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R. Casanova, A.L. Cabrera, H. Heinemann,
and G.A. Somorjai

December 1982

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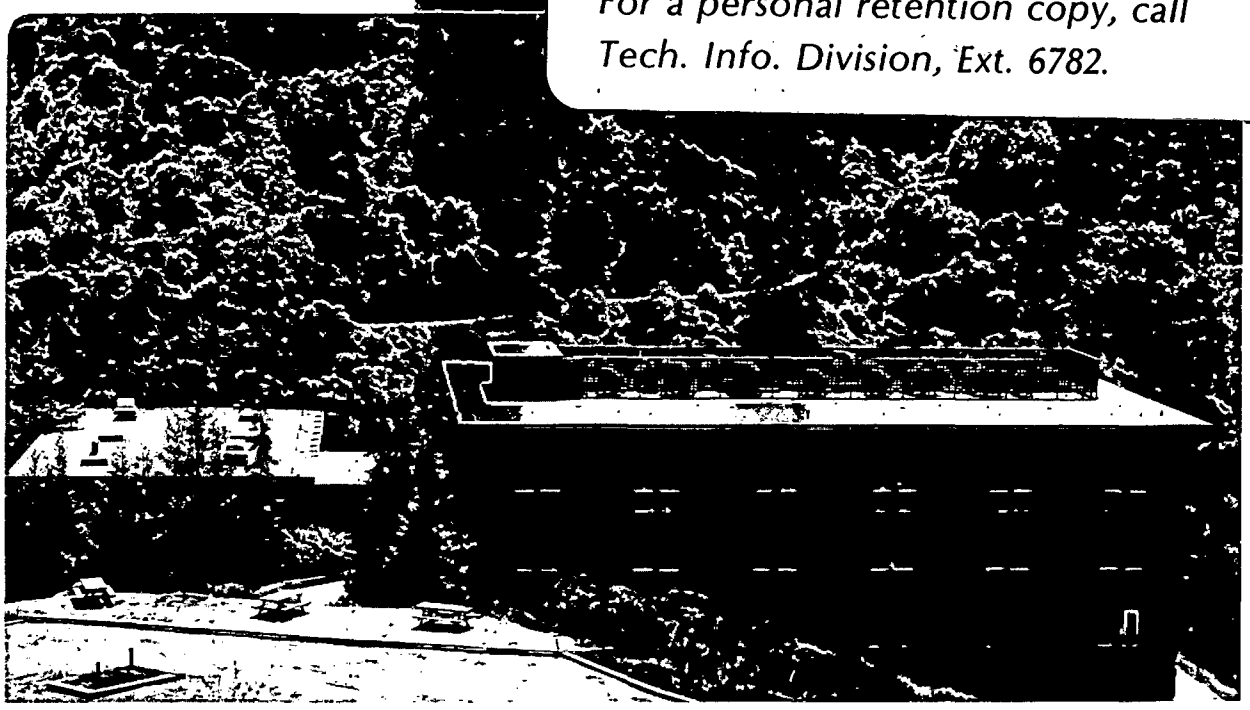

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CALCIUM OXIDE AND POTASSIUM HYDROXIDE CATALYZED LOW TEMPERATURE METHANE PRODUCTION FROM GRAPHITE AND WATER. COMPARISON OF CATALYTIC MECHANISMS

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ABSTRACT

An experimental study directed to obtain information on the catalytic mechanisms involved in the methanation of graphite using, separately, potassium and calcium as catalysts, and water and/or hydrogen as reactants is reported. The mechanisms for the potassium catalyzed graphite-water reaction appears to be the same in the wide temperature range from 473K to 873K as indicated by the constant 11 kcal/mole activation energy found for the methane production. The intercalation of potassium into the graphite as a possible step in the methane synthesis has been investigated and ruled out. XPS studies indicate the formation of an active form of more positively charged carbon from graphite when graphite is heated at low temperatures in the presence of a calcium catalyst and water vapor. The activation energy for this carbon depolymerization reaction is 16.3 kcal/mole. Methane formation only occurs in the presence of hydrogen due to its reaction with the active carbon. The activation energy for the methane production in this case is 25.5 kcal/mole.

INTRODUCTION

The catalytic effects of metals on the kinetics of the reaction between carbon and water vapor have been the subject of intensive investigation for several years. In a recent publication from our laboratory,[1] it was reported that the conversion of high density graphite to methane using potassium compounds as catalysts was achieved in the temperature range 473K < T < 600K, a process that occurs at low-temperatures when compared with those used in current industrial processes.[2] At low temperatures the decomposition probability of most hydrocarbons that may be produced in this reaction is low thus, they may also be the dominant species if the low temperature catalyzed gasification of coal were feasible.

We report here the results of new studies directed to gain insight into the catalytic mechanisms involved in the gasification of graphite with H_2O and H_2. The effects of potassium and calcium catalysts have been investigated in the temperature ranges 673K < T < 873K and 623K < T < 873K respectively. We also utilized potassium intercalated graphite to test its reactivity with H_2O and have been able to rule out K intercalations as an important reaction step during the synthesis of methane.

While potassium readily catalyzes the reaction of water with graphite to produce methane, calcium catalyzes only the depolymerization of graphite to a more reactive form of carbon in this circumstance but not its gasification. Hydrogen addition was necessary to produce methane in the presence of calcium. The potassium catalyzed gasification rate is proportional to the edge area of graphite.

EXPERIMENTAL

The samples used in our experiments were cleaved in air with a razor blade, from a larger piece of highly oriented pyrolitic graphite obtained from the Union Carbide Corporation. The samples had a rectangular shape with a geometric area of ~ 0.32 cm^2 and a thickness of ~ 1 mm. In some of the experiments 2 mm thick graphite samples were utilized.

The sample was mounted on a manipulator using a sample holder made of gold foil spotwelded to two platinum clamps. In this way, we were able to resistively heat the gold foil which was in direct contact with one face of the graphite specimen. Depending on the experiment to be performed, the graphite sample was positioned properly inside the high pressure cell and subsequently exposed to high vacuum. When the pressure in the chamber was less than 2×10^{-9} torr the sample surface was characterized by Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). For the XPS measurements an X-ray source with a Mg anode was used. The electron energy analysis was performed using a high resolution double pass cylindrical mirror analyzer (CMA) from Physical Electronic Industries. After the surface characterization, the sample was isolated in the high pressure cell which was connected to a closed loop reactor, and exposed to water vapor and/or hydrogen. Helium was frequently used as a carrier gas. The reaction products were monitored with a 5880 A HP gas chromatograph. After the reaction was completed the surface of the sample was characterized again. A schematic diagram of the apparatus used is shown in Figure 1A. Detailed description of this system can be found elsewhere.[1,3]

RESULTS

KOH-Graphite System

We have studied the potassium hydroxide catalyzed graphite-water reaction at temperatures ranging from 573K to 873K. The potassium hydroxide covered graphite was exposed to a mixture of 22 torr of water vapor and approximately 1 atm. of helium, and heated at the desired temperature. A plot of the logarithm of the steady state rates per carbon surface atom as a function of the inverse absolute temperature is presented in Figure 2. An activation energy of 11 ± 1 kcal/mole is obtained from this plot. This activation energy does not differ, within the experimental error, from the value reported earlier,[1] in the temperature range 473K < T < 573K. This fact indicates that the activation energy for this reaction is the same in a wider temperature range and perhaps that the catalytic mechanisms involved in this reaction are the same from 573K to 873K.

During our experiments we noticed that an increase in the CH_4 production could be observed when only the thickness of the sample was increased. In Figure 3 two plots of the methane concentration vs. time are displayed for two samples with thicknesses of 1 mm and 2 mm at the reaction temperature of 773K. The difference in the methane production can be explained if we assume that most of the active sites for the KOH catalyzed graphite-water reactions are located at the edges of the graphite crystals. This is supported by a recent electron microscopy study[4] where it was found that the gasification of graphite with water using potassium as a catalyst occurs at the edges and that the potassium particles propagate in a channeling mode along the basal planes. We also found tht increasing the basal plane area of the graphite samples did not increase the methanation rate.

Since gasification occurs preferentially at the prismatic graphite planes

the turnover rates calculated as the methane evolution per surface carbon atom per second are grossly underestimated.

CaO-Graphite System

Calcium oxide has been used in this work as a catalyst in the methane synthesis from graphite, using H_2O and H_2 as reactants. For this purpose, the graphite sample was impregnated with a 1M solution of $Ca(NO_3)_2$ and dried in air. The surface of the graphite sample was characterized by AES and XPS. It exhibits the carbon 15 photoelectron peak at 284.4 eV characteristic for graphite. The sample was then heated in vacuum to allow the calcium nitrate to decompose. Then, the sample was heated in the high pressure cell at a temperature in the range $623K < T < 873K$ for about 4 hours in 22 torr of H_2O and 1 atm of pure helium while the gas composition was monitored by the gas chromatograph. The XPS spectrum taken after this heating cycle showed the appearance of a new peak at a binding energy of 290 eV, which we have attributed to the formation of a new form of carbon on the graphite surface which proved to be much more reactive than graphite, in subsequent studies. This new form of carbon presumably comes from a transformation of the graphitic carbon through a C-C bond breaking process catalyzed by the calcium catalyst and water. No methane could be detected during this step. Then, a reaction with 1 atm of H_2 at the same temperature in the range of 623 to 873K was performed. Methane was readily detected in concentrations higher than those obtained during the potassium catalyzed graphite-water reaction. Typical plots for the accumulation of CH_4 vs. time are presented in Figure 4. An activation energy of 25.5 kcal/mole was obtained for this reaction from the Arrhenius plot shown in Figure 5. Methane production was detected for several hours. From Figure 4 we can see that the hydrogenation is fast during the first few hours but then it slows down. Monitoring the concentration of the new form of active

carbon as a function of time clearly indicates that the active carbon present on the surface is hydrogenated to CH_4 by H_2. After the reaction with H_2 the peak at 290 eV markedly decreased in intensity as can be seen in Figure 6 for T = 773K.

We have also performed experiments using a mixture of 22 torr of H_2O and 32 torr of H_2, in this circumstance there is a balance between the rate of formation of active carbon and the rate of its hydrogenation to methane. Consequently, the stationary state methane productions last longer as can be seen in Figure 7 where the concentrations of the produced methane is plotted against time for several temperatures. The activation energy for the production of methane in the water-hydrogen mixture was found to be 16.3 kcal/mole as obtained from its Arrhenius plot in Figure 5.

We have also studied the hydrogen pressure dependence of the rate of methane production at T = 773K. Figure 8 shows a plot of methane production rate vs. P_{H_2}. From the plot we can conclude that rate = $d\frac{[CH_4]}{dT} = KP_{H_2}$, there is a first order dependence of methane formation on hydrogen pressure.

Potassium Intercalated Graphite System

In recent years considerable effort has been directed toward the understanding of the structure,[5] electronic properties[6] and catalytic properties[7] of alkali-metal-graphite intercalation compounds. We have conducted experiments with C_8K aimed at obtaining information which may be valuable for deciding if intercalation is a possible reaction step during the potassium catalyzed graphite-water reaction for the production of methane.

The surface of the C_8K samples were characterized with AES and XPS. An interesting effect was observed while monitoring the surface by AES. The intensity of the potassium peak increased when the electron beam is left on for about 5 minutes. This can be seen when comparing Figures 9a and 9b. It

appears that potassium diffuses to the surface under the influence of the electron beam. Apparently this effect is not due to local heating by the electron beam because we have purposely heated the sample in the temperature range of 353K to 573K. The intensity of the potassium peak decreased upon heating. This effect is illustrated in Figure 10, when the sample was heated at 573K.

Unintentionally, we modified the composition of the C_8K sample by heating, particularly at temperature close to 573K. Before the heat treatment the sample had a copper-like color and after the heating the color changed to deep blue, which is characteristic of another type of potassium intercalated graphite $C_{24}K$. The XPS spectrum taken of this sample and presented in Figure 11a also confirmed this transformation. We observed the C_{1S} peak at 286.4 eV shifted 2 eV from the C_{1S} peak in graphite (284.4 eV) as shown in Figure 11b. This shift is reasonable if we take into consideration the difference in electronic environment of carbon atoms in this sample compared to that of pure graphite.

According to S.B. Dicenzo[8] the potassium intercelated graphite that has a C_{1S} peak closer to 286 eV has the composition of $C_{24}K$. We have also obtained a full width at half maximum (FWHM) for the C_{1S} peak of 2.1 eV which is in agreement with the results reported by S.B. Dicenzo[98] and Bach[9] for this type of intercalated graphite.

After these surface characterizations we performed a reaction with this sample and 22 torr of water vapor for several hours at 573K. In Figure 12, we present plots of the methane concentrations obtained vs. time for the $C_{24}K$ sample and a KOH-graphite system. Obviously, the methane production is lower for the potassium intercalated graphite sample. After the reaction we observed that the thickness of the sample increased by a factor of 8 from the original thickness due to exfoliation of the graphite, possibly due to water adsorption within the layers. This can be seen in the picture shown in Figure 13. Another

important observation is that the C_{1S} peak shifted back to the typical position of the C_{1S} peak in graphite, as it is illustrated in Figure 11b. It should be noted that we have not observed any shifts in XBS peaks before or after the reaction with water when the KOH-graphite system (in the absence of intercalation) has been used in the methane synthesis.

Our studies allow us to rule out the intercalation of potassium as an important reaction step during the catalytic gasification of graphite in the presence of potassium and water vapor.

DISCUSSION

There are several experimental observations reported here that aid to unravel some of the elementary catalytic reaction steps leading to the formation of methane from graphite.

1) In the presence of potassium as catalyst, water vapor produces methane from graphite in the temperature range of 473 to 873K with an activation energy of 11 ± 1 kcal/mole. In the presence of calcium oxide as catalyst there is no methane evolution under these conditions.

2) Calcium oxide catalyzes the conversion of graphite to a more reactive form of carbon, in the presence of water vapor, and in the temperature range of 628-873K. This is indicated by the appearance of a new photoelectron emission peak corresponding to a carbon 1S electron binding energy of 290 eV. In graphite the C(15) binding energy is 284.4 eV.

3) Once the more reactive form of carbon is produced at the graphite surface, the addition of hydrogen produces methane with an activation energy of 25.5 kcal/mole. Methane formation stops as soon as the active form of carbon is consumed.

4) When a mixture of hydrogen (32 torr) and water vapor (22 torr) was

used in the presence of calcium as catalyst, methane could be produced from graphite in steady state with an activation energy of 16.3 kcal/mole.

5) Increasing the basal plane area of the graphite samples did not increase the reaction rate. Increasing the thickness of the graphite which consequently increases the edge area, increases the methane production rate in proportion. Electron microscopy studies confirm that the catalyzed gasification occurs preferentially at the edges.

6) When using potassium intercalated graphite $C_{24}K$, the rate of methane production was lower than the rate of methane production when KOH was on the external surface of the pure graphite sample.

Potassium and calcium act very differently as catalysts for the production of methane from graphite. While water readily gasifies graphite to methane and carbon dioxide (or carbon monoxide) in the presence of potassium or other alkali metals calcium catalyzes only the depolymerization of graphite to a more reactive form of carbon but not its gasification under the same experimental conditions. XPS studies reveal the appearance of this new form of carbon by a 5.6 eV increase in the carbon 1S electron binding energy in the presence of water vapor on the calcium covered graphite surface. However, the addition of hydrogen was needed to produce methane when calcium oxide served as a catalyst. Thus, we can identify at least two distinct, consecutive reaction steps leading to methane formation in the presence of calcium. First, active carbon forms from graphite,

$$C_{(graphite)} \xrightarrow[H_2O]{CaO} C_{(active)} \qquad (1)$$

then the reactive carbon is hydrogenated in the presence of H_2

$$C_{(active)} + 2H_2 \xrightarrow{CaO} CH_4 \qquad (2)$$

From the temperature dependence of the rate of methane production using pure hydrogen the activation energy for reaction (2) is 25.5 kcal. This value is very similar to the transition metal (Ni, Rh, Ru, Fe, etc.) catalyzed hydrogenation of CO to form methane. From reaction rate studies using a mixture of water vapor and hydrogen we find an activation energy of 16.3 kcal/mole. It is tempting to assign this value to the activation energy needed for reaction (1), for the conversion of graphite to a more active form of carbon.

Both electron microscopy evidence and the increase of methanation rate with sample thickness but not with the increase of surface area indicate that chemical attack occurs at the edges of the graphite basal planes. These edge sites are present in very small concentrations on the highly oriented graphite samples used in these studies. Thus, the turnover rates, when given in units of methane molecules produced per surface graphite atom per second, greatly underestimate the turnover rates at the active edge sites.

The large increase in the binding energy of the carbon 1S electrons when the new type of active carbon forms indicates the presence of a more positively charged carbon species.

About 5.6 eV shift in the C(1S) photoelectron binding energy is observed when compared to that in graphite. Similar shifts of the C(1S) line have been observed by other researchers when studying organic compounds with electron withdrawing substituents like those shown in Table I:

TABLE I

Compound	C(1S) Binding Energy (eV)
$(CH_3)_3\ C^+$	290.1[10]
$HC(OCH_3)_3$	290.0[11]
$O{=}C(COOH)(OH)$	290.2[11]
$O{=}C(ONa)(OH)$	290.3[11]
$O{=}C(CF_3)(OCH_2CH_3)$	290.7[11]

However, while the active carbon appears to be more positively charged, we can not specify its precise electronic state on the surface.

During the catalyzed hydrogenation of carbon monoxide over iron surfaces a carbonaceous deposit forms consisting mostly of CH-species.[12] Photoelectron spectroscopy studies indicate[12] a small shift in the carbon 1S electron binding energy to 283.9 eV. Thus, it appears that the bonding of the active carbon species that form on the graphite surface in the presence of calcium oxide and water is very different from the carbon species present on transition metal surfaces during the CO/H_2 reaction.

Potassium and other alkali metals can catalyze the reaction of water vapor and graphite to produce methane without the need of hydrogen [$2C + 2H_2O \xrightarrow{K} CH_4 + CO_2$]. The activation energy for methane formation is 11.1 1 kcal/mole, appreciably lower than when using calcium as a catalyst. Thus, the mechanism of the alkali catalyzed gasification reaction is very different from the calcium catalyzed reaction. The dissociation of H_2O to OH^- and H^+ is more facile in

the presence of alkali ions than in the presence of calcium. However, the alkali catalyzed reaction between graphite and water must also proceed through a carbon depolymerization and than a subsequent hydrogenation step. Proof for the former comes from our XPS studies that indicated the appearance of a new C(1S) peak corresponding to a binding energy of 292.5 eV when graphite was heated with water vapor in the presence of KOH below the gasification temperature of 473K for several hours. Proof for the hydrogenation reaction step was provided by thermal desorption studies[1] that detected hydrogen evolution from the graphite that was previously reacted with water to produce methane.

Our studies using potassium intercalated graphite ($C_{24}K$) did not yield accelerated reaction rates as compared to KOH covered pure graphite. This is surprising since the edge area greatly increases by swelling of the samples during intercalation and subsequent reaction in the presence of water vapor. While the swelling indicates the absorption of a large amount of water in the graphite this does not increase the rate of gasification in any way. Thus, we must conclude that potassium or water intercalation is not an important reaction step during the low temperature catalyzed gasification of graphite.

While there are certain conclusions that can be reached on the catalyzed gasification of graphite to methane from these and from previous studies on well characterized small area samples, one should be careful when considering the extension of these results to the catalyzed gasification of char or coal. Graphite contains no hydrogen and its unique caizotropic structure and the chemical bonding of its carbon atoms cannot be easily compared with organic molecules and various structural features found in char or coal. Nevertheless, continued comparison of the reactivities of these different systems will help us to unravel the molecular details of their catalyzed depolymerization (or hydrogenolysis) and hydrogenation.

It is likely that the rates of catalyzed depolymerization and gasification of organic systems depend on their structure. Graphite, aliphatic chains or aromatic fused systems are apt to show different reaction rates. Thus, it may be possible to carry out selective hydrogenolysis of complex organic systems that are found in coal and different forms of biomass (wood, etc.). This way new and perhaps desirable organic molecules may be produced.

The question arises whether organic molecules other than methane might also be produced during the gasification at lower temperature. The thermodynamics of producing C_2, C_3 and higher molecular weight hydrocarbons is not unfavorable. It is also clear that alkali and calcium catalysts do not produce molecules other than methane under our experimental conditions. Perhaps the combined application of these catalysts and transition metal compounds that are efficient during CO/H_2 reactions to produce higher molecular weight hydrocarbons will achieve this goal. Studies are in progress in our laboratory to produce C_2 and C_3 organic molecules under conditions that are similar to those needed to produce methane from graphite by using a mixture of catalysts.

CONCLUSIONS

By extending the temperature range to 873K we have confirmed that the catalyzed methanation of graphite is efficient at low temperatures, by using potassium and calcium as catalysts and water and/or H_2 as reactants.

The catalytic reaction mechanisms involved in the potassium catalyzed graphite water reaction, $2C + 2H_2O \xrightarrow[11\ \text{kcal}]{K} CH_4 + CO_2$ seem to be the same in the range of temperatures from 473K to 873K. According to our studies intercalation does not play a role in the methanation of graphite. Calcium catalyzes the transformation of graphitic carbon to an active form of carbon, in the presence of water vapor $C_{(graphite)} \xrightarrow[16\ \text{kcal}]{Ca,\ H_2O} C_{(active)}$. Methane production,

however, requires the addition of hydrogen in this circumstance. $C_{(active)} + 2H_2 \xrightarrow[25\ kcal]{Ca} CH_4$.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Figure 1: (a) Schematic diagram of the apparatus with high pressure cell closed, (b) detail with high pressure cell open.

Figure 2: Logarithm of the CH_4 production rate as a function of the inverse absolute temperature for the KOH-graphite system.

Figure 3: Plots of the number of CH_4 molecules produced during the KOH-catalyzed water-graphite reaction as a function of reaction time, for two different thicknesses of graphite samples.

Figure 4: Number of CH_4 molecules produced during the calcium catalyzed hydrogen-graphite reaction as a function of time for two different temperatures. The sample was pretreated in 22 torr of water vapor before the reaction P_{H_2} = 1 atm.

Figure 5: Arrhenius plots for the calcium oxide-graphite system. The plot for the activation energy of 25.5 kcal/mole corresponds to the sample pretreated in 22 torr of H_2O and then heated in 1 atm of H_2. The plot for the activation energy 16.3 kcal/mole corresponds to the case of 22 torr of H_2O and 32 torr of H_2.

Figure 6: XPS spectrum a) before and b) after the reaction with 1 atm of H_2. The sample was pretreated in 22 torr of H_2O.

Figure 7: Number of CH_4 molecules produced as a function of time for the CaO-graphite system with 22 torr of H_2O and 32 torr of H_2.

Figure 8: Methane production rate as a function of hydrogen pressure at 773K for the CaO-graphite system. Water vapor pressure was not varied.

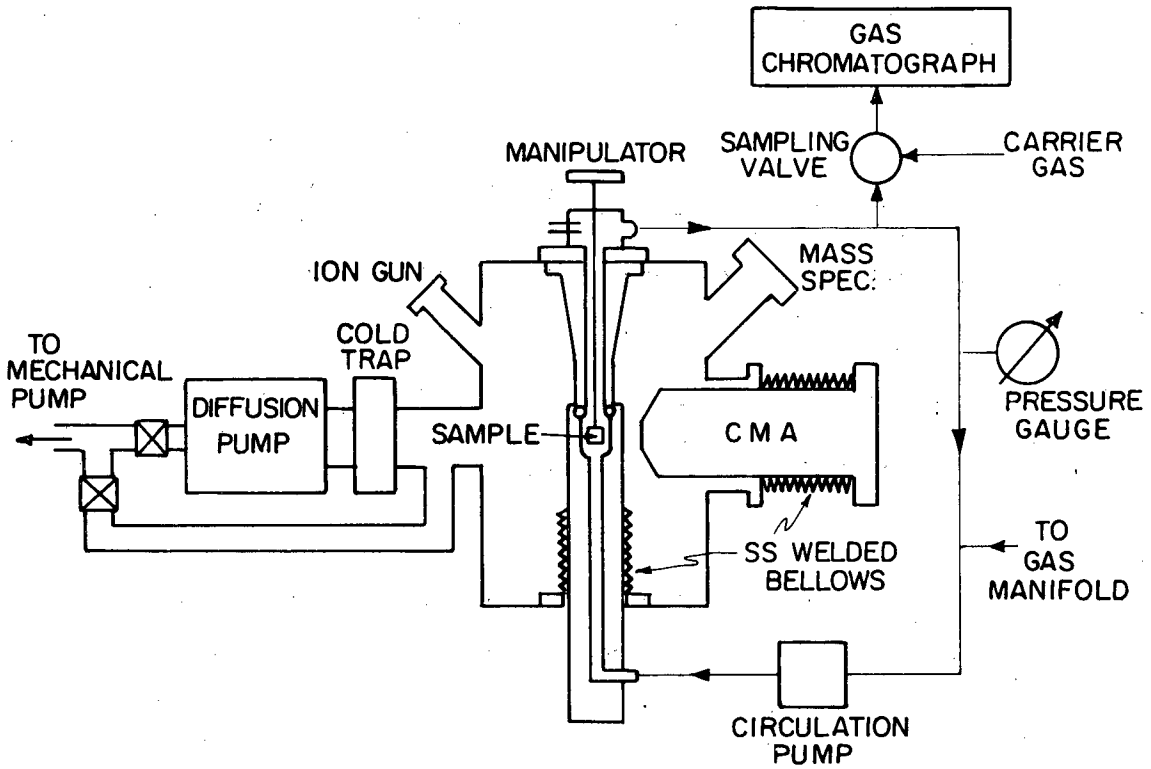
Figure 9: AES spectrum for the K-intercalated graphite sample. a) first spectrum, b) second spectrum 5 minutes apart.

Figure 10: Temperature effect on the intensity of the AES potassium peak for the K-intercalated graphite sample.

Figure 11: XPS spectrum for the $C_{24}K$ sample a) before and b) after the reaction with 22 torr of H_2O at 573K.

Figure 12: Number of CH_4 molecules produced as a function of time during the KOH-catalyzed water graphite reaction and the $C_{24}K + H_2O$ reaction respectively at 573K.

Figure 13: Photograph of two samples of intercalated graphite. Sample above is before reaction while sample below is after reaction.



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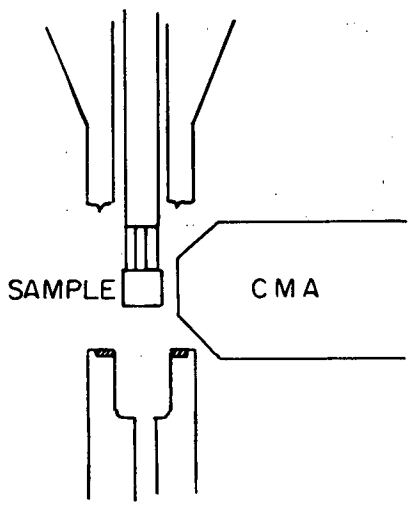

(b)

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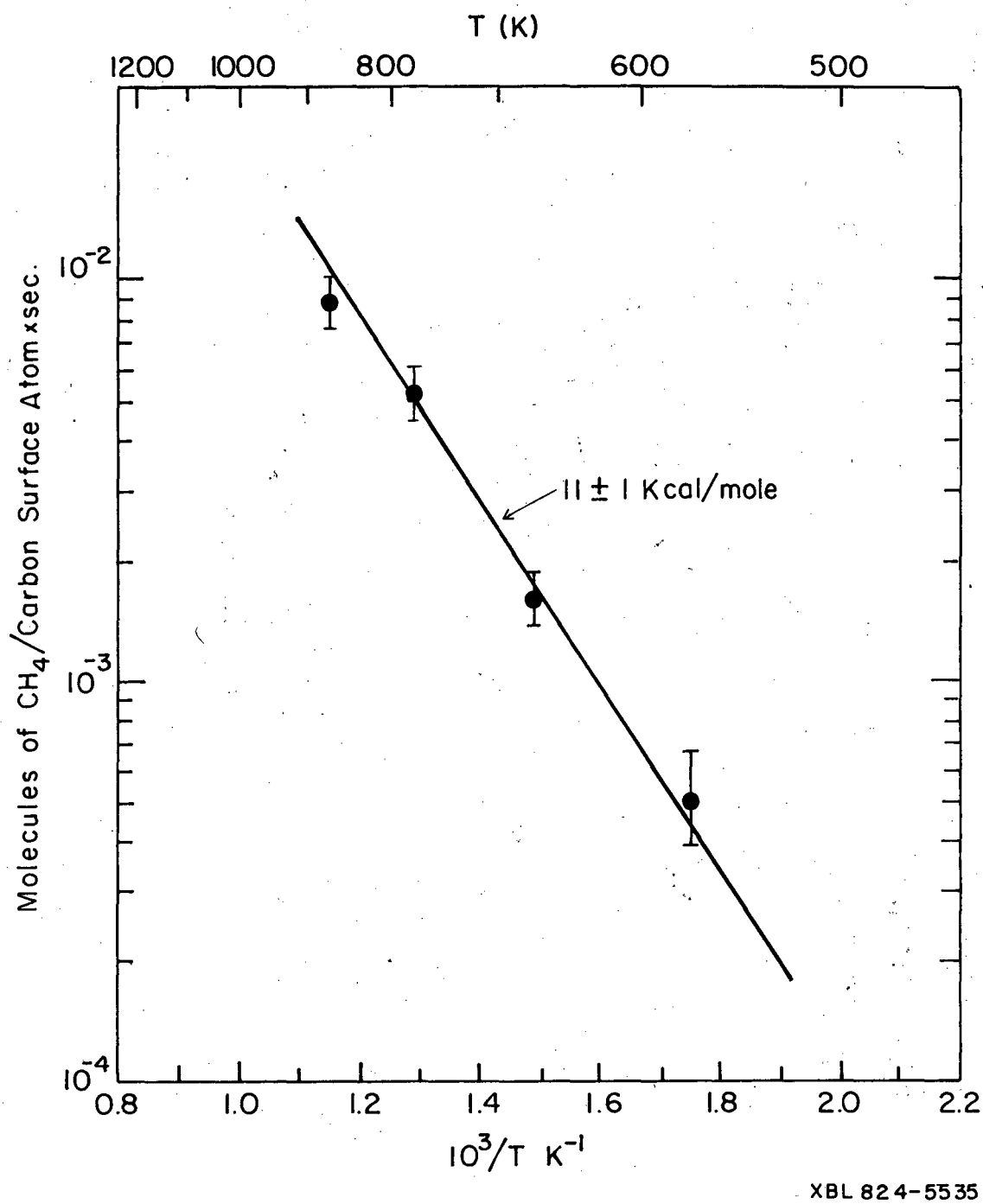
Fig. 1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500
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10^{-3}
10^{-4}
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1.0
1.2
1.4
1.6
1.8
2.0
2.2
$10^3/T$ K^{-1}
XBL 824-5535

Fig. 2

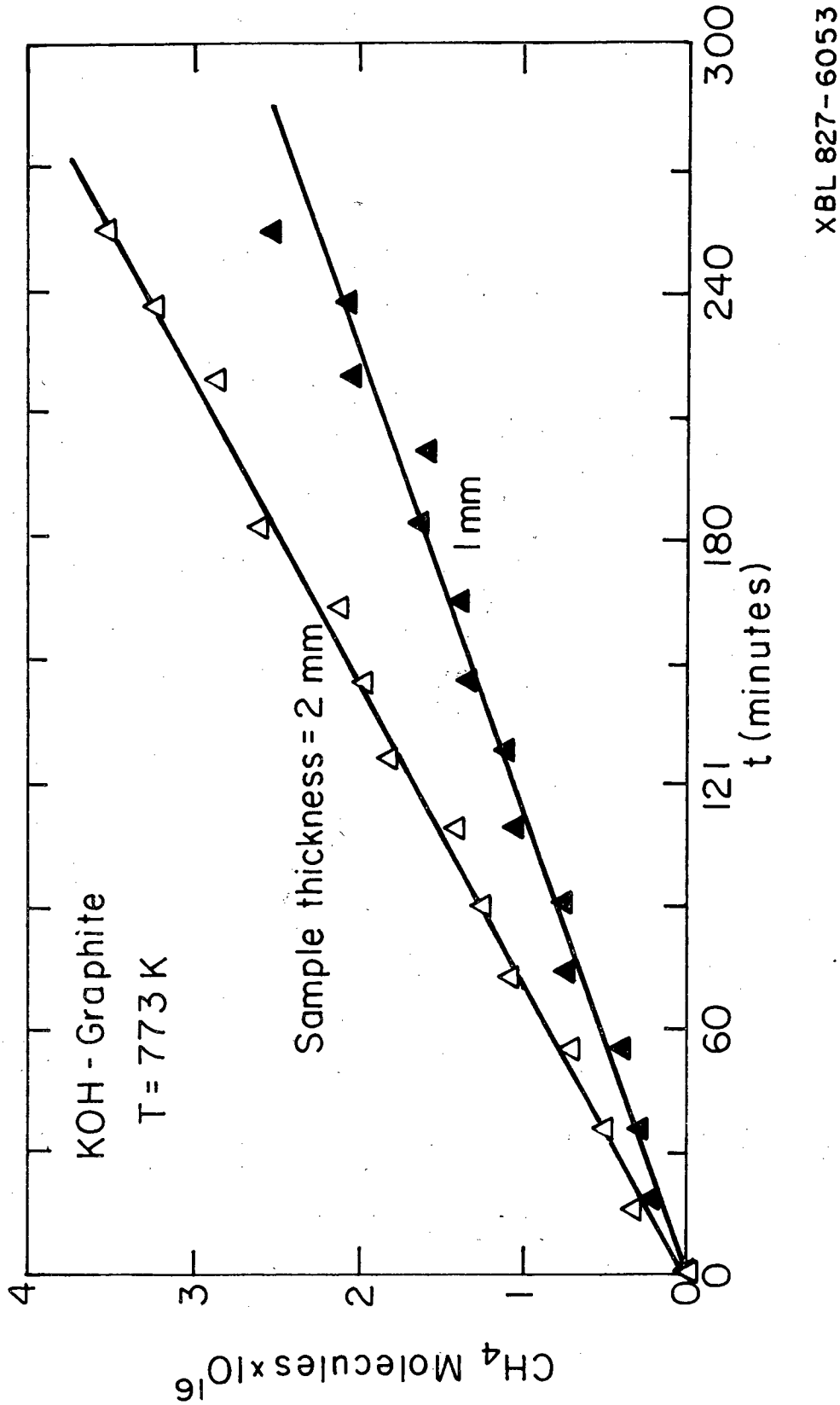

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Fig. 3

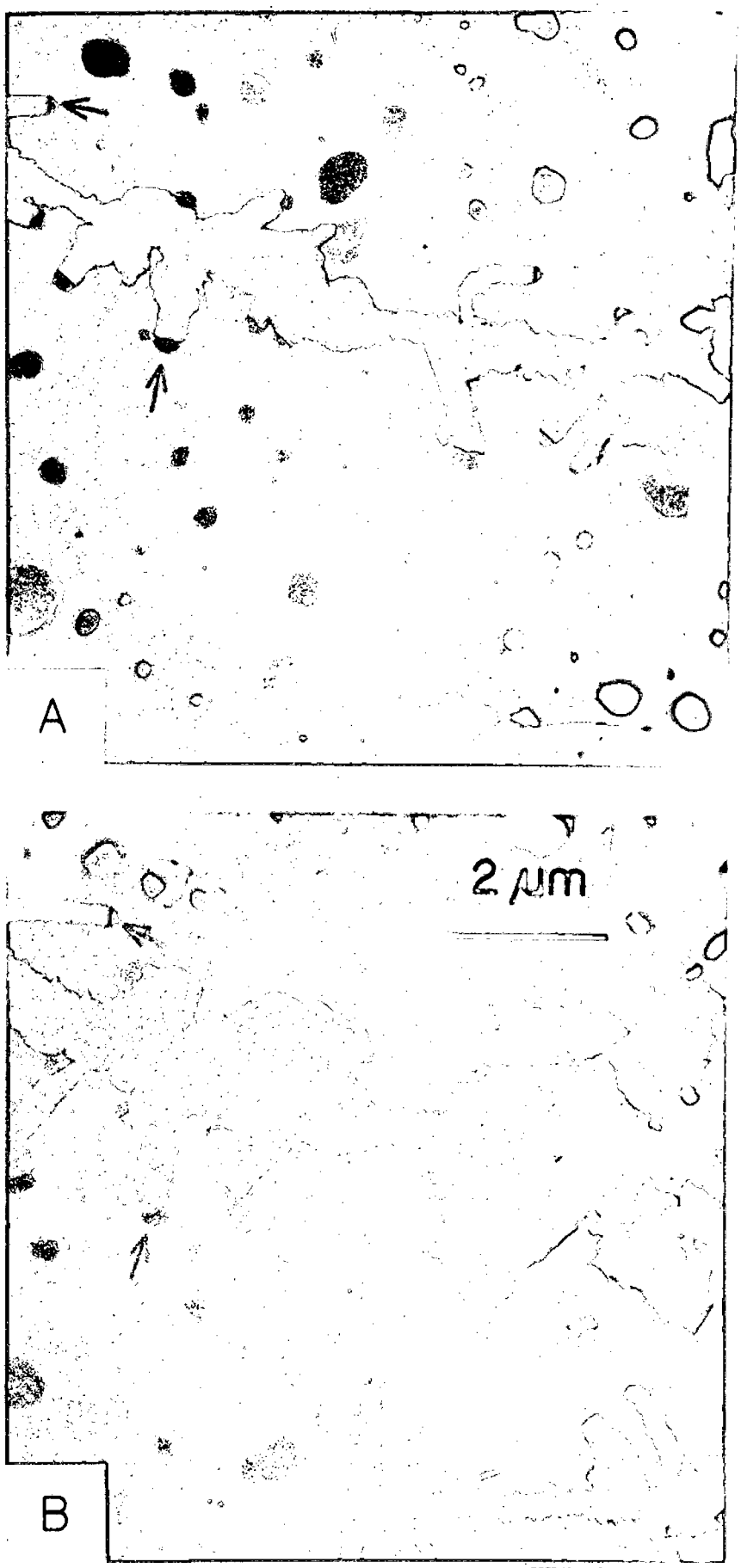

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Fig. 4

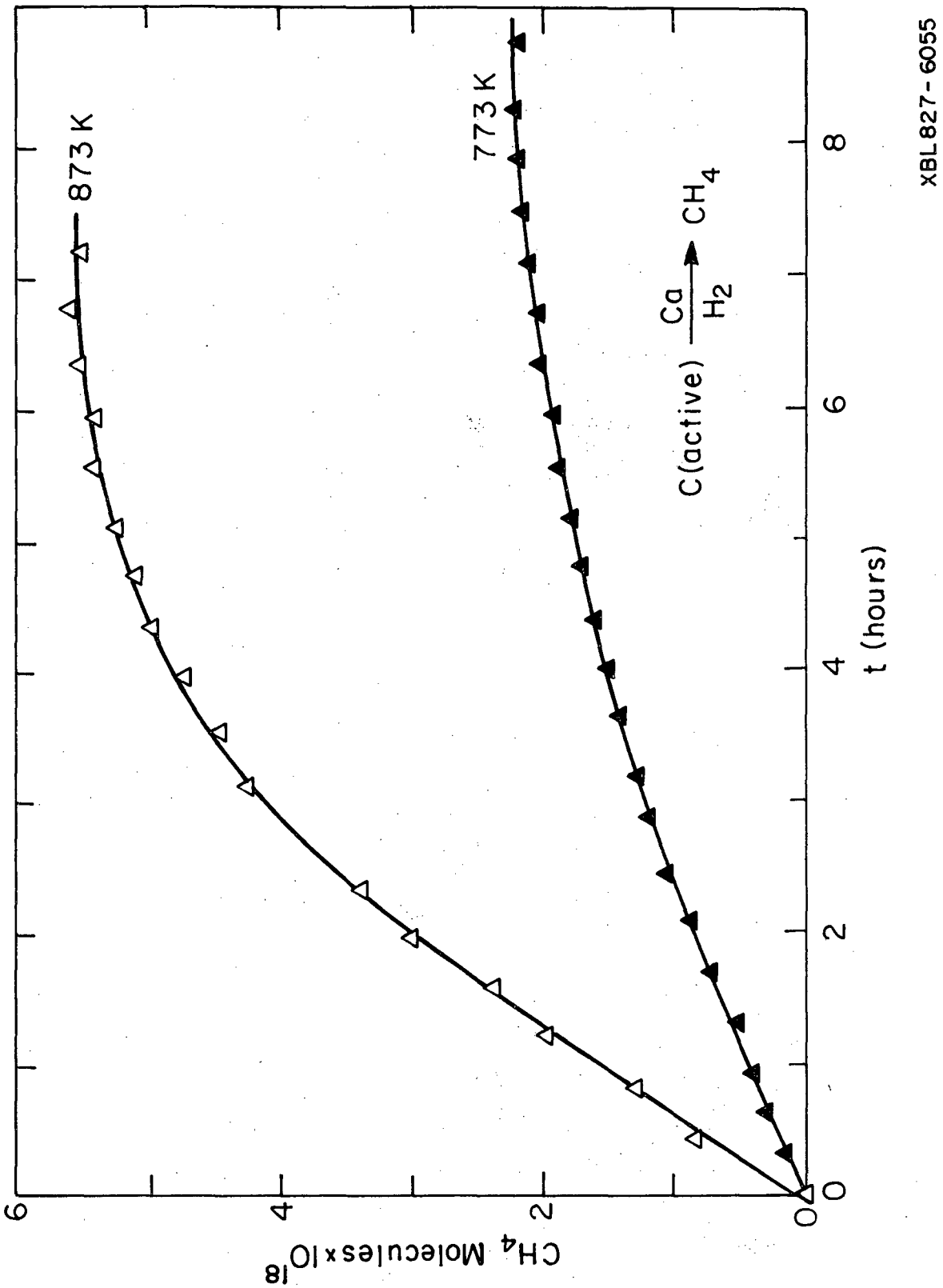
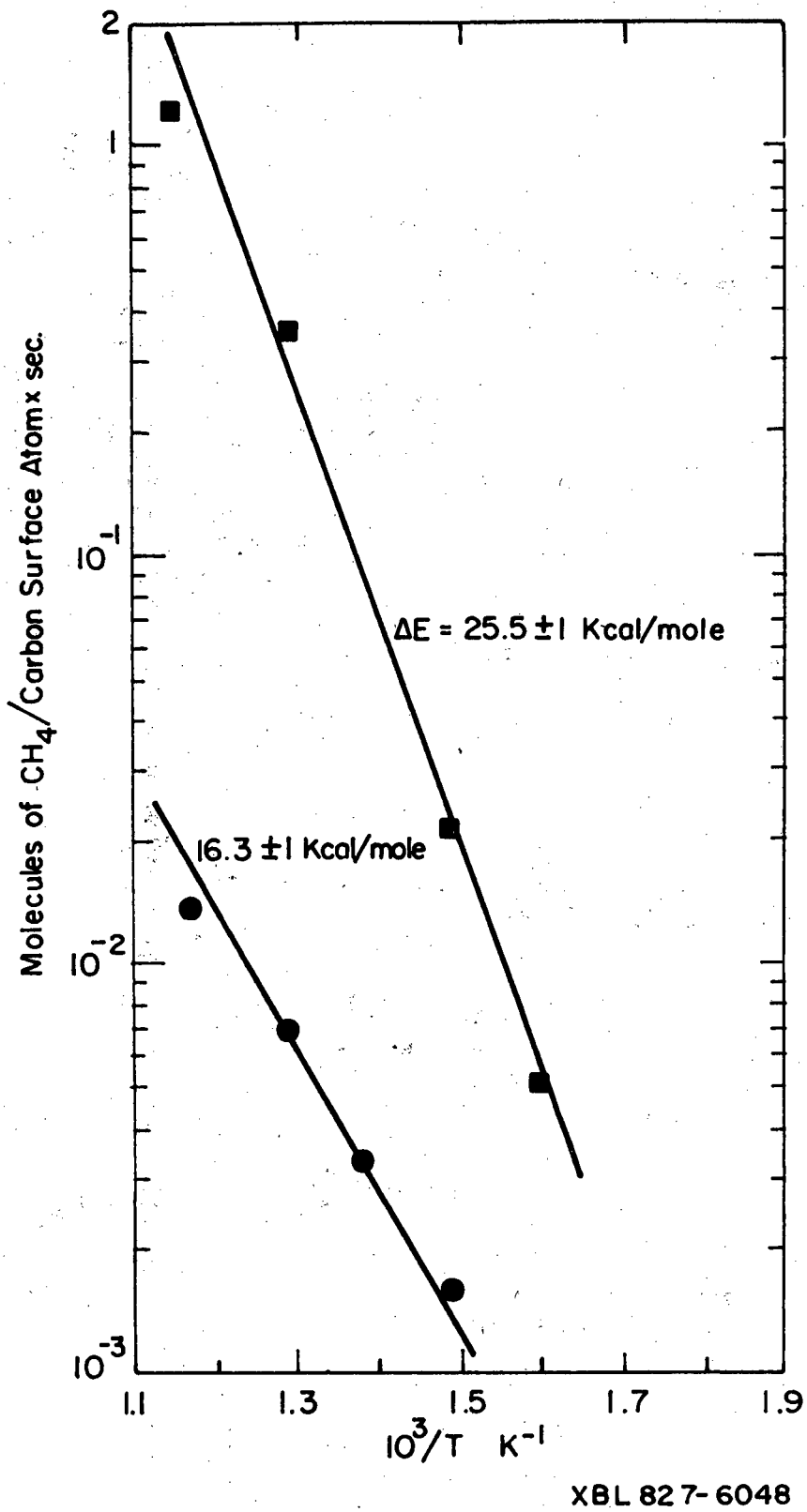

873 K
773 K
C(active) $\xrightarrow[H_2]{Ca}$ CH_4
CH_4 Molecules x 10^{18}
t (hours)
0
2
4
6
8
XBL 827-6055

Fig. 5


2
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10^{-1}
10^{-2}
10^{-3}
Molecules of CH_4/Carbon Surface Atom x sec.
ΔE = 25.5 ± 1 Kcal/mole
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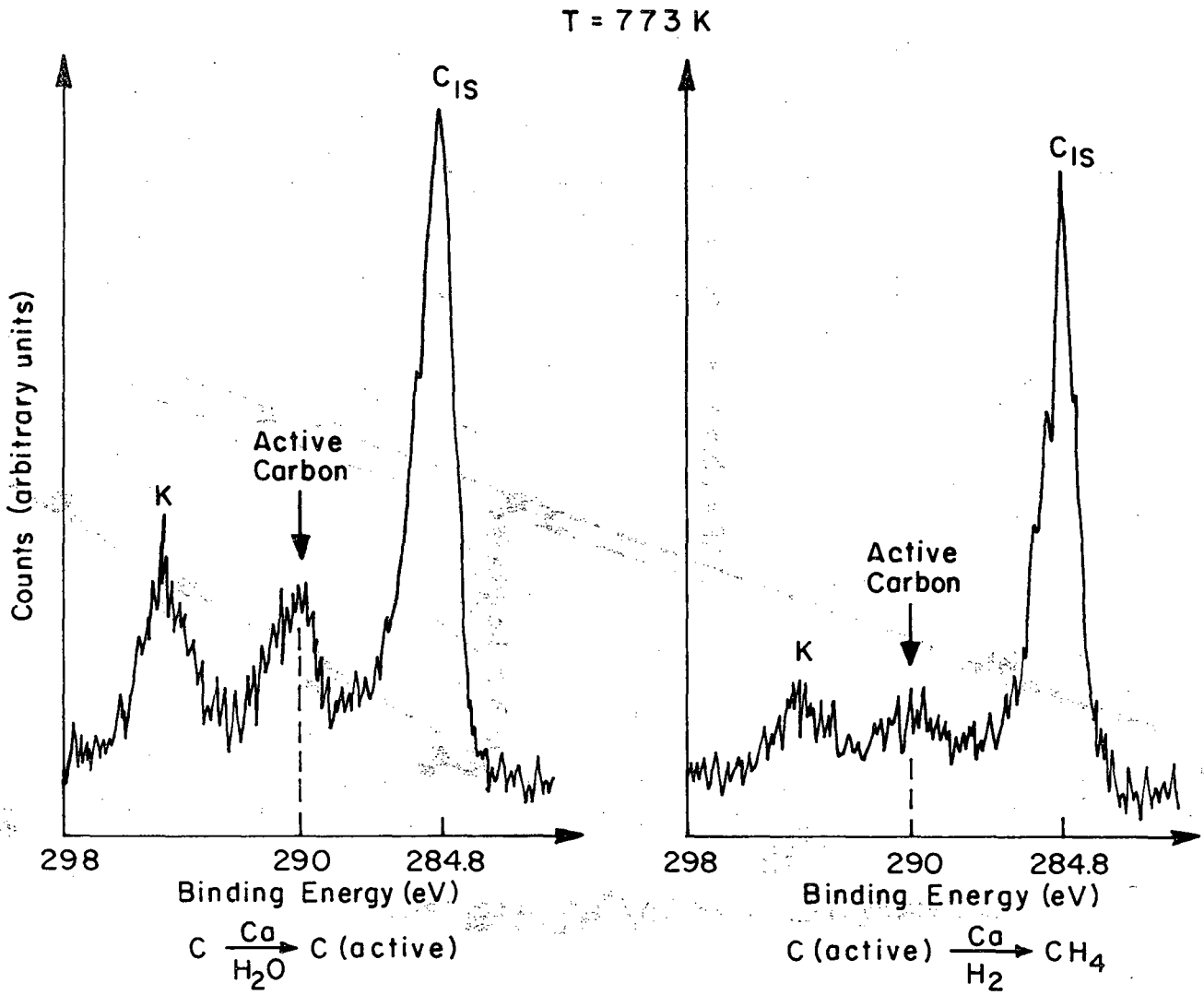
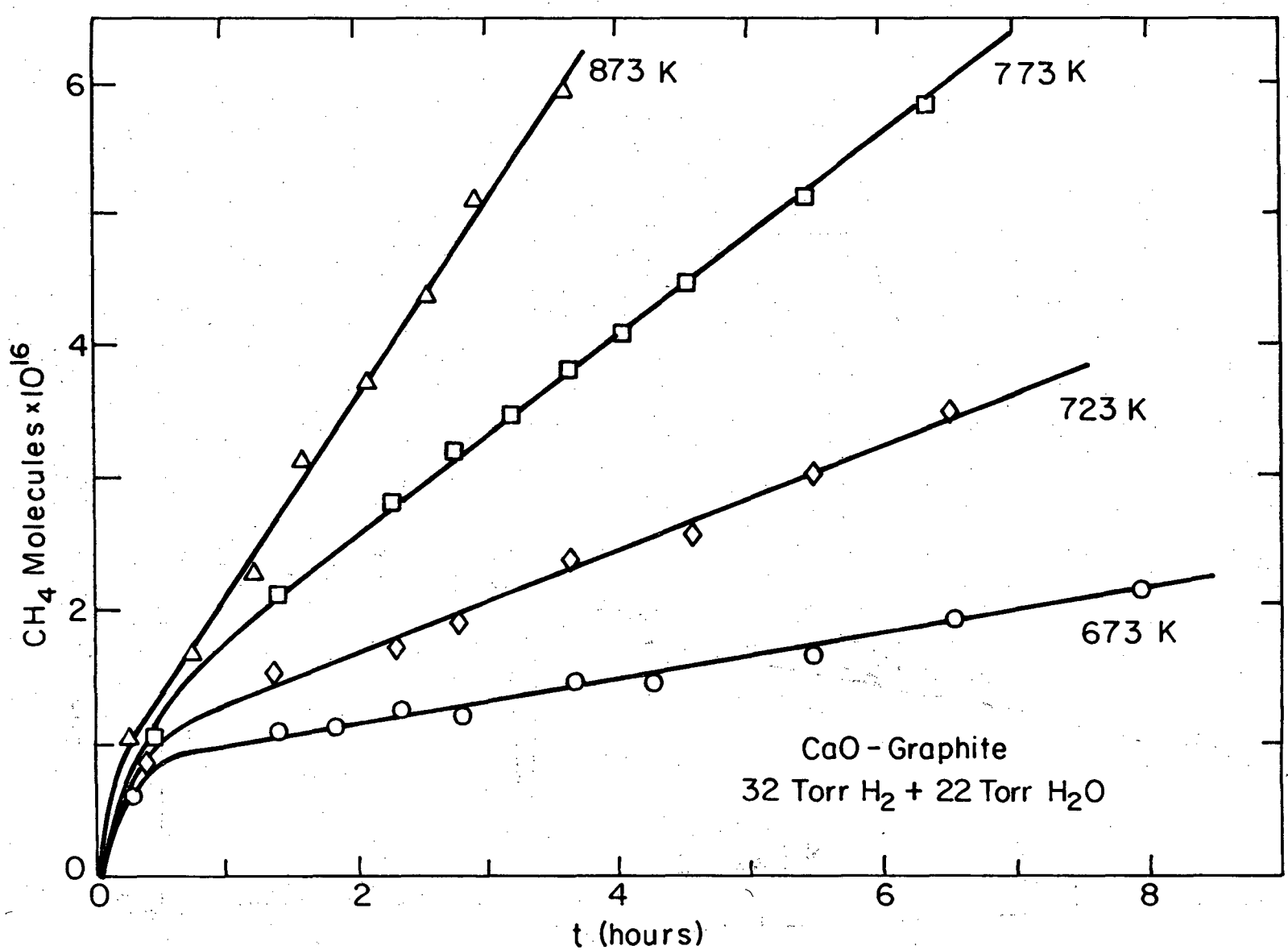
1.1
1.3
1.5
1.7
1.9
$10^3/T$ K^{-1}
XBL 827-6048

Fig. 6



XBL 827-6056

Fig. 7



XBL 827-6054

Fig. 8

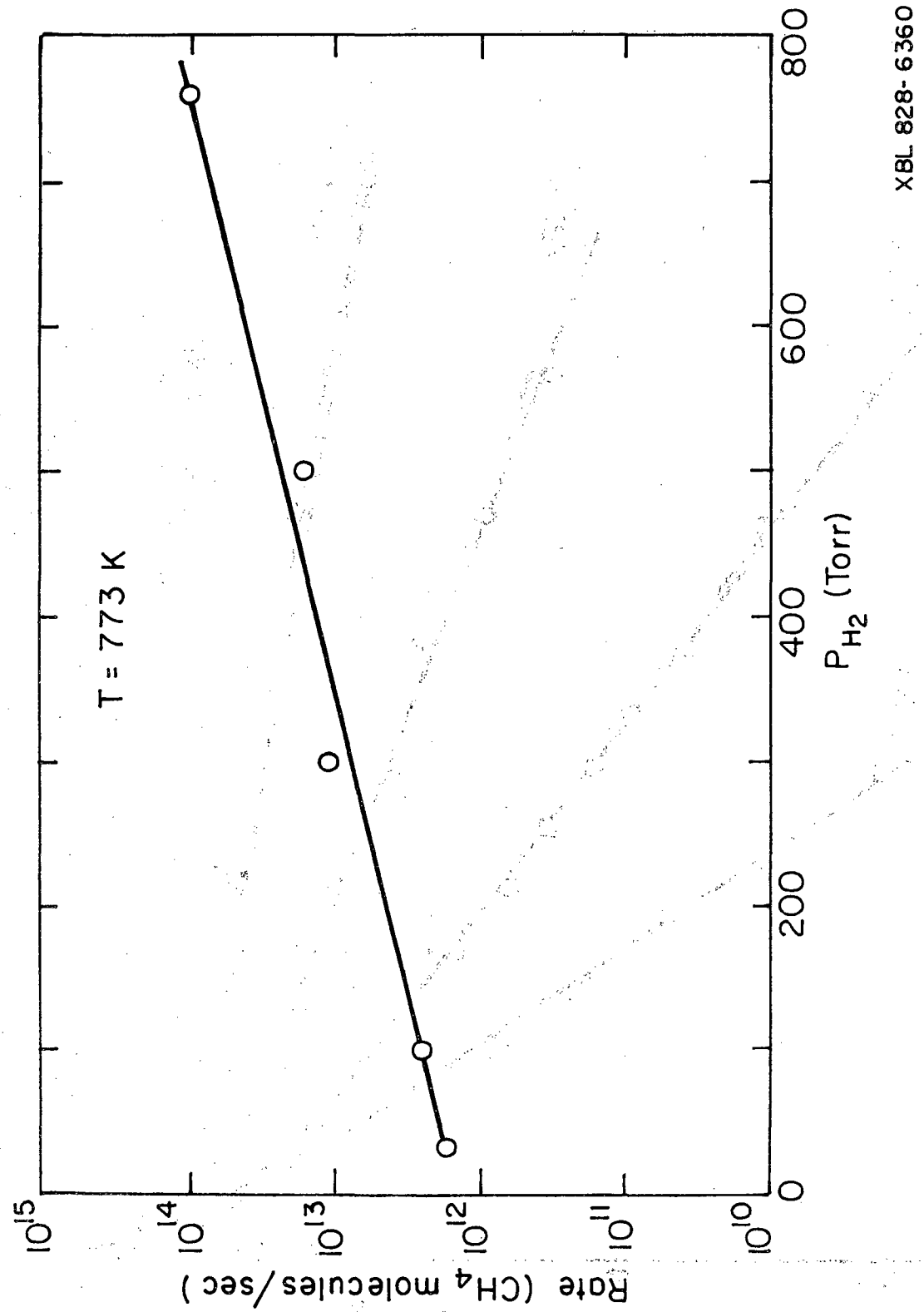
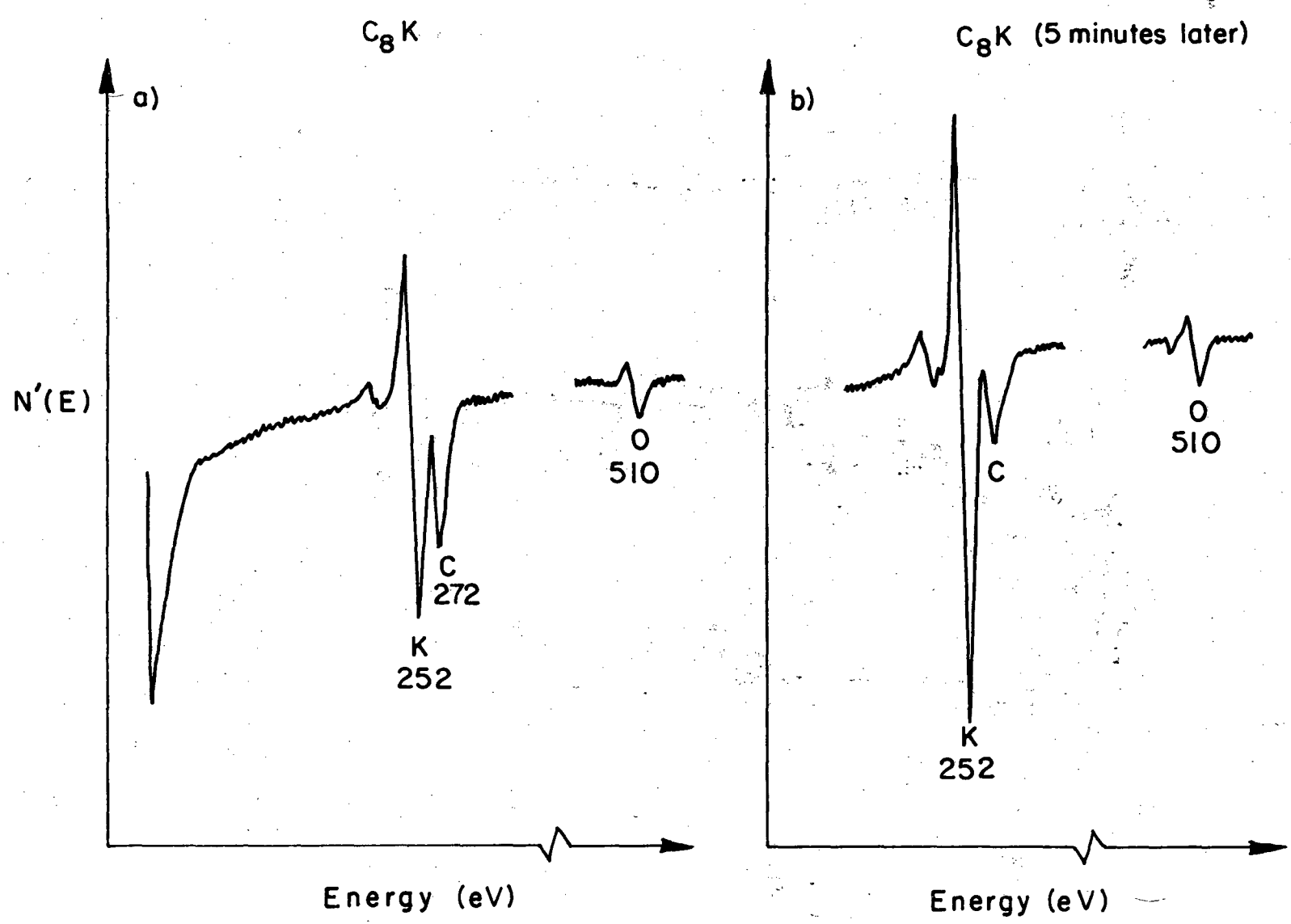

T = 773 K
Rate (CH4 molecules/sec)
10^15
10^14
10^13
10^12
10^11
10^10
0
200
400
600
800
P_H2 (Torr)
XBL 828-6360

Fig. 9



XBL 827-6051

Fig. 10

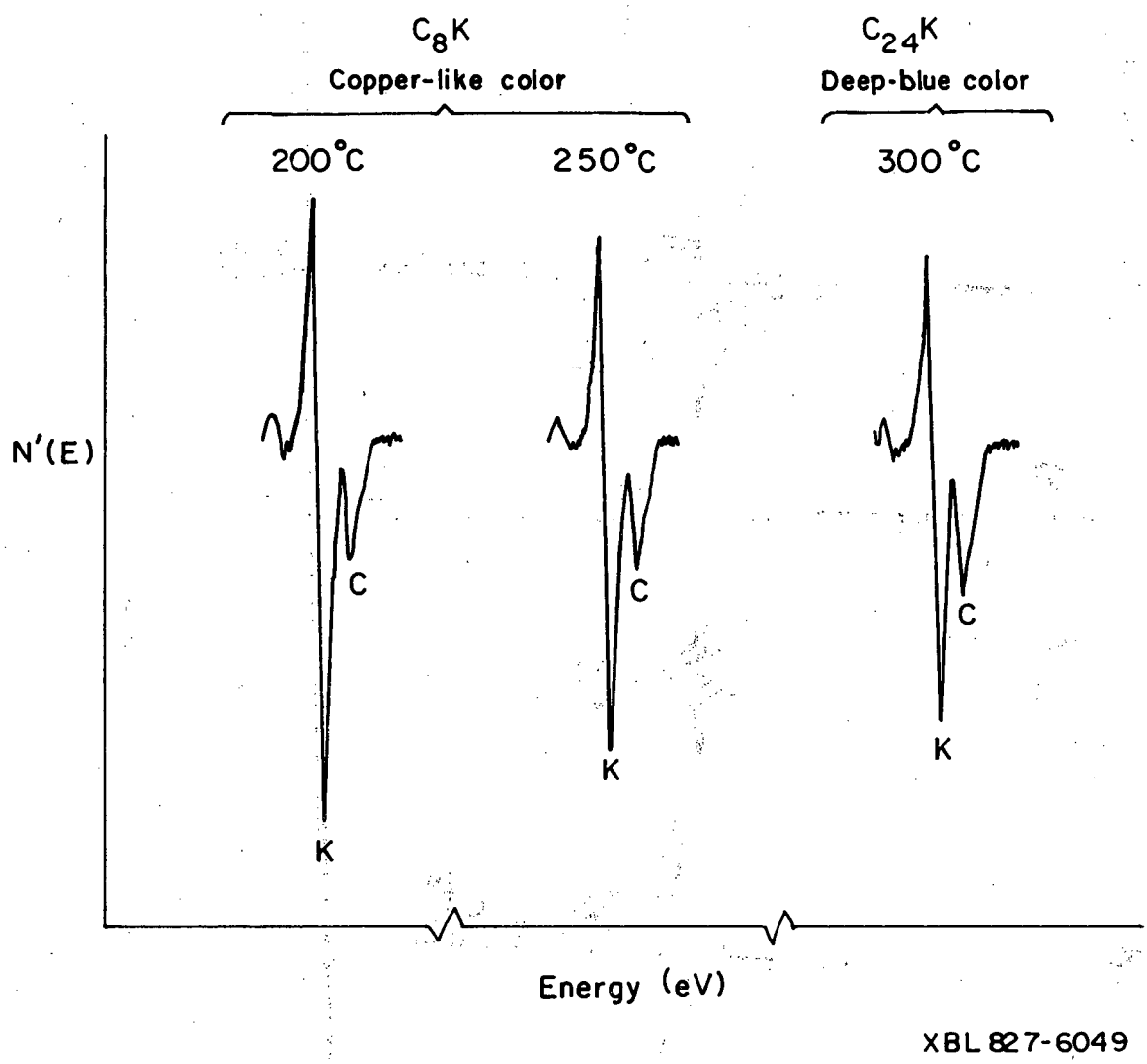
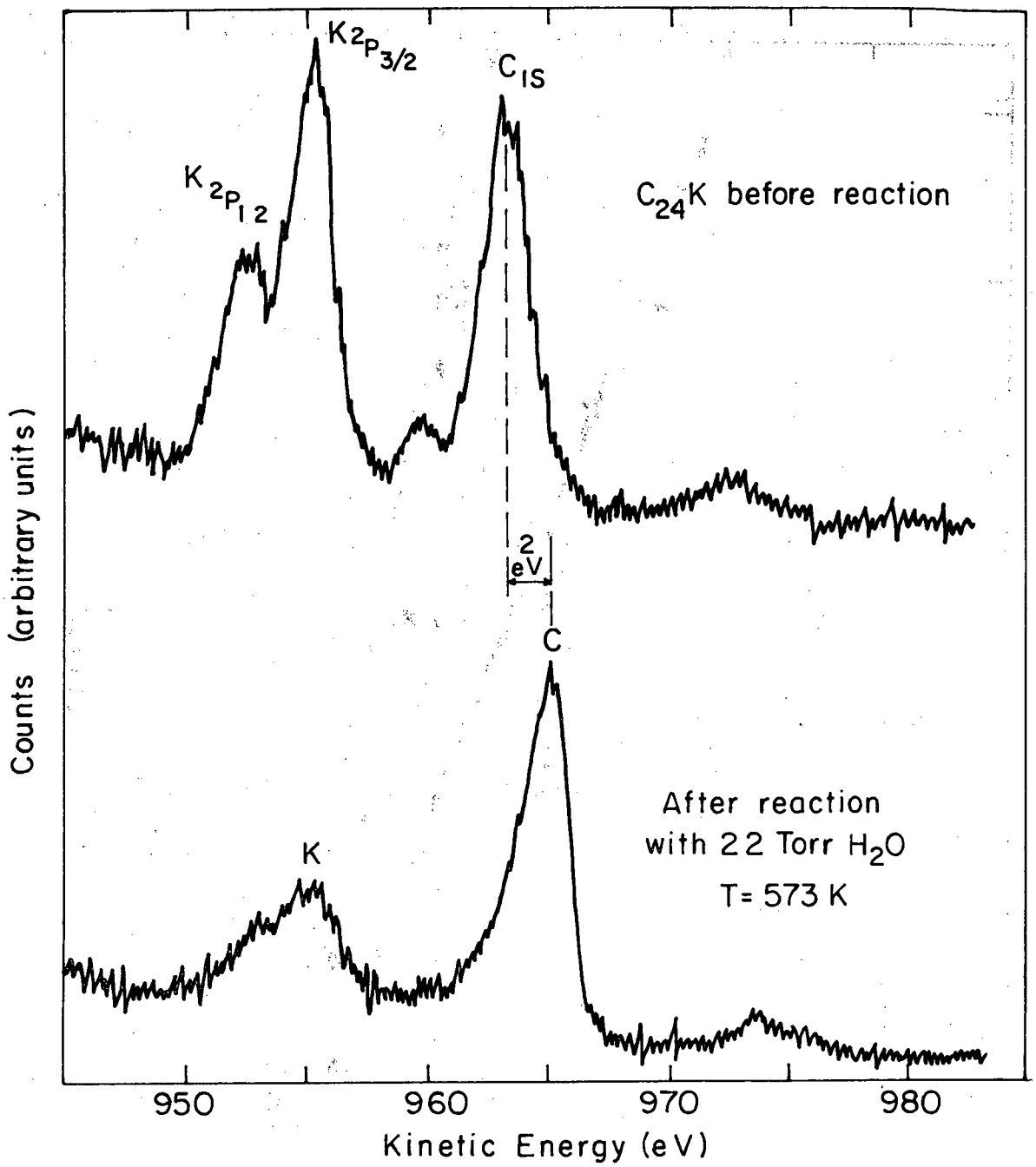

C_8K
Copper-like color
$C_{24}K$
Deep-blue color
200°C
250°C
300°C
N'(E)
C
C
C
K
K
K
Energy (eV)
XBL 827-6049

Fig. 11



XBL 827-6050

Fig. 12

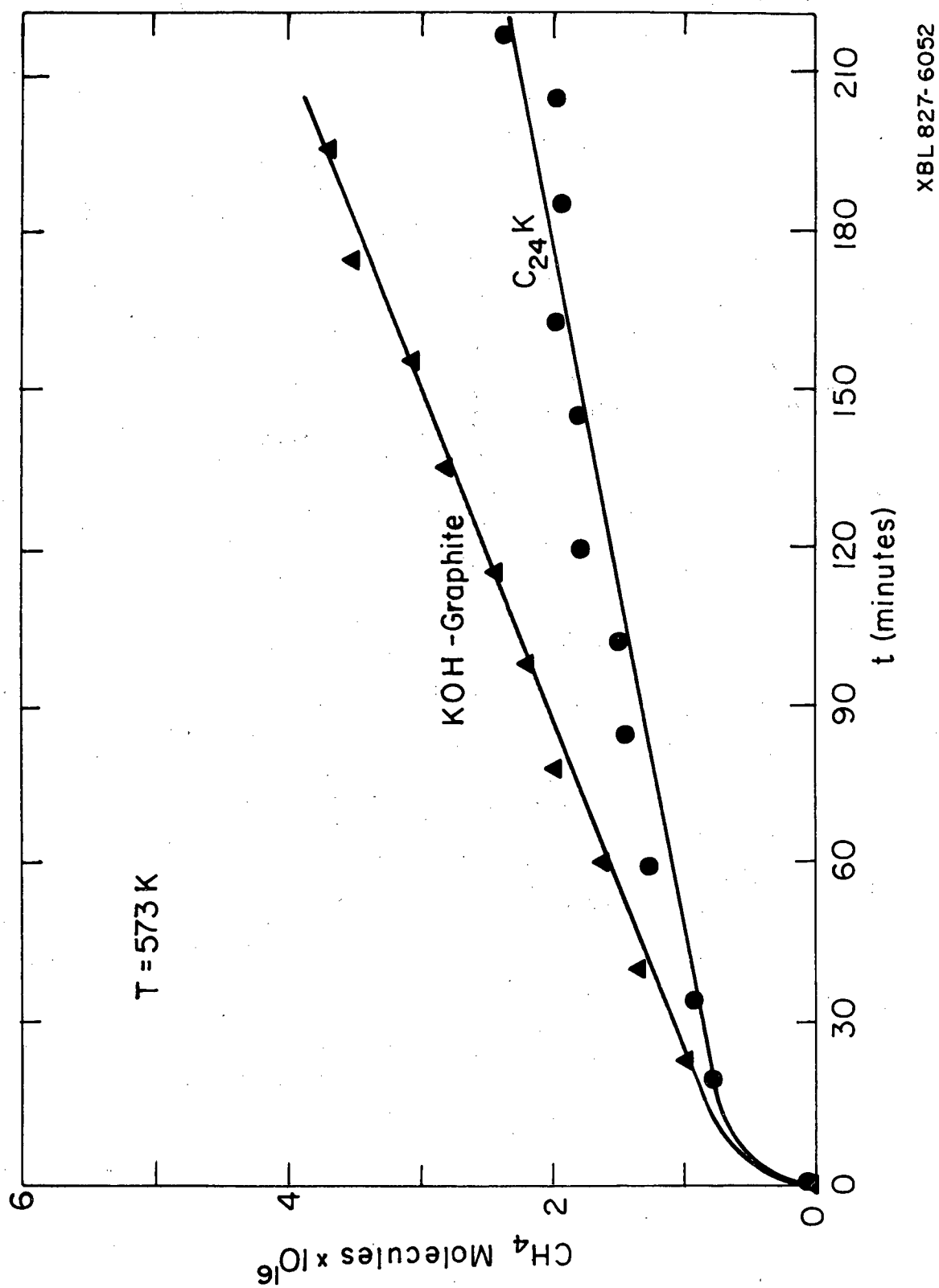

T = 573 K
KOH -Graphite
$C_{24}K$
CH_4 Molecules x 10^{16}
0
2
4
6
0
30
60
90
120
150
180
210
t (minutes)
XBL 827-6052

Fig. 13

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