

The Kinetics of the Water Gas Conversion

III. Influence of H₂S on the Rate Equation

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It has previously been found that the rate of the water gas conversion $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ over a commercial iron oxide chromium oxide catalyst could be adequately described by an expression of the power type. The present article describes how the kinetic expression is modified by the presence of H₂S in the feed gas. Two different concentrations of H₂S have been applied, one (75 ppm) at which only a surface adsorption of H₂S takes place and another (2000 ppm) at which the bulk phase of the catalyst is more or less sulfided. The most characteristic effects of the H₂S are: The strong retarding influence of CO₂ previously found is considerably decreased and a small retarding effect of H₂ is found. The H₂O exponent is increased in the presence of H₂S. The reasons for these changes in the kinetics are discussed. The differences in the form of the kinetic expressions between the two H₂S concentrations are probably within the experimental uncertainty.

The conversion of CO with H₂O according to $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ over iron oxide based catalysts is in industrial practice being performed without or with different concentrations of H₂S as impurity, depending on the source of the feed gas. Roughly, the H₂S concentrations encountered may be divided in the following three groups:

- (1) essentially 0 (less than 1 ppm (part per million)),
- (2) 50-100 ppm and
- (3) a few thousands ppm.

It must be mentioned here that the H₂S concentrations in this article everywhere are based on total (or "wet") feed gas. This is contrary to industrial practice where "dry" feed gas is used as basis.

It seems *a priori* to be likely that the kinetics of the CO-conversion will be influenced by the presence of H₂S, at least in the third group of H₂S-concentrations because in this case the iron oxide catalyst is ordinarily more or less transformed into iron sulfide. The H₂S-concentrations of the second group do

not form iron sulfide, but surface adsorption which may also influence the kinetics is to be expected.

Although the kinetics of the CO-conversion over iron oxide catalysts in a H₂S free gas (or a supposedly H₂S free gas) has been treated by a number of authors (see, *e.g.*, Ref.¹) no work has apparently been published on the kinetics in a H₂S containing feed gas.

In the present series of articles the H₂S free case has been treated in Ref.¹ (atmospheric pressure) and Ref.² (elevated pressure). The present article reports some investigations on the kinetics of CO-conversion with H₂S-concentrations in each of the groups (2) and (3) (approximately 75 ppm and 2000 ppm, respectively) at atmospheric pressure and a temperature of 380°C. It appeared that there are characteristic differences in the kinetics when H₂S is present or not present. The variation of the kinetics with the presence of H₂S may to some extent be put in relation to the state of the catalyst.

EXPERIMENTAL

Gases. The gases applied (CO, CO₂, H₂, N₂) were from the same source and of the same purity as those described previously. Also the purification procedures were similar to the previous ones¹.

Catalyst. The previously applied iron oxide-chromium oxide catalyst was also used for the present experiments and in the same particle size (0.8–1.2 mm). The amount of catalyst was 3.00 g for the experiments with 75 ppm H₂S and 6.00 g for the experiments with 2000 ppm. In both cases the catalyst was diluted with inert material (quartz) to 12.0 cm³ which corresponds to a bed height of 5.2 cm. The catalyst was reduced at 300°C and thereafter stabilized by running for about 2 weeks at working conditions, *i.e.* 380°C and a feed gas containing H₂S in the same concentration as that to be used for the subsequent measurements. When changing the feed gas the catalyst was allowed to run for ample time under the new conditions in order to ensure equilibrium conditions. This was particularly important with the low H₂S concentration (75 ppm).

Experimental set-up. The experimental set-up was identical to that employed previously at atmospheric pressure except that a H₂S-generator was inserted in the feed line. Two different types of H₂S-generators were used, one for the 75 ppm H₂S and another one for the 2000 ppm.

The 75 ppm of H₂S were generated in the following way. H₂ was saturated with water vapour at some suitable temperature (usually in the range 60–80°C) and then passed through an oven containing iron sulfide at 450–500°C. The water then reacts with FeS to form H₂S. A coarse adjustment of the H₂S-content is obtained by varying the temperature of the water bath whereas a finer adjustment was obtained by varying the temperature of the FeS-containing oven. The iron sulfide was obtained by saturating a precipitated and dried iron oxide with H₂S from a cylinder. It is preferable to use hydrogen or a hydrogen-containing gas as carrier gas for the H₂S. The content of H₂S obtained in the feed stream is not far from that calculated from the equilibrium $3 \text{ FeS} + 4 \text{ H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 3 \text{ H}_2\text{S} + \text{H}_2$ when low space velocities are applied. This method has been proposed by Mr. M. H. Jørgensen of this laboratory.

For high concentrations of H₂S the following method was applied. A solution of Na₂S was added at a constant rate through a capillary tube to a half-concentrated solution of oxalic acid at 60°C. The H₂S generated was carried off by the feed gas to the CO-converter.

The first of these methods is preferred for low concentrations of H₂S because it is easier to obtain a constant level of H₂S in the feed gas under these conditions whereas it is less suited at higher concentrations because in this case the temperature of the water bath must be above 90°C.

Analytical procedure. CO and CO₂ were as usual determined in an Orsat apparatus. At the high concentrations of H₂S the CO₂ was obtained by correcting the amount

adsorbed in the KOH-solution for the H_2S present in the gas. When the degree of conversion was calculated from H_2 concentrations this component was determined by gas chromatography. H_2S was determined by an iodometric method. The gas to be analyzed was passed through a 1 M Cd-acetate solution and a wet gasmeter. To the precipitated CdS was added a KI_3 solution (0.1 N with respect to I_2) and hydrochloric acid. Surplus I_2 was back-titrated with a 0.1 N thiosulfate solution.

LIST OF SYMBOLS

- f = feed rate of CO (mole/h)
 k = reaction rate constant for forward reaction.
 K = equilibrium constant for the CO-conversion.
 l, m, n and q = exponents occurring in eqn. (1)
 $(CO), (H_2O), (CO_2)$ and (H_2) = partial pressures (atm.) of CO, H_2O , CO_2 and H_2 , respectively. Suffix 0 indicates initial partial pressure. Suffix e indicates partial pressure at exit of the reactor.
 (H_2S) = concentration of H_2S in ppm.
 r = net reaction rate (mole CO converted/(h)·(g catalyst))
 r_f and r_b = forward and backward reaction rates, respectively.
 x = degree of conversion of CO (moles CO converted/mole CO in feed gas)
 w = weight of catalyst (g)
 $\beta = (CO_2)(H_2)/K(CO)/(H_2O)$

EVALUATION OF
EXPERIMENTAL RESULTS

As usual the degree of conversion, x , was calculated from the equation $x = (CO_2)_e / ((CO)_e + (CO_2)_e)$ when no CO_2 was present in feed gas. When CO_2 was present in feed gas it was not practical to base the calculation of x on CO_2 determinations in feed and exit gas, the uncertainty becoming too large. Instead the H_2 determinations were applied to the following equation

$$x = ((H_2)_e - \frac{(H_2)_0}{(CO)_0} (CO)_e) / ((H_2)_e + (CO)_e)$$

in which $(H_2)_0$ usually was small. These equations are valid whether the symbols entering refer to "wet" gas or to "dry" gas partial pressures. As the analytical determinations were on dry gas it was the more practical to apply dry gas partial pressures. Anywhere else in this article the symbols refer to "wet" gas partial pressures.

It was previously found that the kinetics of CO-conversion in the temperature range 330–500°C in the H_2S free case could be adequately expressed by a power function * of the type

$$r = f \cdot \frac{dx}{dw} = r_f - r_b = k \cdot (CO)^l (H_2O)^m (CO_2)^n (H_2)^q (1 - \beta) \quad (1)$$

* In the previous articles the somewhat less correct expression "exponential equation" has been used.

The exponents l , m and n vary to some extent with temperature. At 380°C it was found that $l = 1.00$, $m = 0.25$ and $n = -0.60$ (the values of m and n are the corrected ones as used in Ref.²). q was found to be zero over the whole temperature range.

It seemed reasonable to try to express the kinetics of a H₂S containing feed gas in a similar manner. The technique applied for obtaining a kinetic expression has been the same as that described previously. In each series of runs the concentration of one of the reactants or products in the feed gas was varied. From each series a preliminary value of one of the exponents l , m , n or q , depending on which component was varied, was obtained by the graphic method described in Ref.¹ By inserting the exponents in eqn. (1) and applying the electronic digital computer the value of the rate constant k which made the calculated conversion equal to the experimental conversion was found for each run in the way described in Ref.² l , m , n or q was changed in steps of 0.05 until the value of k showed no systematic variation within each series. Only very minor variations of the preliminary constants were necessary.

It was not practically possible to obtain completely identical H₂S concentrations from one run to another within each series. The analytical uncertainty of the H₂S determination in the 75 ppm range is about ± 3 ppm. In several cases the variation of (H₂S) from one run to another has been somewhat larger than this. The effect of the variation of (H₂S) on the rate constant was therefore investigated. It was found that with a feed gas consisting of 25 % CO, 10 % H₂, 25 % N₂ and 40 % H₂O the variation of k with (H₂S) in the range 30–100 ppm H₂S could be expressed by $k = a (\text{H}_2\text{S})^{-0.35}$, a being a constant, assuming the same rate equation to be valid over the whole range. This means that a variation of (H₂S) from 70 to 80 ppm causes a variation of k of 5 %. The correction necessitated by varying (H₂S) is generally less than the experimental uncertainty caused by other factors. The values of k obtained in the Tables 1–5 have, nevertheless, been corrected for deviations of (H₂S) from the average obtained in each series. At 2000 ppm H₂S the rate constant has not been corrected for varying (H₂S), the correction being negligible.

Finally a series of runs at each of the two H₂S concentrations has been made by varying the reaction temperature (after stabilization of the catalyst at the highest temperature applied) in order to determine the apparent energy of activation. In this case no attempt has been made to correct for deviations due to varying (H₂S).

The following series of runs have been performed.

Approx. 75 ppm H₂S in feed gas:

- Variation of (CO)₀ with constant (H₂)₀ and (H₂O)₀, no (CO₂)₀; Table 1.
- Variation of (CO)₀ with constant (H₂)₀, (H₂O)₀ and (CO₂)₀; Table 2.
- Variation of (H₂O)₀ with constant (CO)₀ and (H₂)₀, no (CO₂)₀; Table 3.
- Variation of (CO₂)₀ with constant (CO)₀, (H₂O)₀ and (H₂)₀; Table 4.
- Variation of (H₂)₀ with constant (CO)₀ and (H₂O)₀, no (CO₂)₀; Table 5.
- Variation of temperature, Table 6.

Approx. 2000 ppm H₂S in feed gas:

- Variation of (CO)₀ with constant (H₂O)₀ and (H₂)₀, no (CO₂)₀; Table 7.
- Variation of (H₂O)₀ with constant (CO)₀ and (H₂)₀, no (CO₂)₀; Table 8.

Variation of $(\text{CO}_2)_0$ with constant $(\text{CO})_0$ and $(\text{H}_2\text{O})_0$, no $(\text{H}_2)_0$; Table 9.

Variation of $(\text{H}_2)_0$ with constant $(\text{CO})_0$ and $(\text{H}_2\text{O})_0$, no $(\text{CO}_2)_0$; Table 10.

Variation of temperature, Table 11.

The tables contain total amount of feed gas, composition of feed gas, degree of conversion, rate constant k , amount of H_2S in wet feed gas and, for the experiments with $(\text{H}_2\text{S}) \simeq 75$ ppm, the rate constant corrected for deviation of (H_2S) from the average. The rate equation employed for the forward reaction is given above each table. It is pointed out that the reverse reaction has been taken into consideration in the calculations (factor $(1-\beta)$ in eqn. (1)).

DISCUSSION

Before discussing the variation of the exponents with (H_2S) it may be preferable to consider the state of the catalyst in the two cases. If it is assumed that the reaction between Fe_3O_4 , H_2S and H_2 occurs according to the equation $\text{Fe}_3\text{O}_4 + 3 \text{H}_2\text{S} + \text{H}_2 \rightleftharpoons 3 \text{FeS} + 4 \text{H}_2\text{O}$ it can be calculated from thermodynamic data that when the feed gas contains 75 ppm H_2S Fe_3O_4 is the stable compound for any of the feed conditions applied in the present investigation. On the other hand when the feed gas contains 2000 ppm H_2S the stable compound should be FeS (except perhaps in a short zone at the entrance when no H_2 is added to the feed gas). Analytical determinations of sulphur in used catalysts are in agreement with these calculations. Several catalysts having been applied in the 75 ppm H_2S range have been analysed and sulphur contents of 0.5–1.0 % have been found. This quantity is not higher than it may well be assumed to be adsorbed at the surface. However, the catalyst contains a minor amount of Cr (about 7 % as Cr_2O_3) and it is possible that some of the sulphur is combined with Cr.

Table 1. 75 ppm H_2S . Variation of $(\text{CO})_0$. Amount of catalyst 3.00 g. Rate equation for forward reaction:

$$r_f = k(\text{CO})^{0.75}(\text{H}_2\text{O})^{0.50}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.15}$$

No.	Total feed mole/h	Feed gas composition %					Conv. exp. %	Rate constant k uncorr.	ppm H_2S in wet gas	Rate constant k corr.
		CO	CO_2	H_2	N_2	H_2O				
1	2.296	30.7	0	11.3	18.3	39.7	28.2	0.168	81	0.171
2	2.325	41.5	0	12.0	7.3	39.2	23.8	0.157	75	0.155
3	2.317	23.9	0	11.7	25.4	39.0	28.4	0.155	75	0.153
4	2.371	12.3	0	12.7	36.9	38.1	35.5	0.165	72	0.161
5	2.379	12.6	0	10.9	38.7	37.8	34.7	0.163	80	0.165
6	2.358	6.2	0	12.2	43.6	38.0	41.7	0.155	83	0.160
7	2.371	18.4	0	11.4	32.8	37.4	29.6	0.152	80	0.154
8	2.321	24.5	0	12.0	27.1	36.4	27.4	0.156	76	0.155
9	2.367	36.1	0	10.9	15.1	37.9	23.8	0.151	78	0.152
10	2.304	41.5	0	12.8	5.7	40.0	26.0	0.176	72	0.172
Average:									77	0.160

Table 2. 75 ppm H₂S. Variation of (CO)₀. Amount of catalyst 3.00 g. Rate equation for forward reaction:

$$r_f = k(\text{CO})^{0.80}(\text{H}_2\text{O})^{0.50}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.10}$$

No.	Total feed mole/h	Feed gas composition %					Conv. exp. %	Rate constant <i>k</i> uncorr.	ppm H ₂ S in wet gas	Rate constant <i>k</i> corr.
		CO	CO ₂	H ₂	N ₂	H ₂ O				
1	2.446	24.9	11.4	5.08	20.1	38.5	34.9	0.261	70	0.256
2	2.413	36.1	11.7	6.08	8.4	37.7	29.1	0.238	75	0.239
3	2.396	12.1	11.9	5.83	32.6	37.6	37.9	0.235	75	0.236
4	2.500	21.8	10.9	5.40	25.1	36.8	32.6	0.239	76	0.241
5	2.396	30.4	11.5	4.26	15.9	37.9	31.7	0.240	75	0.241
6	2.358	5.6	11.9	4.06	40.2	38.2	48.0	0.247	74	0.247
Average:									74	0.243

Table 3. 75 ppm H₂S. Variation of (H₂O)₀. Amount of catalyst 3.00 g. Rate equation for forward reaction:

$$r_f = k(\text{CO})^{0.75}(\text{H}_2\text{O})^{0.50}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.15}$$

No.	Total feed mole/h	Feed gas composition %					Conv. exp. %	Rate constant <i>k</i> uncorr.	ppm H ₂ S in wet gas	Rate constant <i>k</i> corr.
		CO	CO ₂	H ₂	N ₂	H ₂ O				
1	2.333	24.1	0	4.4	21.5	50.0	29.1	0.127	80	0.129
2	2.321	24.8	0	3.9	8.1	63.2	32.5	0.130	77	0.130
3	2.367	24.3	0	3.7	2.5	69.5	32.9	0.127	73	0.124
4	2.358	24.0	0	3.9	32.5	39.6	26.0	0.124	81	0.126
5	2.288	24.8	0	3.9	45.3	26.0	22.0	0.123	78	0.124
6	2.325	24.9	0	3.9	36.8	34.4	26.0	0.135	77	0.135
7	2.296	25.2	0	3.9	54.4	16.5	18.1	0.125	75	0.124
8	2.325	24.2	0	3.6	28.8	43.4	27.4	0.124	76	0.123
Average:									77	0.127

Table 4. 75 ppm H₂S. Variation of (CO₂)₀. Amount of catalyst 3.00 g. Rate equation for forward reaction:

$$r_f = k(\text{CO})^{0.75}(\text{H}_2\text{O})^{0.50}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.15}$$

No.	Total feed mole/h	Feed gas composition %					Conv. exp. %	Rate constant <i>k</i> uncorr.	ppm H ₂ S in wet gas	Rate constant <i>k</i> corr.
		CO	CO ₂	H ₂	N ₂	H ₂ O				
1	2.229	19.1	35.5	6.58	10.9	27.9	27.8	0.210	65	0.197
2	2.363	17.1	50.1	6.63	0.3	25.9	25.1	0.211	67	0.200
3	2.388	20.1	7.0	5.99	40.4	26.5	30.3	0.216	66	0.204
4	2.421	19.6	21.7	5.90	26.0	26.0	27.2	0.214	82	0.219
5	2.317	20.0	31.3	6.64	15.5	26.6	25.2	0.197	83	0.203
6	2.279	20.1	0	6.09	46.7	27.1	33.5	0.203	87	0.213
7	2.471	18.2	45.2	6.66	5.1	24.8	22.5	0.197	86	0.206
Average:									77	0.206

Table 5. 75 ppm H₂S. Variation of (H₂)₀. Amount of catalyst 3.00 g. Rate equation for forward reaction:

$$r_f = k(\text{CO})^{0.75}(\text{H}_2\text{O})^{0.50}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.15}$$

No.	Total feed mole/h	Feed gas composition %					Conv. exp. %	Rate constant <i>k</i> uncorr.	ppm H ₂ S in wet gas	Rate constant <i>k</i> corr.
		CO	CO ₂	H ₂	N ₂	H ₂ O				
1	2.400	23.6	0	13.0	25.8	37.6	24.5	0.135	75	0.136
2	2.350	23.9	0	6.9	31.3	37.9	24.1	0.120	84	0.126
3	2.371	23.4	0	35.9	2.7	38.0	21.9	0.131	73	0.130
4	2.363	23.6	0	24.3	13.8	38.3	23.4	0.136	72	0.135
5	2.304	24.2	0	16.5	20.2	39.1	26.0	0.143	71	0.139
6	2.288	24.0	0	27.1	9.4	39.5	23.5	0.132	73	0.131
7	2.292	24.4	0	18.0	18.3	39.3	25.0	0.137	68	0.133
Average:									74	0.133

Table 6. 75 ppm H₂S. Variation of temperature. Amount of catalyst 3.00 g. Catalyst stabilized at 500°C. Rate equation for forward reaction:

$$r_f = k(\text{CO})^{0.80}(\text{H}_2\text{O})^{0.45}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.15}$$

No.	Total feed mole/h	Feed gas composition, %					Conv. exp. %	Rate constant <i>k</i>	ppm H ₂ S in wet gas	Reaction temperature °C
		CO	CO ₂	H ₂	N ₂	H ₂ O				
1	2.329	24.3	22.4	13.0	0.8	39.5	61.0	1.36	73	500
2	2.404	23.7	23.2	13.6	0.7	38.8	49.4	0.606	73	460
3	2.400	24.7	23.6	13.6	0.1	38.0	28.2	0.250	74	420
4	2.363	24.3	23.4	13.7	0.3	38.3	30.4	0.269	68	420
5	2.413	24.2	23.5	13.7	0	38.7	12.5	0.0931	74	380
6	2.346	24.3	0	11.7	26.5	37.5	14.7	0.0790	78	380
7	2.458	25.4	0	14.0	26.7	33.9	4.6	0.0231	79	330

Table 7. 2000 ppm H₂S. Variation of (CO)₀. Amount of catalyst 6.00 g. Rate equation for forward reaction:

$$r_f = k(\text{CO})^{0.35}(\text{H}_2\text{O})^{0.40}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.10}$$

No.	Total feed mole/h	Feed gas composition, %					Conv. exp. %	Rate constant <i>k</i>	ppm H ₂ S in wet gas
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.425	24.6	0	6.70	30.9	37.8	17.5	0.0495	2010
2	2.400	35.9	0	6.79	18.9	38.4	15.6	0.0474	2030
3	2.392	5.2	0	6.50	49.8	38.5	23.4	0.0448	1960
4	2.454	15.2	0	6.47	41.1	37.2	18.6	0.0471	2070
5	2.413	50.8	0	6.41	3.2	39.6	14.3	0.0470	1870
Average:									1990

Table 8. 2000 ppm H₂S. Variation of (H₂O)₀. Amount of catalyst 6.00 g. Rate equation for forward reaction:

$$r_f = k(\text{CO})^{0.85}(\text{H}_2\text{O})^{0.40}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.10}$$

No.	Total feed mole/h	Feed gas composition, %					Conv. exp. %	Rate constant <i>k</i>	ppm H ₂ S in wet gas
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.338	24.6	0	6.84	55.8	12.8	7.7	0.0283	2080
2	2.363	24.2	0	7.09	0.4	68.3	13.8	0.0282	2000
3	2.267	25.0	0	6.71	19.2	49.1	13.3	0.0298	1950
4	2.325	24.6	0	6.68	46.7	22.0	9.8	0.0296	1970
5	2.329	24.3	0	6.55	35.4	33.8	11.8	0.0306	1870
Average:									1970

Table 9. 2000 ppm H₂S. Variation of (CO₂)₀. Amount of catalyst 6.00 g. Rate equation for forward reaction:

$$r_f = k(\text{CO})^{0.85}(\text{H}_2\text{O})^{0.40}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.10}$$

No.	Total feed mole/h	Feed gas composition, %					Conv. exp. %	Rate constant <i>k</i>	ppm H ₂ S in wet gas
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.383	24.3	6.3	0.15	43.6	25.7	14.9	0.0474	1960
2	2.375	24.2	3.4	0.15	45.8	26.5	16.1	0.0489	2010
3	2.471	23.3	18.5	0.14	32.6	25.5	13.7	0.0484	1970
4	2.400	24.1	0	0.15	50.1	25.7	15.7	0.0430	1940
5	2.400	25.2	29.7	0.17	19.0	25.9	12.5	0.0449	1970
6	2.363	25.0	47.6	0.16	1.3	25.9	12.5	0.0463	2050
Average:									1980

Table 10. 2000 ppm H₂S. Variation of (H₂)₀. Amount of catalyst 6.00 g. Rate equation for forward reaction:

$$r_f = k(\text{CO})^{0.85}(\text{H}_2\text{O})^{0.40}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.10}$$

No.	Total feed mole/h	Feed gas composition, %					Conv. exp. %	Rate constant <i>k</i>	ppm H ₂ S in wet gas
		CO	CO ₂	H ₂	N ₂	H ₂ O			
1	2.288	24.8	0	35.9	13.1	26.2	12.7	0.0432	1900
2	2.267	23.0	0	12.5	37.3	27.2	14.2	0.0426	1920
3	2.258	24.0	0	6.1	42.6	27.3	15.6	0.0453	1880
4	2.288	24.6	0	1.7	46.7	27.0	16.5	0.0460	1850
5	2.263	23.6	0	23.9	26.0	26.5	14.0	0.0453	2090
6	2.250	22.2	0	0.16	50.9	26.7	17.0	0.0428	2000
Average:									1940

Table 11. 2000 ppm H₂S. Variation of temperature. Amount of catalyst 6.00 g. Catalyst stabilized at 500°C. Rate equation for forward reaction:

$$r_f = k(\text{CO})^{0.80}(\text{H}_2\text{O})^{0.45}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.10}$$

No.	Total feed mole/h	Feed gas composition, %					Conv. exp. %	Rate constant <i>k</i>	ppm H ₂ S in wet gas	Reaction temperature °C
		CO	CO ₂	H ₂	N ₂	H ₂ O				
1	2.338	22.3	0	25.0	27.0	25.7	43.2	0.241	2160	504
2	2.333	23.0	0	26.4	24.9	25.7	25.0	0.100	2070	458
3	2.333	23.2	0	23.0	28.1	25.7	12.3	0.0400	2070	418
4	2.346	23.3	0	25.4	25.7	25.6	5.5	0.0159	2070	385
5	2.371	23.4	0	25.7	25.6	25.3	1.0	(0.0024)	2160	313
6	2.388	23.2	0	25.1	26.6	25.1	40.6	0.228	2160	504

On the other hand the sulphur content of a catalyst which had run for about one month with a feed gas containing 2000 ppm H₂S amounted to 22 %. Assuming it to be combined with iron as FeS this corresponds to about 60 % of the iron being present as FeS. It is likely that a run of longer duration under such conditions will result in a still higher S-content as complete sulfidation is likely to be a slow process.

It appears from Tables Nos. 1–5 and Nos. 7–10 that it is possible with 75 ppm H₂S as well as with 2000 ppm H₂S to establish exponential rate equations which are valid with good approximation over the whole concentration range applied.

The series of experiments given in Tables 1 and 2 have both been intended at a determination of the exponent *l* (at 75 ppm H₂S), different CO₂-concentrations having been applied in the two cases. The two values of *l* obtained (0.75 and 0.80) are well within the experimental uncertainty which is of the order of ± 0.05. Somewhat arbitrarily *l* = 0.75 has been applied for the subsequent calculations.

As expected the activity of the catalyst is essentially lower with 2000 ppm H₂S in feed gas than with 75 ppm H₂S. Also, within each of the two H₂S concentrations the activity of the catalyst has been somewhat different for the different series of runs.

The exponents obtained at 380°C with 0, 75 and 2000 ppm have been summarized in Table 12. Although the present investigation is less extensive than the previous one with sulphur free gas there is no doubt that the kinetic expression is greatly influenced by the presence of H₂S. On the other hand the differences in the exponents obtained with 75 ppm H₂S and with 2000 ppm H₂S are so small that they may probably be explained as being due to experimental uncertainty.

The changes of some of the exponents with the presence of H₂S can be given a reasonable explanation by considering the influence of the H₂S on the state of the catalyst surface.

Table 12. Values of exponents l , m , n and q obtained with different H₂S concentrations.

	l	m	n	q
0 ppm H ₂ S	1.00	0.25	-0.60	0
75 ppm H ₂ S	0.75-0.80	0.50	-0.10	-0.15
2000 ppm H ₂ S	0.85	0.40	-0.10	-0.10

The CO exponent, l , is lower when H₂S is present. This is not easily put unambiguously into relation to the changed state of the catalyst surface. The difference in the values obtained at 75 ppm and at 2000 ppm are within the experimental uncertainty. On the other hand the rise in the value of m (the water exponent) when passing from 0 to 75 ppm H₂S is probably due to an influence of the concentration of H₂O in the gas phase on the amount of H₂S adsorbed. Such a dependency seems likely considering that the bulk phase equilibrium between Fe₃O₄, H₂O, FeS and H₂ is established at not very much higher H₂S concentrations. At the highest H₂S concentrations (2000 ppm) the catalyst is sulfided to a considerable extent in the bulk phase. It is possible that the water dependency is again somewhat lower.

The CO₂ exponent, n , is also considerably influenced by the presence of H₂S. In this case the effect seems to be that the CO₂ adsorption is considerably decreased already at low H₂S concentrations, probably because the parts of the catalyst surface which are able to adsorb CO₂ to a large extent are prevented from that by preferential adsorption of H₂S. Preliminary experiments indicate that a large effect is obtained already with 10-15 ppm H₂S in the feed gas. The consequence of this effect is that the conversion obtained is much less decreased by high CO₂ concentrations when H₂S is present than when no H₂S is present. It appears from Table 12 that there is a small retarding effect of H₂ when H₂S is present.

To sum up, the rate equations found for the three cases at 380°C are:

$$r = k(\text{CO})(\text{H}_2\text{O})^{0.25}(\text{CO}_2)^{-0.60}(\text{H}_2)^0(1-\beta) \quad (2)$$

for no H₂S being present

$$r = k(\text{CO})^{0.75}(\text{H}_2\text{O})^{0.50}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.15}(1-\beta) \quad (3)$$

for 75 ppm H₂S

$$r = k(\text{CO})^{0.85}(\text{H}_2\text{O})^{0.40}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.10}(1-\beta) \quad (4)$$

for 2000 ppm H₂S.

As the two last equations with regard to the exponents are identical within experimental uncertainty it is reasonable to assume that for the present catalyst an "average" equation

$$r = k(\text{CO})^{0.80}(\text{H}_2\text{O})^{0.45}(\text{CO}_2)^{-0.10}(\text{H}_2)^{-0.10}(1-\beta) \quad (5)$$

for all practical purposes may be valid for H₂S concentrations in the whole range from 50 ppm to several thousands ppm.

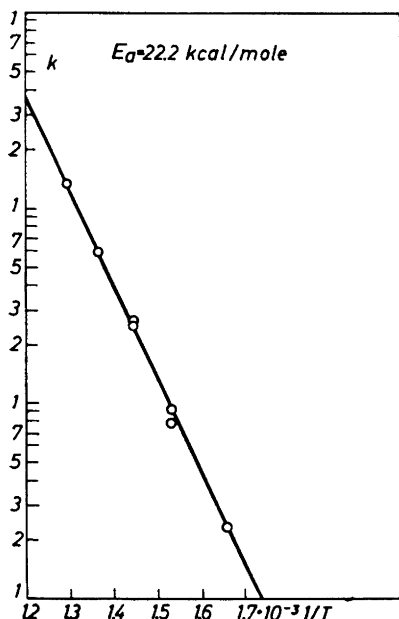


Fig. 1. Plot of $\ln k$ vs. $1/T$. 75 ppm H_2S in feed gas. Experimental data are given in Table 6.

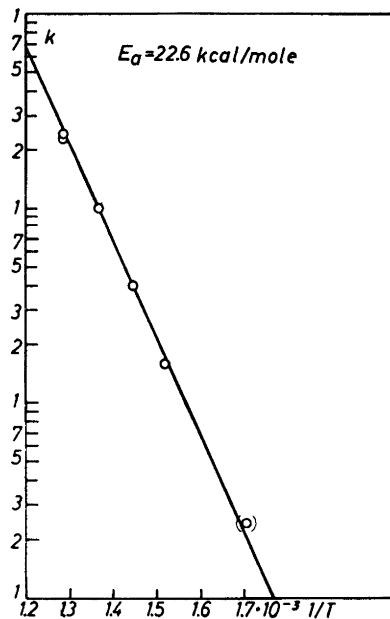


Fig. 2. Plot of $\ln k$ vs. $1/T$. 2000 ppm H_2S in feed gas. Experimental data are given in Table 11.

It was mentioned above that the effect of the variation of (H_2S) on the rate constant within the range 30–100 ppm may be expressed by $k = a(H_2S)^{-0.35}$. In principle it is therefore possible also to include the effect of the variation of (H_2S) within this range in eqn. (3). However, the experimental uncertainty of the H_2S exponent, although good enough for correction purposes, is larger than that of the other exponents.

For the calculation of the rate constants in Tables 6 and 11 the "average" rate eqn. (5) has been applied. By plotting $\ln k$ vs. $1/T$ (Figs. 1 and 2), the apparent energy of activation has been found to be 22.2 kcal/mole for the 75 ppm case and 22.6 kcal/mole for the 2000 ppm case, *i.e.* practically identical. The rate constant obtained at 313°C (Table 11) is rather uncertain due to the low conversion and has therefore been put in parenthesis.

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