LA-UR-78-847

CONF-780807--4

TITLE: The Decomposition of Hydrogen Bromide using Iron Bromide and Magnetite.*

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SUBMITTED TO: To be considered for presentation at the 2nd. World Hydrogen Energy Conference, 21-24 August 1978, Zurich, Switzerland, and to be published in the proceedings.

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*Work completed under the auspices of the Division of Basic Energy Sciences, United States Department of Energy.

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ENERGY RESEARCH AND
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CONTRACT W-7405-ENG. 36

THE DECOMPOSITION OF HYDROGEN BROMIDE USING IRON BROMIDE AND MAGNETITE*

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ABSTRACT

A means of thermochemically decomposing hydrogen bromide has been investigated experimentally using the reaction between magnetite and HBr as the bromine producing step. A high yield of Br_2 was formed in a short time (90% in 0.5 h). For the hydrogen producing step, the direct hydrolysis of ferrous bromide was confirmed as having an unfavorable equilibrium (3.61×10^{-3} at 849 K). However introduction of magnesium oxide into an aqueous solution of $FeBr_2$ and subsequent heating of the insoluble product gave H_2 and Fe_3O_4 in good yields. Further, Br_2 could be regenerated from this Fe_3O_4 by treatment with HBr. All the reactions were demonstrated to be fast, going to about 85% completion. The main drawback is the heat required to dry and dehydrate magnesium bromide in order to reform MgO by hydrolysis. These reactions are discussed within the framework of a thermochemical cycle.

INTRODUCTION

With the evolution of the study of the regenerative chemical reactions for the production of hydrogen from water many of the early ideas have had to be modified. However one problem which has remained constant throughout is finding a thermochemical method for decomposing HBr. This can then be linked with the two well known reactions:

$$SO_2 + Br_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr \qquad (1)$$

$$H_2SO_4 \rightarrow H_2O + SO_2 + 1/2\ O_2 \qquad (2)$$

to form a cycle which has the possibility of a high thermal efficiency. [1] One attractive theoretical possibility was using chromium bromides:

$$CrBr_2 + HBr \rightarrow CrBr_3 + 1/2\ H_2 \qquad (3)$$

$$CrBr_3 \rightarrow CrBr_2 + 1/2\ Br_2 \qquad (4)$$

These reactions, with many modifications, have been studied extensively at Los Alamos [2,3], the conclusion being reached that high thermal efficiencies are incompatible with high yields and fast rates.

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Therefore we have switched our attention to iron compounds which are economically attractive. In the iron system the +3 state is stabilized by the formation of the oxide. This paper describes a study undertaken to estimate the feasibility of using such reactions for splitting HBr in a thermochemical hydrogen process. Some time after the initiation of this work it was learned that some Japanese workers [4,5] had been investigating some of the same reactions but coupling them to Br_2/Cu_2O as the oxygen producing step.

RESULTS AND DISCUSSION

1. Bromine Formation

The bromination of Fe_3O_4 using HBr:

$$Fe_3O_4(c) + 8HBr(g) \rightarrow 3FeBr_2(c) + 4H_2O(g) + Br_2(g) \qquad (5)$$

$$\Delta H^o_{298} = - 301.7 \text{ kJ}$$

has been shown [6] to proceed fast with high product yields, (80-90% in 0.5 h) over a wide temperature range, 500-900 K with the stoichiometry as indicated. Surface effects probably account for the reaction not going to completion. In the hydrogen chloride reaction:

$$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + Fe_2Cl_6 + 4H_2O \qquad (6)$$

only small amounts of Cl_2 are formed. About 10% of Fe_2Cl_6 decomposes to $FeCl_2$ and Cl_2. [7]

The free energy change for this reaction is negative at low temperatures and becomes zero at 880 K. At temperatures below 880 K the negative free energy results in high entropy production due to the irreversibility. For example at 700 K, the entropy production is 184 kJ/kmol H_2 K which results in a loss factor (i.e. loss of available energy with respect to the overall change in energy of the incoming water) of .23. This represents 43% of the total loss factor (.54) which is allowable for an overall cycle efficiency of 50% when coupled to a heat source with a temperature range 1200 K to 500 K. [8]

However, by reducing the entropy production to zero we now introduce energy losses connected with separating H_2, HBr and H_2O. Also, if a stoichiometric deficiency of HBr is used some Fe_2O_3 will be formed at temperatures greater than 800 K:

$$Fe_3O_4 + 2HBr \rightarrow Fe_2O_3 + FeBr_2 + H_2O \qquad (7)$$

where the free energy of (7) becomes more negative than that of (5).

2. Hydrogen Formation

In cycles involving $FeCl_2$, H_2 has been generated by the direct hydrolysis of $FeCl_2$. Therefore, as an initial study of H_2 formation from $FeBr_2$, the direct hydrolysis was investigated.

a) Direct Hydrolysis of $FeBr_2$.

$$3FeBr_2 + 3H_2O \rightarrow 3FeO + 6HBr \qquad (8)$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \qquad (9)$$

The equilibrium constant of reaction (8) was measured as described in the experimental section and the results are given in Table I. Reaction (9) was found to occur spontaneously once FeO had been generated in reaction (8). Some relevant thermodynamic data are shown in Figure 1, taken from [9]. As a consequence of the low equilibrium constant a very high $H_2O:H_2$ ratio is obtained. Figure 2 shows the theoretical percentage of water converted and the amount of HBr produced at equilibrium at 940 K as a function of moles of input water. (At temperatures higher than 940 K, the vapor pressure of $FeBr_2$ becomes so great that $FeBr_2$ will distill out of the hot zone of the apparatus, 12.5 mm at 940 K, mp 960 K). This plot indicates clearly that, as more HBr is produced, so is more unconverted water carried over resulting in very dilute HBr. Concentrating this HBr to be used in reaction (5) and the concurrent separation problems makes this step uneconomic.

As has been pointed out by van Velzen and Langenkamp [7] for the $FeCl_2$ hydrolysis these inefficiencies in themselves are sufficient to make the whole cycle unprofitable. For $FeBr_2$ hydrolysis the situation is even worse since the equilibrium constant is lower (0.0106 vs. 0.1240 at 940 K).

Reaction (8) can be carried out in a H_2 atmosphere in order to suppress (9). The rationale being that the temperature can then be lowered to where (9) becomes more favorable (see Fig. 1.) thus requiring less energy input. In addition the separation problems should be eased. However much this modification improves reaction (9) it does not affect reaction (8), which is still too inefficient to be employed. Therefore an alternative route for obtaining H_2 from $FeBr_2$ was considered.

b) Base Hydrolysis of $FeBr_2$

The following steps were postulated:

$$3FeBr_2(aq.) + 3MgO(c) \rightarrow 3FeO(c) + 3MgBr_2(aq.) \qquad (10)$$

$$3FeO(c) + H_2O(g) \rightarrow Fe_3O_4(c) + H_2(g) \qquad (11)$$

$$3MgBr_2(aq.) \rightarrow 3MgBr_2(c) \qquad (12)$$

$$3MgBr_2(c) + 3H_2O \rightarrow 3MgO + 6Br(g) \qquad (13)$$

which in the fashion written and when coupled with (1), (2) and (5) give a thermal efficiency (or figure of merit as defined by Funk [10]) for water decomposition of 53%. Therefore these steps were examined experimentally.

i) When aqueous $FeBr_2$ solution and MgO were mixed together (reaction 10), slow H_2 evolution was observed together with the immediate appearance of a blue green precipitate. This precipatate was identified, by its x-ray diffraction pattern [11], to be a mixed valent iron hydroxy bromide of the general form $[Fe(OH)_2]_A[FeOOH]_B[FeOBr]_C$ where A >> B + C known as "green rust." The details of this reaction are discussed elsewhere [6] and are summarized in Fig. 3. The maximum amount of H_2 which was obtained was 53% of that which would accompany the complete formation of Fe_3O_4, the rate being significantly catalyzed by palladium black. Reaction (10) can be rewritten:

$$3FeBr_2(aq.) + 3MgO(c) \rightarrow H_2 + \text{green rust} + MgBr_2(aq.) \qquad (14)$$

$$\text{green rust} \xrightarrow[< 373\ K]{} H_2 + \text{oxidized green rust} \qquad (15)$$

(14) taking place rapidly, followed by a slow rate determining (15). The amount of magnesium bromide formed in (14) is in the range 85-95% of that required by the stoichiometry of (10) and (11). It does not appear possible to obtain pure $Fe(OH)_2$ in the presence of bromide ions. A similar reaction was obtained when MgO was replaced with magnesium hydroxide, basic magnesium carbonate or basic magnesium bromide. These modifications can be incorporated into the cycle if a resultant gain in efficiency would be obtained.

ii) Since it has been shown [12] that $Fe(OH)_2$ decomposes to H_2, Fe_3O_4 and H_2O at temperatures above 373 K:

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2 \qquad (16)$$

it was decided to heat green rust at higher temperature. The H_2 yields obtained are shown in Fig. 4. At 723 K, 72% of the total possible H_2 was evolved in 1 h. (In the absence of Pd black, the amount of H_2 evolved in (14) and (15) is small, about 2% in 1 h). The main reaction path on heating green rust results in the formation of Fe_3O_4 (as shown by x-ray):

$$\text{green rust} \rightarrow Fe_3O_4 + H_2 + H_2O \qquad (17)$$

showing that the main component of green rust is iron in the + 2 state, only small amounts of FeOOH and FeOBr being present. The other reaction paths are:

$$2FeOOH \rightarrow Fe_2O_3 + H_2O \qquad (18)$$

$$3FeOBr \rightarrow Fe_2O_3 + FeBr_2 + 1/2\ Br_2 \qquad (19)$$

However no lines corresponding to Fe_2O_3 or $FeBr_2$ were seen in the product x-rays indicating that (18 and 19) are minor pathways. Of course small amounts of Fe_2O_3 and $FeBr_2$ would not be seen. In any case Fe_2O_3 does not harm the regenerative nature of the cycle:

$$Fe_2O_3 + 6HBr \rightarrow 2FeBr_2 + Br_2 + 3H_2O \qquad (20)$$

Reaction (19) decreases the H_2 yield since HBr would be formed. However the cyclisation is unaffected, $FeBr_2$ being carried through the process until, in aqueous solution, it reacts with MgO. At 823 K the yields were decreased, presumably because an alternate reaction path:

$$4Fe(OH)_2 \rightarrow Fe_3O_4 + Fe + 4H_2O \qquad (21)$$

has a lower free energy (ΔG^{o}_{823} = -245.2 kJ vs. -192.5kJ for (16)). Fe will easily react with steam liberating H_2:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \qquad (22)$$

so the formation of Fe does not detract from the overall process.

A study was also undertaken to see the effect of mixing time for the $FeBr_2$/MgO reaction (that is reactions 14 and 15) on the H_2 yields on heating the product green rust (reaction 17). With the uncatalyzed reaction, the H_2 yield increased from 1% after .25 h to 7% after 15 h and no appreciable effect was seen on the thermal decomposition of the green rust formed. This is further support for the mechanism proposed for green rust formation; that is fast precipitation from solution followed by intramolecular oxidation, both stages being accompanied by H_2 formation.

iii) With the experimental proof that both H_2 and Br_2 can be generated in high yields we then proceeded to study the regenerative formation of $FeBr_2$. Fe_3O_4, formed by the thermal decomposition of green rust, was treated with HBr. $FeBr_2$, Br_2 and H_2O were formed as in the case of pure Fe_3O_4 in reaction (5). The results are shown in Table II. In all cases the Br_2 yields are lower than the H_2 yields which is not surprising considering the nature of green rust and also that even when pure Fe_3O_4 was used only 80-90% of the Br_2 theoretically possible was obtained. If, as is thought, that this is partly due to surface effects, then it should be possible to decrease their importance with efficient stirring.

iv) In order to complete the study of this method of splitting HBr, the hydrolysis of $MgBr_2 \cdot 6H_2O$ was examined and found to go quantitatively when heated to 970 K for 1.5 h. The dehydration and hydrolysis of the hexahydrate was studied as a function of temperature for a constant time interval of 0.5 h. It is clear that little reaction occurs below the melting point of the hydrate.

The drying and dehydration of $MgBr_2$ requires a very large heat input:

$$3MgBr_2(aq.) + 66H_2O(l) \rightarrow 3MgBr_2\cdot 6H_2O(c) + 48H_2O(g) \qquad (23)$$

$$\Delta H^o_{298} = +\ 2147\ kJ$$

$$3MgBr_2\cdot 6H_2O(c) \rightarrow 3MgBr_2(c) + 18H_2O(g) \qquad (24)$$

$$\Delta H^o_{298} = +\ 1317\ kJ$$

The amount of water was dictated by the need to assure adequate mixing of $FeBr_2$ solution and MgO slurry in reaction (14). Although it was experimentally found that if all the water is replaced by acetone (or methanol) no reaction occurs, due to lack of solubility of MgO it is possible to substitute most of the water to a minimum of 6 moles per $MgBr_2$ since the hydrate is soluble in acetone:

$$3MgBr_2(aq.) + 18H_2O(l) + 48CH_3COCH_3(l) \qquad (25)$$

$$\rightarrow 3MgBr_2\cdot 6H_2O(c) + 48CH_3COCH_3(g)$$

$$\Delta H^o_{298} = +1500\ kJ$$

This is a 30% reduction over a totally aqueous system but is hardly enough to influence a thermochemical cycle.

Another approach to decreasing the heat requirement was to use basic magnesium bromide hydrates, $(MgBr_2)_a(Mg(OH)_2)_b(H_2O)_c$, in place of MgO, thereby reducing the need to dehydrate. These hydrates are found as intermediates in the hydrolysis of $MgBr_2\cdot 6H_2O$:

$$MgBr_2\cdot 6H_2O \rightarrow (MgBr_2)_a(Mg(OH)_2)_b(H_2O)_c \rightarrow MgO + 5H_2O + 2HBr \qquad (26)$$

and were shown to react like MgO in (10). If the reaction was such that the hydrolysis occurred before the dehydration then the intermediate could be used. However, from Figure 5 one can see that most of the water is removed before extensive hydrolysis occurs.

CONCLUSIONS

It is apparent from this study that the base hydrolysis of $FeBr_2$ does give a method of splitting HBr thermochemically. Br_2 and H_2 are obtained in high yields at acceptable rates. Many of the reactions can be carried out over wide temperature ranges which will make thermal matching from a high temperature heat source easier. All the reactions occur at relatively low temperatures suggesting that the process could be coupled to a solar energy collector.

Table III lists all the reactions as they occur. The temperatures of the reactions and the accompanying enthalpy changes are given in Table IV. Green rust has been written as $Fe(OH)_2$ for simplification. It shows clearly that the formation of hydrates as an intermediate in the formation of dry $MgBr_2$ from solution (either acetone or water) incurs an extremely large heat penalty. This has previously been noted in the case of the chromium cycle.[3] The relatively high temperature at which the dehydration of $MgBr_2$ takes place makes it impossible to utilize all the heat generated by the low temperature exothermic reactions.

When these reactions are coupled with the formation and decomposition of sulfuric acid and the efficiency calculated in the usual way (10) an efficiency of 16% is obtained. Obviously the acceptable rates are at the expense of the overall efficiency. This method of splitting HBr will only be of practical value if an auxillary low temperature heat source is made available.

EXPERIMENTAL

1. Reagents. The $FeBr_2$ used was obtained from Roc/Ric Research Chemicals and was characterized by its x-ray diffraction pattern and by being oxidized to give an Fe:Br ratio of 1:2. Other chemicals were obtained from Mallinckrodt Chemical Co., characterized by x-ray patterns and used without further purification. HBr was obtained from Scientific Gas Products, Inc.

2. Analytical Methods. Gas samples were analyzed by mass spectrometry and, in all cases, were shown to be H_2, usually 99% with air and acetone as the balance. Solid products were identified by x-ray powder patterns and Br_2 estimated using standard titration techniques.

3. Standard Experimental Techniques.

a i) H_2 Evolution Experiments, Direct Hydrolysis of $FeBr_2$.
$FeBr_2$ (7.0×10^{-3} mole) was packed in a narrow quartz tube (6 mm diameter) and held in position with quartz wool and placed in a tube furnace. Preheated steam was introduced into the tube with a very slow flow of argon gas. The exit gases were passed through a water bath to remove HBr and the residual gas flow measured using an inverted vertical burette. The steam input rate was controlled by a syringe pump. The amount of HBr collected in half hour intervals was estimated.

a ii) H_2 Evolution Experiments, in the presence of MgO.
The low temperature reaction between $FeBr_2$ solution and MgO was carried out in an evacuated system as previously described.[6] In order to thermally decompose green rust, it was first isolated by freezing the products from this step. The tube was then evacuated and placed in an oxygen free chamber. After thawing, green rust was separated by filtration using a Schlenk filter stick. The precipitate was dried with acetone and transferred to a pyrex tube which was connected to a pressure transducer and

a gas sample bulb. The whole system was evacuated and the tube placed in a furnace. After designated lengths of time, the tube was removed, cooled and the pressure reading taken.

b) Br_2 Evolution Experiments. Weighed amounts of Fe_3O_4 formed in a ii) were placed in quartz boats in a quartz tube inside a tube furnace. HBr flowed over the boats and left the system through two salt ice traps, one trap of aqueous KI and finally through an oil bubbler. The furnace was heated to 873 K and maintained at that temperature until no more Br_2 could be seen, about twenty minutes.

c) $MgBr_2 \cdot 6H_2O$ Experiments. The solid was heated in a stream of helium to the desired temperature and maintained there for half an hour. The weight loss and acid formed were measured. The compound is hygroscopic so the weights were taken immediately on cooling.

ACKNOWLEDGMENTS

Acknowledgment is gratefully given to M. G. Bowman and J. D. Farr for continuing support and to K. E. Cox, C. Hollabaugh, W. M. Jones, C. L. Peterson and W. G. Witteman for discussions and to M. A. David for experimental assistance.

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TABLE I.

COMPARISON BETWEEN THEORETICAL AND EXPERIMENTALLY OBTAINED EQUILIBRIUM CONSTANTS FOR FERROUS BROMIDE HYDROLYSIS

Temperature K	Experimental Equilibrium Constant	Theoretical Equilibrium Constant
849	3.691×10^{-3}	3.610×10^{-3}
849	3.572×10^{-3}	3.610×10^{-3}
910	1.651×10^{-2}	1.415×10^{-2}

TABLE II

REGENERATIVE FORMATION OF $FeBr_2$ AND Br_2

H_2 Formation on Heating Green Rust		Br_2 Formation on Reacting Produce Fe_3O_4 with HBr. 673 - 873 K	Br_2/H_2
Temp. K	% H_2 Formed		
566	58	42	0.72
628	87	56	0.64
726	80	63	0.79
823	56	45	0.80

TABLE III

REACTIONS INVOLVED IN SPLITTING HBr

$$\begin{aligned}&\mathrm{3FeBr_2(aq.) + 3MgO(c) + 21\ H_2O(\ell) + 51(CH_3)_2CO(\ell)}\\ &\quad\rightarrow \mathrm{3Fe(OH)_2(c) + 3MgBr_2(aq.) + 18H_2O(\ell) + 51(CH_3)_2CO(\ell)}\end{aligned}\tag{A}$$

$$\mathrm{3Fe(OH)_2(c) \rightarrow Fe_3O_4(c) + H_2(g) + 2H_2O(g)}\tag{B}$$

$$\mathrm{Fe_3O_4(c) + 8HBr(g) \rightarrow 3FeBr_2(c) + Br_2(g) + 4H_2O(g)}\tag{C}$$

$$\begin{aligned}&\mathrm{3MgBr_2(aq.) + 18H_2O(\ell) + 48(CH_3)_2CO(\ell)}\\ &\quad\rightarrow \mathrm{3MgBr_2\cdot 6H_2O(c) + 48(CH_3)_2CO(g)}\end{aligned}\tag{D}$$

$$\mathrm{3MgBr_2\cdot 6H_2O(c) \rightarrow 3MgBr_2(c) + 18H_2O(g)}\tag{E}$$

$$\mathrm{3MgBr_2(c) + 3H_2O(g) \rightarrow 3MgO(c) + 6HBr(g)}\tag{F}$$

$$\mathrm{3FeBr_2(c) \rightarrow 3FeBr_2(aq.)}\tag{G}$$

$$\mathrm{21H_2O(g) \rightarrow 21H_2O(\ell)}\tag{H}$$

$$\mathrm{51(CH_3)_2CO(g) \rightarrow 51(CH_3)_2CO(\ell)}\tag{I}$$

TABLE IV

REACTION TEMPERATURE AND ΔH^{o}_{298} FOR THE REACTIONS INVOLVED IN SPLITTING HBr

Reaction	Temperature, K	ΔH^{o}_{298}, kJ
A	< 373	$- 156.3^{*}$
B	573 - 773	+ 103.8
C	473 - 873	- 283.0
D	≥ 329	+ 1500.2
E	723	+ 1316.7
F	773 - 1073	- 255.3
G	< 373	$- 243.5^{*}$
H	≤ 373	- 924.3
I	≤ 329	- 1557.7

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*An estimated enthalpy of formation of $FeBr_2$(aq.) used here.

FIGURE CAPTIONS

Fig. 1. The free energy changes as a function of temperature of some reactions of iron compounds.

Fig. 2. The theoretical percentage of water converted and the amount of HBr produced as a function of the moles of input water for the hydrolysis of $FeBr_2$ at 940 K.

Fig. 3. Rate ( ) and yield ( ) of H_2 production formed by reacting $FeBr_2$ solution (2.3 mol ℓ^{-1}) with MgO in the presence of palladium black (0.1 mol ℓ^{-1}) at 298 K.

Fig. 4. H_2 yield as a function of temperature obtained on heating green rust at the specified temperatures.

Fig. 5. Dehydration and hydrolysis of $MgBr_2 \cdot 6H_2O$ after heating for 0.5 h at the specified temperature.

$$MgBr_2 \cdot 6H_2O \rightarrow MgO + 2HBr + 5H_2O.$$

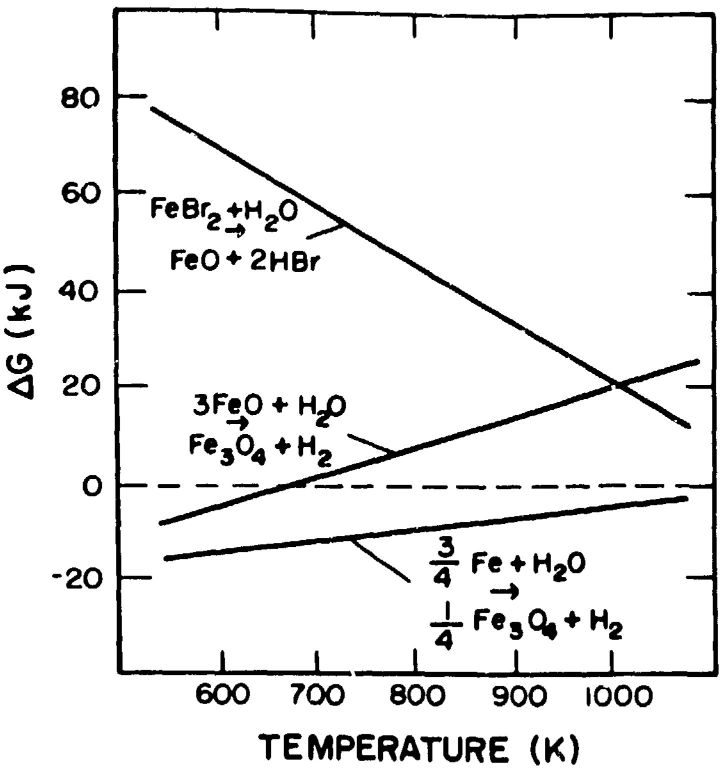

80
60
40
20
0
-20
ΔG (kJ)
$FeBr_2 + H_2O \rightarrow FeO + 2HBr$
$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$
$\frac{3}{4} Fe + H_2O \rightarrow \frac{1}{4} Fe_3O_4 + H_2$
600
700
800
900
1000
TEMPERATURE (K)

Fig. 1

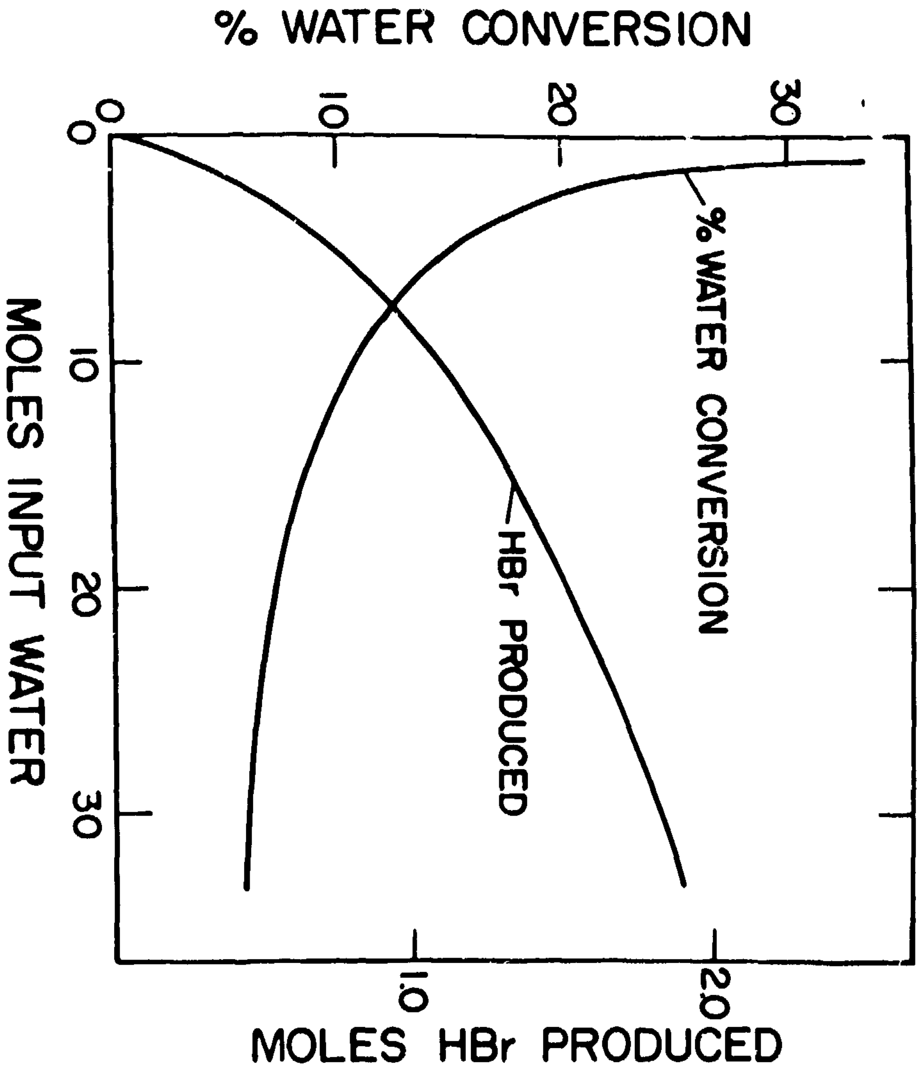

% WATER CONVERSION
0
10
20
30
MOLES INPUT WATER
0
10
20
30
MOLES HBr PRODUCED
1.0
2.0
HBr PRODUCED
% WATER CONVERSION

Fig. 2

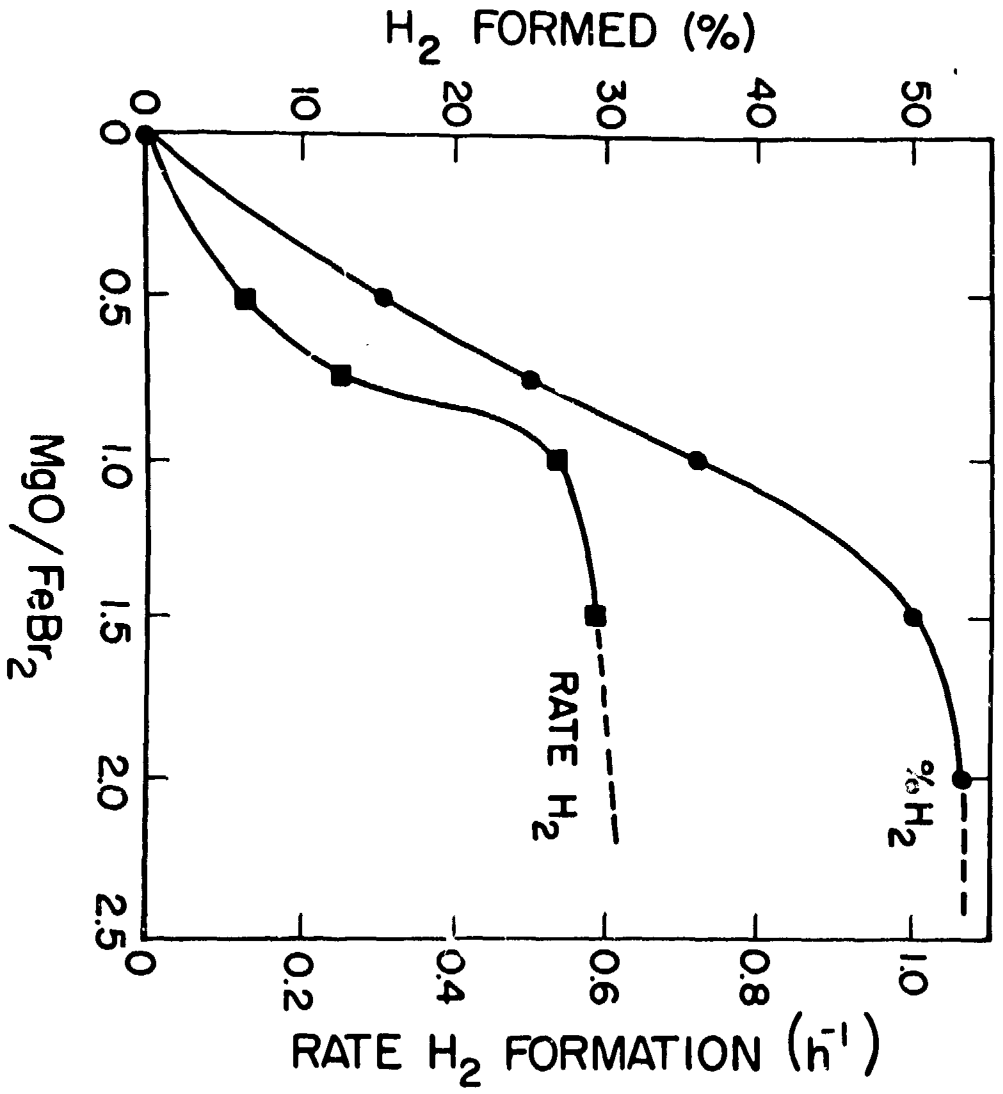
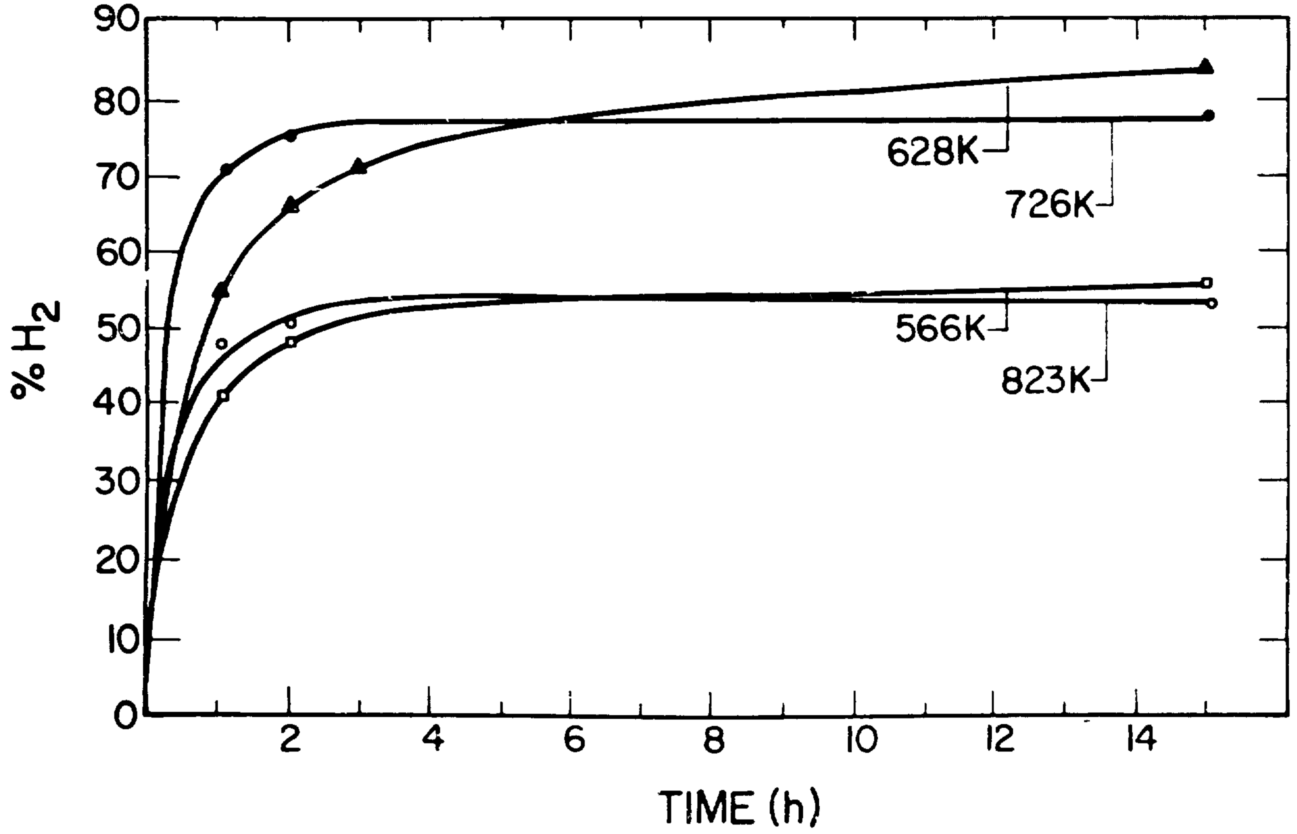
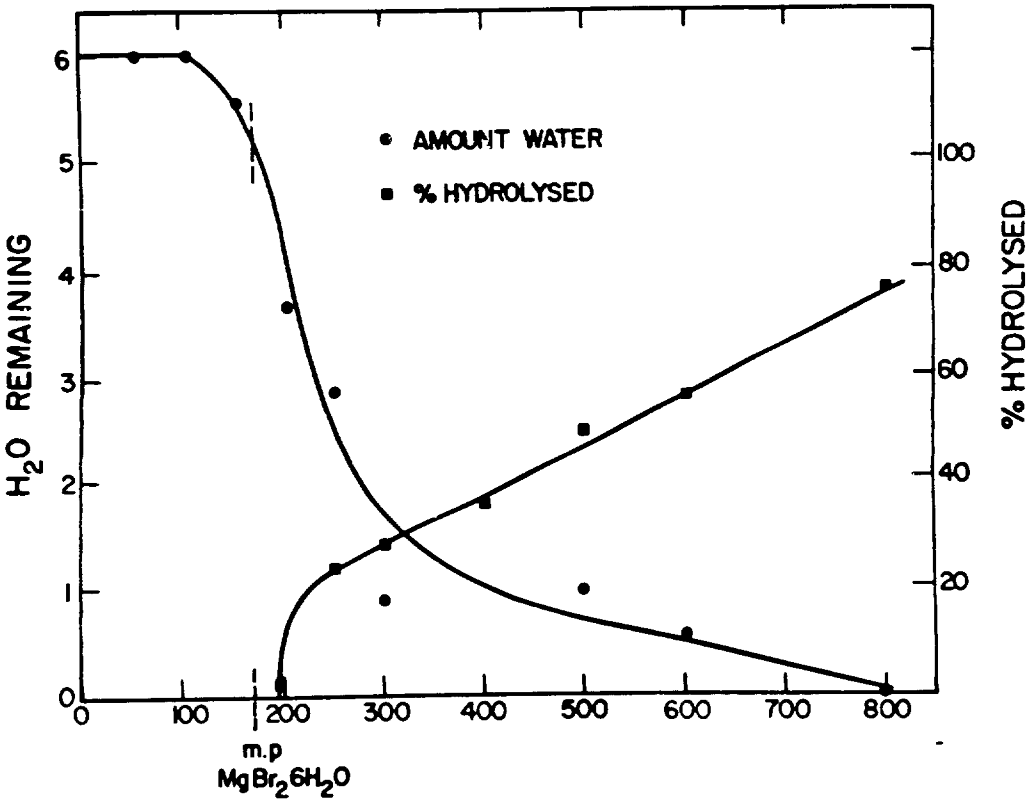

H$_2$ FORMED (%)
0
10
20
30
40
50
0
0.5
1.0
1.5
2.0
2.5
MgO/FeBr$_2$
0
0.2
0.4
0.6
0.8
1.0
RATE H$_2$ FORMATION (h^{-1})
RATE H$_2$
% H$_2$

Fig. 3



90
80
70
60
50
40
30
20
10
0
% H_2
2
4
6
8
10
12
14
TIME (h)
628K
726K
566K
823K

Fi·. 4



H_2O REMAINING
% HYDROLYSED
● AMOUNT WATER
■ % HYDROLYSED
0
1
2
3
4
5
6
20
40
60
80
100
0
100
200
300
400
500
600
700
800
m.p
$MgBr_2 6H_2O$

Fig. 5