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THE ROLE OF KOH IN THE LOW TEMPERATURE STEAM GASIFICATION OF GRAPHITE: IDENTIFICATION OF THE REACTION STEPS

F. Delannay, W.T. Tysoe, H. Heinemann,
and G.A. Somorjai

May 1983

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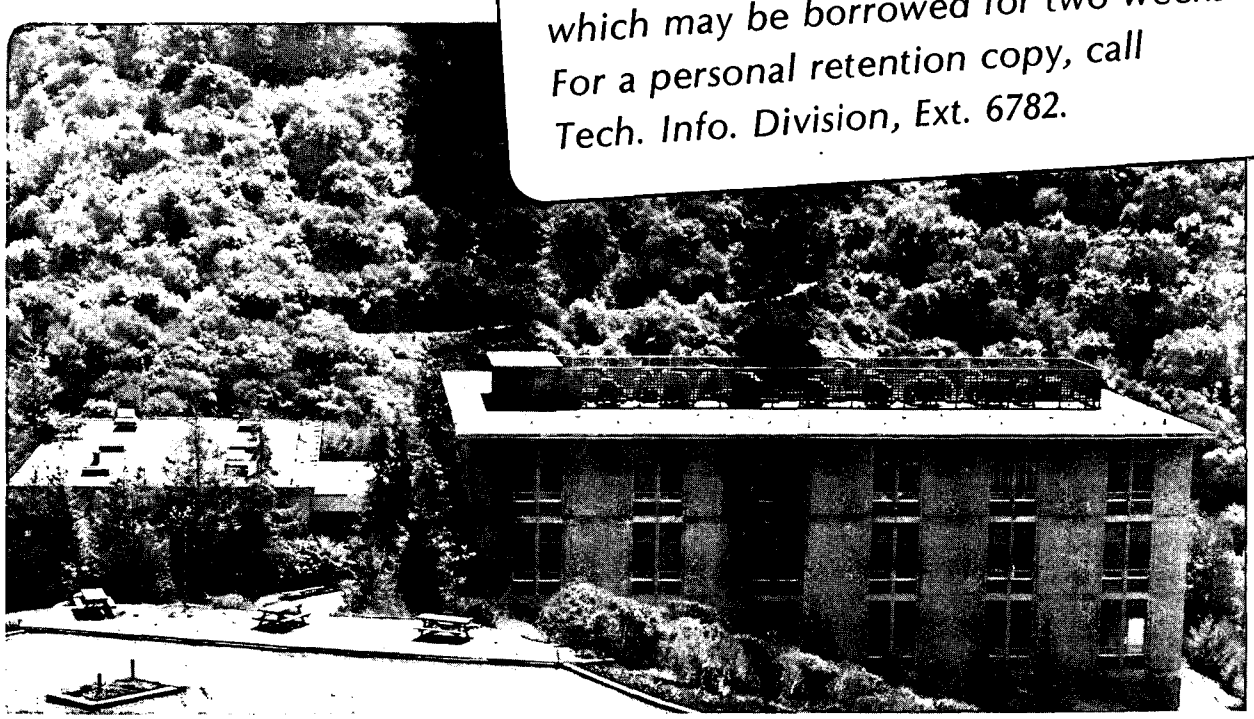

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THE ROLE OF KOH IN THE LOW TEMPERATURE STEAM GASIFICATION OF GRAPHITE: IDENTIFICATION OF THE REACTION STEPS

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The Role of KOH in the Low Temperature Steam Gasification of Graphite: Identification of the Reaction Steps

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Abstract

The reaction of a KOH loaded graphite powder with atmospheric pressure of steam in the temperature range 700-900K proceeds via two successive stages. During stage I, hydrogen and hydrocarbons are evolved at a high rate but no CO or CO_2. This stage ceases after the equivalent of 0.5 molecules of H_2 per potassium in the sample are produced. During stage II gasification proceeds catalytically at a much reduced rate with the production of one CO molecule per equivalent H_2 molecule. The absence of CO or CO_2 evolution during stage I indicates the formation of a stable oxygen containing compound. This compound may be decomposed thermally by heating the sample up to 1300K. CO evolves almost exclusively during this high temperature treatment. These results suggest a step reaction mechanism involving (1) the dissociative adsorption of water forming C-H and C-OH (phenol) groups, (2) the formation of a K-O-C entity (phenolate), from the reaction of KOH with the phenol groups, (3) the decomposition of these K-O-C entities to give CO, K_2O and perhaps metallic potassium and (4) the formation of KOH from reaction of K_2O with water. The transition from stage I to stage II is due to the consumption of KOH to form K-O-C species. The rate of the catalytic reaction (stage II) is controlled by the slowest step (3).

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1. INTRODUCTION

Steam gasification of carbon to produce hydrogen and carbon monoxide is usually conducted at a temperature higher than 1000K. The need for such high a temperature is a consequence of the highly endothermic nature of the reaction.

$$C + H_2O \longrightarrow H_2 + CO \qquad (1)$$
$$\Delta H_{300K} = + 31.4 \text{ kcal/mole}$$

Hydrocarbons can subsequently be synthesized from H_2 and CO by methanation or Fischer-Tropsch reactions on suitable catalysts. These reactions are exothermic and are carried out at relatively low temperatures (500-800K).

The direct production of methane according to the reaction

$$2C + 2H_2O \longrightarrow CH_4 + CO_2 \qquad (2)$$
$$\Delta H_{300K} = 3.65 \text{ kcal/mole}$$

is virtually thermoneutral. This has prompted the search for catalysts able to activate this reaction at low temperature. Low temperature operation is also necessary to avoid decomposition of other hydrocarbons that might be formed.

Alkalis are known to catalyse reaction (1) [1,2,], and the presence of alkali hydroxides has been reported to bring about the formation of methane from the reaction of graphite with water vapor in the temperature range 500-800K[3,4]. These experiments used small pices (~ $1cm^2$) highly oriented pyrolytic graphite (Union Carbide) which was exposed to 20

Torr of water vapor in a recirculation type reactor. At 500K, surface carbon atoms were shown to be converted into CH_4 with an apparent turnover frequency of 1 to $5x10^{-4}$ s^{-1}.

The influence of KOH on the low temperature reaction of carbon with water vapor has now been studied on larger surface area powder graphite samples exposed to atmospheric pressure of steam. It was found that KOH indeed promotes the production of hydrogen, methane and other hydrocarbons at temperatures below 800K but that this reaction is stoichiometric rather than catalytic. The present paper studies the stoichiometric versus catalytic behaviors observed in the temperature range 600-1000K. It is shown that both behaviors can be rationalized within the framework of the same reaction mechanism. A subsequent paper [5] will deal with the influence of experimental conditions on the distribution of the hydrogen and hydrocarbon reaction products.

2. EXPERIMENTAL

The carbon used in these experiments was spectroscopic grade graphite powder (Ultra Carbon Corp., Type UCP-2, 325 mesh) having a BET surface area of 30 m^2g^{-1}. Incipient wetness impregnation was performed by mixing equal weights of graphite powder and of a solution of KOH or K_2CO_3 (Mallinckrodt, analytical grade) in distilled water. The potassium/carbon loading was varied by changing the solution concentration. The sample was then dried at 375K for about 30 minutes.

Figure 1 presents a diagram of the experimental setup. The reactor was a 3.7 mm ID alumina tube in which 0.5 g of sample was deposited

between two alumina wool plugs. Quartz or stainless steel were avoided because, under reaction conditions, these materials were found to react with KOH and/or affect the rate and product distribution of the reaction. The reactor furnace temperature could be adjusted from 300K to 1300K.

The sample could be exposed to either pure argon or pure steam. Steam was produced by pressurizing a distilled water reservoir with argon so as to force water through a heated tube (steamer) where it was vaporized. The steam pressure in the reactor was thus equal to the argon pressure. Usually, a pressure slightly in excess of atmospheric pressure yielded a flow rate of about 50cc of gas min^{-1}. This produced a sufficiently high water vapor space velocity that the reaction was far from equilibrium over the whole temperature range.

At the outlet of the reactor, steam was condensed in an open ended U-shaped tube immersed in water. The gas products which bubbled out of the tube were collected in a 3cc graduated burette filled with water. This allowed a precise measurement of the rate of gas evolution. The whole collecting system contained less than 40 ml of water so as to minimize the possibility of dissolution of the gas products. At the top end of the burette, a septum allowed sampling of the gases for immediate analysis. The products could also be stored in a vacuum container for later analysis after completion of the reaction.

The products were analysed by gas chromatography and mass spectrometry

A thermal conductivity detector with a column consisting of six feet Chromosorb 102 + six feet Chromosorb 101 with argon carrier was used for the analysis of H_2, CO, CO_2, and CH_4. A flame ionization detector with a six feet long Chromosorb 102 column and argon carrier was used for the analysis of the hydrocarbons. Mass spectrometry of the products was performed by leaking the gas stored in the vacuum container into an ultra high vacuum chamber equipped with a EAI quadrupole mass spectrometer [3]. Mass spectrometry was mainly used to assess whether Ar, O_2 or air were present in the products. A small amount of argon was usually found due to solution in the water. In some experiments involving low gas production rates, this amount of argon had to be subtracted in order to determine the volume of gas products accurately.

3. RESULTS

Three types of experiments were conducted: isothermal reactions in the presence of steam; temperature programmed reactions with steam, and temperature programmed heating in an argon atmosphere.

a) Isothermal Reactions

In these experiments, the sample was first exposed to steam at about 400K. The temperature of the reactor was then raised quickly ($\sim$ 160K min^{-1}) up to a reaction temperature in the range 700-900K. Figure 2 shows the amount of gas collected as a function of time at 800K for a sample having a KOH/carbon molecular ratio of 0.043 (corresponding to 20% of KOH by weight). The shape of this plot is typical of all reactions

in this temperature range (700-900K) for KOH/C ratios varying from 0.01 to 0.065. The amount of gas produced has been normalized to the number of KOH molecules in the sample. After an initial burst of gas, a first steady state production was observed for a few hours. During this first steady state, the products were only hydrogen and hydrocarbons with virtually no detectable CO and CO_2. The hydrocarbon/hydrogen molecular ratio during this phase ranges from 0.5×10^{-2} to 5×10^{-2}, the largest hydrocarbon component being methane. However, higher hydrocarbons up to C_6 are easily detectable in the product gas. Their proportions depend on reaction time and temperature and alkali loading.[5]

The reactivity of the sample then decreased usually over a fairly short period. This phenomenon always occurred as soon as the equivalent of 0.5 H_2 molecule per potassium atom in the sample had been collected. The gas production subsequently proceeded with a much reduced rate. CO was found in the products during this second steady state, as indicated by the dashed line in Figure 2. The rates of production of CO and H_2 during this low rate were approximately equal as expected from reaction (1). A few of percent of CO_2 could also be detected.

The first and second steady states exhibited in Figure 2 may for the present be assumed to be due to two different reactions. These reactions will be referred to in the following as reactions I and II respectively.

In order to assess whether reaction I is due to the mere dehydrogenation of KOH, the sample was heated under an argon atmosphere instead of flowing steam. No gas was produced, indicating that water is required for the reaction.

The activation energy of reaction I was measured on samples with a KOH/C ratio of 0.043 (corresponding to a C/KOH ratio of ~23) in the temperature range 850-1000K. The determination was made after the collection of about 0.15 to 0.2 gas molecules per potassium. As shown by the Arrhenius plot of Figure 3, these rates yield an accurate activation energy of 44.8 kcal/mole.

As shown on the semilog plot of Figure 4, the rate of reaction I at 800K (expressed as number of gas molecules per potassium per unit time) increased drastically when increasing the KOH/C ratio from 0.01 to 0.04 (corresponding to a decrease in C/KOH ratio from 100 to 25). No marked change was observed from 0.04 to 0.065.

In order to check whether the behavior of potassium carbonate was identical to that of potassium hydroxide, an isothermal reaction was conducted at 800K on a sample with a K_2CO_3/C molecular ratio of 0.0215 (so that it contains the same number of potassium atoms as an alkali hydroxide loaded sample with KOH/C=0.043). Apart from a burst of gas which corresponds to the formation of about 0.01 gas molecule, per potassium atom, no type I reaction was observed, merely a much slower type II reaction.

b) Temperature Programmed Reaction

In these experiments, the sample was exposed to steam at 500K (ie. before significant reaction had commenced) and the temperature of the reactor was increased at a constant rate of 5K min^{-1}. The open circles in Figure 5 show the resulting rate of gas production as a function of temperature for a sample with a KOH/C ratio of 0.043. A maximum is observed at a temperature of about

900K. The decrease in rate after this maximum reflects the same phenomenon as the transition from reaction I to reaction II in isothermal reactions (Figure 2). The total gas produced at the end of this decrease corresponds again to about 0.5 equivalent hydrogen molecules per potassium. When the temperature is increased further, the reaction rate once again starts to increase exponentially with increasing temperature. This stage of the reaction apparently corresponds to reaction II in isothermal experiments. (Extrapolating this steeply increasing plot down to 800K would yield a rate corresponding approximately to the slope of the plot in region II of Figure 2).

The solid points in Figure 5 are the rates of production for a similar experiment for a sample containing K_2CO_3 instead of KOH (K_2CO_3/C=0.0215). Only the high temperature type II reaction is observed. This rate is however lower than for the KOH loaded sample.

A blank experiment with a sample of pure graphite powder in the absence of KOH exhibited a gas production which was too low to allow an accurate measurement of its temperature dependence. At 1050K, the gas production rate in the absence of alkali was about 40 times lower than for the sample with KOH/C=0.043.

Figure 6 replots the data of Figure 5, in Arrhenius form. In the case of a KOH loaded sample, the rates at temperatures below the maximum (reaction I) do not follow a single straight line.

For reaction above 900K (reaction II), the KOH loaded sample exhibits an apparent activation energy that is 10 kcal/mole lower than that for a K_2CO_3 loaded sample.

c. Temperature Programmed Heating Under Argon

If all the hydrogen produced during reaction I comes from the steam alone, the corresponding amount of oxygen should be accumulated in the sample in the form of an oxygen containing compound. We have attempted to thermally decompose this compound. A sample with a KOH/C ratio of 0.043 was reacted isothermally with steam at 800K up to the completion of reaction I. After flowing argon for about 1 hour at the reaction temperature in order to remove all remaining water, the argon flow was turned off and the sample heated at a linear rate of 15K min^{-1} without gas flow. Gas desorption caused gas to issue from the reactor into the collecting burette, allowing an accurate measurement of the rate of desorption (after correction for the thermal expansion of gas in the reactor). Fig. 7 shows plots of the time dependence of reactor temperature and gas desorption rate. The temperature of the reactor could not be increased above 1300K so that the position of the maximum desorption rate has little kinetic meaning as it merely coincides with the start of the isothermal period. Figure 8 presents an Arrhenius plot of the rate of desorption at the beginning of the temperature treatment (up to the desorption of 10% of the total). This yields an apparent activation energy of 35.4 kcal/mole.

The gas desorbed during this heat treatment was almost exclusively CO, containing only a few percent CO_2. The total CO accumulated after 3 hours

of treatment at 1300K corresponded to a CO/K ratio of about 0.8. A small amount of gas production continued after this period. However, even after overnight heating the total CO/K ratio never reached 1.

No gas was collected during a similar heat treatment of a pure graphite sample.

If the sample was again exposed to steam at low temperature after this heat treatment, it recovered part of its original reactivity. Figure 9 compares the gas production at 800K for a freshly prepared sample and for the same sample after heat treatment and reexposure to atmospheric pressure of steam at 400K. In this case, no linear steady state region was observed, merely a continuous decrease of reaction rate with time. Depending on the duration of the high temperature (1300K) treatment, the amount of hydrogen collected during a 2 hour period corresponded to a H_2/K ratio of 0.08 to 0.15.

4. DISCUSSION

The high gasification rate referred to as reaction I is a specific property of the hydroxide loaded graphite sample. This reaction is evidently not catalytic: water reacts with carbon and potassium hydroxide to produce hydrogen and hydrocarbons whereas oxygen remains in the sample in the form of an unknown oxygenated species. The accumulation of this species eventually results in the deactivation of the sample. As this deactivation always occurs after the production of the same H_2/K ratio, whatever the KOH loading, it appears that this species is associated with potassium in a fixed stoichiometric ratio.

One potential reaction scheme is the conversion of potassium hydroxide into a carbonate according to the equation

$$2KOH + H_2O + C \longrightarrow K_2CO_3 + 2H_2 \qquad (3)$$

This reaction has been proposed in a patent by Shalit et al. [6]. It is only slightly endothermic (ΔG_{800K}= + 11.2 kcal/mole). However, our results do not seem to be in accord with such a reaction since it involves the production of one H_2 per potassium on the sample, whereas only half this amount is evolved. In addition, if KOH had, in fact, been completely converted into K_2CO_3 after completion of reaction I, it should subsequently behave like a K_2CO_3 loaded sample. Figure 6 indicates, however, that the two samples exhibit a 10 kcal/mole difference in apparent activation energy for reaction II.

An alternative reaction scheme is presented in Figure 10. The first step would be the dissociative adsorption of a water molecule on the prismatic planes of graphite to form a phenolic and a C-H group. Such a dissociative adsorption with high sticking probability has been inferred by Olander et al. [7] from molecular beam scattering experiments. In the absence of alkali, these groups rapidly recombine to yield a water molecule once again. A strong base such as KOH would, however, neutralize the weakly acidic phenol group to give a potassium phenolate salt and a water molecule (step 2). In this case, the hydrogen remaining adsorbed on the carbon surface may either desorb as H_2 or sequentially form C-H bonds to yield a hydrocarbon. The ratio of hydrogen to potassium predicted by this reaction scheme (0.5) corresponds to that observed experimentally.

Moreover, the existance of such phenolate groups as intermediates in the catalytic gasification of carbon has been previously postulated by Mims and Pabst [8,9]. It should, however, be noted that, in the present case, the number of potassium atoms in the sample is much larger than the number of accessible edge sites on the graphite surface. Thus it is necessary to assume that the interaction of potassium with the carbon surface induce weakening and, eventually, scission of the C–C bond so as to create new surface sites for reaction. Such a fragmentation of the aromatic rings due to the interaction with potassium has, for example, been suggested by Sancier [10] on the basis of the e.s.r. analysis of a heat treated K_2CO_3-carbon mixture. The chemical nature of the compound containing the K–O–C groups is unknown. It might be suggested that these groups end up as potassium carbonyl entities stabilized by some interaction (eg. intercalation) with graphite.

Heat treatment of the sample after complete conversion of the KOH induces the decomposition of these K–O–C groups to yield, either metallic potassium and CO, or K_2O, CO and carbon (step 3 in Figure 10). Metallic potassium evaporates at a high rate at 1050K, so that much of the metallic potassium could sublime from the sample during heat treatment at 1300K. (Some intercalation might also occur [11]). K_2O remains in the sample and converts into KOH under subsequent exposure to steam so as to restore part of the activity of the sample (step 4). If the ratio m = CO/K collected during heat treatment equals 0.85, 30% of the original KOH loading is then

available for reaction. When the sample is reexposed to steam, the resulting gas production should yield an amount of H_2 corresponding to $H_2/K=0.15$ (with respect to the original KOH loading) which corresponds to that observed experimentally.

It is worth noting that the amounts of gas collected during the first reaction, high temperature treatment and subsequent reaction, all rule out the conversion of KOH into K_2CO_3 during reaction I. This is because the collection of a ratio $CO/K < 1$ would imply the decomposition of K_2CO_3 into K_2O, and, in such a case, the original activity of the sample should be completely restored under reexposure to steam. This did not occur, as shown on Figure 9.

The various stages of reaction may thus be rationalized as follows. The initial burst may correspond to the fast reaction of KOH already in contact with prismatic edges of the graphite. The subsequent steady state (reaction I) is controlled by transport of the remaining KOH to these edges and presumably also by the breaking of the C–C bonds necessary to provide enough reaction sites. According to Figure 3, these phenomena have an activation energy of about 45 kcal/mole. (The slopes of the Arrhenius plots for reaction I reported in Figure 6 cannot be taken as accurate activation energies as, in this experiment, one of the reactant phases (KOH) progressively disappears.)

After completion of reaction I, the gas production is controlled by the decomposition of the K–O–C groups (step 3 in Figure 10). The mechanism of reaction II (which is obviously catalytic) involves the whole set of sequential

steps as proposed in Figure 10, step 3 being the rate limiting one. The apparent activation energy measured on the Arrhenius plot in Figure 8 is probably fairly close to the true activation energy for the decomposition of the K-O-C groups (as less than 10% of these groups have been consumed during this experiment so that their coverage remains constant). It is striking that this value corresponds nicely to the activation energy of reaction II measured in Figure 6.

Several authors [12,13] have proposed that the decomposition of alkali carbonate in the presence of carbon to give metallic alkali and CO was the rate limiting step in the alkali carbonate catalyzed steam gasification of carbon. Our conclusions concerning the role of KOH are similar, except that the oxygen containing intermediate appears not to be K_2CO_3. The activation energy for the KOH catalyzed reaction (reaction II) is 10 kcal/mole lower than in the case of K_2CO_3.

5. CONCLUSION

The high rate of carbon gasification promoted by KOH at temperatures even lower than 800K is a striking phenomenon. As discussed in the subsequent paper [5], significant amounts of hydrocarbons are produced under such reaction conditions. This reaction cannot be sustained in a catalytic way, due to the high stability of the oxygen containing potassium compound (K-O-C) that is formed. If a compound can be found that plays the same role as potassium hydroxide while yielding a less stable oxygen containing intermediate it would allow the attainment of catalytic gasification without requiring high temperature operation.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Fig. 1: Diagram of experimental apparatus.

Fig. 2: Plot of gas production as a function of reaction time at 800K for a sample with a KOH/C loading equal to 0.043 (molecular ratio).

Fig. 3: Arrhenius plot of the temperature dependence of gasification rate after the collection of 0.15 to 0.2 gas molecule per potassium in the sample.

Fig. 4: Plot of dependence of the rate of reaction I on the KOH/C loading.

Fig. 5: Plot of the temperature dependence of the gas production rate during a temperature programmed reaction at a heating rate of 5K min^{-1}. The open circles and full dots correspond to KOH and K_2CO_3 loaded samples respectively. The K/C ratio equals 0.043 in both cases.

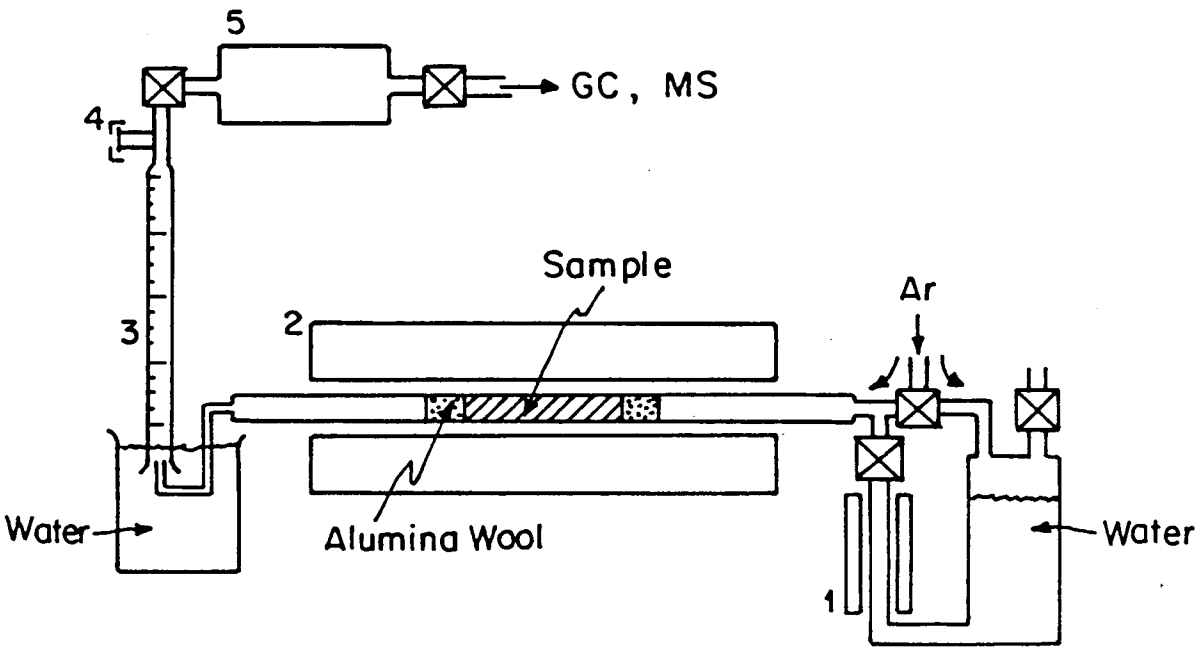
Fig. 6: Arrhenius plots of the temperature dependence of the gas production rate displayed in Figure 5.

Fig. 7: Plot of the temperature dependence of the CO desorption rate during high temperature treatment of a sample with KOH/C=0.043 after completion of reaction I.

Fig. 8: Arrhenius plot of the temperature dependence of the CO desorption rate at the beginning of the linear heating of a sample during the same experiment as displayed in Figure 7.

Fig. 9: Plot of a comparison of the gas production as a function of time for a freshly prepared KOH loaded sample (a) and for the same sample after high temperature treatment (b).

Fig. 10: Mechanistic model for the reaction of water with graphite in the presence of KOH.



1 Steamer
2 Reactor
3 Burette
4 Septum
5 Vacuum Container

XBL 832-5326

Fig. 1

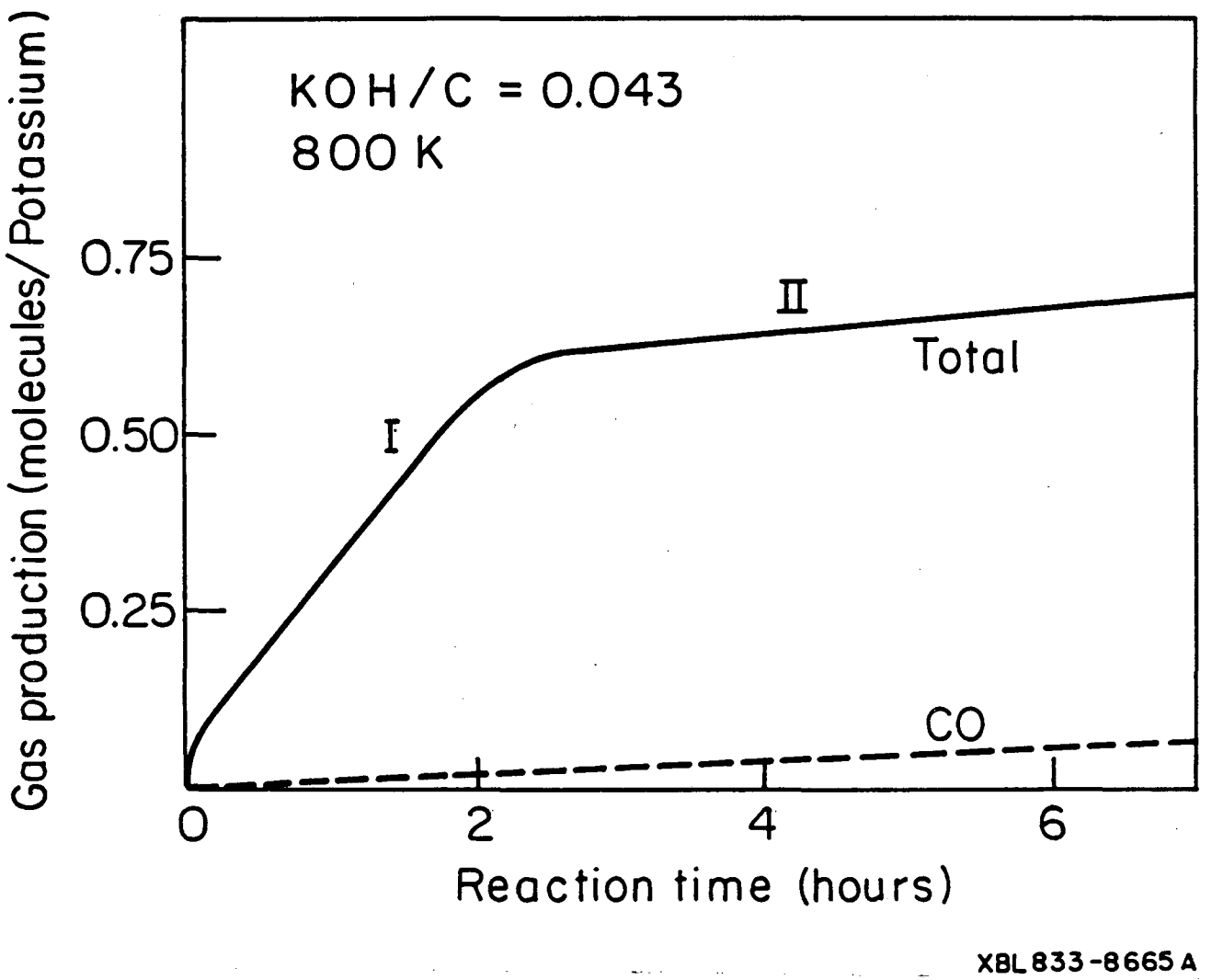

KOH/C = 0.043
800 K
0.75
0.50
0.25
I
II
Total
CO
0
2
4
6
Gas production (molecules/Potassium)
Reaction time (hours)
XBL 833-8665 A

Fig. 2

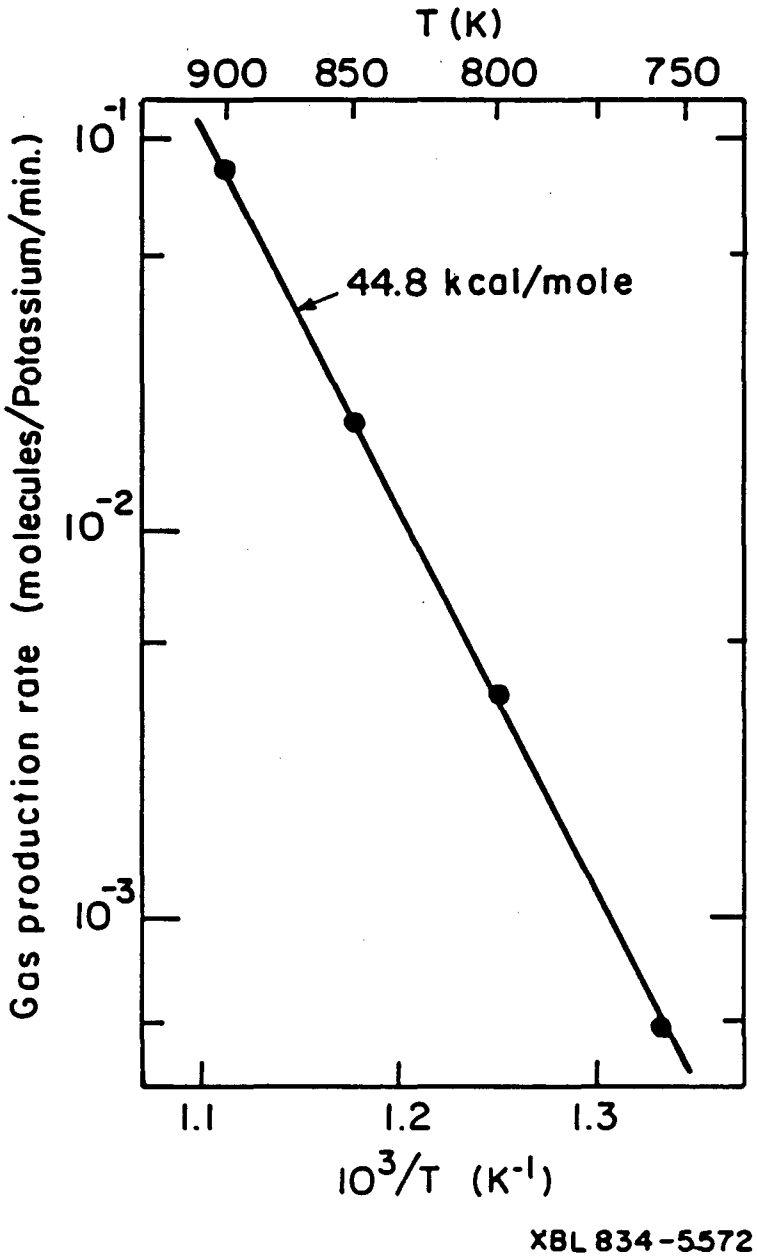

T (K)
900
850
800
750
10^{-1}
10^{-2}
10^{-3}
44.8 kcal/mole
Gas production rate (molecules/Potassium/min.)
1.1
1.2
1.3
$10^3/T$ (K^{-1})
XBL 834-5572

Fig. 3

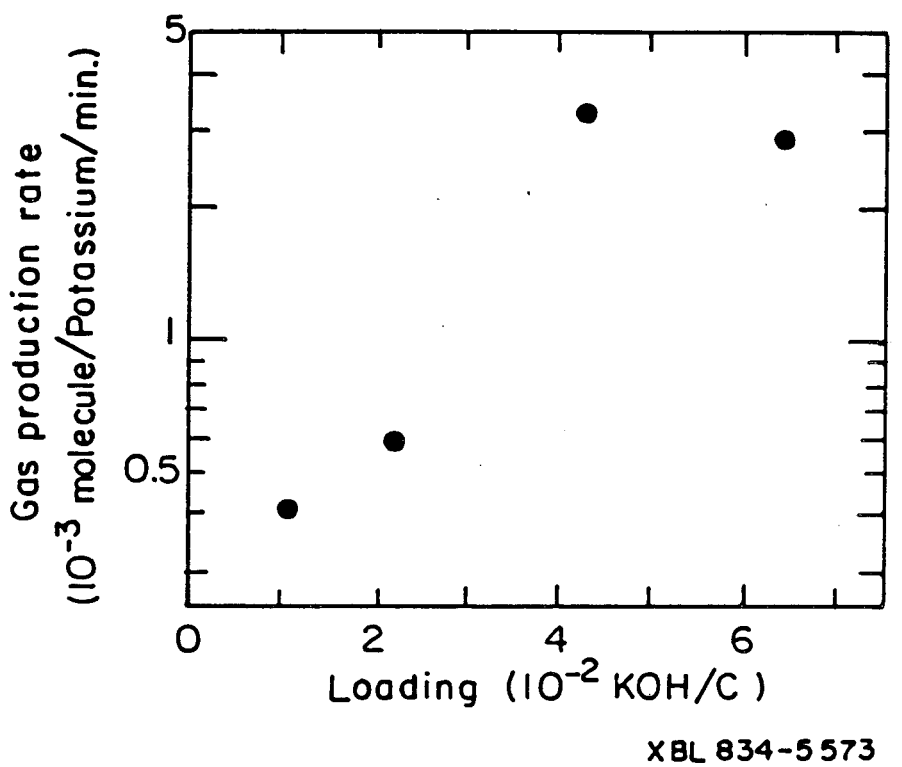

5
1
0.5
0
2
4
6
Gas production rate
(10^{-3} molecule/Potassium/min.)
Loading (10^{-2} KOH/C)
XBL 834-5573

Fig. 4

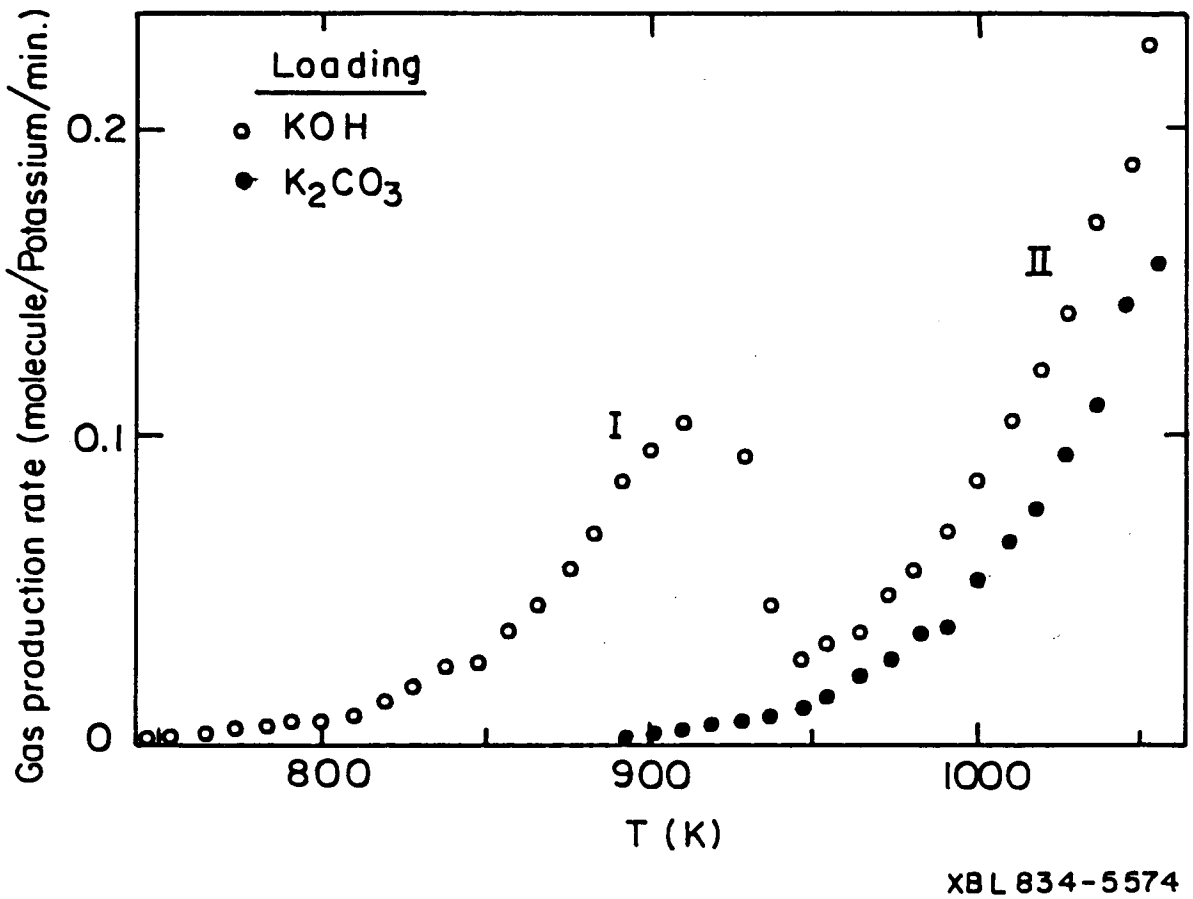

Loading
KOH
K_2CO_3
I
II
0.2
0.1
0
800
900
1000
T (K)
Gas production rate (molecule/Potassium/min.)
XBL 834-5574

Fig. 5

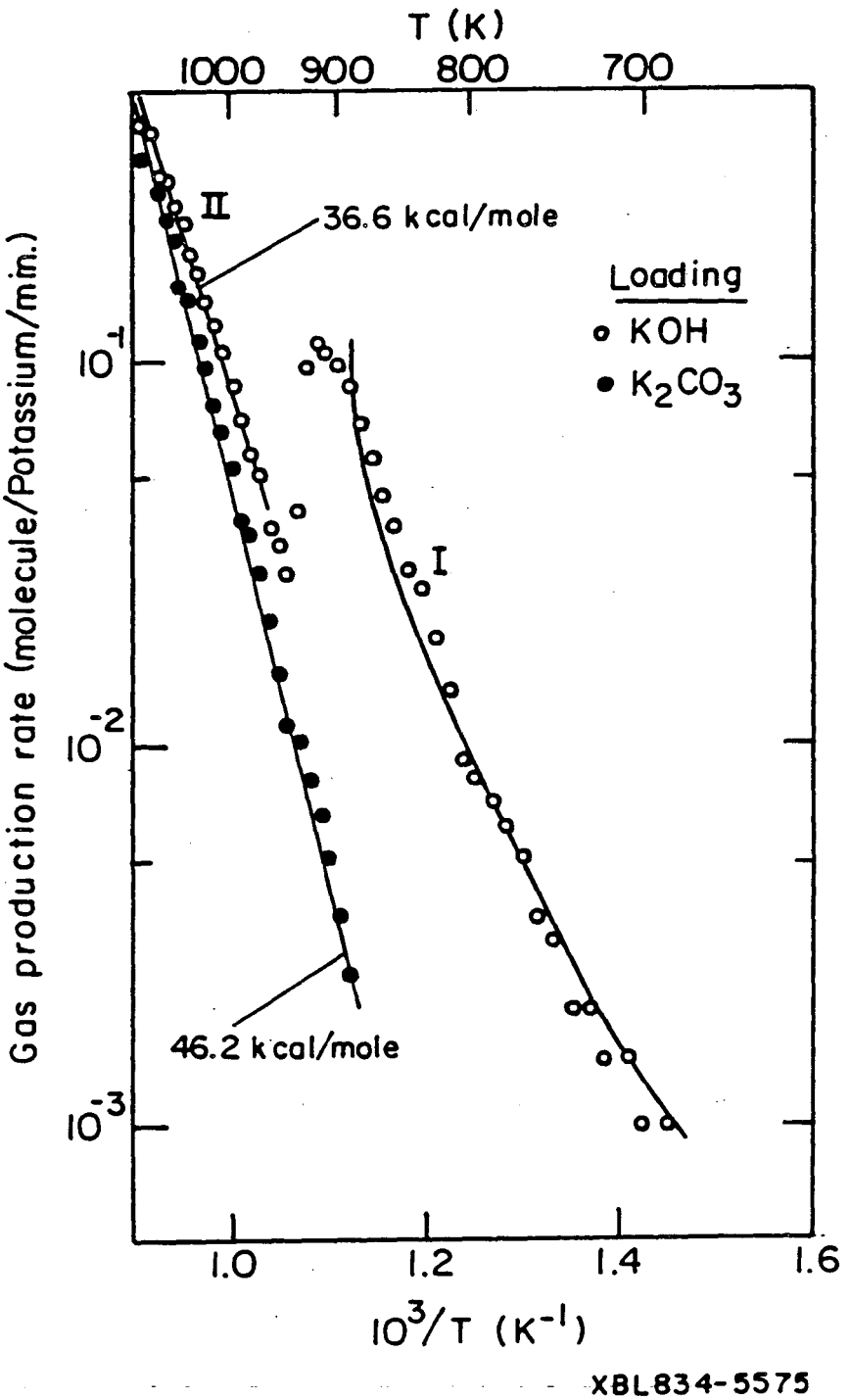
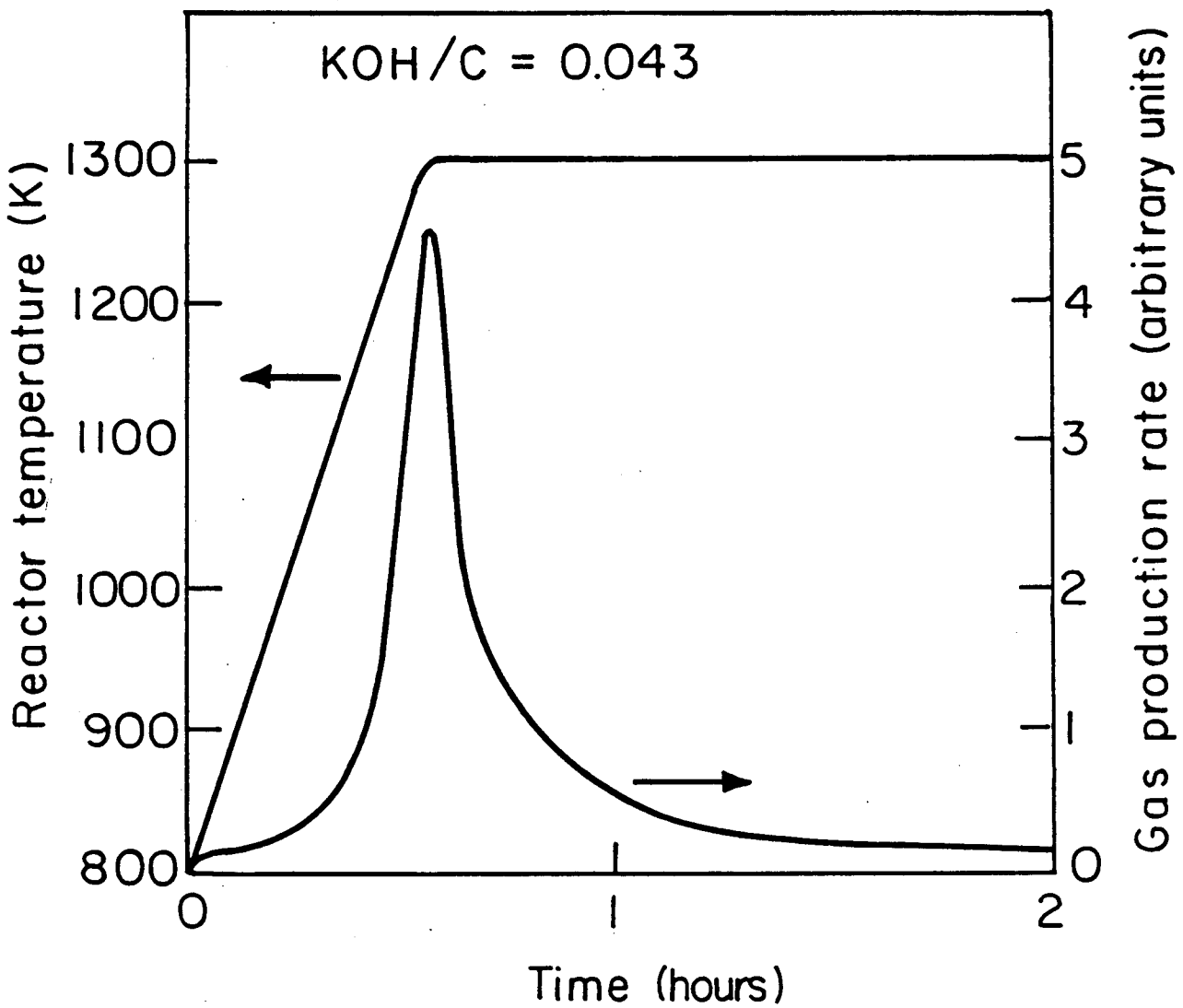

T (K)
1000
900
800
700
II
36.6 kcal/mole
Loading
KOH
K_2CO_3
I
46.2 kcal/mole
10^{-1}
10^{-2}
10^{-3}
Gas production rate (molecule/Potassium/min.)
1.0
1.2
1.4
1.6
$10^3/T$ (K^{-1})
XBL834-5575

Fig. 6



XBL 833-8713A

Fig. 7

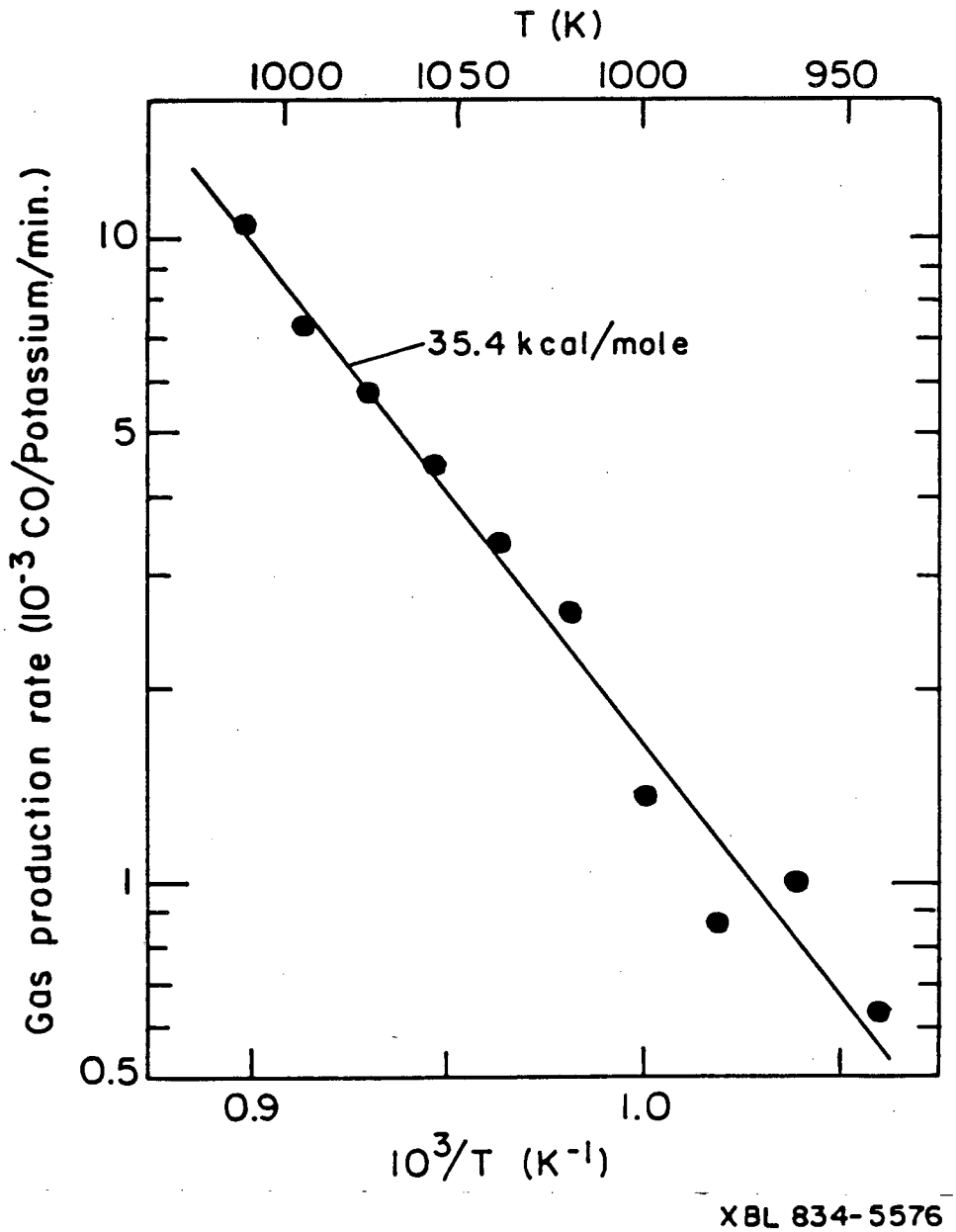

T (K)
1000
1050
1000
950
10
5
1
0.5
Gas production rate (10^{-3} CO/Potassium/min.)
35.4 kcal/mole
0.9
1.0
$10^3/T$ (K^{-1})
XBL 834-5576

Fig. 8

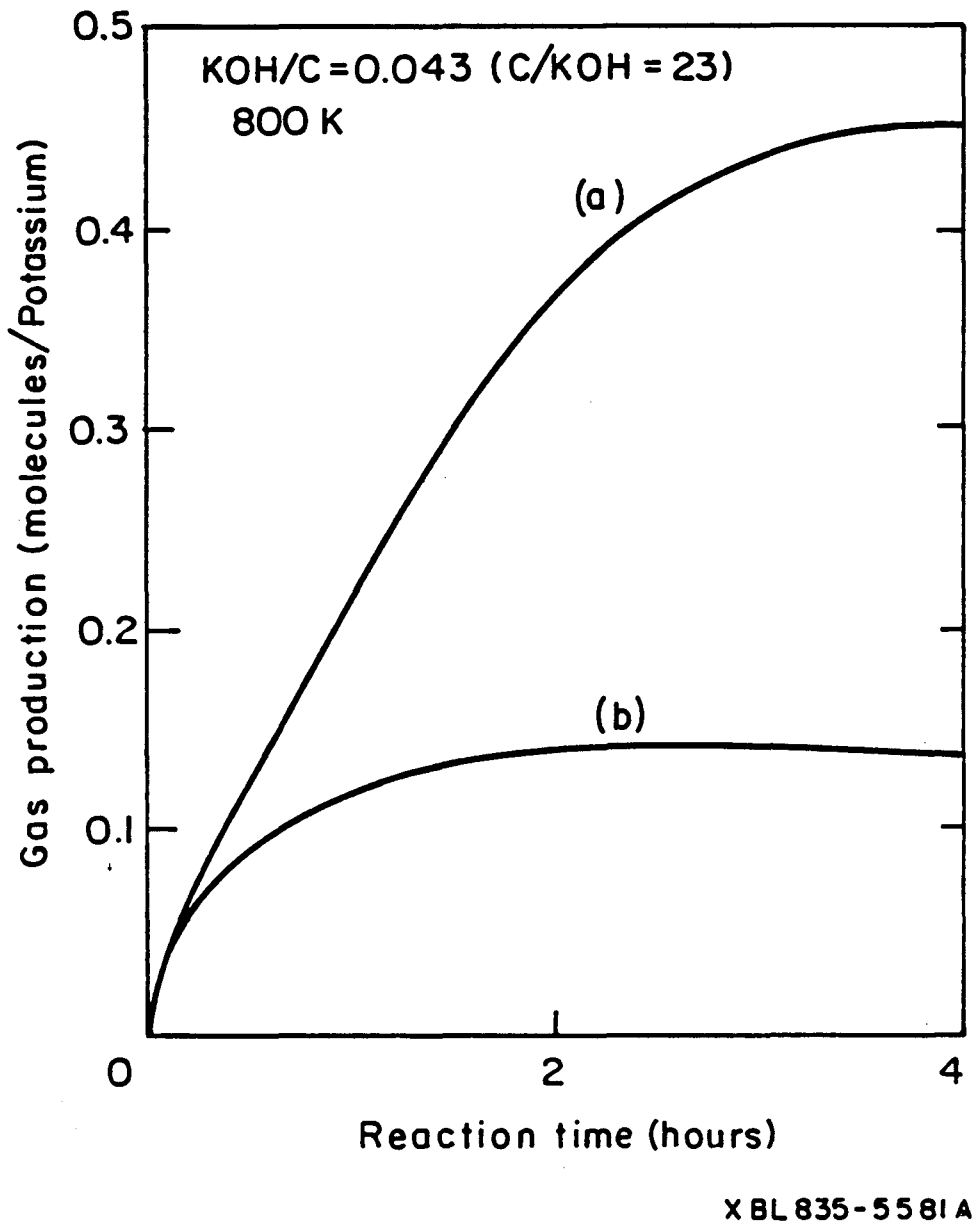

KOH/C=0.043 (C/KOH = 23)
800 K
(a)
(b)
0.5
0.4
0.3
0.2
0.1
0
2
4
Gas production (molecules/Potassium)
Reaction time (hours)
XBL835-5581A

Fig. 9

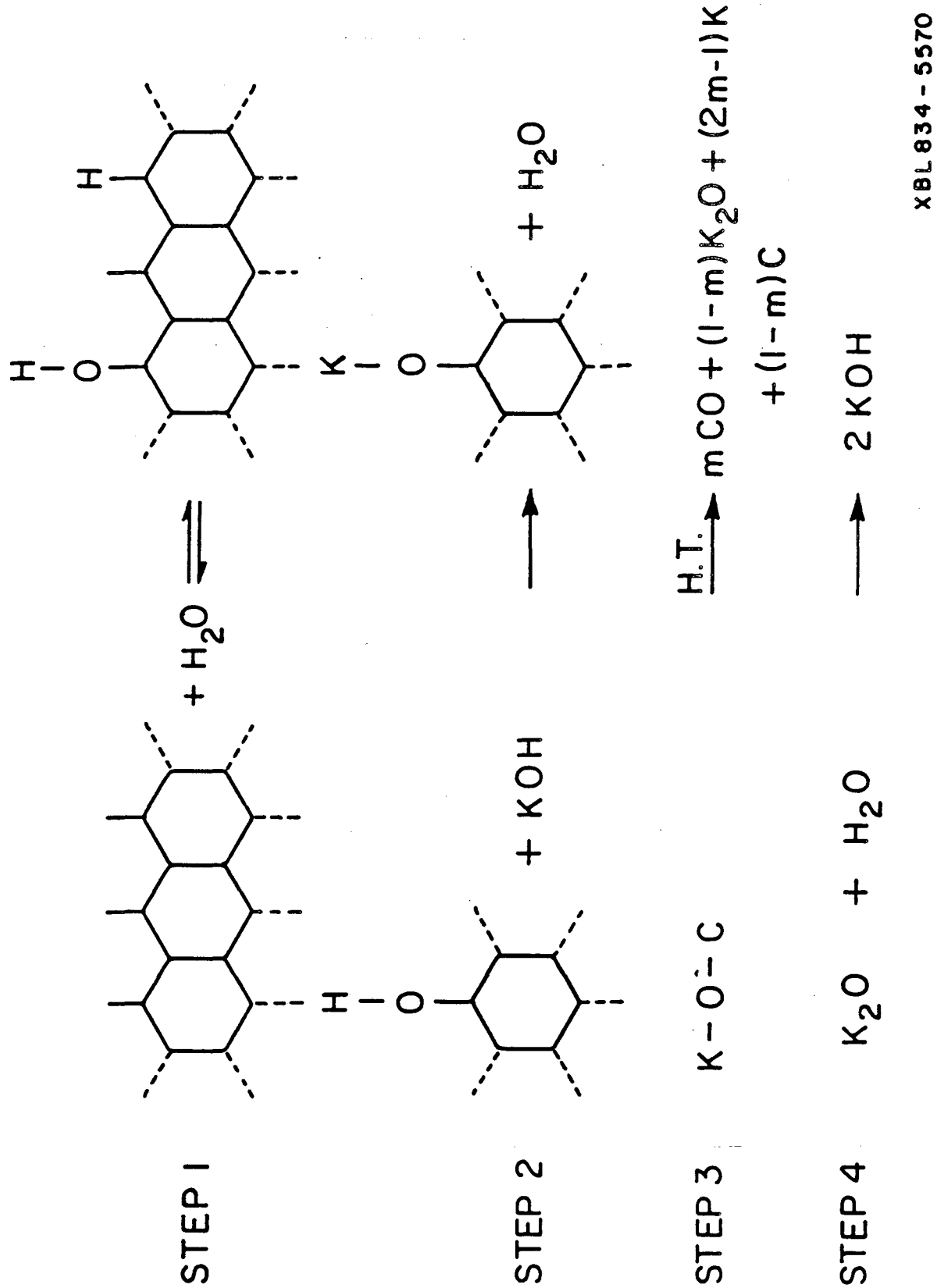

STEP 1
STEP 2
STEP 3
STEP 4
H
H – O
+ H2O
K – O
+ H2O
+ KOH
H – O
K – O̅ – C
K2O + H2O
H.T.
m CO + (1-m) K2O + (2m-1) K
+ (1-m) C
2 KOH
XBL 834 - 5570

Fig. 10

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