On Reaction Kinetics for the Thermal Decomposition of Hydrogen Sulfide

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New kinetic data for the hydrogen sulfide decomposition reaction obtained from quartz tubular reactors over a temperature range of 800−1,250°C are reported. The study shows that the overall decomposition reaction has a first-order dependency on H_2S *concentrations at these temperatures. The regression of our experimental data gave an overall hydrogen sulfide decomposition reaction rate constant as* $k\ (m^3/kmol \cdot s) = (1.68 \pm 0.86) \times 10^{11}\ \exp\ [(-28{,}940 \pm 840)/T]$. *Moreover, for the first time, kinetic data from higher temperature (1,500−3,100°C) shock-tube studies (Olschewski et al., 1994; Woiki and Roth, 1994) and the lower temperature flow reactor study (this work) are reconciled. A single rate constant for* H_2S *decomposition reaction,* $k\ (m^3/kmol \cdot s) = (1.12 \pm 0.11) \times 10^{11}\ \exp\ [-(28{,}360 \pm 200)/T]$ *over a wide temperature range of 800−3,100°C was found to represent satisfactorily the three sets of data.*

Introduction

Hydrogen sulfide is produced during various hydrocarbon upgrading processes associated with the petroleum refining and the natural gas industries. It is normally converted to and recovered as sulfur in the modified Claus process via the following overall reaction:

$$H_2S + 1/2\,O_2 \leftrightharpoons 1/x\,S_x + H_2O \qquad (1)$$

In Claus plants, the conversion of H_2S to sulfur is achieved in two distinct reaction steps. In the first step, sulfur dioxide is produced from the partial combustion of H_2S in a refractory lined vessel called the reaction furnace. In the second step, the sulfur dioxide is then reacted with the unreacted hydrogen sulfide over alumina or titania catalysts in converters to produce elemental sulfur. The Claus plant reaction furnace typically operates between 1,250−1,600 K where the gas residence times range from 0.5−2.0 s. The combustion or oxidation of hydrogen sulfide in the reaction furnace is accompanied by the thermal decomposition of hydrogen sulfide.

Several experimental studies on the oxidation of hydrogen sulfide in flames and in shock tubes have been reported in the literature (Levy and Merryman, 1965; Merryman and Levy, 1967; Bradley and Dobson, 1967; Muller et al., 1979; Frenkenlach et al., 1981; Cambot et al., 1981; Tsuchiya et al., 1997). In fact, detailed reaction mechanisms comprising several elementary reactions have been proposed (Frenkenlach et al., 1981; Tsuchiya et al., 1997). Inclusion of the H_2S decomposition reaction is essential in the development of these comprehensive kinetic models for the oxidation process.

The interest in hydrogen sulfide decomposition reaction has not only been limited to H_2S combustion systems and, in fact, the energy crisis of 1973 led to initiation of numerous studies on the production of hydrogen from the decomposition of hydrogen sulfide. Several of the studies involving catalytic processes for splitting hydrogen sulfide into hydrogen were granted patents during the 1980s (Chivers et al., 1980; Berk et al., 1991). Since our interest is mainly in the homogeneous gas-phase thermal reactions occurring in the front-end of Claus plants, these studies will not been discussed here.

The reported studies on the homogeneous gas-phase H_2S decomposition reaction can be broadly classified into two groups on the basis of the reactor type employed. One group constitutes the experiments conducted in shock tubes. A majority of these experiments were conducted at higher temperatures ($>$1,800 K). The other group comprises the experiments conducted in conventional flow or static reactors at lower temperatures ($<$1,500 K). A review of these studies indicates that the reaction kinetics obtained from the two

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groups differ significantly. For example, the flow reactor studies (Raymont, 1975; Kaloidas and Papayannakos, 1989; Tesner et al., 1990; Adesina et al., 1995) have reported activation energies in the range of 195−277 kJ/mol while the shock tube studies (Higashihara et al., 1976; Bowman and Dodge, 1981; Roth et al., 1982; Olschewski et al., 1994; Woiki and Roth, 1994; Shiina et al., 1996) have reported activation energies varying from 268 to 384 kJ/mol. Moreover, the differences between the rate constants obtained from similar reactor systems are also quite significant. In the most recent study on the H_2S decomposition reaction, Shiina et al. (1996) have reported rate constants one-fifth to one-tenth of those reported by Olschewski et al. (1994) and Woiki and Roth (1994). Both of the latter groups in their independent studies came up with almost identical reaction rate constants.

The difference among the reported studies is limited not only to rate constants. There is controversy regarding the overall H_2S decomposition mechanism. While in all the shock tube studies the H_2S decomposition reaction has been considered to be first-order with respect to H_2S concentration, the flow/static reactor studies have reported both first- and second-order dependency on H_2S concentrations. Darwent and Roberts (1953) conducted experiments in static reactors over the temperature range of 773−923 K and reported that the homogeneous and heterogeneous reactions were second- and first-order, respectively, with respect to the H_2S concentration. They estimated that the homogeneous reaction would dominate at temperatures above 923 K. Based on Darwent and Roberts' work (1953), Tesner et al. (1990) assumed that the H_2S decomposition was first- and second-order with respect to H_2S concentration for the homogeneous and the heterogeneous reactions, respectively. They tried to interpret their experimental data based on this assumption, but they did not conduct a systematic study to verify the assumption. The hydrogen sulfide concentrations were not directly measured in either of these studies (Tesner et al., 1990; Darwent and Roberts, 1953), although the rate constant for the H_2S decomposition reaction was reported. While Darwent and Roberts (1953) measured the rate of formation of hydrogen, Tesner et al. (1990) measured the rate of formation of sulfur. Another major shortcoming of the Tesner et al. (1990) study was that they used nitrogen as diluent, containing up to 0.01% oxygen. Now, oxygen present in trace amounts is known to accelerate the hydrogen sulfide decomposition reaction (Higashihara et al., 1976). Since Tesner et al. (1990) did not give consideration to the effects of oxygen in analyzing their experimental data, the rate constants reported for H_2S decomposition in their study are not reliable. In other flow reactor studies, Kaloidas and Papayannakos (1989) and Adesina et al. (1995) examined the H_2S decomposition reaction over the temperature ranges of 873−1,133 K and 1,040−1,084 K, respectively. They found the overall reaction rate for H_2S decomposition to be first-order with respect to the H_2S partial pressure.

From the review of the literature, it can be inferred that there is a great deal of controversy and discrepancy regarding the overall reaction kinetics and the mechanism for hydrogen sulfide decomposition. Despite the fact that detailed reaction schemes composed of elementary reactions have been proposed, their application or extrapolation to lower temperatures remains questionable.

The objective of this work is to report new experimental data for H_2S decomposition over the temperature range (1,073−1,523 K) encountered in the front-end of a Claus plant for which reliable reaction kinetic data are not available. Further, the issue of the order of dependency of H_2S concentration on the overall H_2S decomposition reaction was investigated. Finally, an attempt was made to reconcile the higher-temperature reaction kinetic data (shock tube studies) with our lower-temperature data.

Experimental Studies

The details of the experimental setup have been described elsewhere (Karan, 1998; Karan et al., 1998). The apparatus consisted of a coiled quartz tubular reactor of 5.0 mm ID (available in lengths of 3.2, 6.4 and 16 m) placed in a Thermolyne electric furnace that could be operated from 600 to 1,700°C. The gas-flow rates were maintained using an eight-channel Linde mass-flow controller. The hot product gases from the reactor were first quenched in less than 20 ms to temperatures less than 400−600°C by a combination of free and forced convection in a short length of reactor extending out of the furnace. Further cooling was attained in a water-cooled cocurrent double pipe quartz exchanger where the gases flowed in the inside tube. Any sulfur present in the product stream was removed partially in the quartz heat exchanger and completely in a sulfur trap consisting of a 25-mm-diameter glass tube packed tightly with glass wool. The H_2S concentrations in the feed and the sulfur free product streams were analyzed on an on-line 3400C_X Varian gas chromatograph equipped with a thermal conductivity detector and a pulsed flame photometric detector. The gas chromatograph was calibrated for H_2S concentration using standard gas mixtures. The H_2S concentrations determined by gas chromatography were accurate to $\pm 4\%$ of the measured values.

Experiments were conducted under dilute conditions (dilution $\geq 98\%$) in three tubular quartz reactors of lengths 3.2 m, 6.4 m, and 16 m over a temperature range of 800−1,250°C at a total gas-flow rate of 4.0 ± 0.1 L/min (expressed at 20°C and 101.3 kPa). The inlet pressure varied from 110 kPa to 165 kPa. The isothermal gas residence time (t_{res}) calculated for the plug flow of gas ranged from 200 ms to 2.0 s. The required concentrations of hydrogen sulfide were prepared by diluting 50 mol. % H_2S with pure nitrogen, both supplied by Praxair Canada Ltd.

For reactor characterization, the temperatures along the reactor were measured with shielded thermocouples. The reactor operations were verified using propane pyrolysis experiments for which detailed reliable intrinsic kinetics are available in the literature. The reactor was found to operate isothermally and very close to plug flow (Karan et al., 1998).

Results and Discussion

Effect of temperature

The effect of temperature on the H_2S conversion is shown in Figure 1. The equilibrium H_2S conversions for a feed of 1.0 mol. % H_2S in nitrogen at total pressures of 110 and 165 kPa have also been reported in Figure 1. The two pressures correspond to the minimum and maximum inlet pressures for our experiments. The equilibrium conversions were calcu-

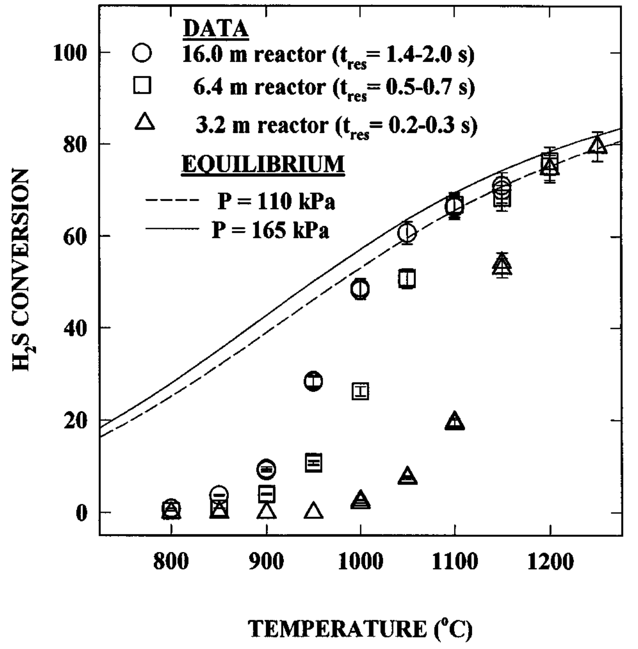

Figure 1. Experimentally measured H_2S conversions in three quartz reactors with gas residence times ranging from 0.2 to 2.0 s.

lated from the Gibbs free energy minimization for an H_2S-H_2-S_x-N_2 system, where S_x represents the sulfur allotropes S_1, S_2, ..., S_8. The free energy of formation data for all species were obtained from JANAF thermochemical Tables (Chase et al., 1985). It is known that the H_2S decomposition is severely restricted by the thermodynamic equilibrium at lower temperatures (< 500°C). It can be seen from Figure 1 that even at 800°C the equilibrium conversions are approximately 25 and 30% for total pressures of 165 and 110 kPa, respectively. At the highest temperature investigated in this study (1,250°C), the equilibrium conversions lie in the range of 79–82%. The experimentally measured H_2S conversions in the three quartz reactors of lengths 3.2, 6.4, and 16.0 m are also shown in Figure 1. The H_2S conversions below 850°C are less than 5% even in the longest reactor for gas residence time of approximately 2 s. However, at temperatures exceeding 1,200°C, experimental H_2S conversions close to equilibrium conversions are achieved even in the shortest reactor within a residence time of approximately 200 ms. This clearly shows that the H_2S decomposition reaction is very rapid at higher temperatures.

Effect of initial concentration

To find out the order of dependency of H_2S concentration for H_2S decomposition reactions, experiments were conducted at 900°C and 1,000°C in the 16.0 m long reactor for three initial H_2S concentrations of 0.5, 1.0, and 2.0 mol. % and at 1,100°C in the 3.2 m reactor for four initial H_2S concentrations of 0.2, 0.5, 1.0, and 2.0 mol. %. The results of these experiments are presented in Figure 2. The measured H_2S conversions for initial H_2S concentrations varying by four to ten fold are found to yield a constant value within experimental errors. This proves that the reaction rate is first-order with respect to the H_2S concentration.

Kinetic model

The initial step in hydrogen sulfide decomposition, until the studies of Woiki and Roth (1994) and Olschewski et al. (1994), was considered to be hydrogen abstraction via the following reaction

$$H_2S + M \rightleftharpoons SH + H + M \qquad \Delta H_{298} = 377.8 \text{ kJ/mol} \quad (2)$$

where M is an inert collisional molecule (which in our case is the diluent gas nitrogen) that acts as an energy transfer agent. These two studies, however, reported reaction rate constants that were significantly higher than those reported in the previous shock tube studies. They argued that the initial dissociation of H_2S takes place according to the energetically favorable reaction

$$H_2S + M \rightleftharpoons H_2 + S(^3P) + M \qquad \Delta H_{298} = 297.6 \text{ kJ/mol} \quad (3)$$

where $S(^3P)$ represents a sulfur atom in a ^3P electronic state. The initial rates of hydrogen sulfide decomposition, according to either of the reactions 2 or 3, can be expressed as follows

$$-r_{H_2S} = k_1 \, C_M \, C_{H_2S} \quad (4)$$

where C_M and C_{H_2S} are the concentrations of M and H_2S in kmol/m^3, respectively, and k_1 (in m^3/kmol·s) is the reaction rate constant for reaction 2 or reaction 3, as the case may be.

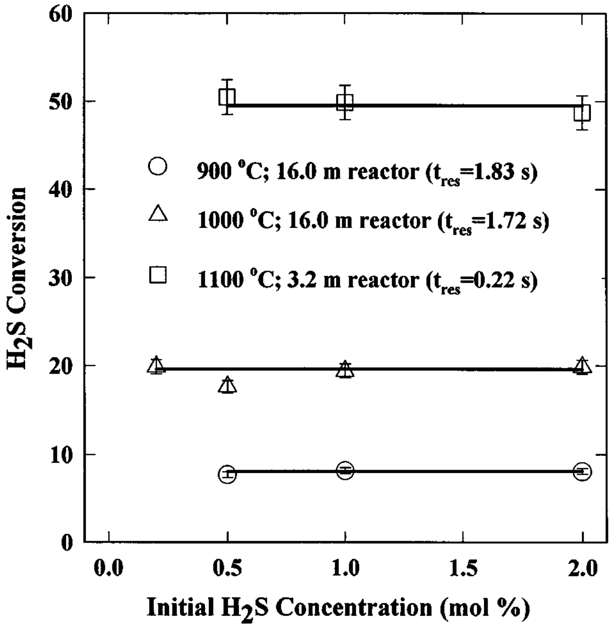

Figure 2. Effect of initial H_2S concentration on H_2S conversion measured at three different temperatures.

Table 1. Selected Reactions for H_2S Decomposition

Reaction	A $m^3/(kmol \cdot s)$	E_a (kJ/mol)	Reference
(1) $H_2S + M \leftrightarrow H_2 + S + M$	1.90×10^{11}	274.3	Woiki and Roth (1994)
	2.00×10^{11}	274.4	Olschewski et al. (1994)
	2.18×10^{11}	268.6	Shiina et al. (1996)
(2) $H_2S + M \leftrightarrow H_2 + S + M$	4.64×10^{11}	345.0	Roth et al. (1982)
	1.99×10^{11}	310.0	Bowman and Dodge (1976)
(3) $H_2S + S \leftrightarrow$ products	8.31×10^{11}	30.9	Shiina et al. (1996)
	5.70×10^{11}	63.2	Woiki and Roth (1994)
(4) $H_2S + H \leftrightarrow SH + H_2$	1.90×10^{11}	20.7	Woiki and Roth (1994)
(5) $H_2 + S \leftrightarrow SH + H$	15.84×10^{11}	82.5	Shiina et al. (1996)
	6.00×10^{11}	100.3	Woiki and Roth (1994)
(6) $S + SH \leftrightarrow S_2 + H$	0.20×10^{11}	0	Woiki and Roth (1994)
(7) $S_2 + M \leftrightarrow 2S + M$	0.48×10^{11}	322.16	Woiki and Roth (1994)
(8) $H_2 + M \leftrightarrow 2H + M$	2.20×10^{11}	401.9	Woiki and Roth (1994)

Woiki and Roth (1994) measured the initial rates of formation of the H and S atoms and found that the rates of formation of the S atoms were 10–20 times that for the H atoms. Based on these experimental facts, they proposed that reaction 3 was the primary step in H_2S decomposition. Irrespective of whether reaction 2 or reaction 3 dominates the initial decomposition of H_2S, the production of radical SH and atoms S and H is followed by subsequent rapid reactions of H_2S with the atoms. The atoms and radicals also react very rapidly with each other. The net result is that the overall rate of disappearance of H_2S is found to be twice the rate of H_2S consumption via reaction 2 or 3. Hence, the overall H_2S decomposition rate (in $kmol/m^3 \cdot s$) can be expressed as

$$-r_{H_2S} = k\, C_M\, C_{H_2S} \qquad (5)$$

where k (in $m^3/kmol \cdot s$) is two times k_1 ($k = 2k_1$). At very low initial concentrations of H_2S (< 100 ppm), a majority of the H_2S will be decomposed by the primary reaction step and, therefore, the overall rate of H_2S disappearance will equal the initial rate of H_2S decomposition. Some of the important reactions and the associated kinetic parameters reported in the literature are presented in Table 1.

Estimation of Parameters. From our experiments, we have established the overall H_2S decomposition rate to be first-order with respect to H_2S concentration. The rate of disappearance of H_2S was calculated via Eq. 5 and the rate constant k was determined using the experimental data which corresponded to H_2S conversions less than 90% of the equilibrium conversions.

The parameters for the irreversible forward reaction rate (k), that is, the H_2S decomposition reaction were obtained by least-squares minimization of the difference between the model predicted and experimentally observed H_2S conversions. The results are reported in Table 2. The regressed rate constant k in $m^3/(kmol \cdot s)$ was found as

$$k = (1.68 \pm 0.86) \times 10^{11} \exp\left[(-28{,}940 \pm 840)/T\right] \qquad (6)$$

Comparison with previous studies

Comparison of Activation Energy. The activation energy, from Eq. 6, for the overall H_2S disappearance rate corresponds to 240.6 kJ/mol which is in excellent agreement with the recent lower temperature (1,030–1,070 K) study by Adesina et al. (1995) who reported the activation energy to be 240 kJ/mol. However, it is significantly higher than the 195 kJ/mol value reported by Kaloidas and Papayannakos

Table 2. Experimental Conditions and the Rate Constant k (Computed from Eq. 5) for Overall H_2S Decomposition Reaction

Temp. (°C)	Pressure (kPa)	Initial Conc. (mol. %)	Residence Time (t_{res}) (s)	H_2S Conversion (%)	k $(m^3/kmol \cdot s)$
800	158	1.0	1.95	0.9	0.260
800	158	1.0	1.95	1.0	0.291
850	159	1.0	1.88	4.9	1.560
850	159	1.0	1.88	5.0	1.570
900	162	1.0	1.83	8.6	2.980
900	162	1.0	1.83	8.1	2.800
950	164	1.0	1.77	30.8	12.90
950	164	1.0	1.77	29.0	12.00
1,000	165	1.0	1.72	49.3	25.40
1,000	165	1.0	1.72	50.0	26.00
850	144	1.0	0.68	0.6	0.568
850	144	1.0	0.68	0.6	0.568
900	147	1.0	0.66	5.6	5.790
900	147	1.0	0.66	2.5	2.600
950	148	1.0	0.64	11.5	12.90
950	149	1.0	0.65	11.2	12.40
1,000	149	1.0	0.62	25.6	33.40
1,000	149	1.0	0.62	25.3	33.00
1,050	152	1.0	0.61	51.2	85.20
1,050	152	1.0	0.61	50.9	84.60
1,000	112	1.0	0.23	5.8	24.20
1,000	112	1.0	0.23	5.3	22.00
1,050	114	1.0	0.23	7.4	32.80
1,050	114	1.0	0.23	7.7	34.20
1,100	115	1.0	0.22	19.2	94.60
1,100	115	1.0	0.22	19.6	96.60
1,150	117	1.0	0.22	37.4	218.0
1,150	117	1.0	0.22	40.1	244.0
900	161	0.5	1.83	7.7	2.660
900	162	1.0	1.83	8.2	2.820
900	162	2.0	1.83	8.1	2.800
1,000	165	0.5	1.72	50.5	26.20
1,000	165	1.0	1.72	49.8	25.60
1,000	166	2.0	1.73	48.7	24.60
1,100	115	0.2	0.22	17.6	98.60
1,100	116	0.5	0.22	19.4	85.40
1,100	116	1.0	0.22	19.4	95.20
1,100	116	2.0	0.22	19.8	97.20

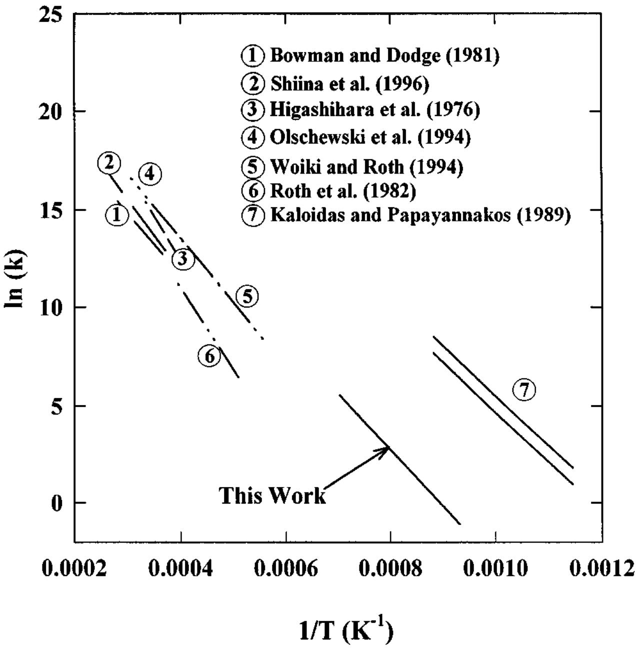

Figure 3. Comparison of published rate constants for H_2S decomposition reaction (k in $m^3/(kmol \cdot s)$).

(1989) who conducted their experiments at temperatures ranging from 873 to 1,133 K in tubes made of alumina, in which catalytic effects may have been significant. In a recent study, Harvey et al. (1998) have shown that the surface reactions in alumina reactors may account for up to 70% of the total rate. The activation energies of 273.2 kJ/mol, 274.4 kJ/mol, and 268.6 kJ/mol reported in the high temperature (1,800–3,300 K) shock tube studies of Woiki and Roth (1994), Olschewski et al. (1994), and Shiina et al. (1996), respectively, are all somewhat higher than that obtained from our experiments.

The comparison of activation energies is often used to show the relative goodness of one's kinetic data with respect to other published work. This is very misleading, because similar activation energies do not ensure similar rate constants. Therefore, we wanted to find out how our rate constants compared to those reported in the literature.

Comparison of rate constants

A comparison of the rate constants obtained in our study with those reported in literature is shown in Figure 3. It must be noted that we have obtained the rate constant (k) for overall H_2S decomposition reaction defined by Eq. 5. However, the high-temperature shock tube studies have reported the rate constant (k_1) for the initial decomposition reaction, which is equal to one-half the overall rate constant (k). To be consistent in comparison, we divided the overall rate constant (k) obtained from our experiments by two.

In their study, Kaloidas and Papayannakos (1989) expressed the rate of disappearance of H_2S (in $mol/cm^3 \cdot s$) in a form different than Eq. 5

$$(-r_{H_2S}) = k_f \, P_{H_2S} \qquad (7)$$

where k_f is in $mol/cm^3 \cdot s \cdot atm$ and P_{H_2S} (in atmospheres) is the partial pressure of hydrogen sulfide in the reacting mixture. For comparison, this rate expression was transformed into a form consistent with Eq. 5 and expressed as $k_f = 10^{-3} \times kP_t/[RT]^2$, where P_t is the total system pressure in atmospheres, T is in Kelvin, and the corresponding value of R is 82.0562 $cm^3 \cdot atm/(mol \cdot K)$. The rate constant k was then calculated from this expression. However, since the total pressure in their experiments varied from 1.3 to 3 atm, a range of rate constants rather than a single line is shown for the kinetics proposed by Kaloidas and Papayannakos (1989) in Figure 3.

From Figure 3, it can be seen that there is a considerable disagreement among the reported rate constants both in the lower- and higher-temperature regions. These differences can be attributed partially to the different experimental techniques used in these studies. Among the high-temperature shock tube studies, different research groups have measured different chemical species (such as S, H, S_2, H_2 or H_2S) and determined the rate constant from the temporal concentration profiles of these species.

For example, Olschewski et al. (1994) and Woiki and Roth (1994) measured the S atom concentration in their experiments. From the S atom production rate at initial times, they obtained the reaction rate constant for the initial decomposition of H_2S, which is expected to proceed via reaction 3. In an earlier work, Roth et al. (1982) had monitored the H atom concentrations during H_2S decomposition. They calculated the initial H_2S decomposition rate from the H atom production rates at initial times. The underlying assumption here is that the initial H_2S decomposition proceeded according to reaction 2. In their recent study, Woiki and Roth (1994) found the initial H atom production rate to be 10–20 times lower than the initial S atom production rate. This explains why the rate constants reported by Roth et al. (1982), as shown in Figure 3, have lower values than those reported in their recent work (Woiki and Roth, 1994). Among the other studies, the rate constants proposed by Shiina et al. (1996), Bowman and Dodge (1981) and Higashihara et al. (1976) are in good agreement with each other. Both Shiina et al. (1996) and Bowman and Dodge (1981) determined the reaction rate by monitoring the H_2S concentration. While Shiina et al. (1996) used infrared emission spectroscopy to determine the H_2S concentration, Bowman and Dodge (1976) had employed ultraviolet absorption spectroscopy. Although different techniques were used to monitor the H_2S concentrations, in the two studies similar rate constants were obtained. In their experiments, Higashihara et al. (1976) monitored the S_2 concentration by ultraviolet absorption and determined the rate constant from these measurements. The rate constants reported by them lie between the rate constants determined by S atom concentration measurement and that determined by H_2S concentration measurement.

At lower temperatures, the only available first-order rate constant was that by Kaloidas and Papayannakos (1989) who measured the H_2S concentrations in the feed stream and product streams of their reactor. It can be clearly seen from Figure 3 that the rate constants reported by Kaloidas and Papayannakos (1989) are greater and significantly different than that obtained in this work. It must be mentioned here that Kaloidas and Papayannakos (1989) suggested that quartz had a catalytic effect on the decomposition reaction and therefore performed their experiments in alumina tubes. The fact that the rate constants reported by them are higher than those obtained in this study indicates that the catalytic effect of quartz, if any, is relatively less than that of alumina. Recently, Harvey et al. (1998) conducted experimental studies on H_2S decomposition in tubular alumina reactors over a temperature range of 1,350–1,600 K. They report that more than 70% of the total rate is composed of the surface reaction. Moreover, in another recent study, Faraji et al. (1998) conducted experiments over 1,273–1,473 K in empty and quartz-packed reactors made of quartz. They concluded that at temperatures greater than 1,273 K the homogeneous gas-phase reaction is much faster than the catalytic reaction on the silica surface.

Extrapolation of rate constants

The errors involved in modeling H_2S decomposition rates by extrapolating the available high-temperature rate constants can be large and the calculated rates may be unrealistically low or high. For example, extrapolation of the rate constants obtained in shock tube studies to the highest temperature (that is, 1,523 K) investigated in this work results in values 3 to 600 times lower than that obtained in our experiments. These differences are even more pronounced at the lower temperatures. At 1,073 K, the extrapolated rate constants are 1/9 to 1/70,000 times that observed in this work. The extrapolation of the rate constant reported at lower temperature also results in values that are significantly higher than those found in this study. For example, the extrapolated rate constant of Kaloidas and Papayannakos (1989) is a maximum of 16 times that found in this study at 1,073 K and 8 times at 1,523 K.

Proposed reconciliation of rate constant over 1,073–3,300 K

The differences in high-temperature shock tube obtained rate constants and those obtained in this study are too large to be explained by experimental errors or by the different experimental conditions and reactor types used. It is important to reconcile these differences.

We wanted to examine the scatter in the experimental data of this work and other reported studies, and any bias it could have on regression of the parameters. An observation of Figure 3 shows that the rate constant obtained from this study falls in line with the rate constants reported by Olschewski et al. (1994) and Woiki and Roth (1994). Fortunately, both Olschewski et al. (1994) and Woiki and Roth (1994) had reported the rate constants and the corresponding temperatures in a tabular form. These data along with the data obtained in this study are shown in Figure 4. The kinetic parameters corresponding to the three sets of data are reported in Table 3.

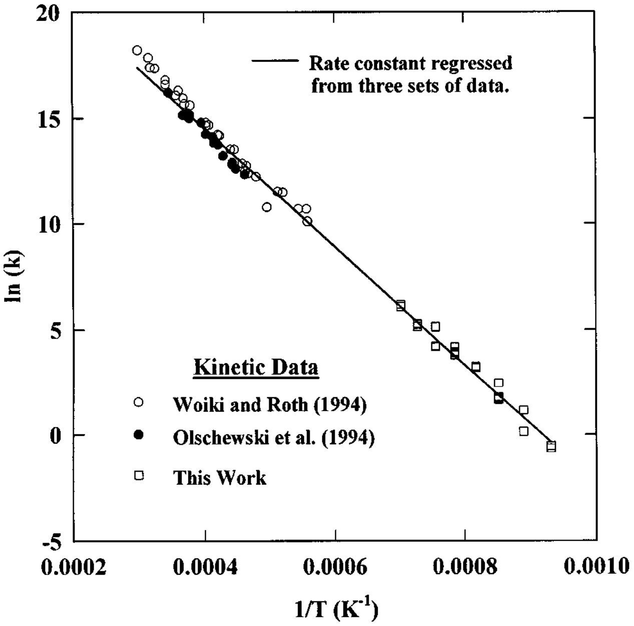

Figure 4. New rate constant for H_2S decomposition over the temperature range 1,073–3,350 K (k in m^3 kmol^{-1} s^{-1}).

In Figure 4, the solid line represents the best fit line obtained by the least-squares minimization of the three sets of data. The new rate constant (in m^3/kmol·s) is given as:

$$k = (1.12 \pm 0.114) \times 10^{11} \exp\left[(-28{,}360 \pm 200)/T\right] \quad (8)$$

The activation energy corresponding to Eq. 8 is equal to 235.8 kJ/mol and is lower than those obtained in all shock tube studies. Figure 4 shows that the shock tube study data and our data are in remarkably good agreement. This plot demonstrates that the rate constants for H_2S decomposition obtained from two entirely different experimental techniques and at a vastly different temperature range are highly consistent.

Conclusions

An experimental study on hydrogen sulfide decomposition over the temperature range 800–1,250°C at H_2S concentra-

Table 3. Kinetic Parameters for H_2S Decomposition Reaction Obtained from Different Sets of Data

	Ea_1* (kJ/mol)	A_1* (m^3/kmol·s)	Data Points	Correlation Coefficient (R^2)
Olschewski et al. (1994)	274.36 (260.18)**	2.00×10^{11} (2.00×10^{11})**	30	0.9838
Woiki and Roth (1994)	273.19 (277.74)**	2.00×10^{11} (2.78×10^{11})**	17	0.9821
This study	240.12	0.84×10^{11}	38	0.9706
3 Sets combined	235.78	0.51×10^{11}	85	0.9959

*Corresponds to the rate constant $k_1 = A_1 \exp(-Ea_1/RT)$ where R equals 8.314×10^{-3} kJ/mol·K and T is in Kelvin.
**Calculated from the data reported in the reference.

tions of 0.2 to 1.0 mol. % in nitrogen was reported. The experiments clearly established that the reaction was first-order with respect to H_2S concentration. The rate constants obtained by regression of our data are slightly lower than those reported from other flow tube study. The extrapolation of this rate constant to higher temperatures results in values greater than those found in a majority of the reported shock tube studies. However, an examination of selected high-temperature raw data (Olschewski et al., 1994; Woiki and Roth, 1994) in conjunction with our data showed that a single rate expression could describe the three sets of data encompassing a large temperature range of 800−3,100°C. The regression of the three sets of data resulted in a new rate constant k (in $m^3/(kmol \cdot s)) = (1.12 \pm 0.114) \times 10^{11}$ exp $[(-28{,}360 \pm 200)/T]$, which fits the data obtained at high and low temperatures from two different experimental techniques satisfactorily.

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