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CATALYTIC GASIFICATION OF GRAPHITE OR CARBON
Quarterly Report, April 1 - June 30, 1985

H. Heinemann

June 1985

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Quarterly Report

April 1 - June 30, 1985

CATALYTIC GASIFICATION OF GRAPHITE OR CARBON

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TABLE OF CONTENTS

I.	Task Description for FY 1985	1
II.	Highlights	2
III.	Progress of Studies	3

I. TASK DESCRIPTION FOR FY 1985

This program is designed to look at the basic chemistry of the reaction of carbonaceous materials with water in the presence of catalysts to produce hydrocarbons and/or synthesis gas. Much of the work is being carried out with graphite as a carbon source to insure that hydrogen in hydrocarbons is derived from water. Relatively low temperatures are being used to favor the equilibrium $C+2H_2O \rightarrow CH_4+CO_2$, which is almost thermally neutral. Our earlier work has shown that, in the presence of KOH as catalyst, higher hydrocarbons up to C_6 can be formed. This raises the question whether hydrocarbons are a primary product and syngas a secondary one formed by steam reforming. The formation of hydrocarbons is a stoichiometric reaction in which each H_2 in water reacts to form a phenolate and a hydrocarbon: $5C+4KOH \rightarrow 4COK+CH_4$. We have shown the presence of phenolate by surface spectroscopy and have found that it can be decomposed over metal oxides to make the reaction truly catalytic: $4COK \xrightarrow{MeOx} 2K_2O+2C+2CO$; $2K_2O+2H_2O \rightarrow 4KOH$. Future work is directed toward combining flow reactor studies with ultrahigh vacuum surface studies to follow the mechanism, to find the best catalysts for phenolate decomposition, to measure and improve kinetics, and to study the effect of added gases, such as CO or COS.

II. Highlights

1. A pressure flow reactor has been built and tested. This unit will be used to study the effect of water partial pressure on the kinetics of catalysed steam gasification.
2. Studies with isotopic labeled CO and CO₂ (using both ¹³C and ¹⁸O) on graphite have shown that the CO disproportionation ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$) readily proceeds at 800-850K. The formation of reactive carbon species from this reaction may explain the previously reported increase in the gasification rate when CO is added to the feed. An intermediate oxygen containing species on the graphite permits ready oxygen exchange.
3. It has previously been reported that nickel is a good gasification catalyst, but that it is rapidly poisoned even in graphite gasification. Nickel oxide alone is not a catalyst for gasification but mixtures of NiO and KOH are and are greatly superior to KOH alone. The possibility is being considered and investigated that catalytically active compounds of nickel and potassium may be formed before or during the reaction, compounds which are not subject to the poisoning occurring with metallic nickel. If such compounds are identified, it may be possible to produce a family of new and improved catalysts.

III. Progress of Studies

a) Pressure flow reactor

Work in the published literature indicates that the gasification rate of carbonaceous material in the presence of alkali carbonate rapidly increases with steam pressure (P. A. Lefrancois et al., *Advances in Chemistry* 69, 65, 1967). All work on graphite and char gasification in the present program has been carried out at atmospheric pressure. Rates of gasification at this condition and at the relatively low temperatures used in the present work are comparatively low and are shown in Figure 1. It is, therefore, important to determine whether more practical rates can be obtained at higher pressure.

During the present quarter, a new flow reactor system has been designed and constructed. Figure 2 shows a schematic of the new system. The improvements over the previous model are the following:

- a) Capability for higher steam pressure reactions (~75 psig).
- b) More reproducible and controllable flow of steam.
- c) More homogeneous mixing of inlet gases with steam.
- d) More reproducible gas analysis system.

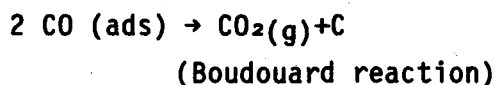
- e) Analysis of steam content in the inlet and outlet stream, which allow us to determine directly the fraction of gas consumed in the reaction.

The detailed functioning of the reactor is as follows: the steam flow is produced by pumping a controllable flow of water through a heating element (point A in Figure 2); the steam is mixed with all the other inlet gases used in a small drum (point B); at this point, all the gases achieve the same temperature; any condensed water is drained from valve C and the gas flow is measured with a rotameter (point D); a sample valve (valve E), with a sampling loop of 0.5 ml is used to determine the inlet gas composition; the gases are then introduced into the reactor and passed through the sample; outlet samples are obtained with a sampling valve (point F) in order to determine the gas composition; the pressure inside the reactor is controlled by valve G; the outlet gases are cooled to room temperature by a condensor (point H); the condensed water is separated from the gas products with a flash drum (point I) and both the rate of water flow through the sample and gas production can be measured at point J. The gas composition is determined by gas chromatography, using He as a carrier gas and a thermal conductivity detector. A Carbosive SII, 3-foot column is used to separate the gases.

The flow reactor has been built. The optimum gas chromatography conditions in order to analyze the gases have been recently obtained. Some experiments previously done with the old system will be repeated in order to check if the results are consistent. The system is now in full operation.

b) UHV/High pressure cell experiments

In the December 1984 quarterly report we discussed the results obtained when ^{13}CO and $^{13}\text{CO}_2$ were adsorbed over clean graphite. In summary, we found that in a temperature programmed desorption experiment (TPD) after adsorption of either $^{13}\text{CO}_2$ or ^{13}CO over ^{12}C (graphite), a peak of mass 45 ($^{13}\text{CO}_2$) at 723K and two peaks of mass 28 (^{12}CO) at around 1000 and 1200K were obtained. Since both gases presented the same TPD features, it was concluded that they should both form the same intermediate on the surface. Also, since the only peak that contains ^{13}C is of mass 45, we concluded that CO disproportionates on the graphite surface according to the reaction



It is important to determine the relative amounts of the different gases desorbed on a TPD experiment. For this purpose, a computer program has been adapted to our system, in order to control the mass spectrometer and monitor more than one mass at the same time during a TPD experiment. The program is currently working, but some modifications are still necessary.

Some preliminary TPD results after adsorption of ^{13}CO and $^{13}\text{CO}_2$ over graphite are shown on Figures 3 and 4. As we mentioned before, the TPD results after adsorption of either gas show the same basic features. However, the intensity ratio of the mass 45 peak over the mass 28 peak is different when $^{13}\text{CO}_2$ is adsorbed; a larger amount of ^{12}CO is observed, relative to the case of ^{13}CO adsorption. It is also interesting to

notice that in both cases, besides a low temperature peak due to physisorption, no ^{13}CO is being desorbed from the surface. In both cases, a small mass 44 peak is obtained. This peak can come from the desorption of the small amount of ^{12}C present in the gases. (Both gases and were 90% ^{13}C enriched.)

TPD results after adsorption of $^{12}\text{C}^{18}\text{O}_2$ over graphite are shown in Figure 5. A peak of mass 48 ($^{12}\text{C}^{18}\text{O}_2$) at 739 K is obtained, in agreement with the results discussed earlier. Of the two CO high temperature peaks observed previously, only the peak at 1000K contained ^{18}O . This implies that the 1200K peak is due to some impurity in either the gases or the cell used for the experiments. Also notice that there is a peak of mass 46 ($^{12}\text{C}^{16}\text{O}^{18}\text{O}$) at 739K of the same peak intensity at mass 48. This suggests that CO_2 is dissociated on the surface and that an exchange of oxygen atoms between $^{12}\text{C}^{18}\text{O}_2$ and the oxygen containing impurity is relatively easy.

In order to determine what is the impurity present in the previous experiments, the adsorption of H_2O and O_2 over graphite have been studied. The results are shown in Figures 6 and 7. Both gases show the mass 44 peak at 739K and a high temperature peak of mass 28. However, in the case of H_2O no hydrogen containing molecules besides H_2O were desorbed from the surface. This suggests that in the case of water, the TPD peaks seen in Figure 7 are also due to some contamination in the loop. Also notice that under the same conditions, the amount of O_2 that can be adsorbed on the surface and desorbed as CO is much larger than in the case of CO and CO_2 adsorption. Saturation of the detector at mass 28

is obtained in a TPD experiment, when O_2 is adsorbed on the graphite surface. This suggests that small amounts of O_2 present in the reaction cell from air leaks or high background pressures could be the cause of the impurity problems seen in our TPD results. Improvements to correct these two problems are being carried out.

Even though the results shown in this report are preliminary, several conclusions can be suggested and should be further confirmed. First, these isotope experiments clearly show that there is a high temperature CO peak, coming from gasification of the graphite. Also, it is shown that the adsorption of either CO, CO_2 or O_2 on graphite produces a species on the surface that is able to exchange oxygen relatively fast. Further experiments will be done to determine the nature of this species. Also the effect of depositing KOH and Ni, two common catalysts for the gasification of graphite with steam or CO_2 , on the adsorption of CO, CO_2 , O_2 and H_2O on graphite will be studied.

Figure Captions

Figure 1: Turnover number as a function of time for isothermal reaction at 860K.

Figure 2.a: Schematic of the new flow reactor apparatus.

Figure 2.b: The flow reactor.

Figure 3: Temperature Program Desorption after adsorption of 50 torr of ^{13}CO for 5 minutes.

Figure 4: Temperature Program Desorption after adsorption of 50 torr of $^{13}\text{CO}_2$ for 5 minutes.

Figure 5: Temperature Program Desorption after adsorption of 50 torr of C^{18}O_2 for 5 minutes.

Figure 6: Temperature Program Desorption after adsorption of 50 torr of O_2 for 5 minutes.

Figure 7: Temperature Program Desorption after adsorption of 500 mtorr of H_2O for 5 minutes.

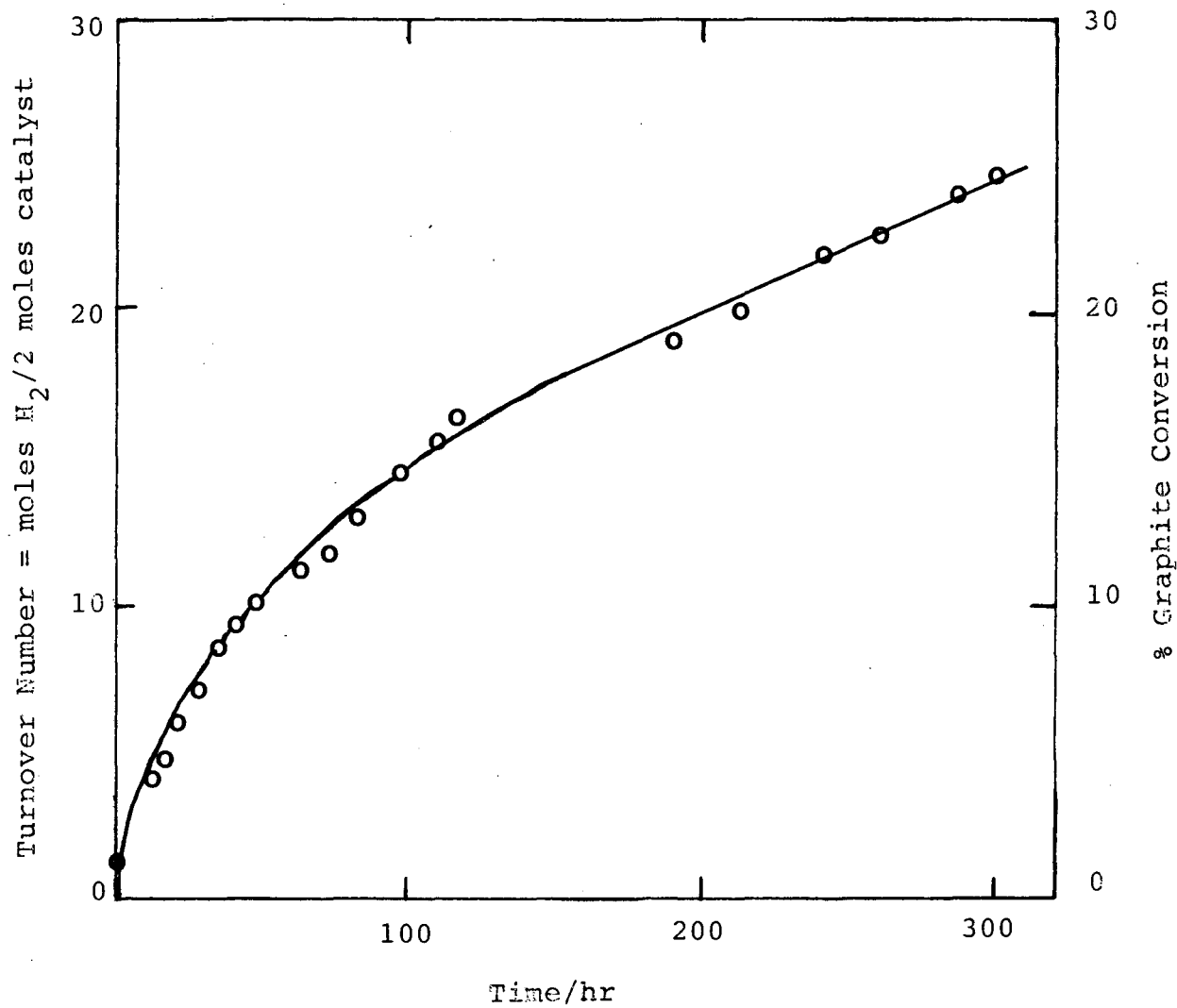


Figure 1

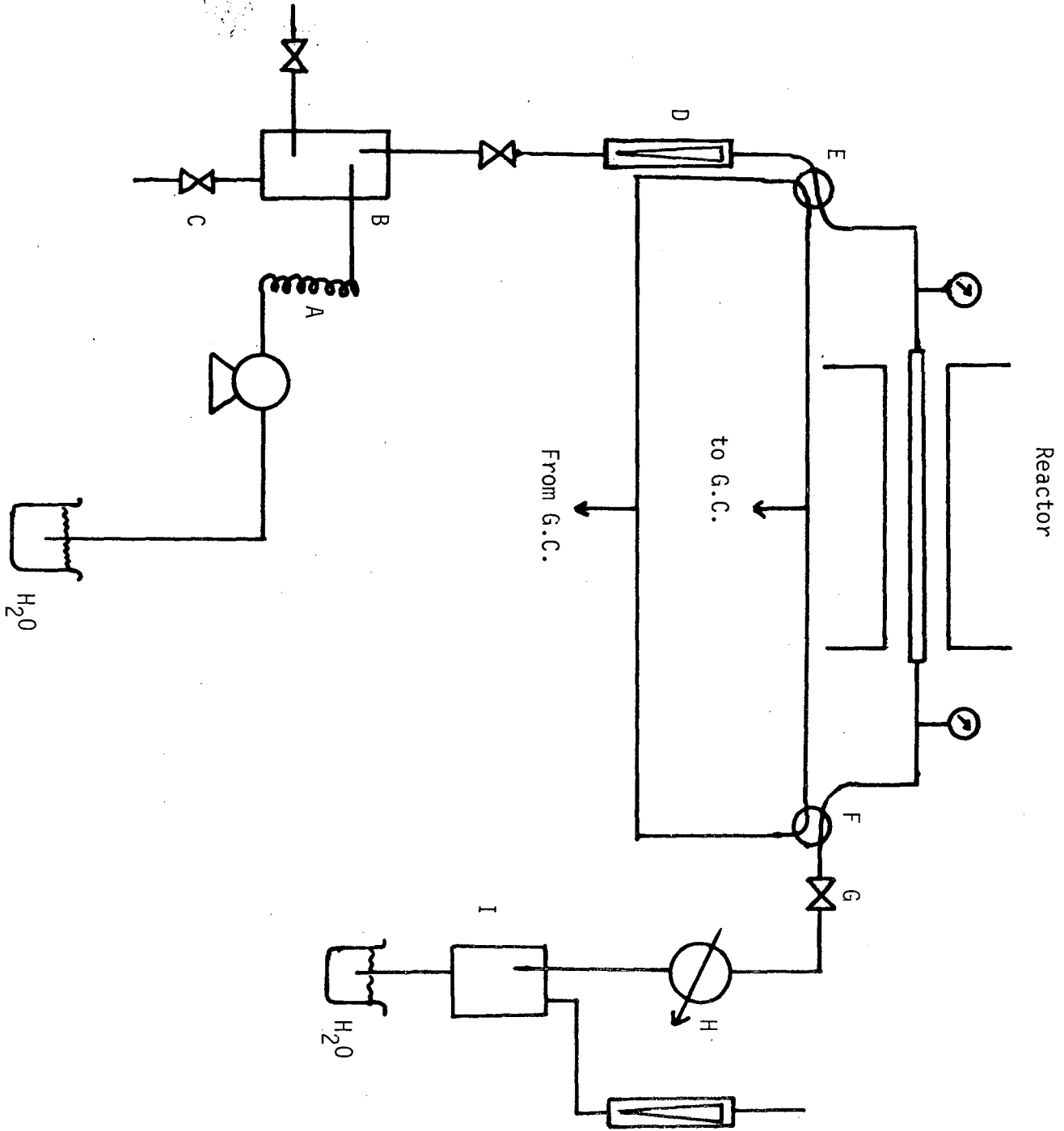
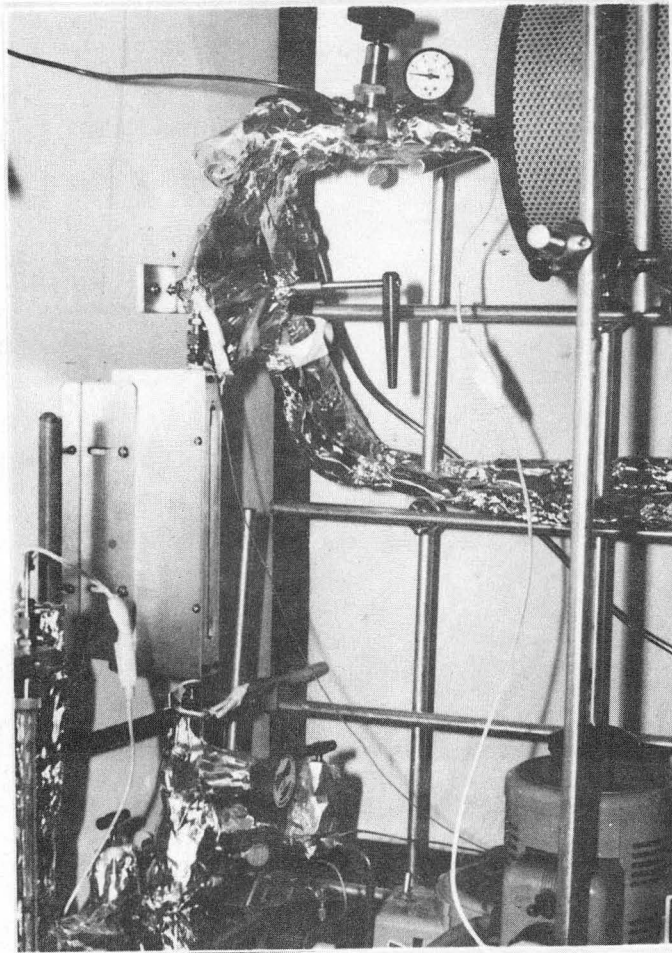
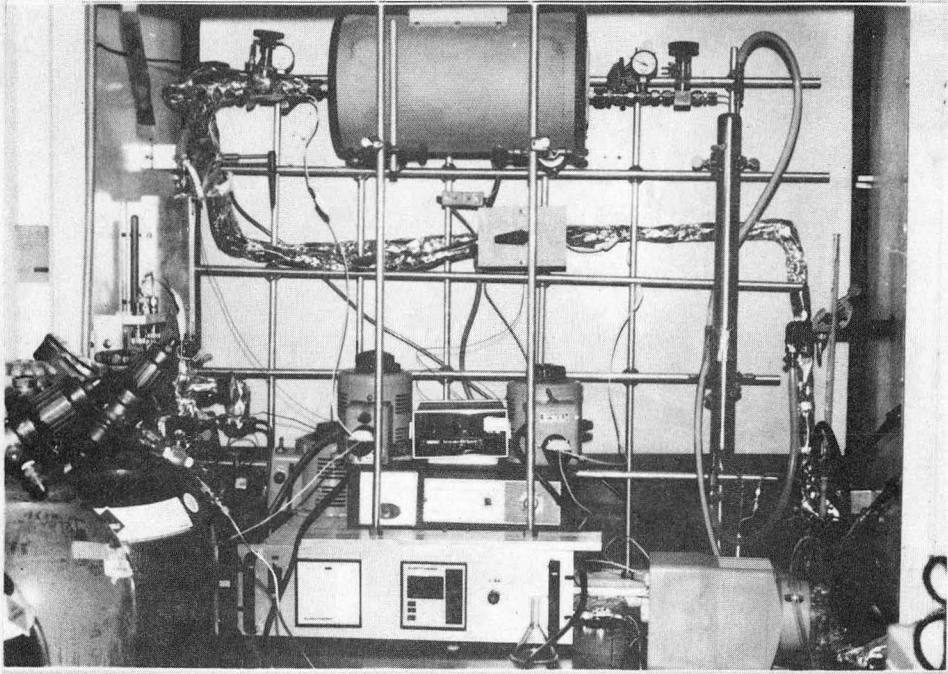
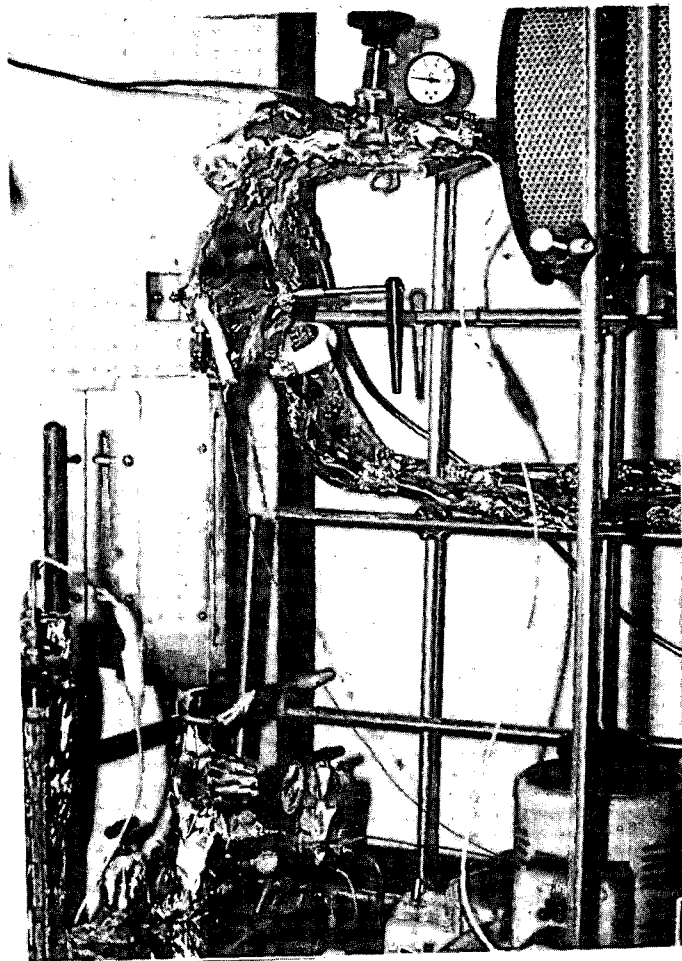
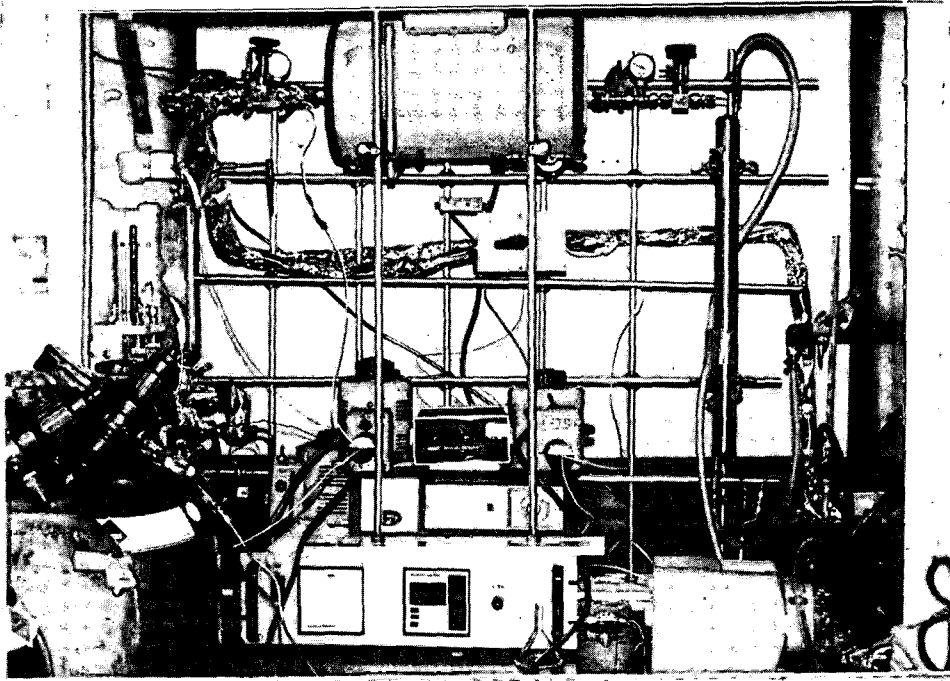


Figure 2a



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Figure 2b



CBB 857-5391

Figure 2b

Figure 3

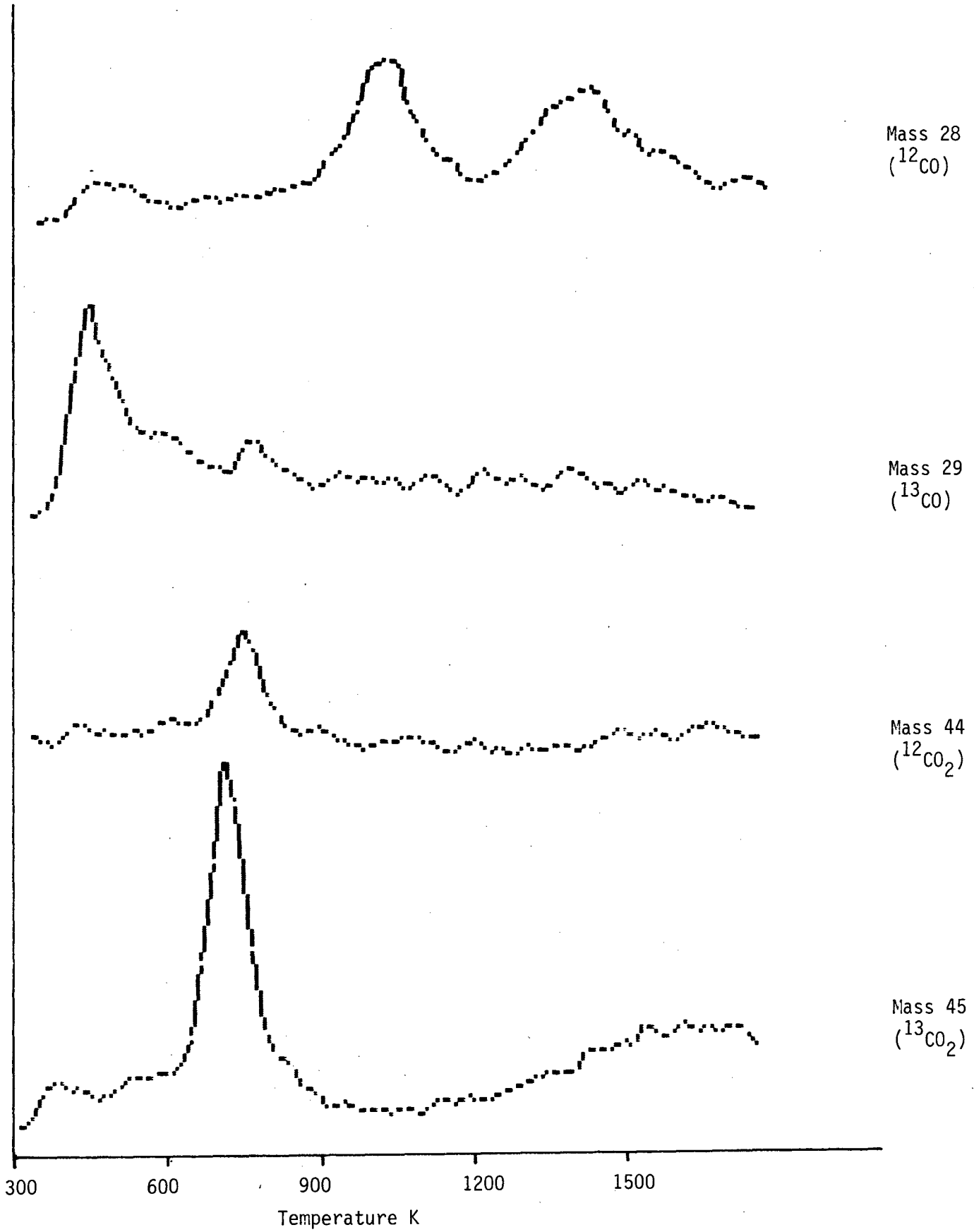
Adsorption of 50 torr ^{13}C
for 5 minutes

Figure 4

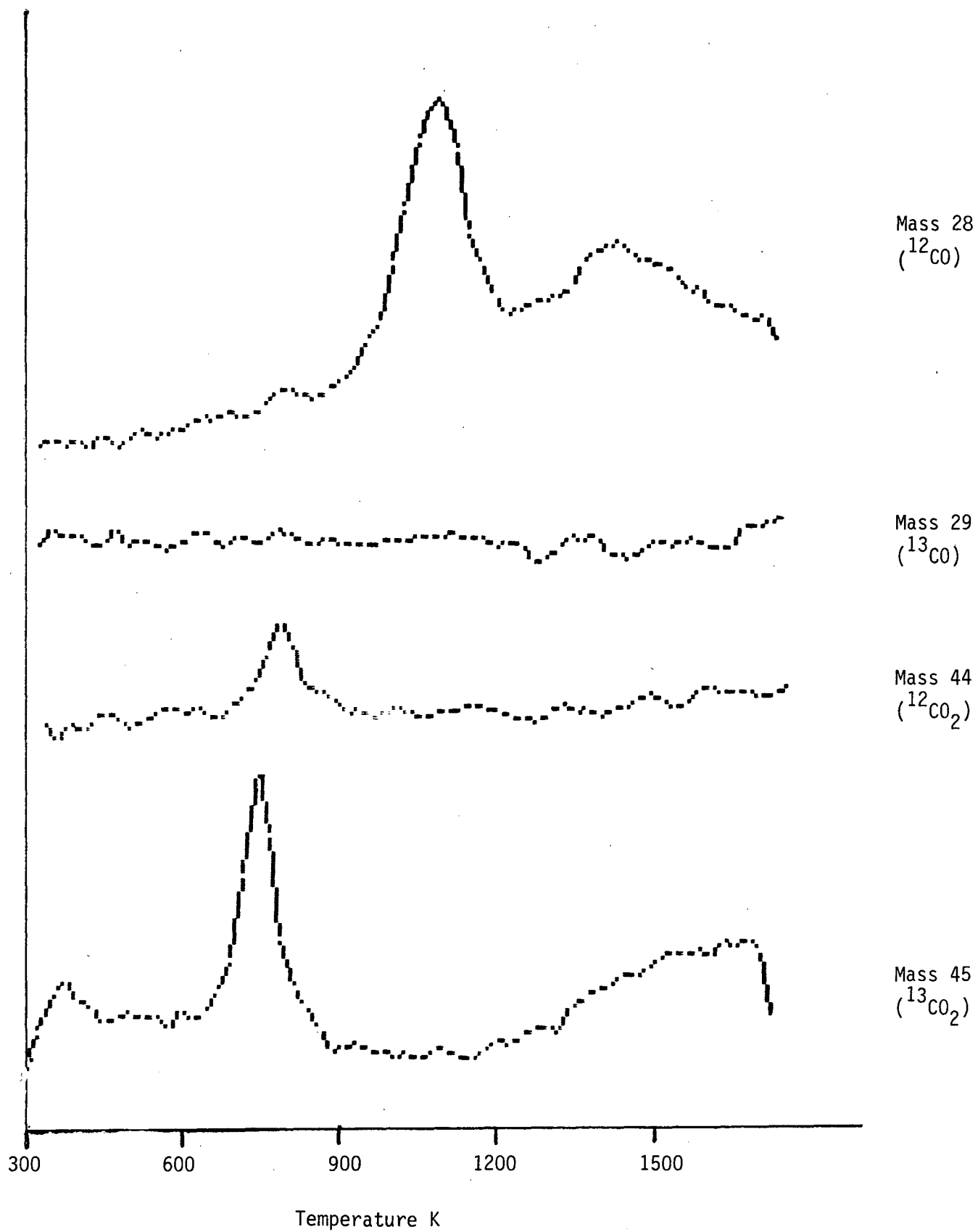
Adsorption of 50 torr $^{13}\text{CO}_2$
for 5 minutes.

Figure 5

Adsorption of 50 torr $^{12}\text{C}^{18}\text{O}_2$
for 5 minutes.

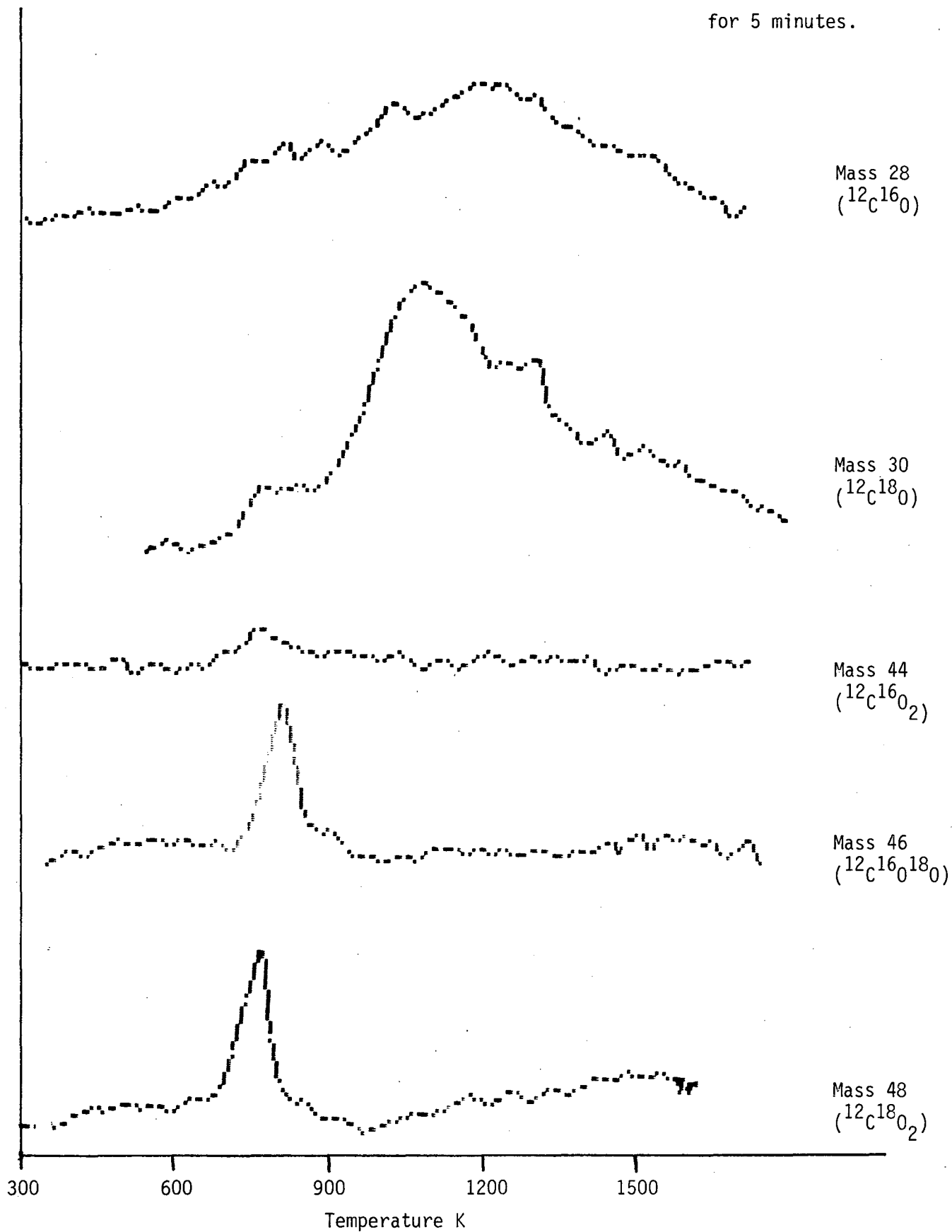


Figure 6

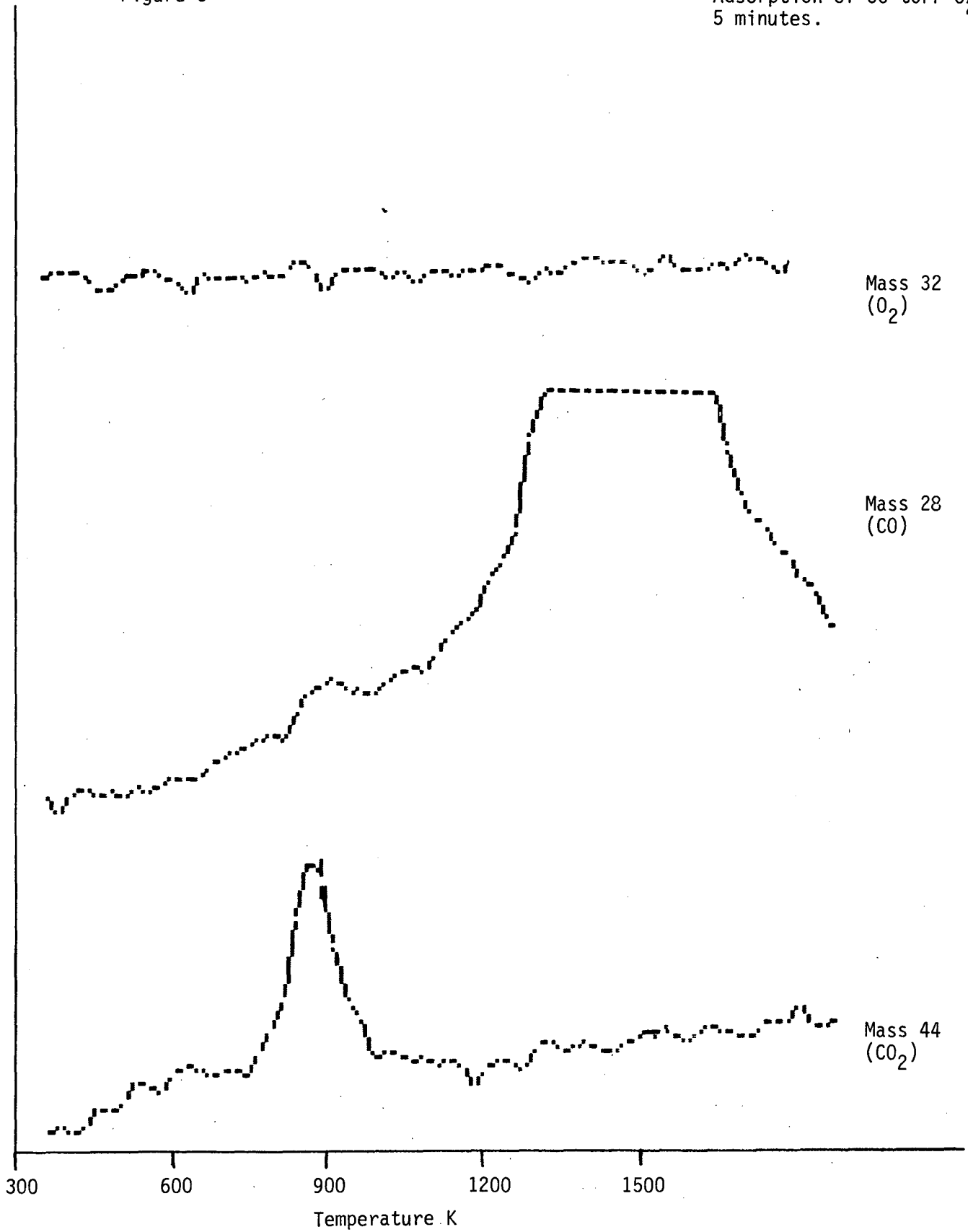
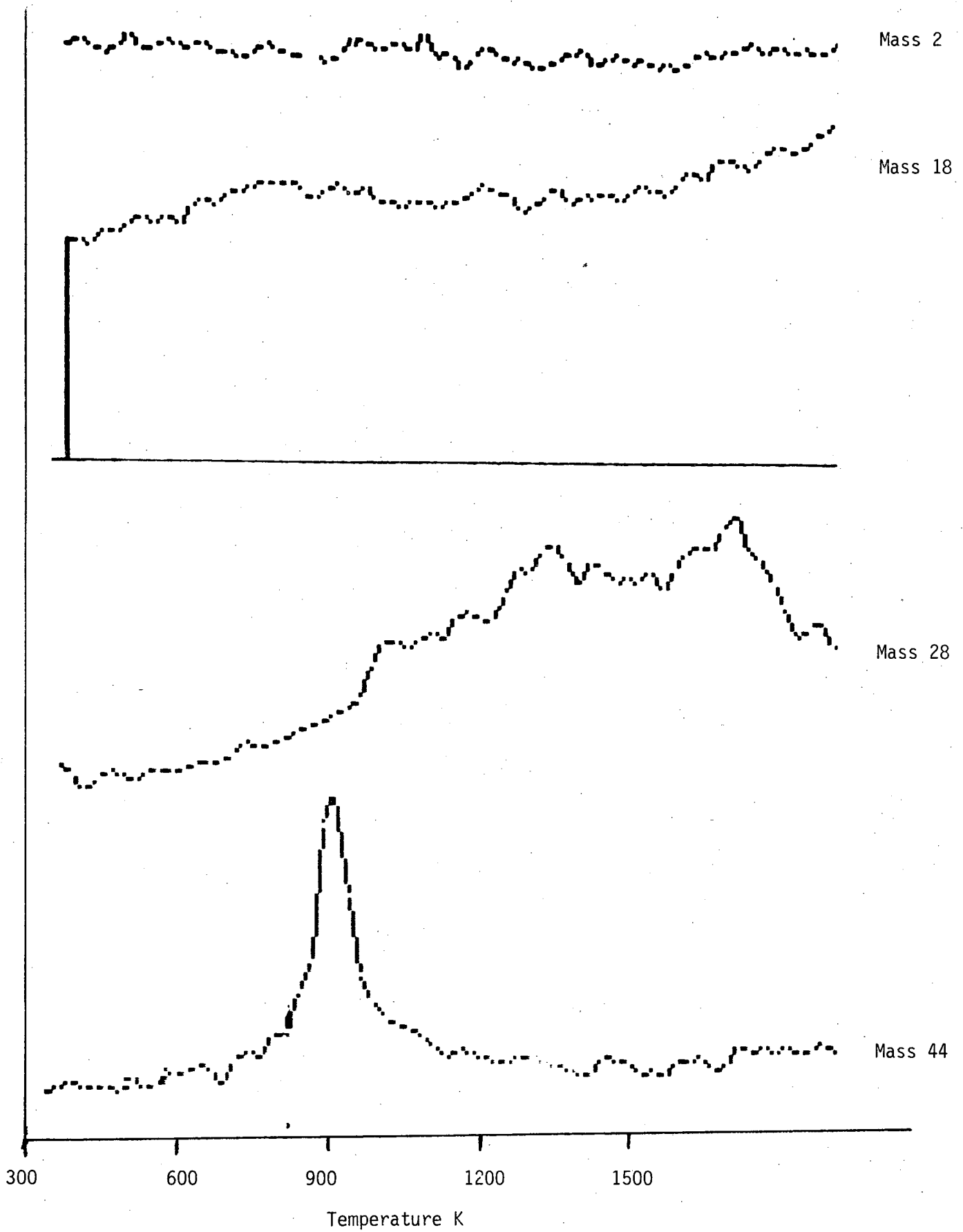
Adsorption of 50 torr O_2 for
5 minutes.

Figure 7

Adsorption of 500 mtorr of
 H_2O for 5 minutes.

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