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CATALYTIC GASIFICATION OF GRAPHITE OR CARBON
Quarterly Report, October 1 - December 31, 1985

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December 1985

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QUARTERLY REPORT

October 1, 1985 - December 31, 1985

CATALYTIC GASIFICATION OF GRAPHITE OR CARBON

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I. Task Description for FY 1986

This program is designed to study the basic chemistry of the reaction of carbonaceous materials with water in the presence of catalysts to produce hydrocarbons and/or synthesis gas. Relatively low temperatures are being used. Earlier work has shown that a combination of KOH and a transition metal oxide, such as NiO, constitutes catalysts superior to either component alone. It is an objective of the present task to identify the optimum ratio of the components and to determine the existence and composition of a potential catalytic compound, e.g. a potassium nickelate. The applicability of the reactions thus far studied with graphite to char, coke and possibly coal will be investigated. Improvements in kinetics will be sought and the effect of added gases, such as H₂S, CO and O₂ will be researched.

II. Highlights

- 1) Two chars (from Illinois #6 coal and from Montana subbituminous coal) were impregnated with KOH-NiO and compared for steam gasification with graphite containing the same catalyst. The rate of H₂ (and CO₂) production at 890K was initially an order of magnitude higher for the chars than for graphite.

- 2) The gasification rate for the chars declined as a function of time. After about 25% of the char was gasified the rate was still three times that of graphite.
- 3) Comparing for the Montana char the catalytic effect of KOH-NiO with K_2O_3 alone, it was found that the former was up to six times more active than the latter.
- 4) Determination of an optimal ratio of K/Ni is underway. While it had previously been shown that in case of KOH impregnation alone the rate of hydrogen production is a function of the amount of KOH present (stoichiometric reaction), it is found that in the case of KOH-NiO there is no dependency on the ratio of catalyst to carbon. The reaction is therefore truly catalytic.
- 5) Thermal desorption studies with CO, CO₂ and O₂ on pure graphite show the presence of carbonyl, lactone, and quinone groups on the graphite edges. Future work will delineate whether the same intermediates exist in the presence of catalysts. Thermal desorption studies using water on the graphite are underway.

III. Progress of Studies

a) Flow Reactor Work

The gasification with steam of two different chars catalyzed by KOH-NiO has been studied. One of the chars was prepared by heating Illinois #6 coal to 1300K for 9 hours under a helium atmosphere. The other was prepared by heating Montana sub-bituminous coal at 1200K under steam for several hours. The catalyst was loaded onto the chars by incipient wetness method, using solutions of KOH and $\text{Ni}(\text{NO}_3)_2$. The molar ratio of K/Ni was equal to 1.0 and the percentage of Ni in the sample is 5%. The samples were pre-treated for 3 hours at temperatures below 500K under an argon atmosphere to decompose the nitrate. We believe that this pre-treatment does not affect the activity of the sample for steam gasification, since the temperature is much lower than under reaction conditions. Both samples were gasified with steam at 893K for several hours. The main products were H_2 and CO_2 . Small amounts of CH_4 and CO were also observed (less than 1%). The rate of H_2 production was monitored as a function of time. The results are shown in Figure 1. In both cases the initial rate of H_2 production is one order of magnitude higher than in the case of steam gasification of graphite. Even though the rate decreases with time, after 6 hours, the rate of gasification of both chars is still three times higher than the initial rate on graphite. The samples were left overnight under reaction conditions.

After 18 hours, the rate of H_2 production in the case of the Montana char was 0.14 ml/min (8.13% of the initial rate) while the Illinois #6 was almost inactive (0.02 ml/min). Integration of the curves shown in Figure 1 gives a 23% carbon conversion in both cases, considering that one mol of carbon is being consumed per each two moles of H_2 produced and that the sample used was entirely carbon. These two assumptions give the most conservative estimate of the carbon conversion.

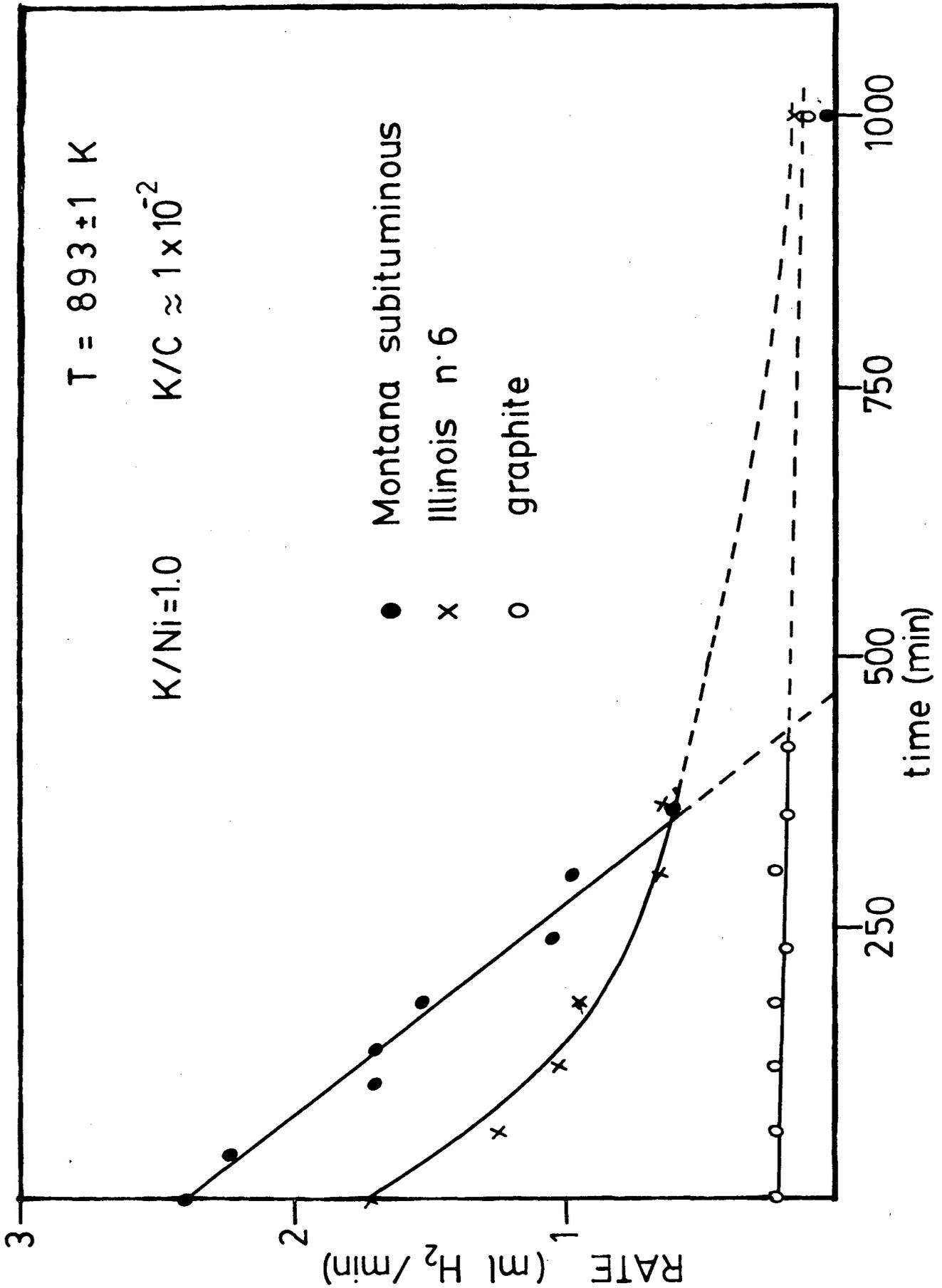
The reasons for the loss of activity with time is not clear. Two possibilities are suggested. Either there is a loss of contact area between the catalyst and the substrate or the catalyst is poisoned during reaction. Atmosphere Controlled Electron Microscopy studies of the two samples will be performed next quarter to investigate the first possibility.

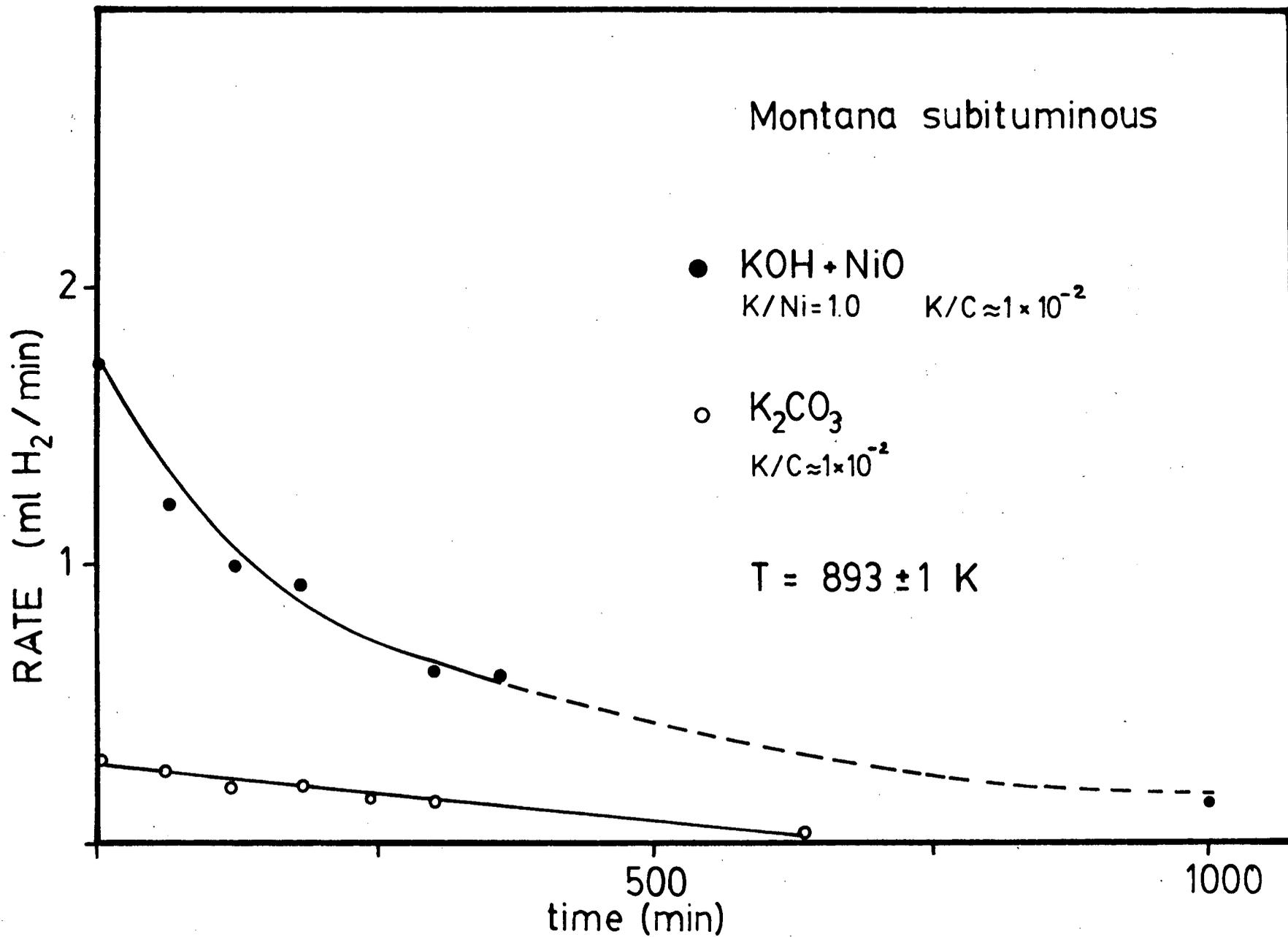
In Figure 2 the activity of KOH/NiO for gasification of the Montana sub-bituminous char is compared with the activity of K_2CO_3 as a function of time. The reaction temperature is 893K. Both catalysts give a similar product distribution. The main products were H_2 and CO_2 . The activity of the KOH-NiO catalysts is initially six times higher than that of K_2CO_3 catalyst and remained higher during the whole period studied (10.5 hours). Similar studies are being done over other carbon substrates. Also comparative studies between the KOH-NiO and Ni metal catalysts will be done.

The rate of graphite gasification as a function of KOH-NiO loading has been studied. The results are shown in Figure 3a. The results obtained by Dellanay, et al (1) for KOH deposited alone over the same substrate are shown for comparison (Figure 3b). Figures 3a and 3b show that in the case of KOH alone the rate of H₂ production is dependent on the amount of catalyst up to a ratio of K/C equal to 0.04. In the case of KOH-NiO, the ratio is independent of the amount of catalyst even at a molar ratio of K/C equal to 2.5×10^{-3} . Further studies are being done to find the optimum KOH/NiO ratio. The KOH/NiO appears to act truly catalytically, while KOH alone has previously been shown to undergo a stoichiometric reaction.

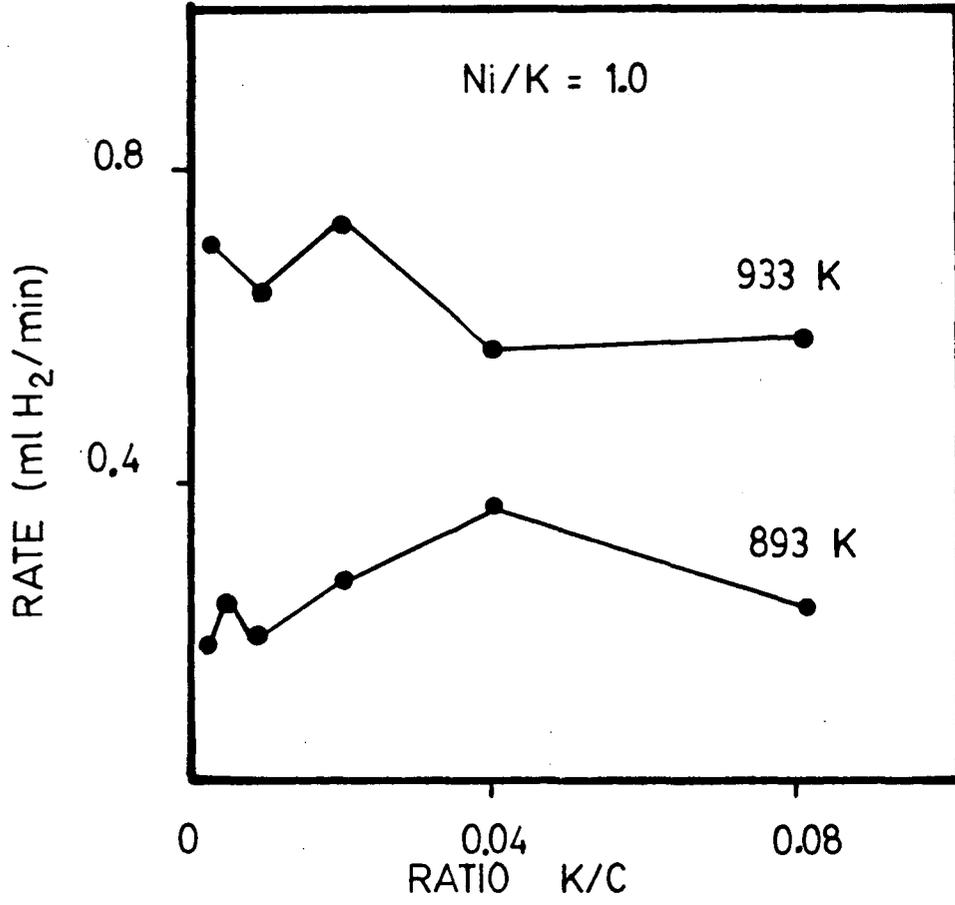
(1) Delannay, F., Tysoe, W.T., Heinemann, H. and Somorjai, G.A., Appl. Catalysis 10 (1984), 111-123.

Figure 1



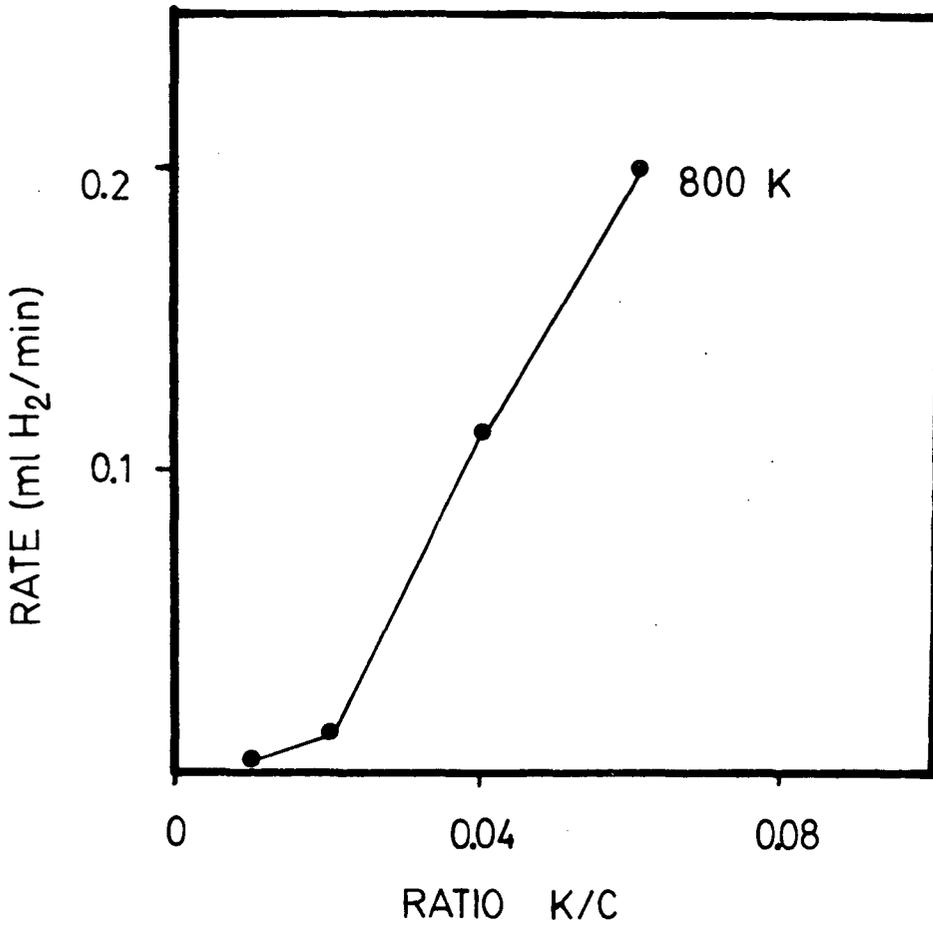


- 9 -
Figure 2



KOH + NiO

Figure 3a



KOH alone

Figure 3b

b) Thermal Desorption Studies on Pure Graphite

It has been previously shown (Annual Report 1985) that TDS experiments under UHV conditions offer a very useful technique in determining the nature of the surface species existing on the edges of pure graphite.

Preliminary experiments after adsorption of CO and H₂O showed that oxygenated species on the surface can desorb at temperatures ranging from 500 to 1300K, indicating different possible chemical sites. Hydrogen and methane have also been detected after H₂O adsorption.

We will now attempt to describe with more detail the nature of these species with the help of additional TDS data after exposure to H₂, CO₂ and O₂. More experiments with CO and H₂O have also been undertaken.

α) Oxygenated species on the graphite surface

(i) CO adsorption:

Figure 4 shows the TDS spectra (29 amu) corresponding to the desorption of ¹³CO, after exposure to 50 torr of ¹³CO at different temperatures. This isotopic derivative was chosen in order to eliminate the problems which can occur when molecular

oxygen is present as a contaminant in the inlet gas. This oxygen would react with graphite to give ^{12}CO and is therefore not interacting with the ^{13}CO we monitor.

In this Figure 4, several desorption peaks can be seen depending on the temperature at which ^{13}CO is adsorbed. At room temperature, only one peak is observed at 250°C , whereas when we dose at 200°C , two peaks at 350 and 500°C appear. Higher temperatures of adsorption give rise to less intense peaks at about 700 , 850 and 1100°C . Some CO_2 (~10% of CO production) is evolved for low T exposures, but no CO_2 desorption peak is observed above 600°C .

(ii) O_2 adsorption:

CO and CO_2 thermal desorption (28 and 44 amu respectively) after adsorption of 50 torrs of oxygen at room temperature are represented in Figure 5. Most of the oxygen comes off as CO at high temperature in a broad massif centered at ca. 700°C with a

tail at 500°C and a small and sharp peak at 1000°C . No molecular oxygen is detected. About 10% comes off as CO_2 at 200°C and 600°C . The total integrated intensities of these two peaks is at least five times greater than the corresponding intensity after adsorption of CO which indicates that we do not reach the saturation coverage, assuming that the number of sites

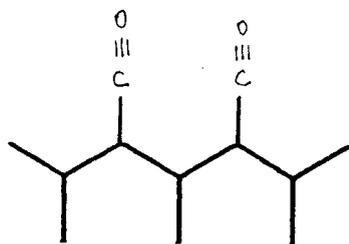
available is the same for both O_2 and CO .

(iii) CO_2 adsorption:

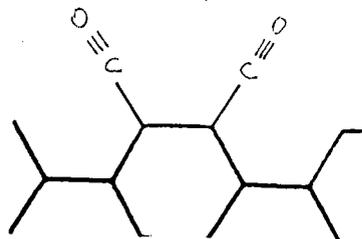
The desorption of oxygenated species after absorption of 8 torrs of $^{13}CO_2$ at room temperature is reproduced in Figure 6. Most of the oxygen is released as ^{12}CO in a way very similar to the one obtained after O_2 adsorption. Some $^{13}CO_2$ (45 amu) desorbs molecularly at $200^\circ C$, whereas almost no $^{12}CO_2$ or ^{13}CO are observed.

(iv) Discussion:

Low temperature desorption peaks of mass 29 amu after ^{13}CO absorption are most likely due to the formation of carbonyl species on the surface. Assuming two types of sites are on the edges of graphite, we can then account for two peaks corresponding to "zig-zag" edges (a) and "arm-chair" edges (b) according to the terminology accepted in the literature.



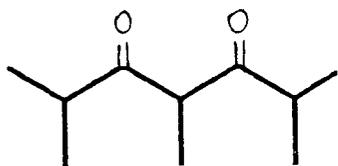
(a)



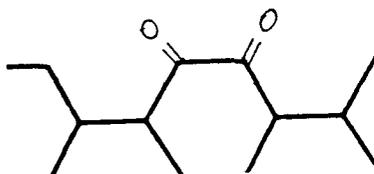
(b)

These two peaks can be the 250 and 350°C features of Figure 4, without defining which site corresponds to which.

The high temperature peaks (mass 28 amu) of CO desorbing after O₂ adsorption (Figure 6) are likely due to quinones, once again either zig-zag (a) or arm chair (b), which are known to be very stable compounds.

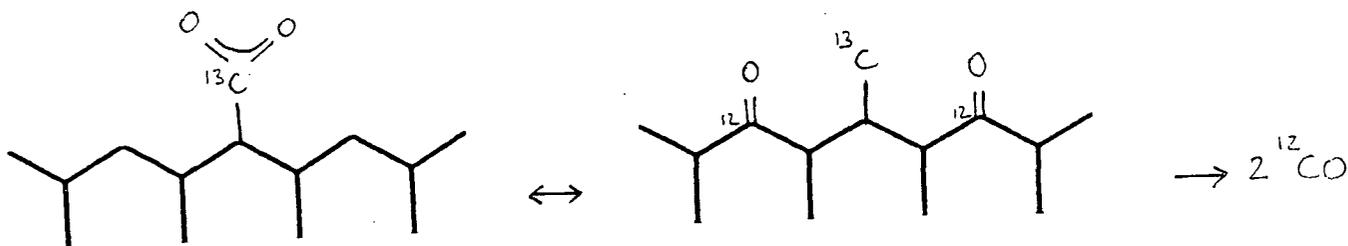


(a)



(b)

The same quinones are found when ¹³CO₂ is put on the surface and desorbs as ¹²CO following this possible scheme:

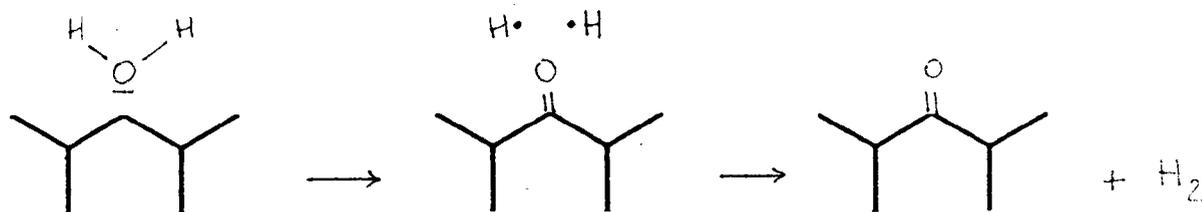


A small amount stays as a carboxyl compound and can desorb at 200°C as ¹³CO₂, as seen in Figure 5.

Finally, the medium temperature CO and CO₂ desorption peaks between 500 and 700°C can be due to more complex species such as lactones or dianhydrides. A summary of the different oxygenated species on the graphite edges we propose is given in Figure 7. The list is obviously not exhaustive, since other species can exist as well on more or less well defined graphite edges and this would account for the broadness of the TDS peaks.

β) Reactivity of H₂O on the Graphite Surface

Figure 8 shows the desorption of H₂ and CO after H₂O absorption on pure graphite. (Once again, only a few percent of CO₂ are observed at low temperature and are not represented in the figure.) The CO peak is at 1000°C, characteristic of quinone formation. Much less H₂ is evolved at about the same temperature. A small percentage of hydrocarbons up to C₆ are produced too as shown in Figure 9 where different masses characteristic of alkanes and/or alkenes are recorded after the same H₂O dose on the surface. The overall amount of hydrogen desorbing during the flash even taking into account the hydrocarbons, is, however, always less than the amount of CO coming off, which indicates that hydrogen is released readily during the adsorption, following this possible scheme:



Further experiments are in progress to ascertain the different mechanisms and species we propose. In particular, XPS studies will be undertaken in order to bring additional proof of the existence of the carbonyls, carboxyls, quinones and the other possible oxygenated species that we now know how to "prepare" on the surface.

We will also try to do the same kind of TDS measurements on a catalyst loaded sample in order to understand better the catalytic behavior of the hydrogasification.

TDS ON CLEAN GRAPHITE AFTER EXPOSURE TO 50
TORRS OF ^{13}CO FOR 30 S AT DIFFERENT TEMPERATURES

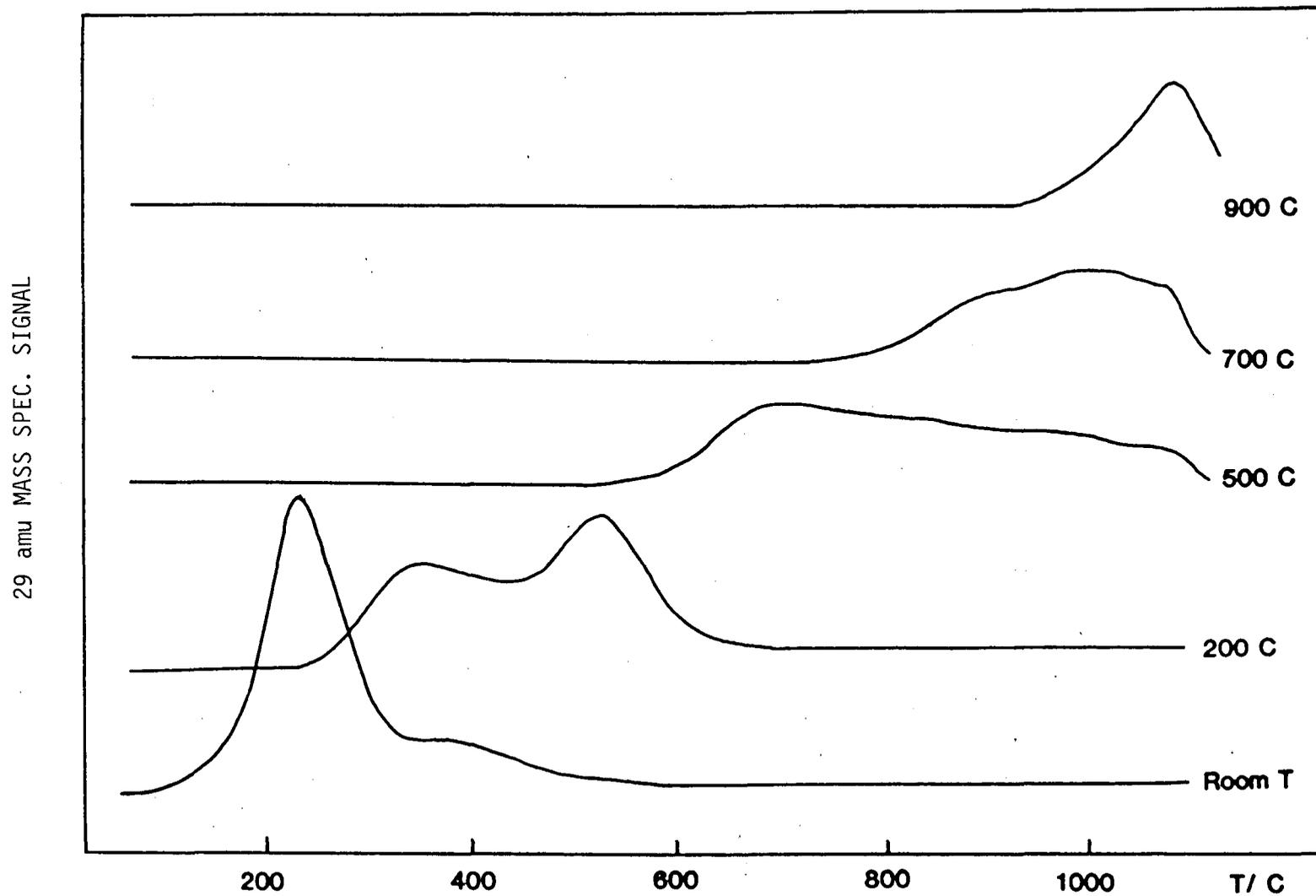


Figure 4

TDS ON CLEAN GRAPHITE AFTER EXPOSURE
TO 50 TORRS OF O₂ FOR 30S

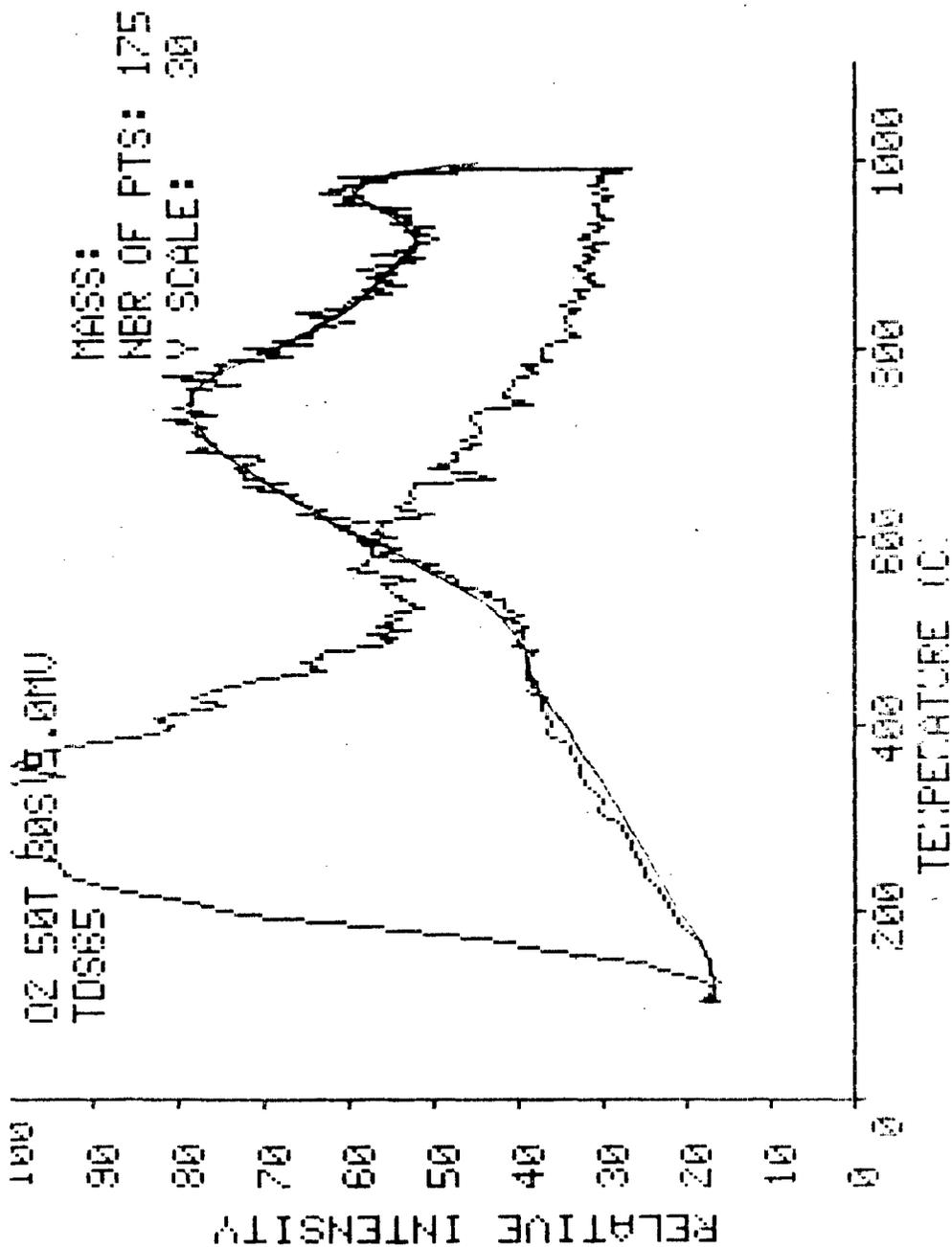


Figure 5

TDS ON CLEAN GRAPHITE AFTER EXPOSURE TO 8 TORRS OF $^{13}\text{C}\text{O}_2$ FOR 60 S

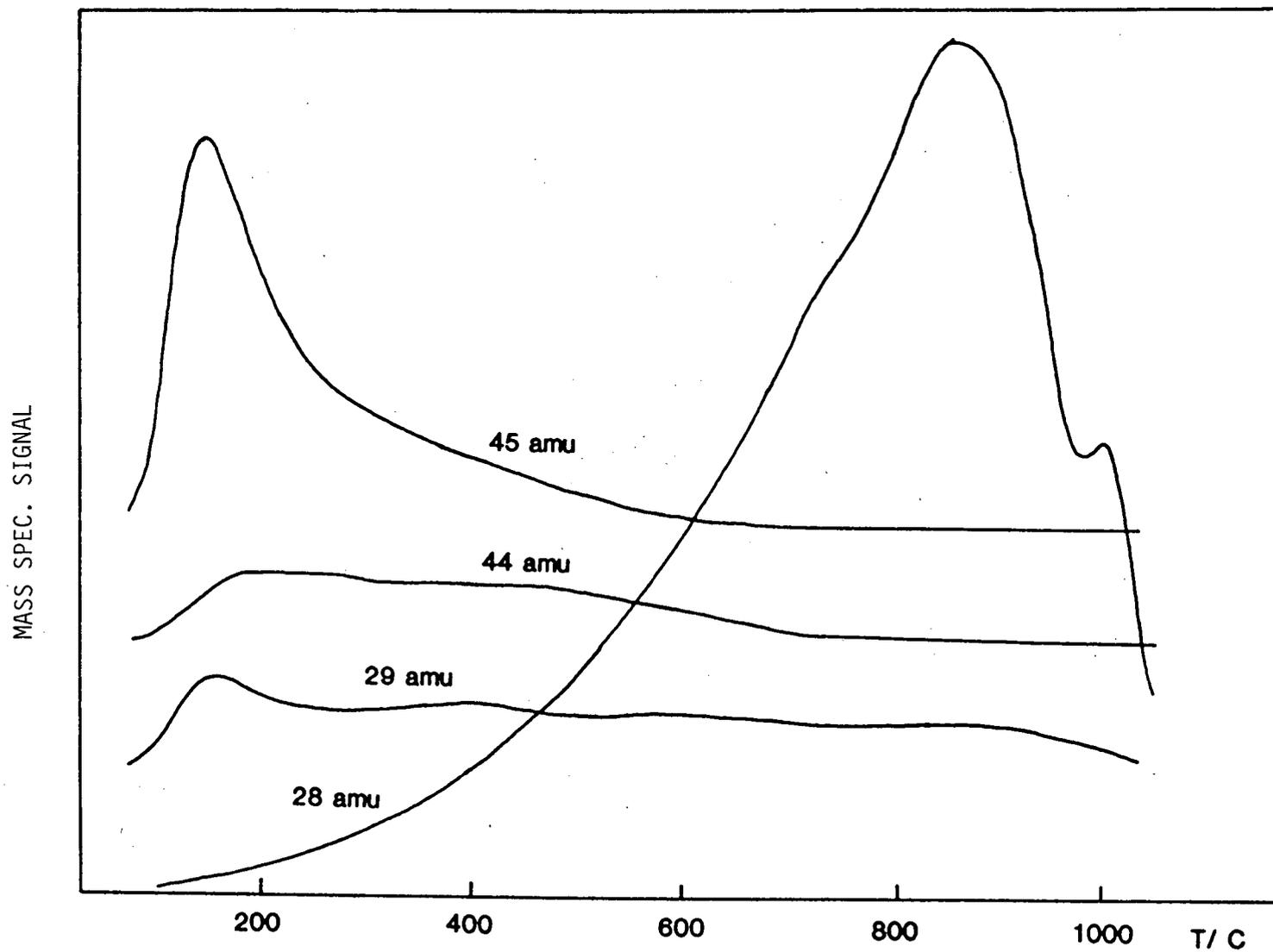


Figure 6

OXYGENATED SPECIES ON GRAPHITE EDGES

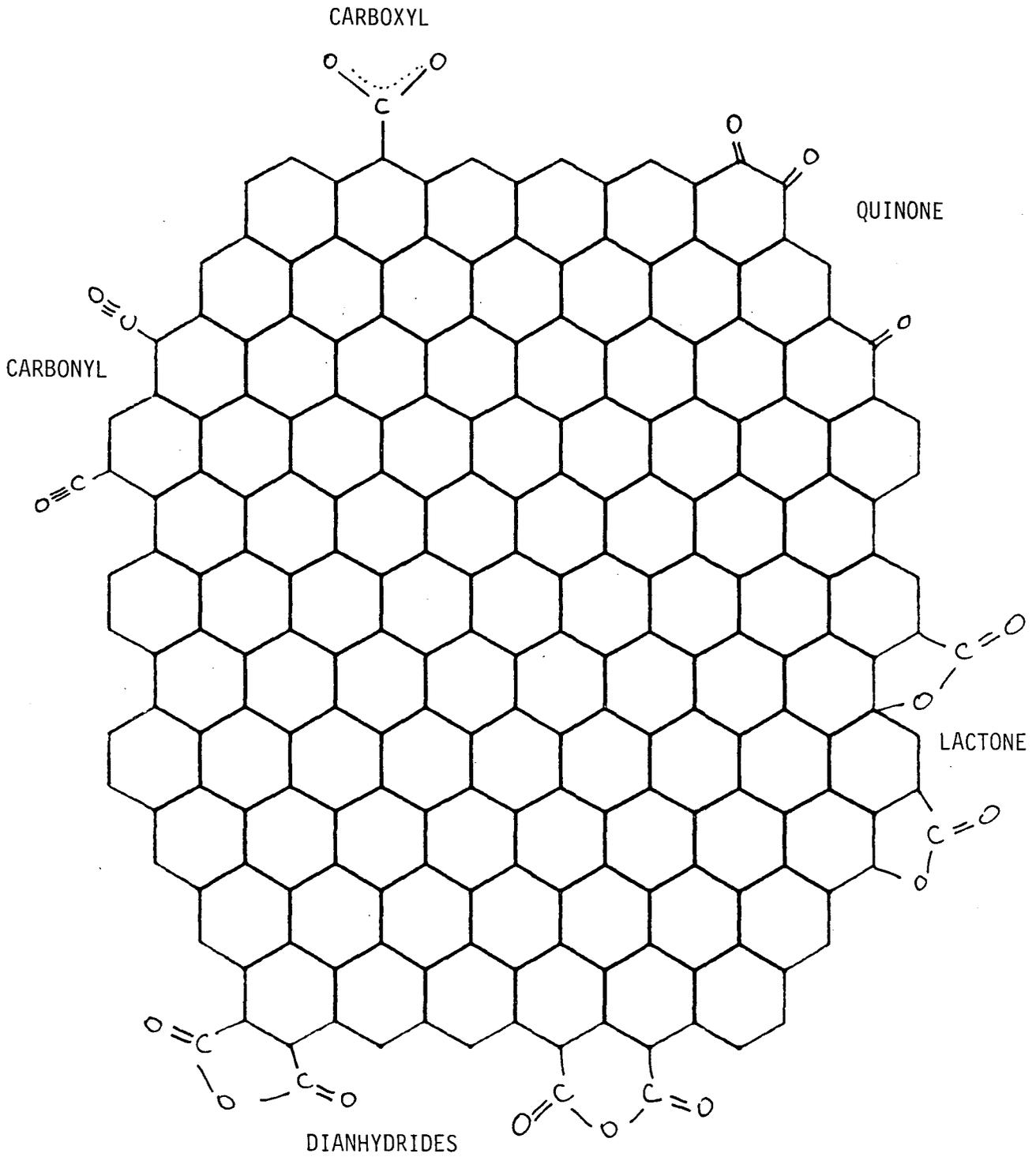
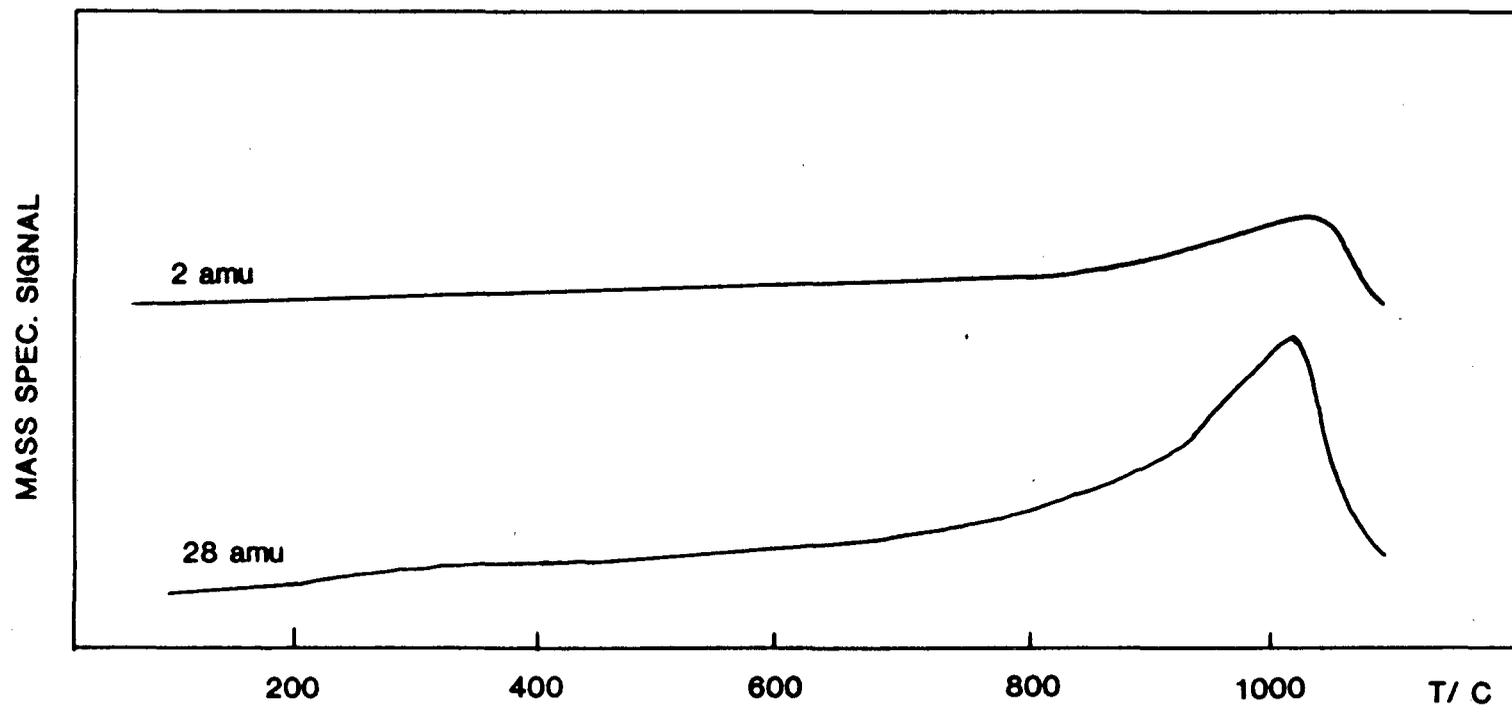


Figure 7



TDS ON CLEAN GRAPHITE AFTER EXPOSURE OF 20 TORRS OF H2O AT ROOM TEMPERATURE

Figure 8

TDS ON CLEAN GRAPHITE AFTER EXPOSURE OF 20 TORRS H₂O AT ROOM TEMPERATURE

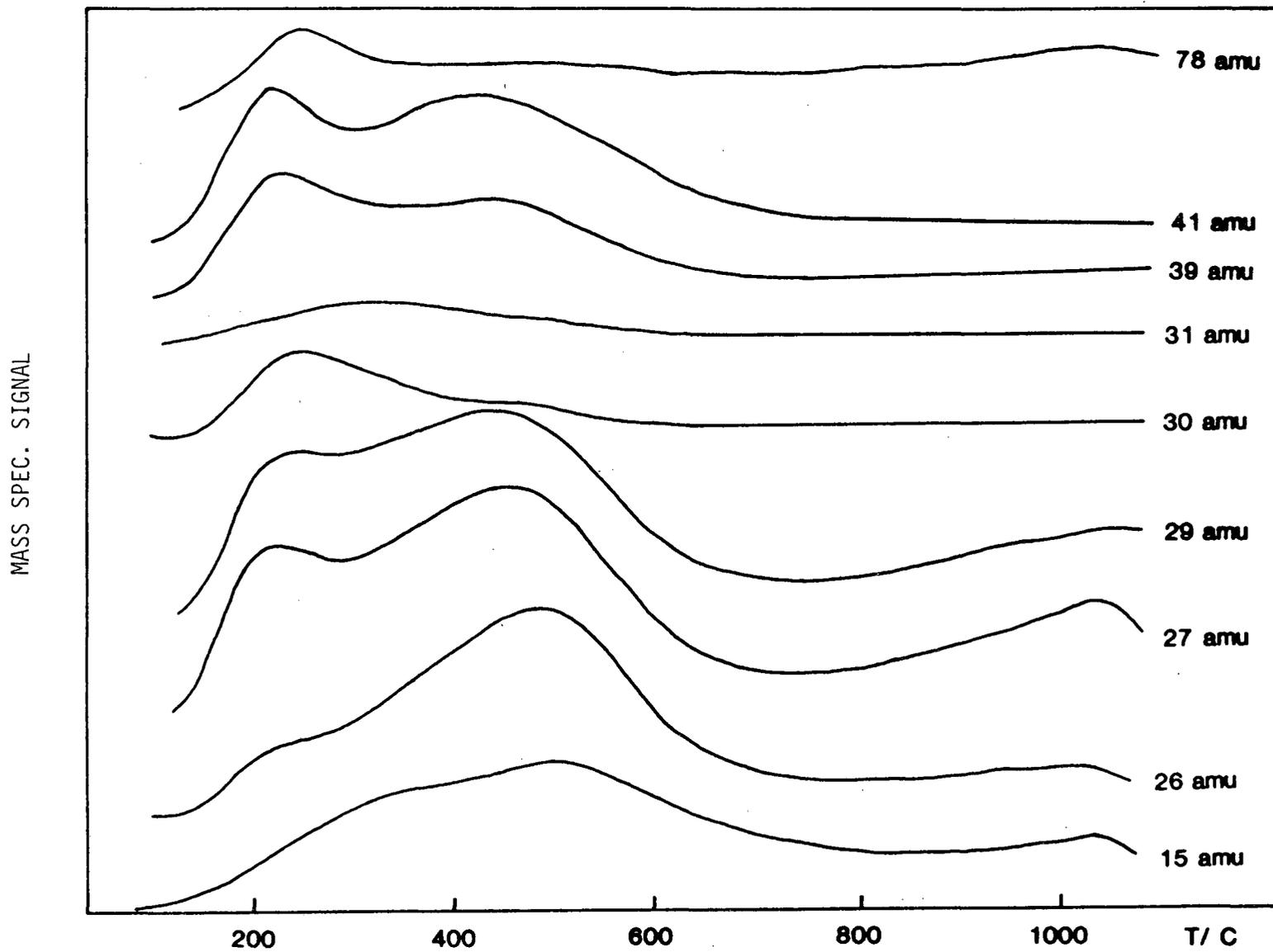


Figure 9

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