface site density of copper increased markedly. During a subsequent cycle, the sulfur-poisoned

sample was partially reactivated. These results suggest that it is feasible to remove sulfur from the catalyst by oxidation.

These data and the results of AES studies (Section 2) indicate that during exposure of the catalyst to H_2S the surface is enriched with copper. This enrichment process is accompanied by catalyst re-construction, since we observe no further copper enrichment during the second regeneration cycle. Whether the reactivated catalyst exhibits methanol synthesis activity remains to be examined. If the copper forms a solid solution with zinc oxide, and this solution is irreversibly modified during sulfidation, then the catalytic activity for methanol synthesis may not be restored.

4.6   Conclusions

* Sulfur chemisorption on Fe and Cu has a considerable exothermic heat of surface segregation with respect to the most stable bulk sulfide, so that catalyst poisoning can occur at H_2S concentration well below the equilibrium concentration of bulk sulfides.

* Regeneration of sulfur-poisoned Fe and Cu catalysts by reaction with pure hydrogen is not practical due to the very low equilibrium H_2S partial pressure at temperatures below which sintering is appreciable.

* Regeneration of sulfur poisoned Cu catalysts by reaction with oxygen is feasible. However, formation of metal oxide layer and reconstruction may not restore catalyst activity.

* Adsorbed sulfur prefers high coordination sites, thereby probably preempting sites required for methanol synthesis intermediates.

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● As the activity of adsorbed sulfur increases, surface
  reconstruction can occur, creating a two-dimensional
  surface compound, a precursor to bulk sulfide. Such a
  surface compound may exhibit drastically altered
  methanol synthesis activity relative to the clean or
  partially sulfur-covered surface.

4.7   References

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Table 4-1

SURFACE STRUCTURES OF ADSORBED SULFUR

Surface	Structures*		Ref. No.
	Adsorbate	Surface Compound	
Fe(001)	C(2x2)	C(22x2) (18x2) (14x2) (10x2)	8, 9, 10
Cu(001)	C(2x2) P(2x1)	$\sqrt{17} \times \sqrt{17}$	11 7
Cu(111)	$\sqrt{3} \times \sqrt{3}$ R 30°	$\sqrt{7} \times \sqrt{7}$	11
Cu(110)	C(2x2) split spots	P(3x2)	1,11

*As determined by low energy electron diffraction (LEED)

Table 4-2

HEAT OF FORMATION OF SURFACE AND
BULK METAL SULFIDES AT 1000 K

Metal	Surface	ΔH_f*	E_B†	Bulk Phase	E_B†	ΔH_{seg}*
Cu	polycryst	-19	86	Cu_2S	79	-7
Fe	supported	-33	99	FeS	84	-15
Ag	(110) (111), (001)	-20 -12	87 78	Ag_2S	67	-20 -11

*ΔH_f, ΔH_{seg}, and E_B have units kcal per mole sulfur atoms.

†E_B represents the binding energy of monatomic sulfur (gas) to the corresponding surface or bulk phase.

Table 4-3

OXIDATIVE REACTIVATION OF SULFUR
POISONED METHANOL SYNTHESIS CATALYST[a]

Catalyst Condition	Oxygen Chemisorbed[b] (g atom x 10^7)	Fraction of Initial Cu Surface Area (%)
(I) Freshly reduced	6.3	100
Sulfided[c]	5.0	79
Reactivated	12.3	195
(II) Freshly reduced[d]	11.0	100
Sulfided[e]	5.3	48
Reactivated	7.0	64

[a] 0.020 grams of catalyst CCI-C79-1.

[b] By exposure to N_2O pulses (cf. Section 3).

[c] Total H_2S exposure = 0.49 x 10^{-6} moles.

[d] Second reactivation cycle on same catalyst sample.

[e] Total H_2S exposure = 1.96 x 10^{-6} moles.

FIGURE 4-1   IRON-SULFUR PHASE DIAGRAM
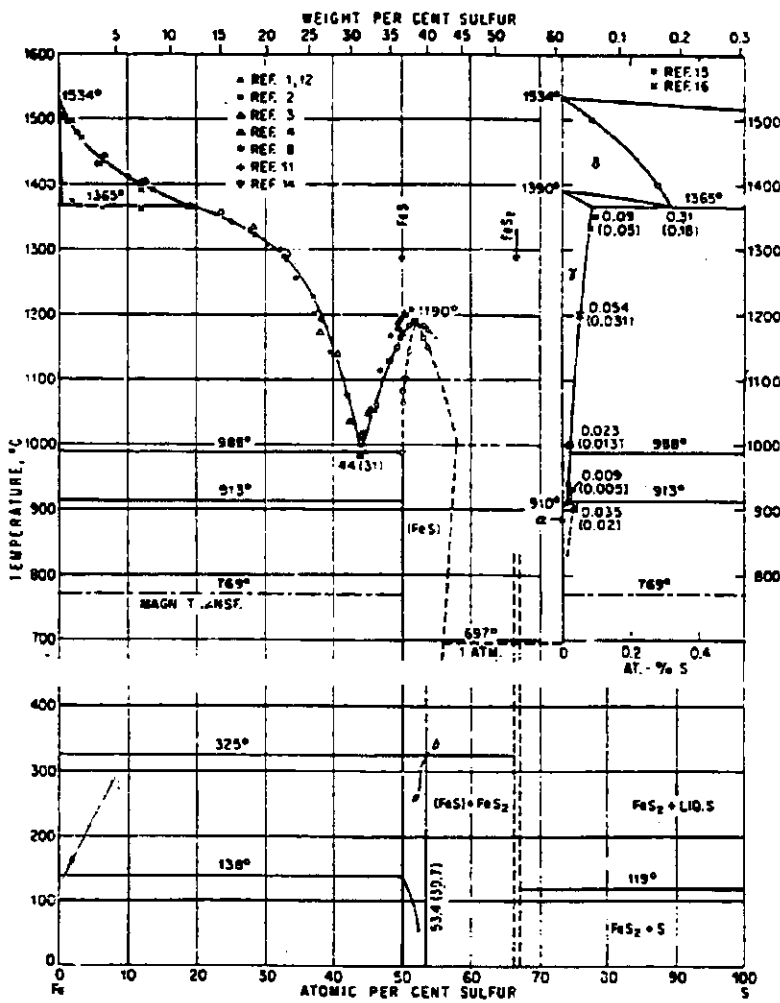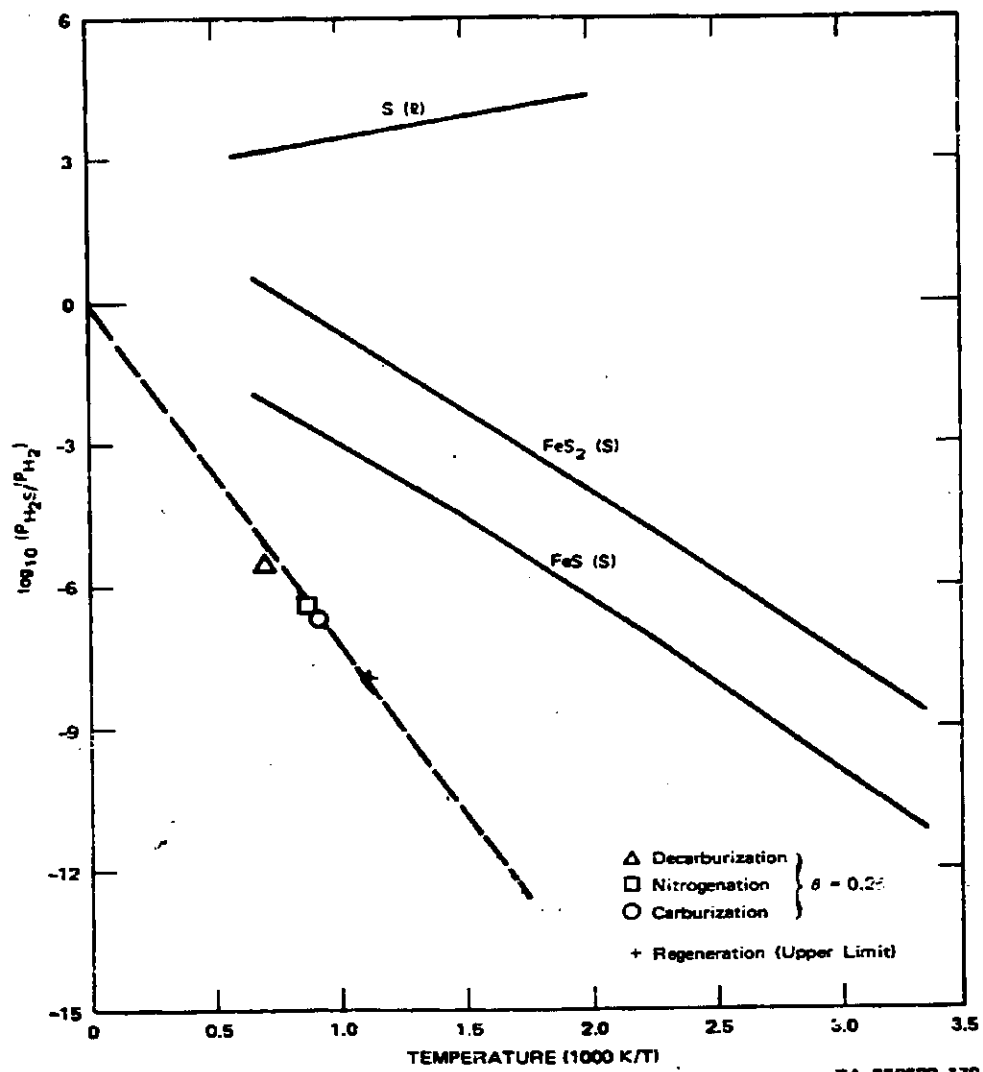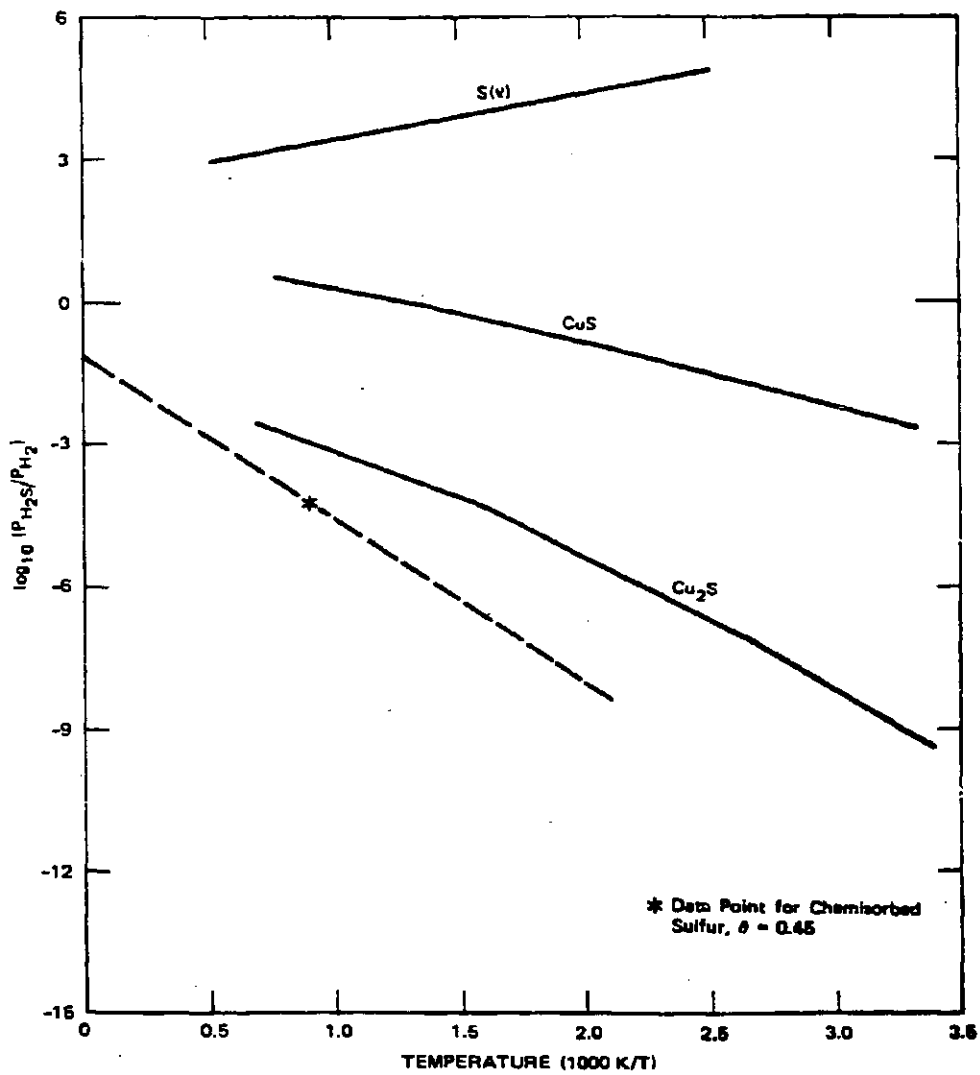
SOURCE: Reference 2.

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FIGURE 4-2   IRON-SULFUR EQUILIBRIUM

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FIGURE 4-3 COPPER-SULFUR EQUILIBRIUM

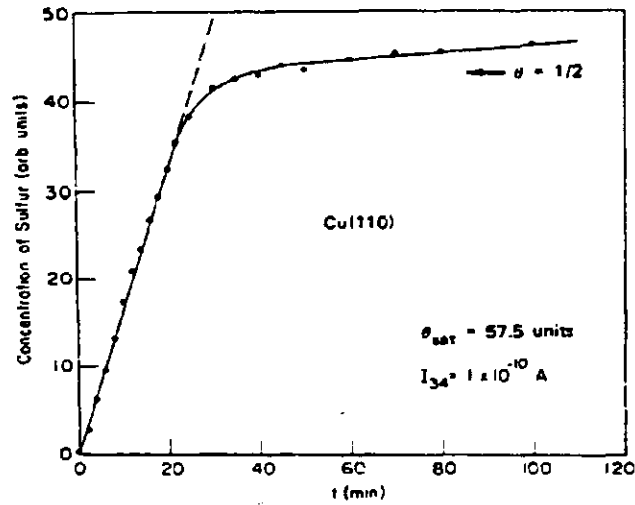$H_2S(g) \rightleftharpoons H_2S(ads)$ MOLECULAR ADSORPTION

$H_2S(ads) \rightleftharpoons HS(ads) + H$
$HS(ads) \rightleftharpoons S(ads) + H$ DISSOCIATION

$S(ads) \longrightarrow MeS(ads)$ RECONSTRUCTION

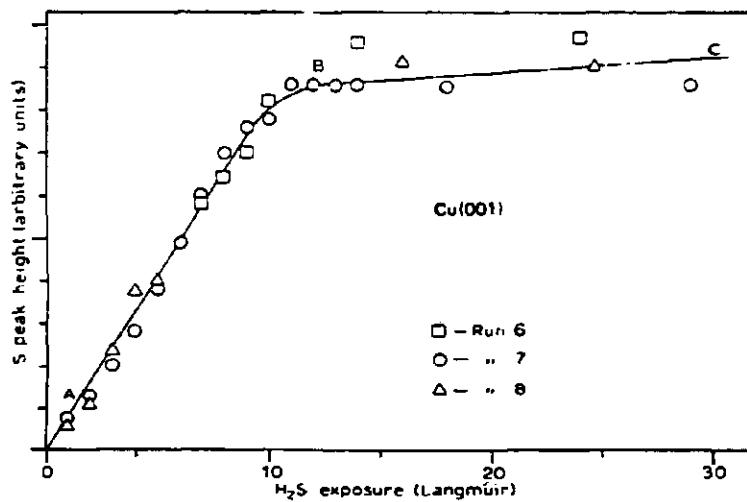$MeS(ads) \longrightarrow MeS(bulk)$ INCORPORATION

TA-350522-172

FIGURE 4-4 HYDROGEN SULFIDE/METAL INTERFACE

SOURCE: Reference 1.

(a) CONCENTRATION OF ADSORBED SULFUR AS A FUNCTION OF TIME AT ROOM
TEMPERATURE AND CONSTANT PARTIAL PRESSURE OF H_2S

SOURCE: Reference 7.

(b) DERIVATIVE PEAK-TO-PEAK HEIGHT OF THE S (150 eV) AUGER PEAK AS A
FUNCTION OF THE EXPOSURE OF Cu(001) TO $H_2S(g)$ AT 295 K

TA-350522-173

FIGURE 4-5   HYDROGEN SULFIDE ADSORPTION ON Cu(110) AND Cu(001)