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PRODUCTION OF TRITIUM BY CONTAINED NUCLEAR EXPLOSIONS IN SALT.

II. LABORATORY STUDIES OF THE REDUCTION OF ALKALINE EARTH SULFATES BY HYDROGEN

W. D. Bond

OAK RIDGE NATIONAL LABORATORY
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AUGUST 1964

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ABSTRACT

The results of this investigation show that tritium produced by a contained nuclear explosion in bedded salt will be mixed with environmental water due to the oxidation-reduction reaction between alkaline earth sulfate impurities and the tritium. The reduction of alkaline earth sulfates with hydrogen occurs in the range of 700 to 900°C at readily measurable rates. Most of the work being reported was performed with magnesium and calcium sulfates, with only a few experiments being performed with strontium and barium sulfates. Dissolving $CaSO_4$ in molten salt did not lower the temperature for the onset of the reduction nor did it increase its rate.

In the presence of excess hydrogen, the solid reduction product of $MgSO_4$ is MgO, whereas with calcium, strontium, or barium sulfates it is mainly the metal sulfide containing a few percent oxide. The experimentally observed reduction products qualitatively agreed with those predicted by thermodynamic calculations. Sulfite was shown to be an intermediate in the reductions. A general mechanism is proposed for the high-temperature reduction of sulfates. The proposed mechanism involves reduction of the sulfate to sulfite, with subsequent thermal decomposition of the sulfite. The final products are determined by the reactions among the sulfite decomposition products and by reactions of the reducing gas with the sulfite decomposition products. The solid reduction product and the gaseous products can be predicted from equilibrium data on the thermal decomposition of the sulfite. In developing the mechanism, several possible reactions among the sulfite decomposition products and the reaction of hydrogen with SO_2 were experimentally investigated.

1. INTRODUCTION

The feasibility of producing tritium by a contained nuclear explosion in salt would be seriously affected if the tritium were diluted by environmental water. Laboratory work was performed on the stoichiometry and on the rate of the oxidation reactions of hydrogen by sulfates which occur as principal impurities in rock salt. If nearly all of the tritium were oxidized to T_2O and mixed with environmental water, isotopic separation of the hydrogen isotopes would be required. Dilution of tritium also occurs by isotopic exchange between T_2 and H_2O. A study of this process was covered in a previous report.[1]

The water content of salt formations is usually less than 1%; the lowest value that can be expected is 0.01% for dome salt.[2] Since about 500 tons of salt are melted per kiloton of explosive,[3] dilution by environmental water would be a serious problem even at 0.01% concentration. Anhydrite ($CaSO_4$), polyhalite ($K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$), and silt are the principal impurities in rock salt, and these materials generally occur in strata.

Any oxidation of hydrogen to water would be due mostly to the oxygen on sulfates.[4] A typical reaction for the oxidation might be:

$$CaSO_4 + 4H_2 \rightleftharpoons CaS + 4H_2O \quad . \tag{1}$$

Depending upon the initial mole ratio of T_2 to environmental water and the equilibrium constant for the reaction, the tritium could be diluted in either of two ways: oxidation of T_2 to T_2O by the forward reaction, or isotopic exchange between water and T_2 by the dynamic equilibrium. In either case the net result is the same: The tritium product is diluted.

Although the literature reports many investigations of sulfate reactions with carbon, methane, or carbon monoxide,[5-12] few studies[12-14] had been reported on the nature of the hydrogen reduction of sulfates. Hegedis and Fukker[13] studied the reduction of sulfates by thermogravimetric methods in regard to the final solid reduction products. Magnesium sulfate was reported to give MgO as the solid reduction product, and $CaSO_4$ was reported to yield CaS. Collectively, the previous literature studies[4-14] indicate that the gaseous reduction products are SO_2, H_2S, S, and H_2O and that the relative amounts of these products are dependent on the temperature, the mole ratio of H_2/sulfate, the hydrogen flow rate, and the particle size of the solid sulfates. Although a general mechanism for sulfate reductions was not prepared, the work of Pechkovskii and Ketov[10] showed that the reduction of barium sulfate by CO involves the sulfite as an intermediate, and that the final reduction products depended upon the thermal decomposition products of the sulfite and their subsequent reaction with the reducing gas.

The author expresses sincere appreciation to H. Kubota and W. R. Laing of the Analytical Division for chemical analysis and to R. E. Blanco, who made many helpful suggestions throughout the course of the work.

2. RESULTS AND DISCUSSION

Thermodynamic data and the chemical analysis of reaction products from experimental reductions are presented to define the reaction products of the hydrogen reduction of $CaSO_4$ and of $MgSO_4$. A few experiments were performed with $SrSO_4$ and $BaSO_4$ for the purpose of investigating sulfite as a general intermediate in sulfate reductions. Rate data were measured for the reduction of $CaSO_4$, $MgSO_4$, and $CaSO_4$ dissolved in molten NaCl. A general mechanism is proposed for sulfate reductions. To verify the mechanism, a few experiments are presented on calcium sulfite decomposition under flow conditions and on secondary reactions of sulfite decomposition products.

2.1 Reaction Products Predicted by Thermodynamic Calculations

Due to the many valence states of sulfur, a great many reactions must be considered to evaluate the products of sulfate reductions. Examination of the literature revealed that all the reactions listed in Table 1 must be considered.

Free-energy data were directly available from the literature for many of the reactions, and the remainder was calculated from free-energy data of the individual compounds. The sources of data for each reaction are listed in Appendix A. Thiosulfates and sulfites were not considered as final products since it is known that these compounds are unstable at temperatures below the reduction temperature of the corresponding sulfates.[15-18]

Table 1. Calculated Standard Free Energy Changes for Some Reactions in the Sulfur-Oxygen-Magnesium (or Calcium) Systems

Reaction No.	Reaction (Me = Ca or Mg)	Me	ΔF (kcal)[a]			
			700°C	800°C	900°C	1000°C
(1)	$MeS + 2SO_2 = MeSO_4 + S_2$[b]	Ca	-4.4	0.3	4.9	9.4
		Mg	0.0	3.0	9.0	13
(2)	$4MeO + 4SO_2 = 3MeSO_4 + MeS$	Ca	-70	-57	-40	-24
		Mg	22	40	51	59
(3)	$4MeO + 2S_2 = 3MeS + MeSO_4$	Ca	-65	-58	-50	-43
		Mg	23	31	37	43
(4)	$MeS + H_2O = MeO + H_2S$	Ca	13	13	13	13
		Mg	-5	-5	-4	-2
(5)	$MeSO_4 + 4H_2 = MeS + 4H_2O$	Ca	-45	-48	-50	-52
		Mg	-45	-49	-52	-55
(6)	$MeSO_4 + 4H_2 = MeO + 3H_2O + H_2S$	Ca	-29	-32	-35	-39
		Mg	-51	-54	-57	-58
(7)	$MeSO_4 + H_2 = MeO + SO_2 + H_2O$	Ca	4.0	-4.0	-9.5	-14.0
		Mg	-16	-22	-26	-30
(8)	$MeSO_4 + 7/2H_2 = MeO + 1/2H_2S + 1/4S_2 + 3H_2O$	Ca	-22	-26	-30	-34
		Mg	-46	-49	-53	-54
(9)	$SO_2 + 2H_2 = 1/2S_2 + 2H_2O$		-24	-22.5	-21.0	-19.5
(10)	$SO_2 + 3H_2 = H_2S + 2H_2O$		-34.5	-31	-29.5	-30.0

[a] Estimated accuracy of $\Delta F°$ for reactions involving MgS is ±10 kcal; all others are ±1.0 kcal.

[b] The sulfur at these temperatures is gaseous dimer.

The thermodynamic data show that the main products of $CaSO_4$ reduction with H_2 should be CaS and H_2O. Small amounts of CaO, SO_2, S_2, and H_2S would be expected since the free-energy change in reactions (7) and (8) are negative. The main products of the $MgSO_4$ reduction reaction are H_2O, H_2S, SO_2, S_2, and MgO. Magnesium sulfite would not be formed as a product because of the hydrolysis reaction given in reaction (4) and the reverse of the reaction given in reaction (2). Thermodynamic evaluations were not made for $SrSO_4$ or $BaSO_4$ reductions, which would be expected to be very similar to that of $CaSO_4$.

The contribution to oxide formation by the hydrolysis of $MgSO_4$ and $CaSO_4$ is negligibly small[19] and need not be considered. Reduction of the sulfates at temperatures above the thermal decomposition temperature was not considered since the only reactions involved would be those of H_2 with SO_2 and with O_2. The respective decomposition temperatures for the $MgSO_4$, $CaSO_4$, $SrSO_4$, and $BaSO_4$ are 895, 1150, 1375, and greater than 1400°C.[20]

2.2 Reduction Products Found by Experiment

Complete reduction of fixed beds of $MgSO_4$ and of $CaSO_4$ showed the reaction products to be those expected from the thermodynamics (Table 2). The experiments were made under flow conditions and were not necessarily at equilibrium. The solid reduction product from $MgSO_4$ was MgO which contained less than 200 ppm of MgS, whereas the solid product from $CaSO_4$ contained about 95% CaS and about 5% CaO. The presence of SO_2 and its hydrogen reduction products, H_2S and elemental S, suggests that sulfite is an intermediate since the reduction temperature is well below those of the decomposition temperatures of the sulfates. The dependence of stoichiometry of the reduction on temperature suggests the temperature dependence of the many reactions involved. The variation of stoichiometry with initial weight of sulfate indicates nonequilibrium reduction.

The partial reduction of $MgSO_4$, $CaSO_4$, $SrSO_4$, and $BaSO_4$ in porcelain combustion boats showed that sulfite was indeed an intermediate, as it could be detected

Table 2. Material Balances on Sulfur and Hydrogen for the Reduction of Fixed Beds of $MgSO_4$ and $CaSO_4$

H_2 Flow Rate = 133 to 155 cc/min
1-in.-diam bed

			% Sulfate Converted to:				Moles H_2 Consumed/mole SO_4^{2-}	
Compound	Temp. (°C)	Init. Wt. of Sulfate (g)	Metal Sulfide	H_2S	SO_2	S^a	From H_2 Off-Gas Measurement	By Chemical Analysis
$MgSO_4$	734	5.00	0	43.4	31.4	25.2	-	2.81
$MgSO_4$	784	5.00	0	18.5	39.8	41.7	2.2	2.39
$MgSO_4$	784	5.00	0	11.9	48.9	39.2	-	2.12
$MgSO_4$	784	2.50	0	33.0	40.8	26.2	2.3	2.51
$CaSO_4$	885	5.00	96	2.04	1.43	$<1^b$	3.9	3.93
$CaSO_4$	885	5.00	96	2.04	1.43	$<1^b$	-	-
$CaSO_4$	885	5.00	96	2.38	1.36	$<1^b$	-	-
$CaSO_4$	885	5.00	97	2.02	1.83	$<1^b$	-	-
$CaSO_4$	885	2.50	94	4.08	2.34	$<1^b$	-	-
$CaSO_4$	915	5.00	95	3.52	1.12	$<1^b$	-	-

[a] Calculated from H_2S/SO_2 analysis and initial amount of sulfate.

[b] By visual observation of sulfur on cold section of furnace tube.

in the solid reduction product (Table 3). Thiosulfate was not detected in the reduction products, as had been previously reported for $BaSO_4$-CO reduction by Pechkovskii and Ketov.[10] This is probably due to the fact that the reaction was not immediately quenched in our experiments. The observed order of the quantity of sulfite produced in the solid products of reduction of the alkaline earth sulfates is: $BaSO_4 > SrSO_4 > CaSO_4 > MgSO_4$, as would be expected from literature data on the thermal decomposition of sulfites.[15-18] Correspondingly, the amount of SO_2 in the off-gas is the reverse of that for the quantity of sulfite intermediate found.

2.3 Rate Studies

Apparent rates of reduction of $MgSO_4$ and of $CaSO_4$ with H_2 were measured in fixed beds of the respective sulfates. Comparative rates were measured for $CaSO_4$ in pure form, and $CaSO_4$ dissolved in molten NaCl and in molten LiCl-KCl.

Fixed-Bed Reductions

The reaction rates of fixed beds of $MgSO_4$ and $CaSO_4$ were studied by measuring the rate of consumption of hydrogen. A known constant hydrogen feed rate was used in conjunction with the rate of hydrogen emerging from the bed, as measured with a wet-test meter. The difference in the two rates was the rate of consumption. Sulfur dioxide and H_2S were removed in a 2 M NaOH solution before the effluent gas was admitted to the wet-test meter. The reductions of $MgSO_4$ and $CaSO_4$ were both autocatalytic (Figs. 1 and 2, and Table 4). Very long induction periods were observed with $MgSO_4$. Magnesium sulfate is clearly the more reactive compound once reduction has begun. Long induction periods do not necessarily indicate the complete absence of chemical reaction. The reaction during induction is, however, immeasurably slow by most methods. Even though the induction period for $MgSO_4$ was very long at 734°C, H_2S was evolved slowly after 2 min of contact with H_2, and it increased with time. No induction period was observed with $CaSO_4$ at the temperature studied. However, it may take place at lower temperatures.

Table 3. Partial Reduction of Sulfates by Hydrogen

H_2 Flow Rate = 150 cc(STP)/min

Material	Init. wt[a] (g)	Temp. (°C)	Reaction Time[b] (min)	Metal Ion	Solid Product Analysis (wt %)			Off-Gas (mg)	
					$SO_3^=$	$S^=$	SO_4	SO_2	H_2S
$MgSO_4$	1.0245	734	14	45.1	<0.2	<0.2	37.4	254	101
	1.0441	734	2[c]	28.1	0.23	<0.05	68.8	121	36
$CaSO_4$	1.1771	885	5	30.8	0.66	7.56	50.0	6.75	0.5
$SrSO_4$	1.5390	885	3	53.3	4.16	2.57	35.2	4.0	0.55
	1.5324	885	10	53.4	2.94	2.23	34.8	-	.04
$BaSO_4$	1.9554	885	6	69.1	7.95	4.95	20.34	1.4	0.9
	1.9496	885	3.5	51.2	3.25	4.11	42.31	-	-

[a] All weights correspond to 0.00835 to 0.00865 mole.

[b] Reaction time from first observation of reaction product, water.

[c] Furnace tube was immediately removed from furnace to quench thermal decomposition of the sulfite.

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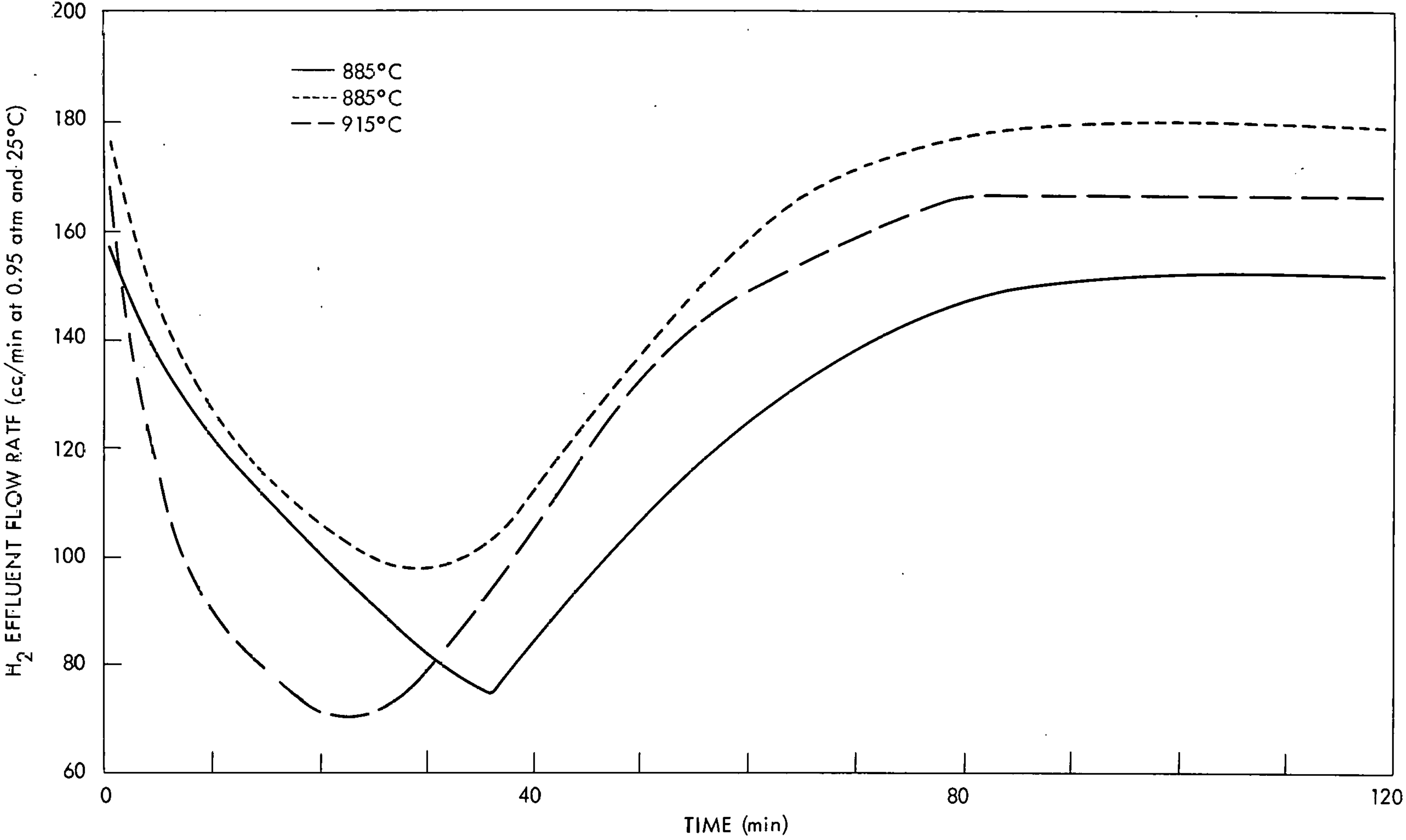

Fig. 1. Reduction of Fixed Beds of Calcium Sulfate by Hydrogen. Five grams of $CaSO_4$ (<325 mesh); surface area, 10 m^2/g; 1-in.-diam bed, 0.9 in. deep.

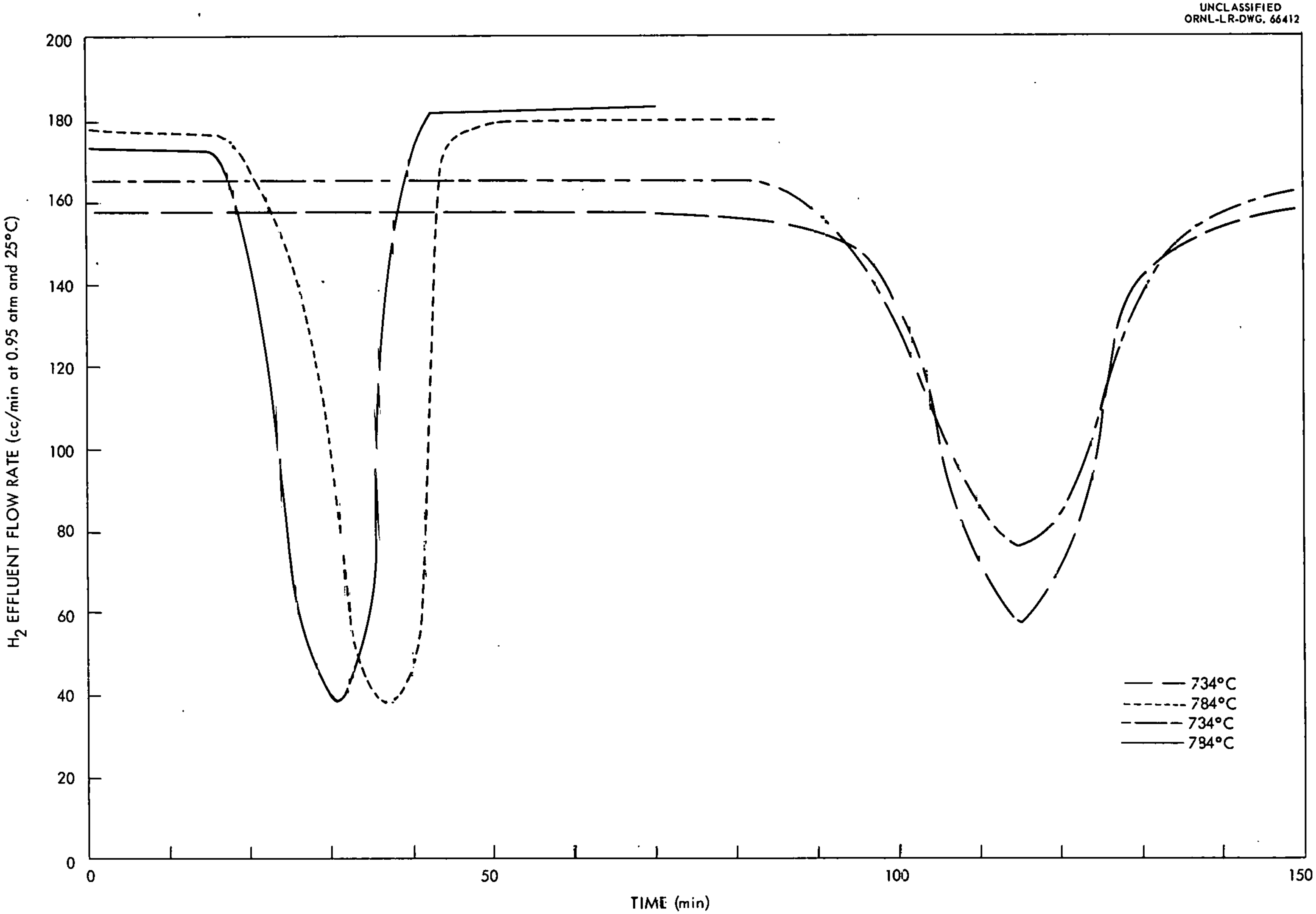

Fig. 2. Reduction of Fixed Beds of Magnesium Sulfate by Hydrogen. Five grams of $MgSO_4$ (<325 mesh); surface area, 0.99 m^2/g; 1-in.-diam beds, 0.5 in. deep.

The total reaction time was independent of the mass of $CaSO_4$ or $MgSO_4$ (Table 4). Calculation of apparent activation energies from the maximum reaction rates by the Arrhenius equation gave 16 kcal for $CaSO_4$ and 18 kcal for $MgSO_4$, which indicates similar processes of reductions for the two compounds. It is doubtful, however, if those reductions have a constant activation energy because the stoichiometry is variable with temperature (Table 2).

Comparative Rates of $CaSO_4$ Alone and of $CaSO_4$ Dissolved in Molten Salt

The rates of reduction of pure $CaSO_4$ and of $CaSO_4$ dissolved in NaCl or molten LiCl-KCl were compared (Table 5). For experiments with $CaSO_4$ or with $CaSO_4$ dissolved in molten NaCl, hydrogen was simply passed over the material when contained by a porcelain boat. In experiments with $CaSO_4$ in molten LiCl-KCl, hydrogen was bubbled into the melt. Comparisons were made by measurement of the water produced in a specified period of time.

Within experimental error, dissolving $CaSO_4$ in molten NaCl did not affect the reduction rate (Table 5). The experiments with LiCl-KCl show that the reaction cannot be initiated at temperatures up to 500°C by dissolving the $CaSO_4$ in molten salt. This result indicates that no marked lowering in the temperature at which reduction of the sulfate is perceptible is caused by having the material dissolved.

2.4 General Mechanism of Sulfate Reductions

The results of the above experiments on the reduction of alkaline earth sulfates with hydrogen suggest a general mechanism for high-temperature reductions of sulfates. The proposed mechanism involves reduction of sulfate to sulfite, with subsequent decomposition of the sulfite and reaction of the reducing gas with the sulfite decomposition products. By this mechanism, the products of a given sulfate reduction can be predicted from thermal decomposition data for the corresponding sulfite, and knowledge of reactions of the reducing gas with the sulfite decomposition products.

Table 4. Reaction Rates of $MgSO_4$ and $CaSO_4$ Powders in Fixed Beds

Powder size: <325 mesh
Bed diam: 1 in.
H_2 flowrate: $145 \pm 10 \frac{cc(STP)}{min}$
Bed depths (in./g): $MgSO_4$ = 0.14; $CaSO_4$ = 0.088
Surface areas (m^2/g): $MgSO_4$ = 0.99; $CaSO_4$ = 10

Compound	Temp. (°C)	Mass (g)	Complete Reduction Time (min)	Induction Time (min)	Maximum H_2 Reaction Rate cc(STP)/min	Time at Maximum Reaction Rate[a] (min)
$MgSO_4$	734	5.00	145	70	87.0	115
$MgSO_4$	734	5.00	150	75	75.5	115
$MgSO_4$	784	5.00	50	8	122	37
$MgSO_4$	784	5.00	50	10	125	31
$MgSO_4$	784	5.00	45	0	123	24
$MgSO_4$	784	2.50	50	10	87.4	32
$CaSO_4$	885	5.00	90	0	66	35
$CaSO_4$	885	5.00	95	0	71	30
$CaSO_4$	885	2.50	90	0	36	20
$CaSO_4$	915	5.00	75	0	82	21

[a] These times include the induction time.

Literature data[10, 18] were available for the decomposition of magnesium and barium sulfites for use in determining the mechanism of sulfate reductions. Some experiments were necessary for determining the decomposition products of $CaSO_3$ under flow conditions that were used in our reduction studies. Strontium sulfite would be expected to behave in the same way as calcium and barium sulfites.

Table 5. Effect on Rate of Reduction of Dissolving $CaSO_4$ in Molten Salts

H_2 Flow Rate = 500 cc(STP)/min

Material	Temp. (°C)	Init. Sample wt (g)	Wt of $CaSO_4$ (g)	Time (min)	$\frac{\text{g of } H_2O}{\text{g of } CaSO_4}$
$NaCl-CaSO_4$	850	3.01	0.903	65	0.165
$NaCl-CaSO_4$	850	2.42	0.727	65	0.135
$CaSO_4$	850	1.00	1.00	65	0.156
$CaSO_4$	850	1.01	1.01	65	0.212
$LiCl-KCl-CaSO_4$	400	55	5.0	80	0
$LiCl-KCl-CaSO_4$	450	55	5.0	20	0
$LiCl-KCl-CaSO_4$	500	55	5.0	15	0

Magnesium Sulfate Reductions

The products of $MgSO_4$ reductions were MgO, SO_2, S, H_2O, and H_2S. The amount of MgS in the reduction product was less than 200 ppm. The fact that the solid reduction product contained only MgO would be predicted from the literature data on $MgSO_3$ decomposition[18] under a stream of N_2, which showed that the decomposition products are mainly MgO and SO_2, with a few percent of the sulfite undergoing auto-oxidation to form $MgSO_4$ and S_2. Thus the reduction products of $MgSO_4$ with H_2 can be explained by the following reactions:

$$MgSO_{4(s)} + H_{2(g)} \longrightarrow MgSO_{3(s)} + H_2O_{(g)} \quad ,$$

$$MgSO_{3(s)} \longrightarrow MgO_{(s)} + SO_{2(g)} \quad ,$$

$$SO_{2(g)} + 2H_{2(g)} \longrightarrow 1/2S_{2(g)} + 2H_2O_{(g)} \quad ,$$

$$SO_2 + 3H_2 \longrightarrow H_2S_{(g)} + 2H_2O_{(g)} \quad .$$

Any small amount of sulfite undergoing auto-oxidation to $MgSO_4$ would in turn be reduced ultimately to MgO by the H_2.

To further check the instability of MgS in an environment of sulfur-bearing gases, attempts were made to form the sulfide by reactions of MgO with S_2, with SO_2, and with H_2S (Table 6). The gases were passed over MgO in a porcelain boat inside a furnace tube. It is seen that very little sulfide is formed in these reactions, indicating the instability of sulfide in these environments. Apparently any sulfide formed reacts with SO_2 to form sulfite or sulfate by the following reactions:

$$2MgS + 3SO_2 \longrightarrow 2MgSO_3 + 3/2S_2 \quad ,$$

$$MgS + 2SO_2 \longrightarrow MgSO_4 + S_2 \quad .$$

With hydrogen present, the sulfite or sulfate ultimately goes to the oxide. Reduction of sulfite with hydrogen gives the same reduction products as the sulfate.[18]

Calcium Sulfate Reductions

The fact that the solid reduction product of $CaSO_4$ was mainly CaS when excess hydrogen was used suggests that CaS is more stable than CaO in the presence of the product gases, which were mainly H_2O with small amounts of SO_2, H_2S, and S_2. The thermal decomposition of $CaSO_3$ under flow conditions similar to those in the present study were not available from the literature. The literature[15, 16] gives the following reaction for $CaSO_3$ decomposition under equilibrium conditions:

Table 6. Reaction of $MgO_{(s)}$ with $S_{2(g)}$, $SO_{2(g)}$, and $H_2S_{(g)}$

Initial amt of MgO = 0.0248 mole MgO (1.00 g)

Reaction	Temp. (°C)	Gas Flow Rate (moles/min)	Mole Ratio of Reactant Gas to MgO[a]	Final Solid Analysis (wt %)		
				S^{2-}	SO_3^{2-}	SO_4^{2-}
$MgO + S_2$	500	9.68×10^{-5}	0.98	0.5	1.51	<0.05
$MgO + SO_2$	800	6.34×10^{-3}	15.5	0.04	<0.04	9.95
$MgO + H_2S$	800	3.57×10^{-3}	8.6	0.46	0.78	<0.05

[a] Computed from gas flow rate, total reaction time, and initial number of moles of MgO.

$$4CaSO_3 \longrightarrow CaS + 3CaSO_4 \quad .$$

Under flow conditions, however, very little CaS was formed after complete decomposition (Table 7). Moderate amounts of free sulfur and SO_2 are evolved. Under the flow conditions used, the decomposition occurred by the following reactions, which were calculated from analysis of the solid product:

$$CaSO_3 \longrightarrow CaO + SO_2 \quad ,$$

$$4CaSO_3 + 2SO_2 \longrightarrow 4CaSO_4 + S_2 \quad ,$$

$$4CaSO_3 \longrightarrow CaS + 3CaSO_4 \quad .$$

The higher the flow rate of the helium sweep gas, the greater was the decomposition to CaO and SO_2. This result is reasonable in that the higher flow rate effectively cuts down the residence time of SO_2 and there is less time for it to react. Measurement of the decomposition in which the weight loss versus time was measured with a semiautomatic recording thermobalance showed that the decomposition was fairly slow at 900°C and appeared to be zero order (Fig. 3). The zero-order dependence indicates bed-diffusion control of the escape of SO_2 and S_2.

Since most of the SO_2 produced by sulfite decomposition would be reduced by the excess H_2 to S_2 and H_2S, the sulfite intermediate is consistent with the observed reaction products. The S_2 or H_2S reacts with any CaO formed to form CaS. The mechanism is given by the following reactions:

$$CaSO_4 + H_2 \longrightarrow CaSO_3 + H_2O \quad ,$$

$$CaSO \longrightarrow CaO + SO_2 \quad ,$$

$$SO_2 + 2H_2 \longrightarrow 1/2S_2 + 2H_2O \quad ,$$

$$SO_2 + 3H_2 \longrightarrow H_2S + 2H_2O \quad ,$$

$$CaO + 3/2S_2 \longrightarrow CaS + 1/2SO_2 \quad ,$$

$$CaO + H_2S \longrightarrow CaS + H_2O \quad .$$

Table 7. Products of the Complete Thermal Decomposition of $CaSO_3$ at 900°C

He Flowrate $\frac{cc(STP)}{min}$	Wt % $CaSO_3$ Decomposed by the Indicated Reaction[a]		
	$6CaSO_{3(s)} \rightarrow 4CaSO_{4(s)} + 2CaO_{(s)} + S_{2(g)}$	$4CaSO_{3(s)} \rightarrow CaS_{(s)} + 3CaSO_{4(s)}$	$CaSO_{3(s)} \rightarrow CaO_{(s)} + SO_{2(g)}$
300	52	17	31
600	40	15	46

[a] Computed from analysis of final solid and material balance. No thiosulfate was detected.

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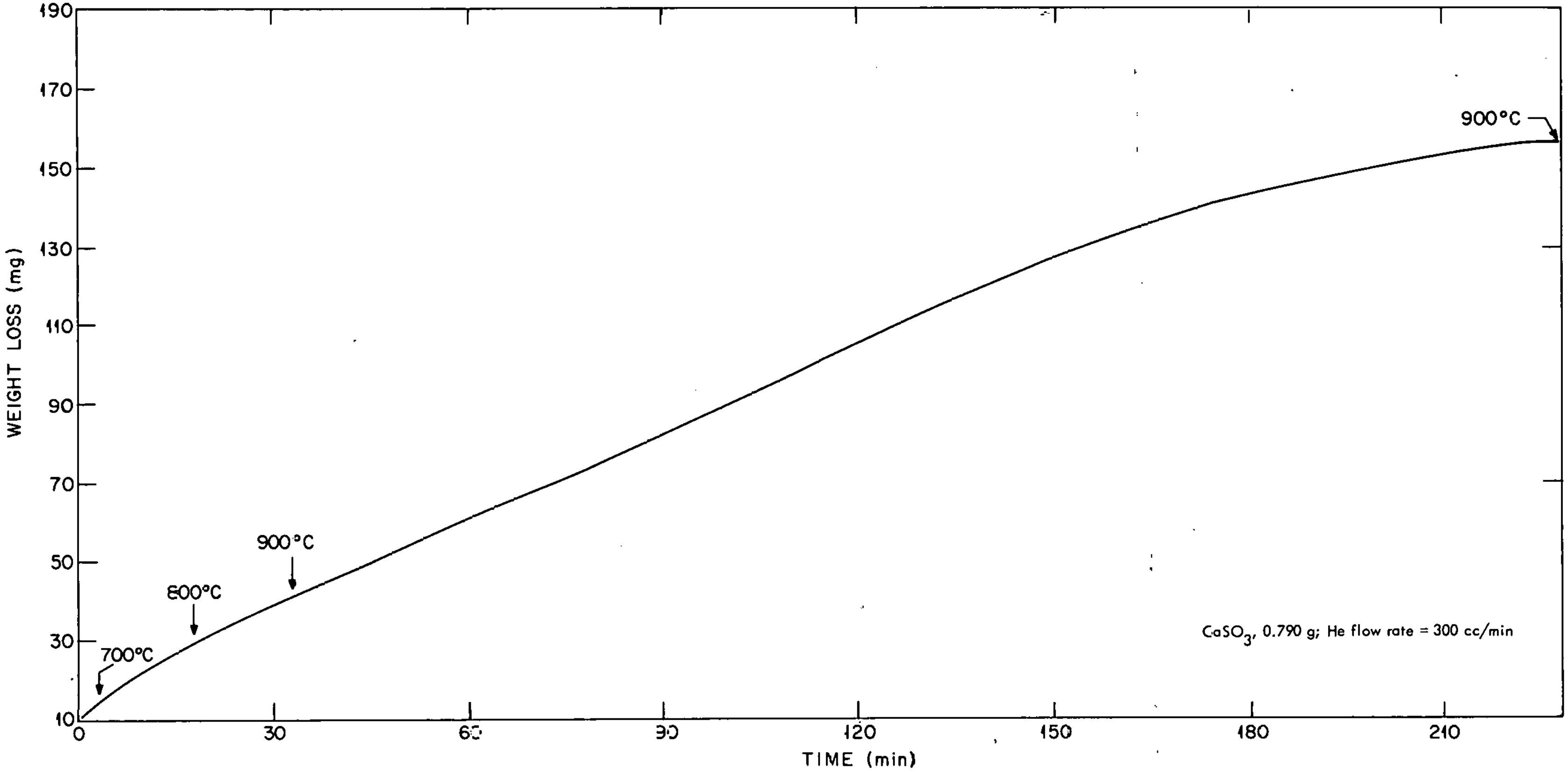

Fig. 3. Rate of Thermal Decomposition of CaSO$_3$.

To further validate the mechanism, several of the reactions were experimentally checked. The reactions of CaO and SO_2, CaO and H_2S, CaO and S_2, CaS and SO_2, CaS and H_2O, and SO_2 and H_2 were briefly investigated. Sulfide is a product of the reactions involving CaO with sulfur-bearing gases (Table 8). No thiosulfate was detected in any of the reaction products. The oxidation of sulfide to sulfate occurs when excess SO_2 is present. The results reported for interaction of CaO and SO_2 are in good agreement with those of Ketov and Pechkovskii.[21]

The following reactions are involved in the reactions in Table 8:

$$CaO + SO_2 \longrightarrow CaSO_3 \quad ,$$

$$4CaSO_3 + 2SO_2 \longrightarrow 4CaSO_4 + S_2 \quad ,$$

$$CaS + 2SO_2 \longrightarrow CaSO_4 + S_2 \quad ,$$

$$2CaO + 3/2S_2 \longrightarrow 2CaS + SO_2 \quad ,$$

$$CaO + H_2S \longrightarrow CaS + H_2O \quad .$$

In sulfate reductions where excess H_2 is present to reduce SO_2, the product of sulfate reduction would be expected to be primarily CaS if the reduction of SO_2 by H_2 is sufficiently fast.

The reaction of SO_2 with H_2 was observed to be very slow at 700 to 900°C, but, when solid CaO or MgO was added, the reaction was very rapid, producing copious quantities of H_2O, S_2, and H_2S. With flow rates of 400 cc/min of H_2 and 400 cc/min or SO_2, and a 1-g sample of MgO or CaO, the MgO was unchanged after 5 min of reaction, but the CaO contained 4.7% sulfide. When H_2 is in excess over SO_2, the solid reduction product would be CaS.

Calcium sulfide is very stable to the reaction-product water. Passing $H_2O_{(g)}$ over 1 g of CaS at 900°C at a rate of 7.5 cc/min for 1.5 hr produced only 2 mg of H_2S (mole ratio $H_2O/CaS = 4.1$), which shows that CaS resists hydrolysis by the reaction-product water.

Table 8. Some Reactions of $CaO_{(s)}$ and of $CaS_{(s)}$ with $SO_{2(g)}$, $H_2S_{(g)}$, and $S_{2(g)}$

Weight of sample: 1.00 g

Temperature: 900°C

Reaction	Gas Flow Rate (cc/min)	Time (min)	Analyses of Solid Product[a] (wt %)		
			S^{2-}	SO_3^{2-}	SO_4^{2-}
$CaO + SO_2$	142	10	0.13	0.34	30.2
$CaO + H_2S$	80	60	13.6	<0.1	<0.1
$CaO + S_2$	22	20	12.7	10.5	7.3
$CaS + SO_2$	142	10	17.7	1[illegible].8	25.2

[a] No thiosulfate was detected.

All the reactions involving the thermal decomposition products of $CaSO_3$ which were tested indicate that CaS should be the most stable product when excess reducing gas such as H_2 is present, as did the thermodynamic calculation. This should also be true for $BaSO_3$ and $SrSO_3$ because lesser amounts of H_2S, S_2 and SO_2 are released during the reduction of the corresponding sulfates (Table 3). Decomposition of $CaSO_3$, $BaSO_3$, or $SrSO_3$[15, 16] under equilibrium conditions proceeds mainly according to the following reaction, where Me = Ca, Ba, or Sr:

$$4MeSO_3 \longrightarrow MeS + 3MeSO_4 \quad .$$

Magnesium sulfite under equilibrium conditions yields MgO and SO_2.

Thus it has been shown that one can predict the final solid products of sulfate reductions on the basis of knowledge of the equilibrium dissociation of the sulfites since their products are the most stable in a system involving hydrogen-sulfur-oxygen-metal. When sulfide is the stable solid product, the product gas is H_2O, and, when oxide is the stable solid product, the product gases are H_2O, SO_2, S, and H_2S. In nonequilibrium flow systems, a few percent of metal oxide is expected to be formed in systems in which the sulfide is thermodynamically more stable than the oxide because SO_2 and its reduction products are swept from the reaction chamber. This prediction also is true for the reductants CO, C, and CH_4.

3. EXPERIMENTAL

3.1 Chemicals

All chemicals used were reagent grade. Calcium sulfite was not available and was prepared by a modification of the procedure of Matthews and McIntosh,[22] in which the hemihydrate was precipitated from a $CaCl_2$ solution by adding a Na_2SO_3 solution until precipitation was complete. The precipitation was conducted under an argon atmosphere. The undried solid resulting contained 23.9% Ca, 46.2% SO_3^{2-}, and 4.5% SO_4^{2-}. This solid was dried at 400°C to the $CaSO_3$ (92% $CaSO_3$, 8% $CaSO_4$).

Hydrogen was purified before use by passing it through a platinum asbestos recombiner, a "Drierite" trap, and then through a charcoal trap cooled by liquid nitrogen to remove O_2 and H_2O.

3.2 Apparatus

The furnace tube used for the fixed-bed reductions is shown in Fig. 4. A similar quartz furnace tube without the silica frit was used for experiments in which the sample was held by porcelain boats. Feed flow rates were measured by calibrated rotameters; H_2 in the off-gas was measured by a wet-test meter after SO_2, S, and H_2S had been removed; free sulfur was removed in a room-temperature glass-wool trap; and SO_2 and H_2S were scrubbed from the gas stream by a 2 <u>M</u> NaOH trap. The 2 <u>M</u> NaOH trap was analyzed for sulfite and H_2S by the procedure of Kurtenacher and Bittner.[23] Temperatures were measured with Chromel-Alumel thermocouples, using a reference ice bath and a potentiometer. Temperature control was maintained by a Pyrovane controller. The thermogravimetric balance used has been described previously.[24]

4. APPENDIX A. SOURCES OF THERMODYNAMIC DATA

The standard free energies for several of the reactions had been calculated previously in the literature. Free energies for the remainder of the reactions were calculated using values for the individual compounds.

4.1 Free Energies of Reactions Available in Literature

$CaS + 2SO_2 \longrightarrow CaSO_4 + S_2$	Ginstling and Volkov[11]
$4CaO + 4SO_2 \longrightarrow 3CaSO_4 + CaS$	Ginstling and Volkov[11]
$4CaO + 2S_2 \longrightarrow 3CaS + CaSO_4$	Ginstling and Volkov[11]
$CaS + H_2O \longrightarrow CaO + H_2S$	Bond and Clark[4]
$CaSO_4 + 4H_2 \longrightarrow CaS + 4H_2O$	Bond and Clark[4]
$CaSO_4 + H_2 \longrightarrow CaO + SO_2 + H_2O$	Bond and Clark[4]

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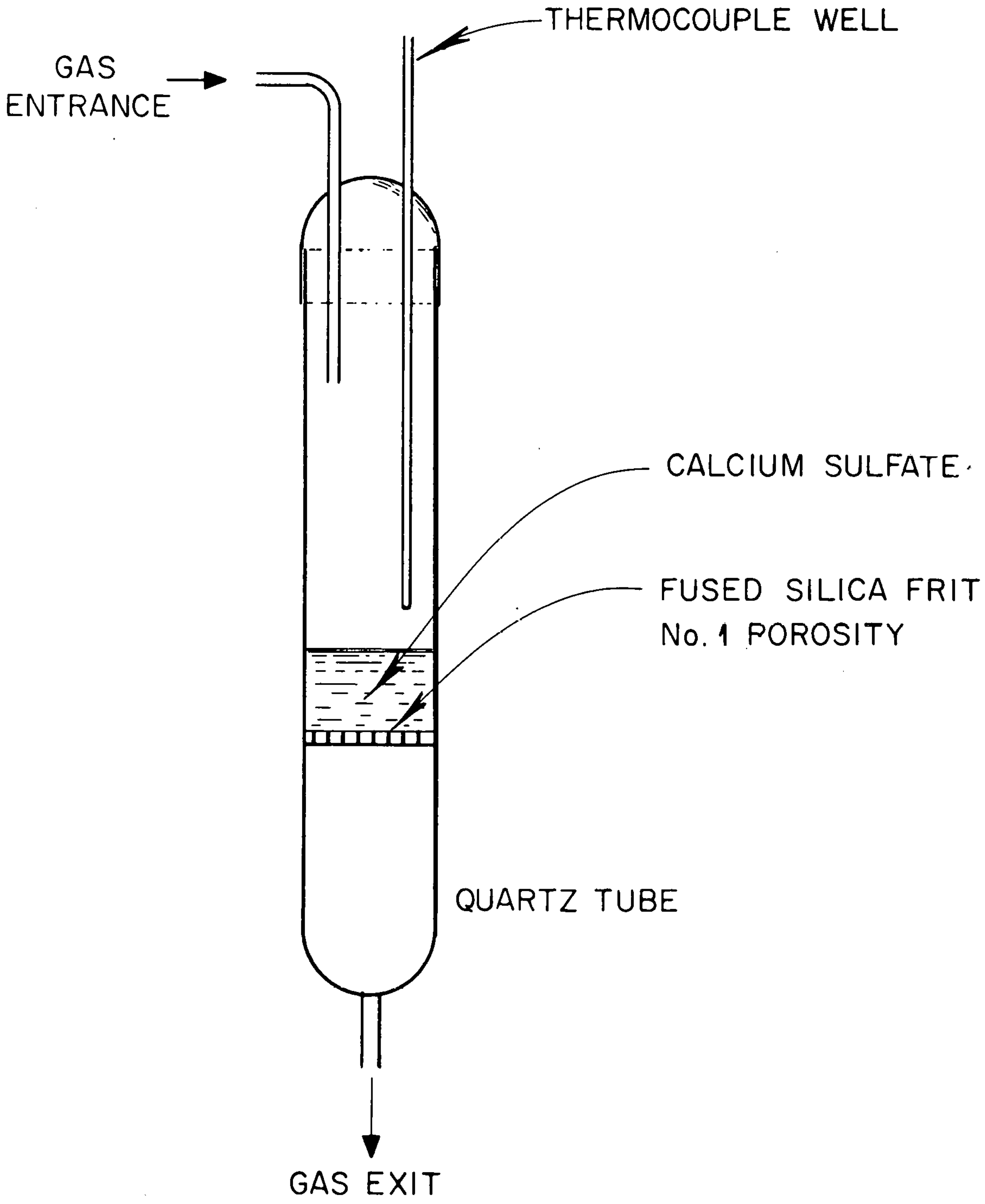

Fig. 4. Schematic Diagram of Furnace Tube for Fixed-Bed Reductions.

4.2 Sources of Free Energy Data for Calculating Other Reactions

Compound	Reference
$CaO_{(s)}$	Glassner[25]
$MgO_{(s)}$	Glassner[25]
$H_2O_{(g)}$	Rossinni, *et al.*[26]
$MgS_{(s)}$	Litz[27]
$MgSO_{4(s)}$	Kelley[28]
$S_{2(g)}$	Kelley[28]
$H_2S_{(g)}$	Kelley[28]
$CaSO_{4(s)}$	Kelley[28]
$CaS_{(s)}$	Kelley[28]

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