



## Chemical kinetics in the gas phase pulse radiolysis of hydrogen sulfide systems

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RISØ-M-2216

CHEMICAL KINETICS IN THE GAS PHASE  
PULSE RADIOLYSIS OF HYDROGEN SULFIDE SYSTEMS

Ole John Nielsen

Abstract. Formations and decays of HS and HS<sub>2</sub> radicals in the gas phase pulse radiolysis of pure H<sub>2</sub>S, H<sub>2</sub>S/Ar and H<sub>2</sub>S/H<sub>2</sub> systems have been followed directly by kinetic spectroscopy. The literature on the subject is reviewed and a complete reaction scheme is discussed. Computer-simulations have been used to check the validity of the proposed mechanisms. Rate constants  $k_{\text{HS}+\text{HS}} = (2.0 \pm 0.4) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$  and  $k_{\text{H}+\text{H}_2\text{S}} = (6.0 \pm 1.2) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  have been determined. The reaction of HS radicals with S atoms is responsible for the HS<sub>2</sub> formation. Pseudo-first order rate constants for reactions of HS with 1,3 butadiene, ethylene and molecular oxygen are reported.

INIS descriptors. ABSORPTION SPECTROSCOPY, CHEMICAL REACTION KINETICS, EXPERIMENTAL DATA, GASES, HYDROGEN SULFIDES, PULSED IRRADIATION, RADIATION CHEMISTRY, RADIOLYSIS, REVIEWS, SIMULATION.

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## PREFACE

This report presents some of the work done by the author during his first year at Risø National Laboratory. The author has tried to make this report short and easily comprehensible.

All of the work has been carried out at the Accelerator, Chemistry and Computer Department of Risø National Laboratory guided by civ.ing. Palle Pagsberg. The author wishes to thank him for his great support and interest in the work.

The author owes great thanks to all the staff at the Chemistry Department Risø for creating such a stimulating environment, furthermore he thanks Risø for supplying the facilities and for financial support.



## 1. INTRODUCTION

When a material is subjected to high energy radiation (e.g.  $\alpha$ -particles,  $\gamma$ -radiation or fast electrons), the primary products are electrons, positive ions and excited atoms and/or molecules. Interaction (e.g. relaxation, combination and decomposition) among these primary products may produce radicals, atoms and molecules, which in turn react to give final stable products.

Pulse radiolysis (irradiations by a short pulse of fast electrons) combined with some kind of transient detection method yields information about the kinetics of different chemical systems. The information obtained by pulse radiolysis is useful in many areas, supplementary and often complementary to information obtainable by other techniques. Recently the pulse radiolysis studies of gases have been excellently reviewed by Sauer (1976).

Only four gas phase pulse radiolysis studies on hydrogen sulfide systems are reported in literature (Willis et al., 1971a; Willis et al., 1971b; Boyd et al., 1973; Perner and Franken, 1969). In three of these studies (Willis et al., 1971a; Willis et al., 1971b; Boyd et al., 1973) the hydrogen yield, absolute dosimetry and the effect of  $SF_6$  and sulfur as electron scavengers in the primary ionic processes were investigated. Only one gas phase pulse radiolysis study (Perner and Franken, 1969) has dealt with the kinetics of the non-ionic secondary reactions involving radicals, atoms and molecules. The transient species HS,  $HS_2$  and  $S_2$  were monitored by kinetic UV/VIS-spectroscopy and rate constants of reaction I and II were evaluated





Determining  $k_I$  involves the usual problem of estimating the initial concentration of HS-radicals just after the pulse. As the extinction coefficient for the observed HS-absorptionband is unknown, Perner and Franken's solution of this problem depends on the  $G(H_2)$  value, where G is the number of molecules produced per 100 eV energy absorbed. Their  $G(H_2)$  value was obtained by assuming a special distribution of the  $H_2$  yield on specified reactions and on the basis of  $G(N_2) = 10.0$  in  $N_2O$ . However, the fact that 12.4 seems to be the correct  $G(N_2)$  value in case of Febetron dose rates (Willis et al., 1968; Willis et al., 1971a) suggests that  $G(H_2)$  should have been increased. With these dubious assumptions the obtained value of  $k_I = (3.2 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  is probably not very reliable. Perner and Franken (1969) also investigated  $H_2S/Ar$  and  $H_2S/Xe$  mixtures. As no complete reaction scheme was set up I have made a more exhaustive and hopefully more elucidating investigation including experiments on pure  $H_2S$ ,  $H_2S/Ar$ ,  $H_2S/He$ ,  $H_2S/H_2$  mixtures and experiments with electron and radical scavengers.

All reactants and reaction products needed to be considered in all reported experiments are listed in table 1 together with the heat of formation,  $H_f^{\circ} 298$ . The values of  $H_f^{\circ} 298$  are taken from Benson (1978) and references therein.

Table 1.  $H_f^{\circ} 298$  in kcal/mole for the considered reactants and products

H	52.1
$H_2S$	-4.9
HS	35
$H_2S_2$	3.8
S	66.3
$S_2$	30.7
$HS_2$	22.1
$H_2$	0
$S_4$	31
$HS_3$	25.3
$H_2S_3$	7.4
$H_2S_4$	10.6

To be sure to consider all imaginable reactions the quadratic array in fig. 1 is set up. In table 2 all these reactions are listed with the standard enthalpy change. The numbering from table 2 is used throughout this report.

Table 2. Considered reactions and the standard enthalpy change in kcal/mole

(11)	$H + H$	$\rightarrow H_2$	-104.2
(12)	$H + H_2S$	$\rightarrow H_2 + HS$	- 12.3
(13a)	$H + HS + M$	$\rightarrow H_2S$	- 92.0
(13b)	$H + HS$	$\rightarrow H_2 + S$	- 20.8
(14a)	$H + H_2S_2$	$\rightarrow H_2 + HS_2$	- 33.8
(14b)		$\rightarrow HS + H_2S$	- 25.8
(15)	$H + S + M$	$\rightarrow HS$	- 83.4
(16a)	$H + S_2 + M$	$\rightarrow HS_2$	- 60.7
(16b)	$H + S_2$	$\rightarrow HS + S$	+ 18.5
(17a)	$H + HS_2 + M$	$\rightarrow H_2S_2$	- 70.4
(17b)	$H + HS_2$	$\rightarrow H_2 + S_2$	- 43.5
(17c)		$\rightarrow HS + HS$	- 4.2
(23a)	$H_2S + HS$	$\rightarrow H_2 + HS_2$	- 8.0
(23b)		$\rightarrow H_2 + H + S_2$	+ 52.7
(25a)	$H_2S + S + M$	$\rightarrow H_2S_2$	- 57.6
(25b)	$H_2S + S$	$\rightarrow H_2 + S_2$	- 30.7
(25c)		$\rightarrow HS + HS$	+ 8.6
(25d)		$\rightarrow H + HS_2$	+ 12.8
(26)	$H_2S + S_2$	$\rightarrow ?$	
(27)	$H_2S + HS_2$	$\rightarrow ?$	
(28)	$H_2S + H_2$	$\rightarrow ?$	
(33a)	$HS + HS + M$	$\rightarrow H_2S_2$	- 66.2
(33b)	$HS + HS$	$\rightarrow H_2S + S$	- 8.6
(33c)		$\rightarrow H_2 + S_2$	- 39.3
(33d)		$\rightarrow H + HS_2$	+ 4.2
(34)	$HS + H_2S_2$	$\rightarrow H_2S + HS_2$	- 21.6
(35a)	$HS + S + M$	$\rightarrow HS_2$	- 79.2
(35b)	$HS + S$	$\rightarrow H + S_2$	- 18.5

cont.

(36a)	$\text{HS} + \text{S}_2 + \text{M} \rightarrow \text{HS}_3$	- 40.4
(36b)	$\text{HS} + \text{S}_2 \rightarrow \text{HS}_2 + \text{S}$	+ 22.7
(37a)	$\text{HS} + \text{HS}_2 \rightarrow \text{H}_2\text{S} + \text{S}_2$	- 31.3
(37b)	$\text{HS} + \text{HS}_2 \rightarrow \text{H}_2\text{S}_2 + \text{S}$	+ 13.0
(38)	$\text{HS} + \text{H}_2 \rightarrow \text{H}_2\text{S} + \text{H}$	+ 12.2
(45a)	$\text{H}_2\text{S}_2 + \text{S} + \text{M} \rightarrow \text{H}_2\text{S}_2$	- 62.7
(45b)	$\text{H}_2\text{S}_2 + \text{S} \rightarrow \text{HS} + \text{HS}_2$	- 13.0
(45c)	$\rightarrow \text{S}_2 + \text{H}_2\text{S}$	- 44.3
(55)	$\text{S} + \text{S} + \text{M} \rightarrow \text{S}_2$	-101.9
(56)	$\text{S} + \text{S}_2 + \text{M} \rightarrow \text{c-S}_3$	- 64.5
(57)	$\text{S} + \text{HS}_2 + \text{M} \rightarrow \text{HS}_3$	- 63.1
(58)	$\text{S} + \text{H}_2 + \text{M} \rightarrow \text{H}_2\text{S}$	- 71.2
(66)	$\text{S}_2 + \text{S}_2 + \text{M} \rightarrow \text{c-S}_4$	- 30.4
(67)	$\text{S}_2 + \text{HS}_2 + \text{M} \rightarrow \text{HS}_4$	
(77a)	$\text{HS}_2 + \text{HS}_2 + \text{M} \rightarrow \text{H}_2\text{S}_4$	- 33.6
(77b)	$\text{HS} + \text{HS}_2 + \text{M} \rightarrow \text{H}_2\text{S}_2 + \text{S}_2$	- 9.7
(77c)	$\rightarrow \text{H}_2 + \text{S}_2 + \text{S}_2$	+ 17.2
(78)	$\text{HS}_2 + \text{H}_2 \rightarrow \text{H}_2\text{S}_2 + \text{H}$	+ 33.8

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## 2. EXPERIMENTAL

The gas samples were irradiated with 2 MeV electrons from a Febetron 705 B field emission accelerator with a pulse duration of 30 nsec and a maximum current of 3000 Amp. The gas mixtures were prepared on a conventional all-glass vacuum line and transferred to a 1 liter stainless steel cell adopted from Gordon et al. (1971) equipped with a set of conjugate mirrors as described by White (1942). This arrangement allows multiple passes of the analyzing light beam through the sample cell. Most experiments were carried out using twelve traversals corresponding to an optical path length of 120 cm. A Varian 150 W high-pressure Xenon lamp with aluminized parabolic reflector and sapphire window provided an analyzing light beam of high brightness in the ultraviolet region. A Hilger and Watts 1 meter

grating spectrometer was used with a 1200 grooves/mm grating blazed at 3000 Å to obtain high efficiency in the spectral range of interest and a reciprocal dispersion of 8 Å/mm. The light intensity passing the exit slit was monitored using a Hamamatsu R928 photomultiplier coupled to a current input operational amplifier with adjustable off-set representing 100% light transmission. The transient signals were sampled and digitized in a transit recorder and transferred to a minicomputer. Here the raw-data may be transformed into absorbance versus time curves or other relevant plot types under control from a teletype. Simple first and second order plots can be inspected on a display screen and plotted on a X-Y recorder. Selected raw-data are stored on magnetic tape for further processing on a large central computer where complex kinetic curves can be compared with simulated models. The experimental set-up is shown in figs. 2 and 3 and described in detail by Hansen et al. (1979).

Dosimetry was performed by monitoring the formation of ozone in 1 atm of oxygen. The in situ measurement of ozone offers an advantage for systems where the electron beam flux and the dose distribution are non-uniform. The average  $O_3$  absorbance at 2550 Å, measured with an optical path length of 120 cm and a band pass of 8 Å, was 0.626. Using  $G(O_3) = 12.8$  (Willis and Boyd, 1976) and the extinction coefficient  $\epsilon(O_3) = 3067 \text{ M}^{-1}\text{cm}^{-1}$  determined by Inn and Tanaka (1953) we calculate a maximum dose of 116 krad per irradiation pulse corresponding to the unattenuated electron beam. Assuming a stopping power of  $H_2S$  equal to that of  $O_2$  the doses in all mixtures can be calculated using the relative stopping powers quoted by Willis et al. (1968), and Bailly and Brown (1959). The irradiation doses could be varied using stainless steel diaphragms as electron beam attenuators.

Care has been taken to check the applicability of the Lambert-Beer law  $A = \epsilon \cdot l \cdot c$ , where  $A$  is the absorbance,  $\epsilon$  the extinction coefficient,  $l$  the optical path length and  $c$  is the concentration. When the used band-pass is wider than the spectral features of the transient absorption bands one has to work with a modified version of the Lambert-Beer relation,  $A = (\epsilon \cdot l \cdot c)^n$ .

Here  $n$  is a fractional power. Applicability of this relation has been investigated in detail by Bourene et al. (1974). The value of  $n$  depends on the line shape and the spectrometer slit setting and must be determined experimentally.

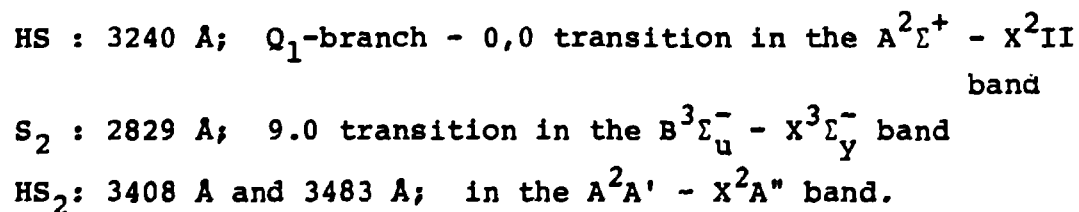
Because of the rather complex reaction system we found it necessary to make use of simulated kinetic models in order to evaluate the absolute rate constants for the most significant reactions involved. A computerprogram, CHEMSIMUL, developed by Ole Lang Rasmussen (1978) was applied. As input, this program accepts reaction schemes in the usual chemical notation, viz.,



etc.

The program translates the "chemical equations" into a pertinent set of differential equations which is solved by numerical integration after specification of initial conditions, G-values and irradiation dose. The effect of parameter variation can be studied by a semi-interactive procedure using a graphical computer terminal.

Formations and decays of HS, HS<sub>2</sub> and S<sub>2</sub> were studied by monitoring absorption bands at the following wavelengths:

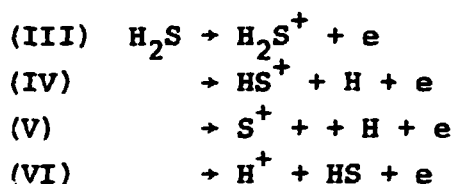


The value of  $n$  in the modified version of the Lambert-Beer relation has in each case been determined by plotting the logarithm of the maximum absorbance vs. the logarithm of the dose, using different doses.

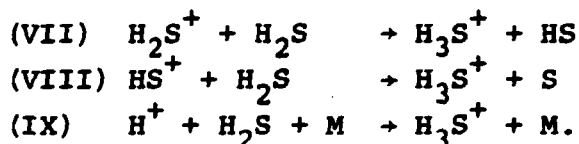
### 3. RESULTS AND DISCUSSIONS

#### 3.1. The pure H<sub>2</sub>S-system

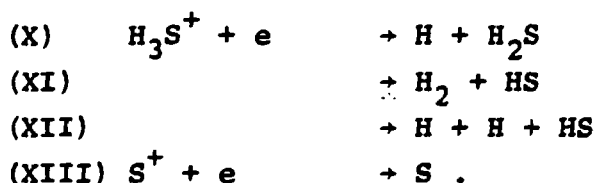
For the sake of completeness the primary ionic processes (also occurring in mixtures) should be mentioned here. From mass-spectrometric studies (Cornu and Massot, 1966) the predominant ions in the radiolysis of H<sub>2</sub>S are H<sub>2</sub>S<sup>+</sup> (52%), HS<sup>+</sup> (22%), S<sup>+</sup> (23%) and H<sup>+</sup> (3%) formed in reactions such as (III)-(VI):



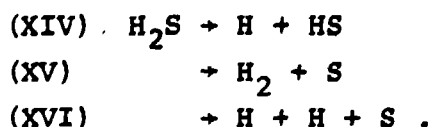
further reactions can be (VII)-(IX):



The fate of sulfur is not clear. Neutralization processes can be (X)-(XIII):

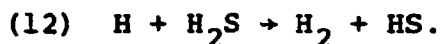


The result of all these ionic and neutralization processes can be described as (XIV)-(XVI):



The relative importance of these reactions are unknown, but reaction (XV) must be very improbable. H atoms are removed

very rapidly in pure  $H_2S$  by reaction 12:



Therefore the only species present in the pure  $H_2S$  system 1  $\mu$ sec after the pulse are  $H_2S$ ,  $H_2$ ,  $HS$  and  $S$ .  $H_2$  will be present in an amount equal to  $[HS] + 1/2[S]$ . A few experiments on the pure  $H_2S$  system have been performed.  $HS$  absorption has been followed for 400  $\mu$ sec in 760 and 380 torr pure  $H_2S$  and for 20  $\mu$ sec in 760 torr  $H_2S$ .  $HS_2$  absorption was followed for 400  $\mu$ sec in 780 torr  $H_2S$ . Unfortunately the  $HS$  absorption in 380 and 760 torr  $H_2S$  were recorded with different slit widths, hence both  $\epsilon$ ,  $n$  and  $c_0$  ( $c_0$  is the start-concentration) are different in these two experiments. In figs. 4 and 5 the experimental curves are shown.

The absence of a typical "second order tail" in fig. 4 indicates contributions from one or more side reactions competing with the simple second order decay (33a-33c). The low residual absorption lasting for 400  $\mu$ sec might be due to spectral overlap from another species. This possibility was checked by monitoring the transient signals above and below the characteristic  $HS$  absorption.

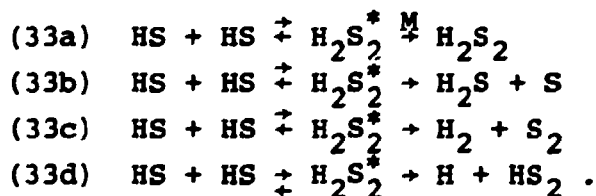
A prompt continuous absorption amounts to approximately 10% of the  $HS$  maximum absorbance. Attempts to fit the experimental data (with and without subtraction of the constant absorbance) to simple first or second order kinetics, were unsuccessful. The decay of both  $HS$  and  $HS_2$  must be of mixed order, predominantly second order.

The exothermic reactions given in table 3 may all contribute to the removal of  $HS$  in the pure  $H_2S$ -system. Reaction 23a has not been taken into account elsewhere, but will be considered here as a possible source of  $HS_2$ . Reactions 33 are definitely taking place since a second order "tail" is observed.

Table 3. HS removal reactions in the pure H<sub>2</sub>S system

	ΔH kcal/mole
(13a) H + HS + M → H <sub>2</sub> S	-92.0
(13b) H + HS → H <sub>2</sub> + S	-20.8
(23a) H <sub>2</sub> S + HS → H <sub>2</sub> + HS <sub>2</sub>	- 8.0
(23b) H <sub>2</sub> S + HS → H <sub>2</sub> + H + S <sub>2</sub>	+52.7
(33a) HS + HS + M → H <sub>2</sub> S <sub>2</sub>	-66.2
(33b) HS + HS → H <sub>2</sub> S + S	- 8.6
(33c) HS + HS → H <sub>2</sub> + S <sub>2</sub>	-39.3
(33d) HS + HS → H + HS <sub>2</sub>	+ 4.2
(34) HS + H <sub>2</sub> S <sub>2</sub> → H <sub>2</sub> S + HS <sub>2</sub>	-21.6
(35a) HS + S + M → HS <sub>2</sub>	-79.2
(35b) HS + S → H + S <sub>2</sub>	-18.5
(36a) HS + S <sub>2</sub> + M → HS <sub>3</sub>	-40.4
(36b) HS + S <sub>2</sub> → HS <sub>2</sub> + S	+22.7
(37a) HS + HS <sub>2</sub> → H <sub>2</sub> S + S <sub>2</sub>	-31.3
(37b) HS + HS <sub>2</sub> → H <sub>2</sub> S <sub>2</sub> + S	+13.0
(38) HS + H <sub>2</sub> → H <sub>2</sub> S + H	+12.2

The reaction, HS + HS → products, can be described as proceeding through an activated intermediate, H<sub>2</sub>S<sub>2</sub><sup>\*</sup>, which might be stabilised at large pressures or decompose:

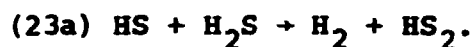


Reaction (33d) is endothermic and no evidence for this recombination route has been presented. In the work of Bradley et al. (1973) the value of  $k_{33b}$  was found to be  $7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Perner and Franken (1969) assume that reaction (33c) is the dominating source of the S<sub>2</sub>.



However, an alternative reaction (25),  $\text{H}_2\text{S} + \text{S} \rightarrow$ , might produce  $\text{S}_2$  via another activated  $\text{H}_2\text{S}_2^{**}$  intermediate. In the OH recombination the reaction analogous to 33b is dominating (Fair and Thrush, 1969). Determination of  $k_{33b}$  involves the problem of estimating the initial HS concentration. Assuming the  $G(\text{HS})$  value equal to that of  $\text{O}_2$ , the initial HS concentration is calculated to be  $c_0(\text{HS}) = 1.04 \times 18.6 \times 120 \times 10^{-9} = 2.3 \mu\text{M}$ . From the experimental decay half-lives the second order rate constant can be calculated  $\tau = \frac{1}{c_0 \cdot k} \Rightarrow k_{33b} \sim 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .

The higher value of  $k_{33b}$  obtained in this and the work of Perner and Franken (1969) compared to that of Bradley et al. (1973) suggests additional removal of HS by e.g. reaction 23a:



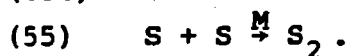
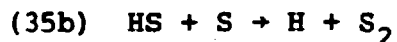
This reaction may also explain the fast appearance of  $\text{HS}_2$  in our experiments. All potential  $\text{HS}_2$  source reactions are listed in table 4. If reaction 23a is the source reaction for  $\text{HS}_2$  then  $\tau(23a) = \ln 2 / (k_{23a} [\text{H}_2\text{S}]_0)$ , i.e. the formation half-life of  $\text{HS}_2$  decreases with increasing concentration of  $\text{H}_2\text{S}$ . This possibility will be investigated in the mixed  $\text{H}_2\text{S}/\text{Ar}$  system. It has not been possible to explain the difference in  $\text{HS}_2$  formation half-life in these and in the experiments of Perner and Franken (1969).

Tabel 4.  $\text{HS}_2$  source reactions

(14a)	$\text{H} + \text{H}_2\text{S}_2$	$\rightarrow \text{HS}_2 + \text{H}_2$
(16a)	$\text{H} + \text{S}_2 + \text{M}$	$\rightarrow \text{HS}_2$
(23a)	$\text{HS} + \text{H}_2\text{S}$	$\rightarrow \text{HS}_2 + \text{H}_2$
(25d)	$\text{H}_2\text{S} + \text{S}$	$\rightarrow \text{HS}_2 + \text{H}$
(33d)	$\text{HS} + \text{HS}$	$\rightarrow \text{HS}_2 + \text{H}$
(34)	$\text{HS} + \text{H}_2\text{S}_2$	$\rightarrow \text{HS}_2 + \text{H}_2\text{S}$
(35a)	$\text{HS} + \text{S} + \text{M}$	$\rightarrow \text{HS}_2$
(36b)	$\text{HS} + \text{S}_2$	$\rightarrow \text{HS}_2 + \text{S}$
(45)	$\text{H}_2\text{S}_2 + \text{S}$	$\rightarrow \text{HS}_2 + \text{HS}$

If the  $k_{33b}$  value from Bradley et al. (1973) and the  $c_o(\text{HS}) = 2.3 \mu\text{M}$  are assumed to be valid it is possible to find a value of  $k_{23a}$  reproducing the experimental HS decay and  $\text{HS}_2$  formation. A computer simulation taking  $k_{23a} = 5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  gives HS half-life 18  $\mu\text{sec}$ , which is in good agreement with the experimental value of approximately 17  $\mu\text{sec}$ .

Since S atoms undoubtedly are among the primary products it is seen from table 4 that reaction 35a, which is 10 times more exothermic than reaction 23a, should be considered as a possible  $\text{HS}_2$  source reaction. Besides reaction 35a there will be two other competitive sulfur consuming reactions:

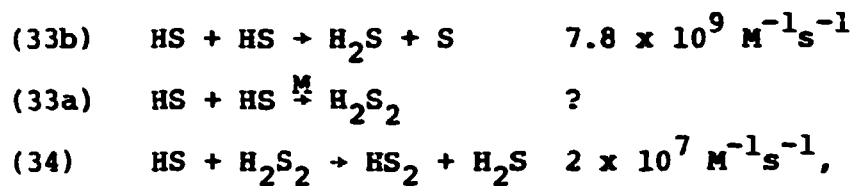


There has been only one determination of  $k_{35b}$  by Mihelcic and Schindler (1970), who found the value of  $k_{35b}$  to be approximately  $3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ . The gas-phase recombination reaction (55) of sulfur atoms is not well understood and there is a large scatter in the published values of the rate constant  $k_{55}$ . The reported values of  $k_{55}$  lie in the range  $10^{12} \times [\text{M}]$  to  $10^{15} \times [\text{M}]$  (Howgate and Barr, 1973; Basco and Pearson, 1967), where  $[\text{M}]$  is the concentration of third bodies.

The only two reactions considered responsible for the  $\text{HS}_2$  removal are reaction 37 and 77.  $k_{37}$  has to be greater than  $10^{11} \text{ M}^{-1}\text{s}^{-1}$  to reproduce the  $\text{HS}_2$  decay. This value seems unrealistic. Taking  $k_{77} = 2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$  the  $\text{HS}_2$  decay are reproduced satisfactorily.

The experimental data on the pure  $\text{H}_2\text{S}$  system are too few to establish a unique complete kinetic model.

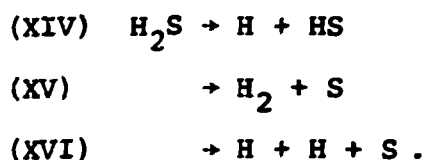
Perner and Franken (1969) proposed another  $\text{HS}_2$  formation mechanism:



where  $k_{34}$  is determined in the work of Perner and Franken (1969). No value of  $k_{33a}$  can reproduce the  $\text{HS}_2$  formation observed experimentally.

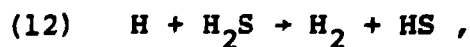
### 3.2. The $\text{H}_2\text{S}/\text{Ar}$ system

In pulse radiolysis of  $\text{H}_2\text{S}/\text{Ar}$  mixtures, energy will be absorbed by  $\text{H}_2\text{S}$  and Ar according to relative stopping powers and relative concentrations. Rare gas sensitized radiolysis of  $\text{H}_2\text{S}$  has been investigated in detail (Jowko et al., 1977; Foryś et al., 1976; Ahmad et al., 1972; Jezierska and Foryś, 1972; Jezierska, 1971). As in the pure  $\text{H}_2\text{S}$  system the result of the primary reactions will be:



Since no molecular hydrogen was observed among the primary products in the experiments of Jezierska and Foryś (1972) the very improbable reaction XV is neglected.

Compared to the pure  $\text{H}_2\text{S}$  case reaction 12:



will remove H atoms and produce HS radicals more slowly because of the smaller  $\text{H}_2\text{S}$  concentration. In fig 6 is shown the variation of HS absorbance in the first 40  $\mu\text{sec}$  after the pulse in 2 torr  $\text{H}_2\text{S}$  with Ar to 1 atm.

If HS removal is neglected the HS formation should consist of a prompt component from reaction XIV and a slower rising component from reaction 12 (see fig. 7). This is exactly what is seen in fig. 6.

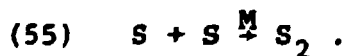
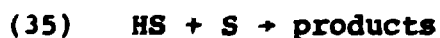
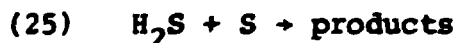
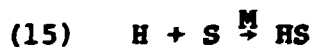
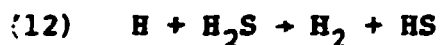
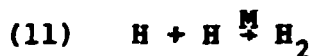
In fig. 8 some typical observed maximum HS absorbances are plotted for different partial pressures of H<sub>2</sub>S backed up with Ar to 1 atm. The increasing HS yield with higher H<sub>2</sub>S partial pressures should cause HS to be removed faster by reaction 33b,



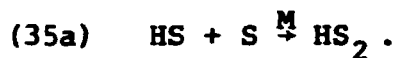
which is definitely taking place. This assumption is in good agreement with the experimental data.

One of the main problems is to determine the relative importance of reaction XIV and XVI. To find a compound scavenging only H atoms and not HS radicals would be a convenient aid in solving this problem. However, in all experiments with H<sub>2</sub>S partial pressures from 1 to 10 torr the ratio between the slower and the prompt rising component of the HS absorbance seems to be constant, around 1:2.

From the complete reaction scheme (table 2) it seems necessary to consider the following reactions:



Reaction 23a and 35a have been proposed as HS<sub>2</sub> source reactions:



The observed HS<sub>2</sub> maximum absorbance for different H<sub>2</sub>S partial pressures is plotted in fig. 9. Experimentally it is found that the rate of formation and the yield of HS<sub>2</sub> are independent of the H<sub>2</sub>S partial pressures. Likewise, the half-life of the HS decay remains independent of [H<sub>2</sub>S]<sub>0</sub>. On this basis it is concluded that reaction 23a contributes only to a minor extent, if at all, to the formation of HS<sub>2</sub>.

### 3.3. The H<sub>2</sub>S/H<sub>2</sub>-system

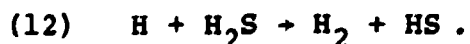
No pulse radiolysis studies of H<sub>2</sub>S/H<sub>2</sub> mixtures have been reported in literature.

Here, as in the H<sub>2</sub>S/Ar-system, the energy will be absorbed by H<sub>2</sub>S and H<sub>2</sub> according to their relative stopping powers and relative concentrations. Assuming stopping power to be proportional to density, the relative stopping powers of H<sub>2</sub> and H<sub>2</sub>S will be 2 to 34. For partial pressures of H<sub>2</sub>S less than 25 torr and H<sub>2</sub> to 1 atm, more than 75% of the energy will then be absorbed by H<sub>2</sub> and the primary consequence is:



#### 3.3.1. Formation of HS

The produced H-atoms will be removed by reaction 12 to produce H<sub>2</sub> molecules and HS radicals:



HS-radical absorbance has been observed after radiation of mixtures of 0.1 to 100 torr H<sub>2</sub>S with H<sub>2</sub> to 1 atm. Observation-

time-intervals ranged from 20 to 400  $\mu\text{sec}$ . Two sets of experiments using different slit widths were carried out. In fig. 10 is shown recorded HS-absorbance in the first 40  $\mu\text{sec}$  after the pulse in 5 torr  $\text{H}_2\text{S}$  with  $\text{H}_2$  to 1 atm. All experimental data are given in tables 5 and 6.

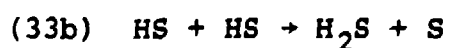
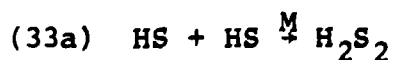
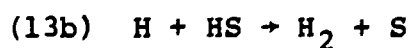
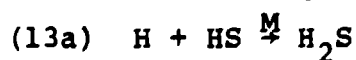
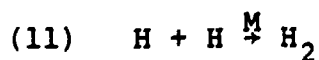
Table 5. Experimental data from the  $\text{H}_2\text{S}/\text{H}_2$ -system

$p(\text{H}_2\text{S})$ in torr	$100 \times A_{\text{max}}$	decay half- life in $\mu\text{sec}$ .	$10^5 \times 1/(\tau_d \cdot A_m)$
5	3.31	63	4.8
5	3.73	83	3.3
10	4.79	64	3.1
10	4.78	70	2.9
15	3.51	60	4.7
15	4.25	64	3.7
20	4.57	63	3.5
20	4.49	64	3.5
25	5.04	56	3.6
25	5.07	64	3.8
50	5.09	57	3.4
50	5.51	58	3.1
100	7.17	45	3.1
100	5.96	50	3.3

Table 6. Experimental data from the H<sub>2</sub>S/H<sub>2</sub>-system

p(H <sub>2</sub> S) in torr	100 x A <sub>max</sub>	formation half- life in μsec.	10 <sup>9</sup> x ln2/(τ <sub>f</sub> ·c <sub>0</sub> )
0.5	2.2	13.5	1.87
0.5	1.9	14.0	1.80
1.0	2.6	6.2	2.00
1.0	2.3	6.5	1.95
2.0	2.7	5.5	1.15
2.0	2.8	5.6	1.13
3.0	2.8	5.0	0.84
3.0	2.6	4.2	1.00
4.0	3.4	4.2	0.75
4.0	3.3	3.8	0.83
5.0	3.0	3.4	0.74
10.0	3.5	2.0	0.63
25.0	3.9	1.4	0.36

Assuming reaction 12 to follow simple pseudo-first order kinetics the rate constant  $k_{12}$  can be determined as  $k_{12} = \ln 2 / (\tau_f \cdot c_0)$ , where  $\tau_f$  is the HS formation half-life and  $c_0$ , the initial H<sub>2</sub>S concentration.  $k_{12}$ -values calculated this way from 13 experiments with H<sub>2</sub>S concentrations ranging from 0.5 to 50 torr are also given in table 6 and plotted in fig. 11. If the simple pseudo-first order assumption was valid the calculated  $k_{12}$ -values should be independent of the initial H<sub>2</sub>S concentration. The too high values of  $k_{12}$  above the dotted line in fig. 11 are significant proof that other H and HS loss reactions have to be considered. These additional reaction are:



The derived "asymptotic"  $k_{12}$ -value of  $2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  is in fair agreement with the value of  $4.35 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  found by Kurylo et al. (1971).

To establish a consistent model for the HS-formation and decay, reactions 11, 12, 13a, 13b, 33a, 33b and 33c should be considered.

There have been numerous investigations of reaction 11 involving different third bodies and  $k_{11} = 3 \times 10^{12} \text{ M}^{-1}\text{s}^{-1}$  with  $\text{H}_2$  as third body (Larkin and Thrush, 1964; Ham et al., 1970) seems to be the most reliable value.

No experimental data on reaction 13a are reported in literature.  $k_{13b} = 1.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$  has been found from discharge flow studies (Bradley et al., 1973).

As seen from table 2 there are three possible exothermic HS recombination reactions. It has been shown that of reactions 33b and 33c, reaction 33b predominates, especially at lower pressures (Forbes et al., 1938; Darwent, 1953; Darwent and Roberts, 1953). This is quite analogous to OH recombination (Fair and Thrush, 1969). It is not possible to presume anything about the importance of reaction 33a.

To simulate the HS formation and removal it is necessary to include reactions 11, 12, 13b, and 33, where reaction 33 is  $\text{HS} + \text{HS} \rightarrow \text{products}$ . The two uncertain parameters in this model are  $k_{33}$  and  $G(\text{H})$ .

Unknowns are determined using a normal simple iterative trial and error method.

$G(\text{H})$  was found to be approximately 12 and  $k_{12}$  to be  $6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  rather than  $4.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ . Model HS concentration variation was not very sensitive to changes in  $k_{33}$ . From the computer simulations it can be seen that  $k_{33}$  must have a value in the range  $7-20 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ .



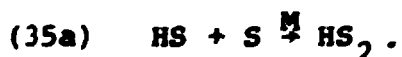
The deviations from simple pseudo-first order kinetics (see fig. 11) is caused by additional H and HS loss reactions taking place. Reaction 11 has been shown to be unimportant as expected. Computer simulations show that reaction 12 becomes pseudo-first order for H<sub>2</sub>S partial pressures above 3 torr. Reaction 13b is expected to be of importance for small H<sub>2</sub>S partial pressures when both H and HS are present in about equal concentrations at the same time. Reaction 33 is expected to be important also at higher H<sub>2</sub>S partial pressures.  $k_{12}$  values from a theoretical model including reactions 11, 12, 13 and 33 are plotted and compared with the experimentally derived values in fig. 11. The agreement is quite good.

### 3.3.2. Decay kinetics

If reaction 33, HS + HS → products, is assumed to be the only HS consuming reaction, then  $2 \times k_{33}/(\epsilon \cdot l)$  is equal to  $1/(\tau_d \cdot A_m)$ , where  $\tau_d$  is the observed HS decay half-life and  $A_m$  the observed HS maximum absorbance. The average value of  $1/(\tau_d \cdot A_m)$  from 14 experiments tabulated in table 5 is  $3.56 \times 10^5 \text{ s}^{-1}$ . An accurate value of  $k_{33}$  can not be calculated until the extinction coefficient  $\epsilon$  of the HS radical has been accurately determined. But estimating  $\epsilon$  to be around  $10^3 \text{ M}^{-1} \text{ cm}^{-1}$  and using the applied optical path length  $l = 120 \text{ cm}$ ,  $k_{33}$  is estimated to be approximately  $2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . This value is in good agreement with the value of  $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  estimated from the present computer simulations and the value  $7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  determined by Bradley et al. (1973).

### 3.3.3. Significance of the absence of HS<sub>2</sub> in the H<sub>2</sub>S/H<sub>2</sub> system

No formation of HS<sub>2</sub> was observed in experiments with H<sub>2</sub>S/H<sub>2</sub> mixtures. This could be due to insufficient contemporary HS and S concentrations to yield HS<sub>2</sub> via the formation reaction proposed in this work:



Deactivation efficiency towards possibly produced  $H_2S_2$  is expected to decrease from  $H_2S$  through  $H_2$  to Ar as third bodies.  $HS_2$  is observed in experiments both in pure  $H_2S$  and in  $H_2S/Ar$  mixtures. Therefore, missing  $HS_2$  in  $H_2S/H_2$  mixtures can not be explained by different deactivation efficiency of  $H_2$  towards  $H_2S_2$ , but must be due to insufficient contemporary HS and S concentrations.

#### 4. REACTIVITY OF THE HS-RADICAL WITH ADDED SUBSTRATES

The reactivity of the HS-radical towards 1,3-butadiene, ethylene and oxygen has been investigated. By adding small amounts of the compound in question to the  $H_2S/Ar$  system the HS-decay is changed to be of pure first order. From the measured HS decay half-lives the corresponding rate constants are estimated. These are shown and compared with those of Perner and Franken (1969) in table 7. The rate constants obtained in the present work seem to be in agreement with those reported by Perner and Franken.

Table 7. Rate constants for HS-radical reactions in  $M^{-1}s^{-1}$

HS + reactant	This work	Perner and Franken
HS	$8 \times 10^9$	$3.2 \times 10^{10}$
1,3-butadiene	$3.8 \times 10^{10}$	$6.0 \times 10^{10}$
1,4-cyclohexadiene		$7.3 \times 10^9$
allene		$8.3 \times 10^7$
ethylene	$8 \times 10^7$	
vinylchloride		$7.4 \times 10^7$
cyclohexene		$4.7 \times 10^7$
$H_2S_2$		$2 \times 10^7$
benzene		$8 \times 10^6$
$O_2$	$<5 \times 10^6$	

## 5. THE FUTURE

More reliable values for the second order rate constants can only be derived when the HS concentration is known more accurately. This is possible when the extinction coefficient for the observed HS absorption band is known. This quantity can be determined from experiments on  $H_2S/H_2$  mixtures if the  $G(H)$  value in pure  $H_2$  was known. It is very surprising that nobody has ever determined this important quantity. We intend to determine  $G(H)$  in  $H_2$  by irradiating  $H_2$  containing small amounts of HI and measuring the yield of  $I_2$ .

## ACKNOWLEDGEMENTS

The author is very grateful to P. Genske, J. Eriksen, O.L. Rasmussen and K. Wojciechowski for invaluable help.

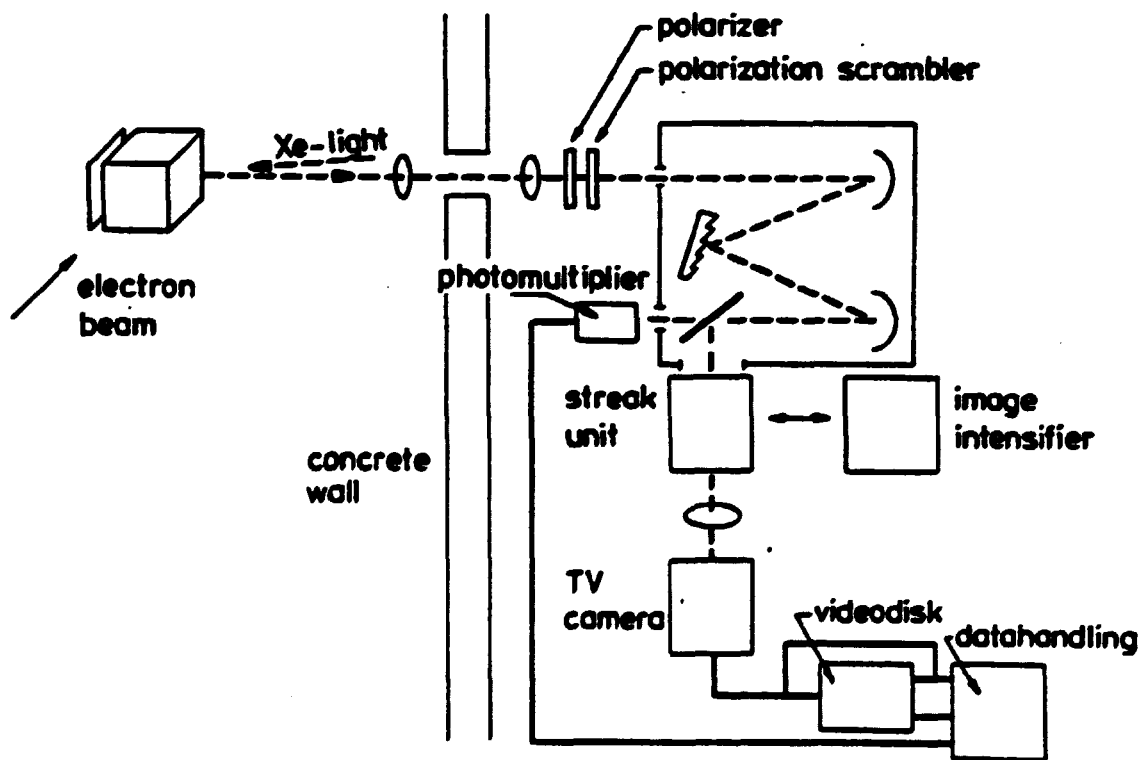
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	H	H <sub>2</sub> S	HS	H <sub>2</sub> S <sub>2</sub>	S	S <sub>2</sub>	HS <sub>2</sub>	H <sub>2</sub>
H	11	12	13	14	15	16	17	-
H <sub>2</sub> S		-	23	-	25	-	-	-
HS			33	34	35	36	37	38
H <sub>2</sub> S <sub>2</sub>				-	45	-	-	-
S					55	56	57	58
S <sub>2</sub>						66	67	-
HS <sub>2</sub>							77	78
H <sub>2</sub>								-

**Fig. 1.** Kvadratic array showing the reactions considered and their numbering used throughout this report.



**Fig. 2.** Experimental setup.

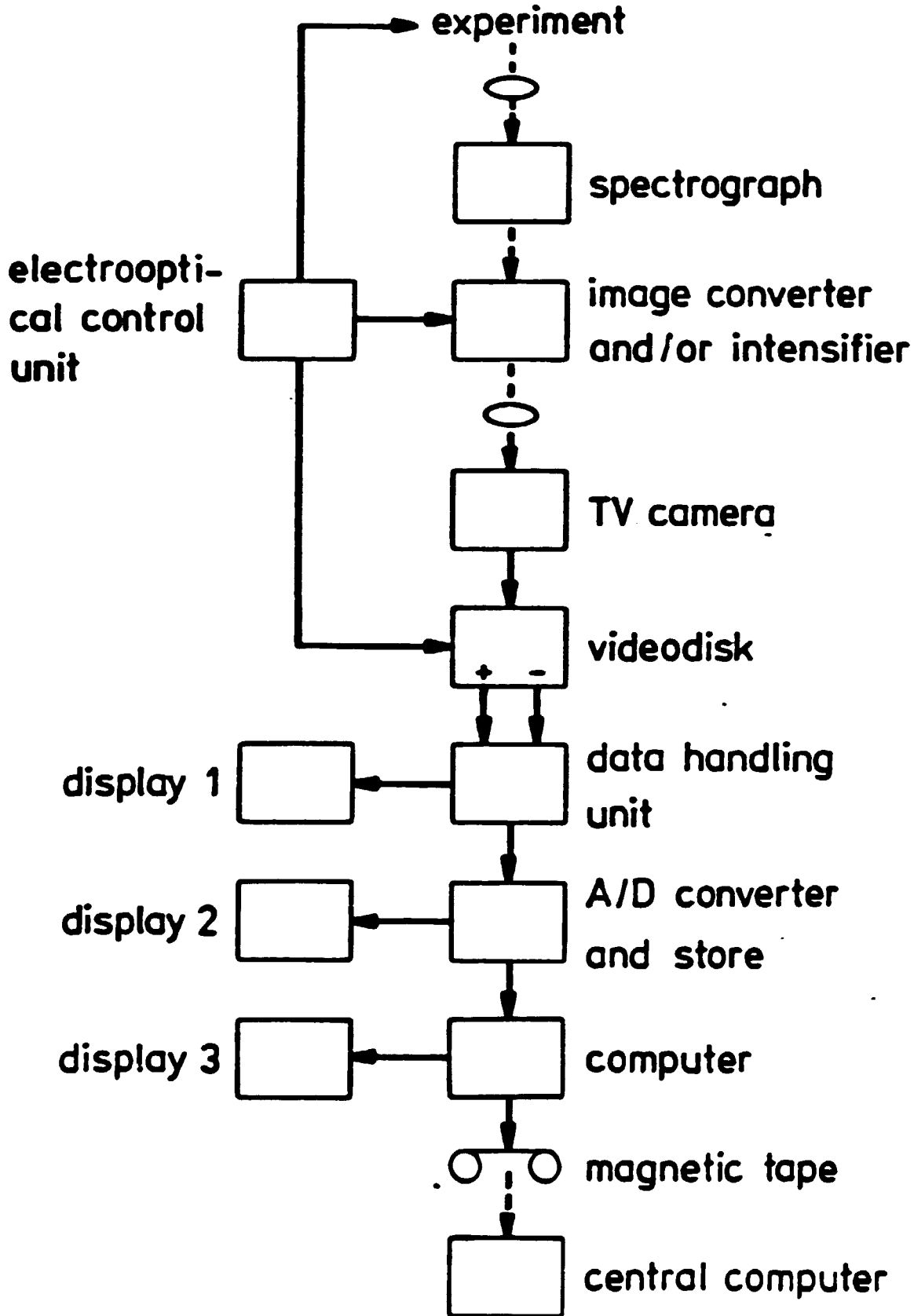


Fig. 3. Block diagram of the detection system.

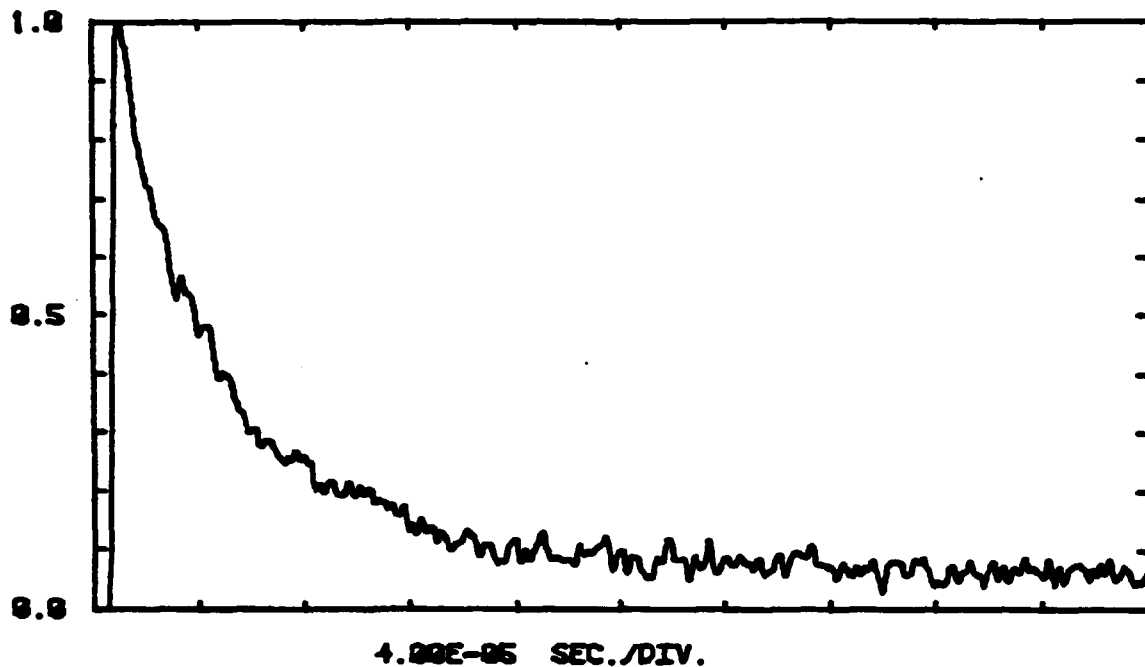


Fig. 4. Experimental HS decay in 760 torr pure H<sub>2</sub>S monitored at 3241 Å. T = 295 ± 1 K.

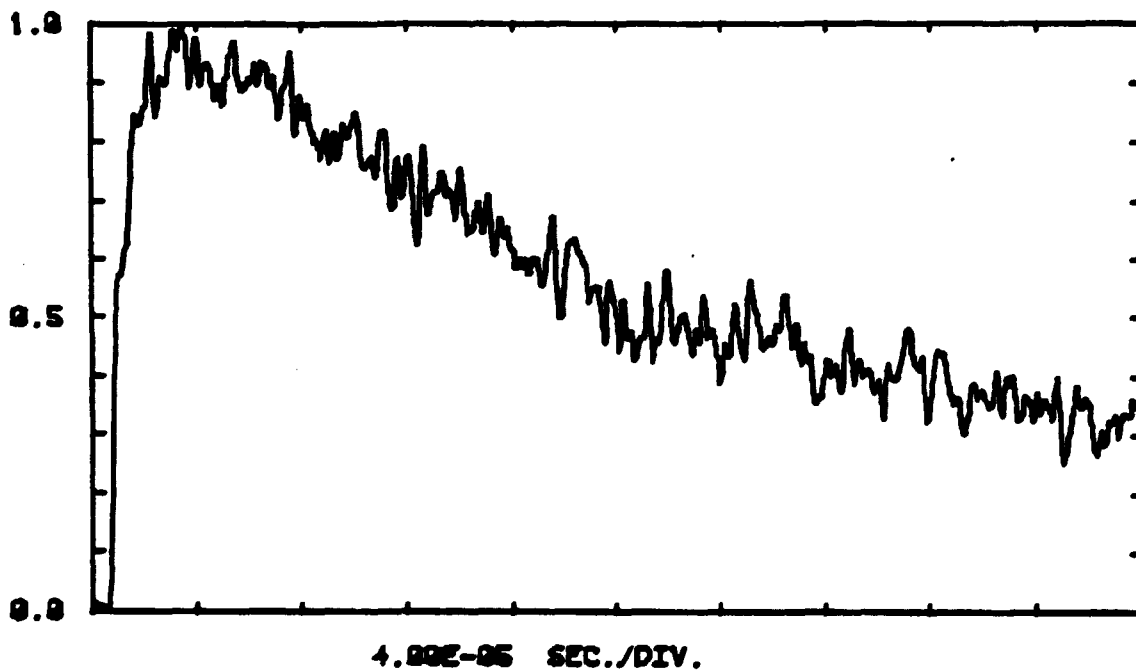


Fig. 5. Experimental HS<sub>2</sub> formation and decay in 760 torr pure H<sub>2</sub>S monitored at 3448 Å. T = 295 ± 1 K.



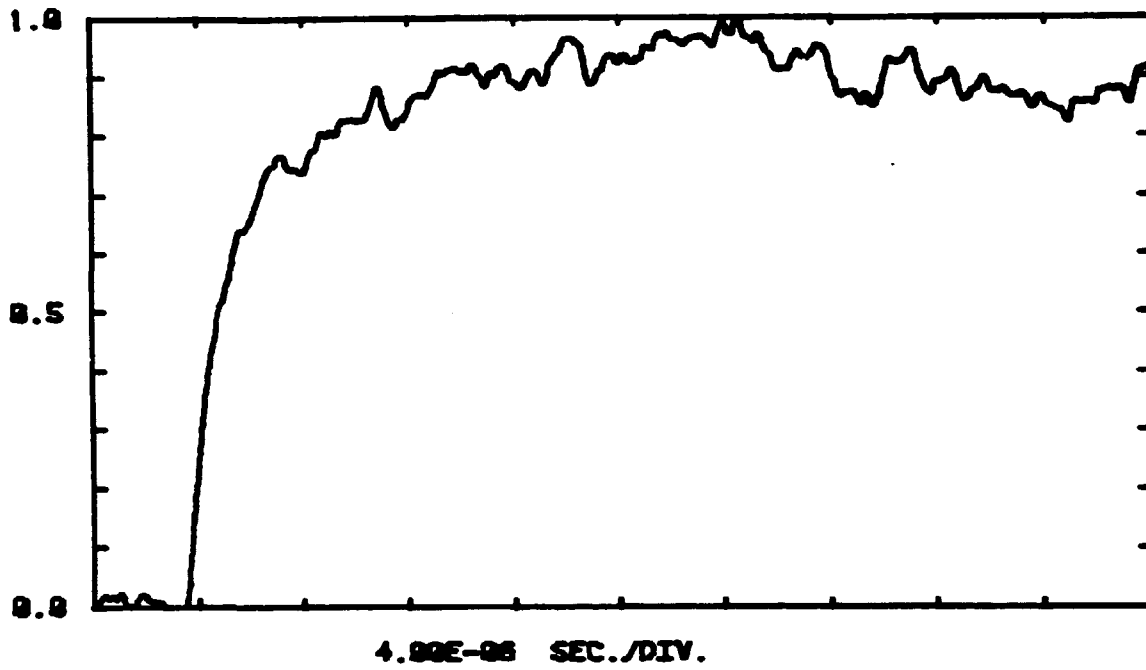


Fig. 6. Experimental HS formation in 2 torr  $H_2S$  with Ar to 760 torr. Monitored at 3241 Å.  $T = 295 \pm 1$  K.

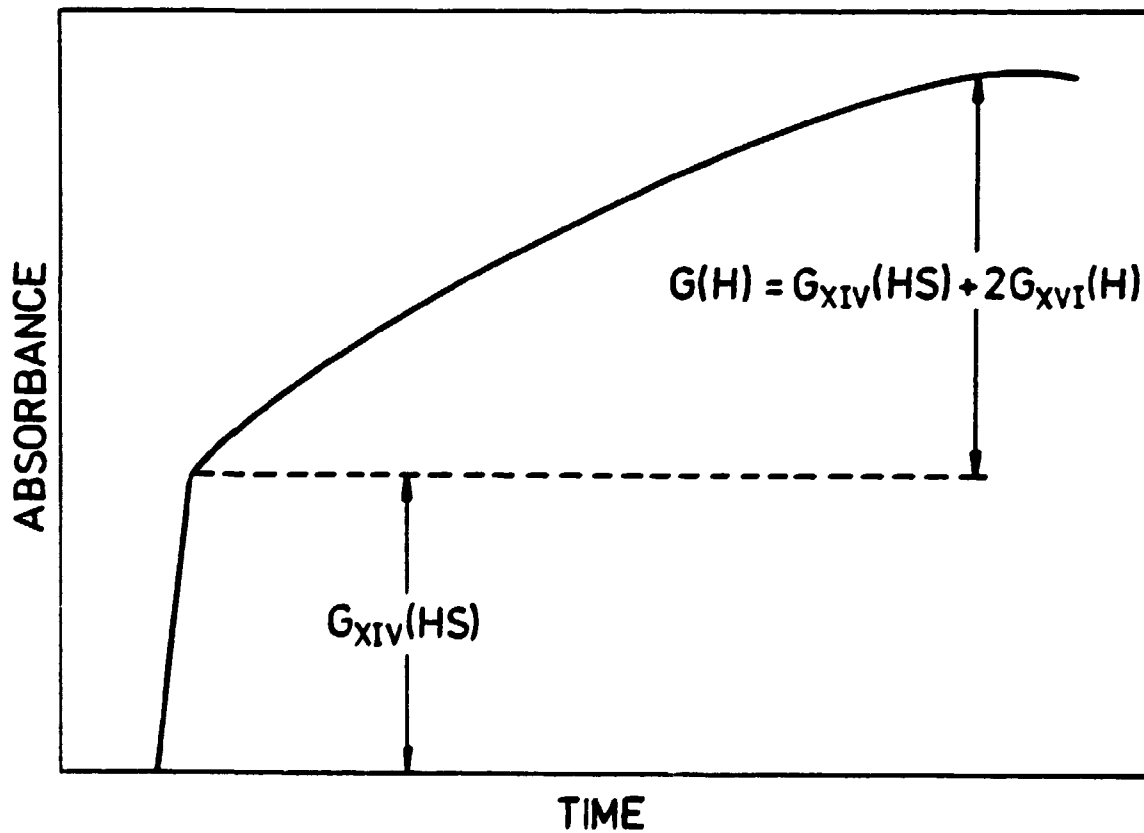
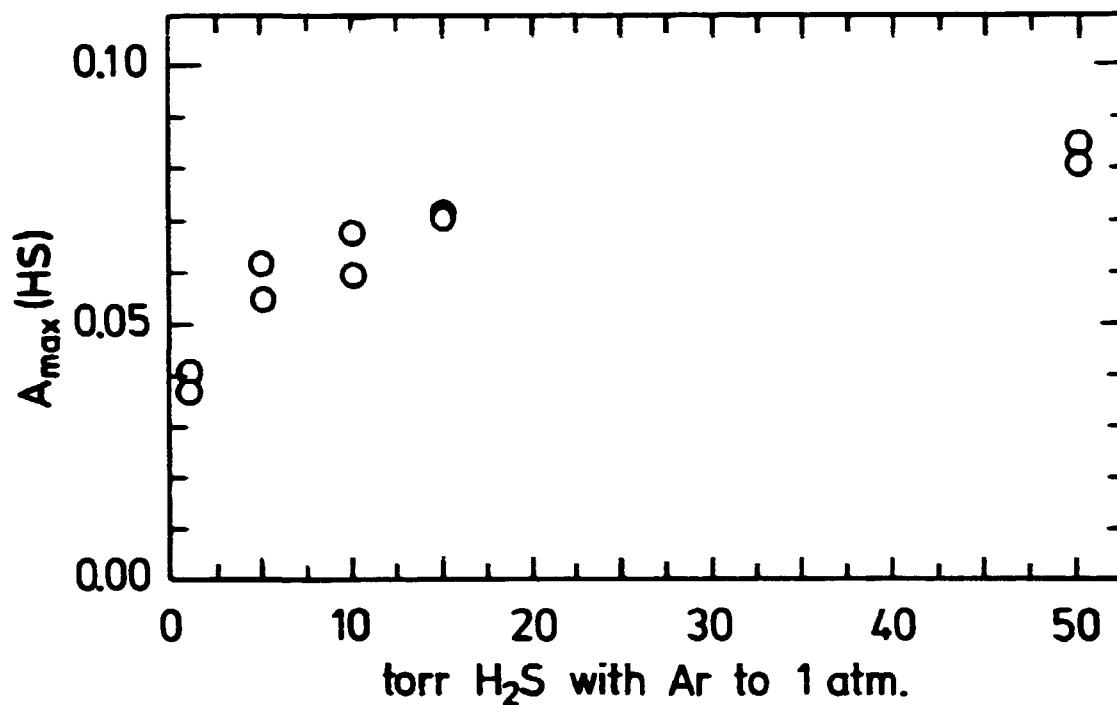
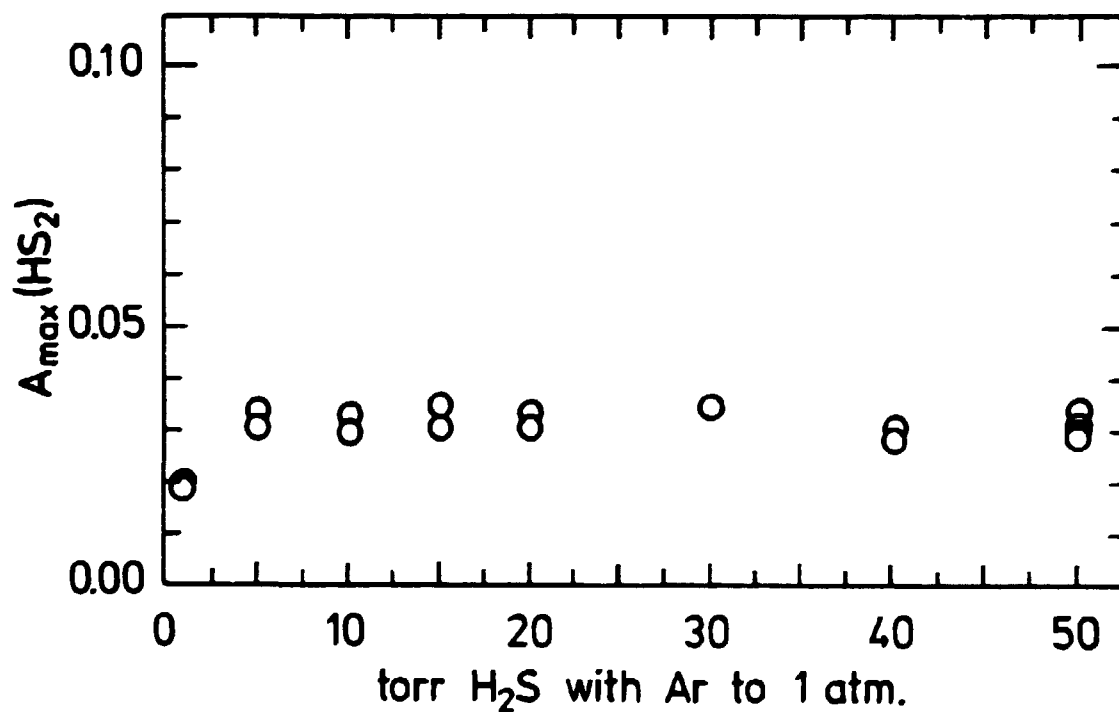


Fig. 7. Theoretically predicted HS formation in  $H_2S/Ar$  mixtures.



**Fig. 8.** Yield of HS in  $\text{H}_2\text{S}/\text{Ar}$  mixtures measured by the maximum HS absorbance at 3241 Å.



**Fig. 9.** Yield of  $\text{HS}_2$  in  $\text{H}_2\text{S}/\text{Ar}$  mixtures measured by the maximum  $\text{HS}_2$  absorbance at 3448 Å.

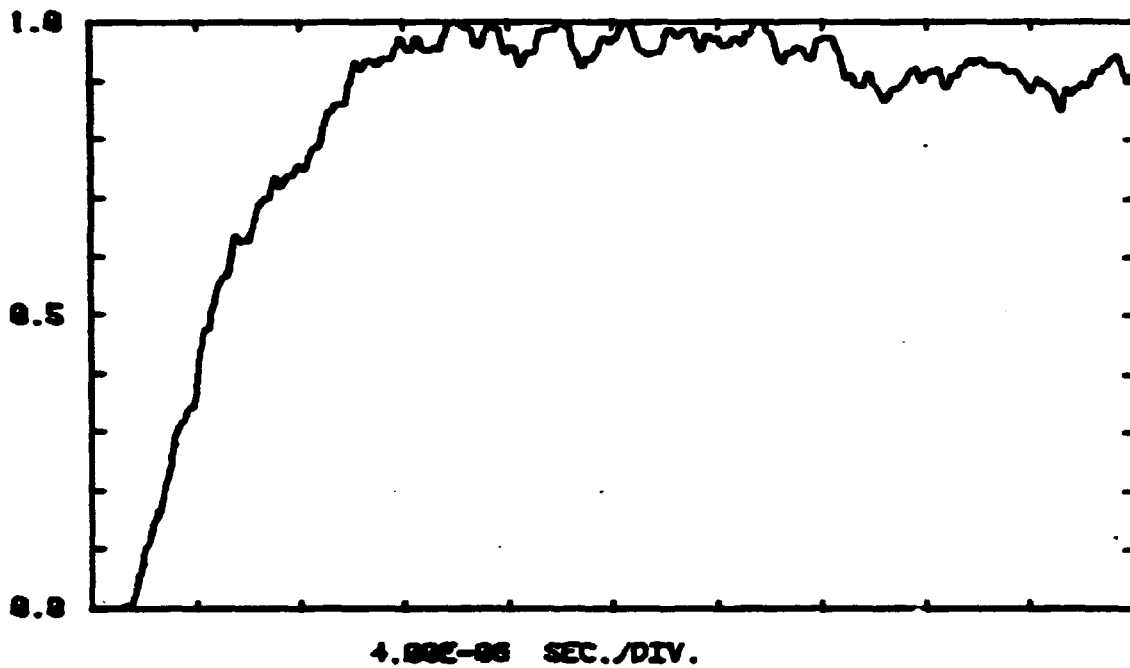
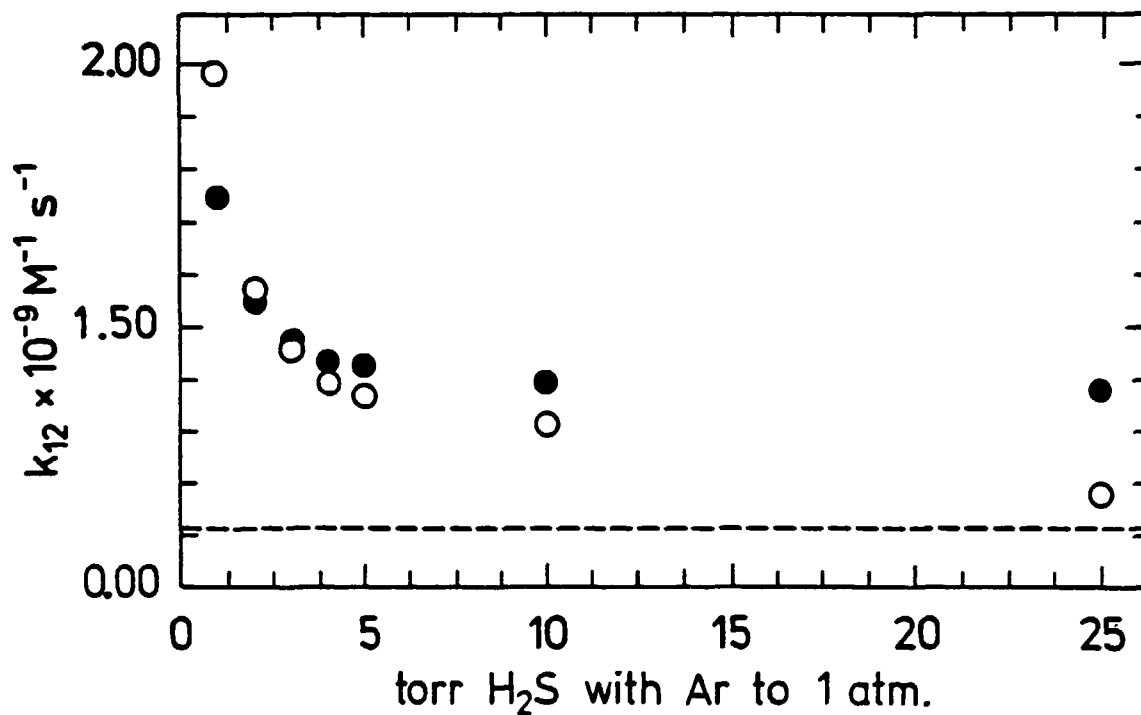


Fig. 10. Experimental HS formation in 5 torr H<sub>2</sub>S with H<sub>2</sub> to 760 torr. Monitored at 3241 Å. T = 295 ± 1 K.



**Fig. 11.** Comparison between experimentally determined values (o) of  $k(\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{HS})$  determined from  $k = \ln 2 / (\tau_f \cdot c_0)$  in  $\text{H}_2\text{S}/\text{H}_2$  mixtures ( $\tau_f$  if the formation half-life of HS and  $c_0$  the initial  $\text{H}_2\text{S}$  concentration) with values (o) derived from a theoretical model including H and HS consuming reactions :  $\text{H} + \text{H} \xrightarrow{M} \text{H}_2$ ,  $\text{H} + \text{HS} \rightarrow \text{H}_2 + \text{S}$ , and  $\text{HS} + \text{HS} \rightarrow \text{products}$ . The asymptote indicates the first order value.

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<p>35 pages + tables + illustrations</p>	
<p>Abstract</p> <p>Formations and decays of HS and HS<sub>2</sub> radicals in the gas phase pulse radiolysis of pure H<sub>2</sub>S, H<sub>2</sub>S/Ar and H<sub>2</sub>S/H<sub>2</sub> systems have been followed directly by kinetic spectroscopy. The literature on the subject is reviewed and a complete reaction scheme is discussed. Computer-simulations have been used to check the validity of the proposed mechanisms. Rate constants <math>k_{\text{HS}+\text{HS}} = (2.0 \pm 0.4) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}</math> and <math>k_{\text{H}+\text{H}_2\text{S}} = (6.0 \pm 1.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}</math> have been determined. The reaction of HS radicals with S atoms is responsible for the HS<sub>2</sub> formation. Pseudo-first order rate constants for reactions of HS with 1,3 butadiene, ethylene and molecular oxygen are reported.</p> <p>Available on request from Risø Library, Risø National Laboratory (Risø Bibliotek), Forsøgsanlæg Risø), DK-4000 Roskilde, Denmark Telephone: (03) 37 12 12, ext. 2262. Telex: 43116</p>	<p>Copies to</p>