

REACTIONS OF CARBON
WITH
ELECTRONICALLY EXCITED GASES

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ABSTRACT

A study has been made of the radiation-induced reaction between CO_2 and carbon at low pressures using low voltage electrons emitted from an oxide coated cathode. Experiments with a flow of CO_2 have shown that the primary radiolysis product responsible for the attack on the carbon is not electrically charged and the evidence presented suggests it is atomic oxygen. The experiments have shown that with carbon present the electron emission current from the oxide coated cathode is being maintained, but that in the absence of carbon the current decays rapidly to quite low values. This has been shown to be due to the competition between the carbon and the cathode for the oxidising species produced in the CO_2 by the accelerated electrons. Use of this effect is made in interpreting results at electron energies at which changes in the gas phase and/or the carbon surface cannot be detected in the present system. The effect of mercury atoms on the behaviour of the CO_2 -carbon reaction has also been investigated.

Studies of the radiation-induced CO_2 -carbon reaction under static conditions has shown that the system rapidly attains some form of steady state condition. Evidence for a reverse reaction involving CO is provided by the deposition of a carbon-like solid observed in these experiments and in similar experiments with CO and CO_2/CO mixtures. A mass balance between products and reactants was never obtained, due to a competition between clean-up and degassing of electrodes, etc.

In spite of the peculiarities of the static systems it has been found that the initial rates of reaction in the static experiments can be compared with the reaction rates in the corresponding flow experiments.

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INTRODUCTION

The first stage of the development of nuclear power in the United Kingdom has been based on the use of graphite as the neutron moderator and carbon dioxide as the coolant gas. In the designs of the Calder Hall reactor and of the first reactors for the Central Electricity Authority these two components are in contact within the reactor core. Studies have therefore been made of the behaviour of these materials under reactor conditions.

The problem set by the compatibility considerations of the CO₂-carbon system in-pile can be divided into two parts. The first part concerns the purely thermal reaction of graphite with carbon dioxide while the second part deals with the influence of the high energy reactor radiation.

It has been shown that the thermal reactions below 600°C are concerned solely with the chemisorbed oxygen on the graphite surface, changes in which are considered unlikely to have any direct technological significance in reactors of the present type. At higher temperatures the gasification reaction will lead to loss of carbon; however methods of protection

against this have been described which may be of value despite the observed ineffectiveness of these methods against radiation induced processes.

The initial work on the influence of reactor radiation quickly showed that a reaction between graphite and carbon dioxide was occurring at temperatures at which the thermal reaction would be negligible. Data from experiments in the Harwell reactor B.E.P.O. showed that this reaction could be interpreted in terms of the radiation decomposition of the CO_2 in the gas phase producing active species which are carried downstream where they could react with the graphite surface to produce CO. In view of the known radiation stability of pure CO_2 it was concluded that the graphite acts as an inhibitor of recombination processes and also as a vehicle for attack by the chemically active species produced by the radiolysis.

It was estimated from the results of the experiments in-pile that for the present Calder Hall reactors the mean rate of loss of carbon from the moderator would be about 0.5 tons per year and that the steady state CO concentration would depend on the gas leak rates but might be expected to lie between 0.5% and 1.5%. Such

results showed that the radiation-induced processes were unlikely to present any operational problems in the present design of reactors of the Calder Hall class or in the reactors being built for the first stages of the United Kingdom civil power programme.

However in future reactor designs economic considerations may decide in favour of higher power ratings (increased radiation intensity) and smaller systems (lower leakage rate and probably a higher ratio of gas to graphite in the core). Both these factors would enhance the importance of the radiation induced processes and due to the almost certain increase in operating temperature would place greater emphasis on the purely thermal reaction between graphite and carbon dioxide.

The results of experiments performed in-pile were of the greatest practical value but added little to the basic knowledge of the reactions. The main trouble was in obtaining good control of all the variables affecting this type of experiment. The results suggested that the behaviour in the pores and at the superficial surface of the graphite was different. Weight changes occurred other than those to be expected in

a purely thermal system and no reliable correlation between CO production and weight loss has so far been obtained. Spectroscopic studies of a high frequency discharge in CO₂ confirmed the presence of most of the species to be expected from the radiolysis but were unable to identify the ones responsible for the carbon removal.

The present work has served to develop apparatus in which gases at low pressure can be bombarded by electrons emitted from an oxide coated cathode in a controlled voltage field. The work has involved the development of gas analytical methods suited to the experiments with minor modifications to the apparatus so as to enable mercury vapour to be removed when necessary and to minimise the amount of reactive metal present in the reaction vessel.

These basic studies are intended to throw light on the processes occurring at much higher gas pressures with high energy radiation in CO₂-cooled and graphite moderated reactors. Of the several assumptions involved in relating the phenomena the most notable is that the principal effect of reducing the gas pressure is to

increase the life-time of the active species and reduce the effect of secondary processes occurring in the gas phase. The principal advantage of this type of experiment lies in the greater facility with which the many variables involved can be controlled independently. The effect of variations in applied voltage, the presence of electrical clearing fields which would eliminate or encourage reactions of charged species and the behaviour in CO_2/CO mixtures has been investigated with the intention of providing information on the nature of the active species responsible for the observed phenomena. The effect of CO_2 on the emission current from the oxide coated cathode has also been investigated in the presence and absence of carbon. Results have been obtained which are of use in interpreting effects observed in the radiation-induced CO_2 -carbon reaction.

LITERATURE SURVEY

(A) Radiochemical reactions in pure CO₂

1. Ionization Processes: In CO₂ these processes have been studied by Smyth and Stueckelberg¹, Kallmann and Rosen² and reviewed up until 1930 by Smyth³, more recent studies have been made by Kambara⁴. Their results are essentially in agreement and are summarised in Table I below.

TABLE I						
Observed Product	Appearance K&R	Potential (ev) S&S	Kambara	Suggested Process	Calculated Minimum Energy	Relative Abundance
CO ₂ ⁺	14	14.4	13.9±0.1	CO ₂ →CO ₂ ⁺		100
O ⁺	17	19.6±0.4	20.3±0.2	CO ₂ →CO+O ⁺	19.0	7
CO ⁺	18	20.4±0.7	20.5±0.2	CO ₂ →CO ⁺ +O	19.7	20
C ⁺	29	28.3±1.5	26.6±0.2	CO ₂ →C ⁺ +O+O	26.7	3
O ₂ ⁺		20.0±1.0		CO ₂ →(CO ₂ ⁺ +CO ₂) →2CO+O ₂ ⁺	18.7	

The values given in the last column were calculated by Smyth directly from heats of dissociation and ionization potentials.

Smyth and Stueckelberg using a modification of Dempsters mass spectrograph and with electron accelerating potentials of the order of 40 volts found that the

O_2^+ ion was only observed at higher CO_2 pressures of about 20μ and considered it to be a secondary ion resulting from the formation of an excited CO_2^+ ion, support for this view comes from the existence of strong CO_2 spectral bands in the corresponding wavelength region. The majority of their observations were made at CO_2 pressures in the ionization tube of the order of 0.8μ where the primary ions CO_2^+ , CO^+ , O^+ and C^+ were found, the relative numbers of these ions at these low pressures and moderately high voltages were of the order of 100, 20, 7 and 3 respectively, however these relative numbers were found to alter with change of CO_2 pressure in the ionization tube. Similar figures have more recently been obtained by Hayakawa and Sugaira⁵. It was observed by Smyth and Stueckelberg that the intensity of the CO^+ ion decreased with increase in CO_2 pressure for CO_2 pressures in excess of 5μ . This was interpreted as the result of a collision of the second kind of the type $\text{CO}^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{CO}$, a process not unlikely in view of the nearness of the ionization potentials of CO and CO_2 . Exchange reactions of this type had been observed earlier by Harnwell⁶ with rare gas mixtures.

The effect of pressure variations in the magnet space of the spectrograph on the relative ion intensities was made and shown to have little effect except with the C^+ ion. The spectrograph was designed so as to minimise thermal dissociation of the CO_2 by the filament, the effect was however, not completely eliminated. Absolute values for the appearance potentials of the different ions were determined by using Argon, whose ionization potential was known, as a standard.

Kambara using a 60° -type mass spectrograph obtained results similar to those of Smyth and Stueckelberg, namely that the O_2^+ ion was not observed at the lower CO_2 pressures in the ion source, furthermore it was found that at low CO_2 pressures the relative ratios among other ions was constant but that at higher pressures the ratio of CO^+ , O^+ and C^+ to CO_2^+ was increased.

The appearance potentials of the various ions can be compared with theoretical expectations. Carbon dioxide is a straight line molecule with the carbon atom in the middle. It was expected therefore that CO_2^+ , CO^+ and O^+ would be obtained at comparatively low potentials whereas to get the C^+ ion both the oxygen

atoms must be broken away and the remaining carbon atom ionised, a process obviously requiring more energy.

The first ionization potential of CO_2 has been determined both spectroscopically and from electron impact work. Electron impact data generally yield slightly higher values of ionization potentials due to the formation of ions in excited states whereas spectroscopic data refer to ions in the ground state. In Table II are listed some values obtained for the first ionization potential of CO_2 using either an electron impact method or a spectroscopic method, also included are two recent values obtained by a photo-ionization method.

TABLE II

Type of method	Ionization potential	Reference
Electron impact	14.4	1
"	13.9 ± 0.1	4
"	13.85	10
"	13.85	11
"	13.88 ± 0.03	12
Spectroscopic	13.79 ± 0.06	7
"	14.4	8
"	13.78 ± 0.01	9
Photo-ionization	14.0 ± 0.3	13
"	13.6 ± 0.2	14

The appearance of the CO_2^+ ion at potentials higher than in Table II has been reported by various workers. Mulliken¹⁵ showed that the ultra-violet emission bands of CO_2 probably represent transitions among 4 electron states of CO_2^+ which correspond to the 4 lowest ionization potentials of CO_2 which were probably 13.72, 17.09, 18.00 and 21.5 volts; similar results have been presented by Weissler et al.¹⁴

2. Excitation Processes: The ultra-violet absorption spectrum has been studied by Leifson¹⁶ and by Lyman¹⁷. Bonhoeffer and Harteck¹⁸ conclude from the data that the continuous absorption spectrum corresponds to a dissociation into carbon monoxide and a normal oxygen atom occurring at 5.5 ev.

It is not usually possible to determine dissociation heats of polyatomic molecules by spectroscopic methods. Combination of thermochemical data with spectroscopically determined values for the heat of dissociation of diatomic molecules, however, frequently enables the heat of formation of the polyatomic molecule to be determined.

Using such a technique Gaydon¹⁹ obtains for the energy required to dissociate CO_2 into CO and O the value 126.2 Kcal/mole or 5.5 ev, while for the complete dissociation into C+O+O, that is the heat of formation of CO_2 , the energy required is 382.3 Kcal/mole or 16.5 ev. However the doubt existing over the heat of dissociation of CO renders this method unreliable for CO_2 .

The above energies refer to the dissociation products in their ground state, i.e., unexcited CO, O, etc.. However, calculations based on the observations of Adel and Dennison²⁰, on the infra-red absorption spectrum of CO_2 , yielded a value of about 300 Kcal/mole for the heat of dissociation of CO_2 into an oxygen atom and a carbon monoxide molecule. The difference between this value and 126.2 Kcal given above corresponding presumably to the excitation energy of CO or O. It was considered that the energy difference was too large to correspond to excitation of the oxygen atom and was more likely to correspond to excitation of the carbon monoxide molecule. Criticisms of the assumptions made in these calculations have, however, been made by Laidler (see ref.22).

Further measurements of the absorption cross-section of CO_2 in the vacuum ultra-violet by Inn et alia²¹

enabled the upper limits of the energy necessary for the process $\text{CO}_2 \rightarrow \text{CO} + \text{O}$ to be determined. These energies are given in column 2 of Table III, the third column of this table contains values for the energy of dissociation of CO_2 into CO and O given by Weekes²² from spectral data. The normal or ground state of CO is indicated by the symbol ($^1 \underline{\Sigma}$), while for oxygen it is indicated by the symbol ($^3 \text{P}$), hence all other symbols refer to excited states of CO or O.

Table III

States	Observed Energy ²¹ (ev)	Observed Energy ²² (ev)
1) CO ($^1 \underline{\Sigma}$) + O($^3 \text{P}$)	6.8	5.4
2) CO ($^1 \underline{\Sigma}$) + O($^1 \text{D}$)	7.7	7.4
3) CO ($^1 \underline{\Sigma}$) + O($^1 \text{S}$)	10.3	9.7
4) CO ($^3 \text{II}$) + O($^3 \text{P}$)	-	11.4
5) CO ($^3 \text{II}$) + O($^3 \text{P}$)	-	13.1

The states of the excited CO_2 molecules from which these products were formed have not been specified, although Wilde et alia²³ suggests that processes (1) and (2) occur via the formation of CO_2 ($^3 \text{II}$) and CO_2 ($^1 \text{II}$) respectively, where the ($^3 \text{II}$) and ($^1 \text{II}$) refer to two low-lying excited states of CO_2

predicted earlier by Mulliken.¹⁵

3. Negative Ion Formation: Loeb²⁴, Wahlin²⁵ and Bradbury and Tatel²⁶ find that carbon dioxide does not have an appreciable electron affinity and no negative ions were observed even at the highest electron velocities attained. Recent confirmation of this has been provided by Rosenbaum and Neuert.²⁷

However it is energetically possible for negative ions to be formed by a process known as "dissociative attachment". This is a reaction in which electrons with some 3.5 ev of energy cause dissociation of the CO₂ molecule into CO + O⁻. For a dissociation of CO₂ into CO + O, the energy required is 5.5 ev, 2.2 ev of this could come from the heat of formation of O⁻. Loeb²⁸ however states that such a process has never been observed.

4. Radiation Stability of CO₂: The apparent stability of CO₂ under the influence of radiation had been observed as far back as 1908 by Cameron and Ramsey who found it to be relatively unaffected by γ -radiation unless Hg or P were present, in which case these substances were oxidised and CO was formed. Further evidence for the stability of CO₂ towards γ -radiation was provided by

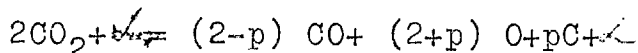
the work of Wourtzell (1920), Lind and Bardwell (1925) and Harteck and Dondes (1955).

With the development of modern reactor technology radiation effects on CO_2 have become of increasing interest, since the CO_2 is a favourable coolant. Thus Davidge and Marsh (1955) and Harteck and Dondes (1955, 1957) have investigated the effect of pile radiation and fission fragments upon CO_2 and have confirmed the earlier results for the ineffectual decomposition of pure CO_2 by radiation.

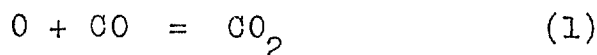
Harteck and Dondes²⁹ carried out further experiments with CO_2 using both γ -radiation and pile radiation and found that the addition of percentages as small as 0.5 per cent of nitrogen dioxide (NO_2) was sufficient to promote considerable decomposition of the CO_2 to give the products carbon monoxide and oxygen. This result showed that CO_2 had no inherent stability towards radiation and that any interference with the reactions involving the radiation produced intermediate species could reduce or eliminate the reactions re-forming CO_2 , confirmation of this was provided by the later work with carbon.

Hirschfelder and Taylor³⁰ basing their analysis on mass spectroscopic and ultra violet absorption studies considered the effect of radiation on CO₂. They assumed that the majority of positive ions formed were CO₂⁺, with a fraction p of the total positive ions present being due to CO⁺, they further assumed that the dissociation of CO₂ into CO and O occurred with a probability equal to that of positive ion formation. Neutralization of CO₂⁺ and CO⁺ was considered to result in the formation of CO + O and C + O respectively, the neutralization of CO₂⁺ to yield C+O+O being thought energetically impossible, although the formation of an excited CO₂⁺ ion was evidently not considered.

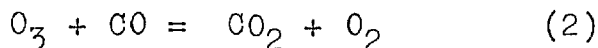
The effect of radiation on CO₂ was expressed as:



they attributed the radiation stability of CO₂ to the recombination reactions



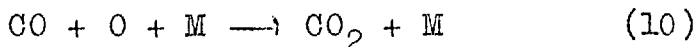
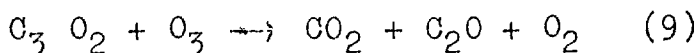
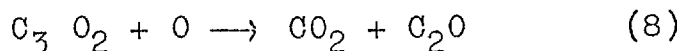
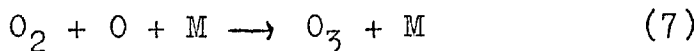
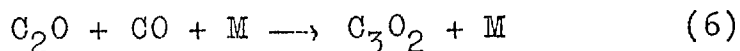
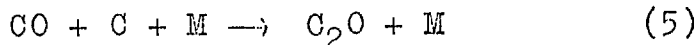
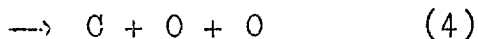
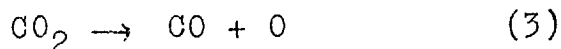
and as O₂ became appreciable and led to O₃ formation



However Jackson³¹ observed that the recombination of CO and O was some 150 times slower than the formation of O₃ via O₂+O = O₃, while Harteck and Dondes^{29,32}

showed that the gas phase reaction between CO and O₃ was hindered by a heat of activation of over 28 Kcal and was therefore probably too slow to be responsible for the reformation of CO₂.

Harteck and Dondes therefore proposed a new reaction mechanism to account for the apparent radiation stability of CO₂, the proposed mechanism is as below:



The mechanism suggests that the formation of carbon sub-oxides, rather than being a side reaction required only in CO-rich mixtures to account for the formation of solids, is here required as an essential step in the CO₂ reformation processes, although there will be partial diffusion of these sub-oxides to the walls to form polymerization products. Wright³³ points

out that the two mechanisms proposed separately by Hirschfelder and Taylor and by Harteck and Dondes are not mutually exclusive. The carbon sub-oxides in the Harteck and Dondes mechanism serve merely as carriers for CO to facilitate reaction with the oxidising species O and O₃. It is to be noted also that carbon atoms play an essential role in the recombination mechanism.

Photolytic or electron impact studies using photon or electron energies sufficient for reaction (3) (5.5 ev = 2250 Å) but insufficient for reaction (4) (16.6 ev = 750 Å) might provide interesting contrasts with radiation chemical studies where both reactions are possible.

(B) Radiochemical reactions in pure CO:

1. Ionization Processes: Simple molecular ionization and dissociative ionization processes in carbon monoxide have been the subject of much study. The work carried out up until 1930 has been briefly reviewed by Smyth³. However Hagstrum³⁴ presents a critical account of the early electron impact work and considers many of the results unreliable. His main objections are (1) that the gas pressures were too high and therefore secondary

processes were almost certainly occurring and (2) the sensitivity of the apparatus was too low. Hagstrum feels that the development of mass spectrometers using magnetically collimated electron beams and retarding potential apparatus enabling the kinetic energy imparted to the ions upon formation to be determined, has rendered the more recent electron impact data much more reliable.

In mass spectrometer studies of ionization processes, the method generally used is for the ions formed by electron impact to be accelerated and collimated into a beam by a system of electrodes at different potentials and then passed through some sort of mass analyser, usually of the magnetic deflection type, the resolved ion beam is then collected and the ion current measured.

The minimum electron energy required to form the particular ion is obtained from the ionization efficiency curve, which is a graph of ion current versus electron energy. The determination of the actual value of this electron voltage is made difficult by the fact that the electrons receive energy from sources other than the potentials applied to the electron accelerating

electrodes. The magnitude of contributions from these sources - the thermal energy of the electrons, contact and surface potentials, potential gradients in the ionization chamber, etc., - cannot be determined directly. However the use of a gas whose ionization potential is known, for example Neon, usually enables the relationship between the voltage applied to the accelerating electrodes, which is the quantity measured, and the actual voltage of the ionizing electrons to be determined.

The minimum electron energy required to completely remove an electron from a molecule, thus forming a molecule-ion, is called simply the ionization potential of the molecule, whereas the term "appearance potential" is generally applied in the case of the formation of a fragment ion from a molecule, that is when ionization and dissociation occur. Theoretically ionization potentials and appearance potentials refer to processes in which all the entities involved are in their ground state and moreover possess no kinetic energy. However when ionization is accomplished by electron impact it is required that the Franck-Condon³⁵ principle is obeyed. Restricting the discussion to diatomic molecules, such a requirement means that if the molecule

and molecule-ion have appreciably different nuclear separations then the molecule-ion will be produced with vibrational energy, while for the case of ionization followed by dissociation the fragment ions may possibly possess kinetic energy as well as excitation energy.

It is known³⁶ that the CO^+ ion is formed with essentially zero kinetic energy and therefore of particular interest in the study of electron collisions in CO are the ionization processes in which the molecule-ion dissociates. To specify completely each dissociative ionization process it is necessary to know (1) the identity of the atomic fragments as to states of ionization and excitation (2) their distribution in initial kinetic energy and (3) the appearance potential for fragments of known kinetic energy. The most recent and probably the best electron impact study of CO is that of Hagstrum³⁷ whose mass spectrometer had special constructional features permitting the determination of the identity of the ion, its appearance potential and its initial kinetic energy. His appearance potential measurements for ions of zero kinetic energy are shown below in Table IV together with the results from sources considered by Hagstrum to be reliable.

Table IV

<u>Observed Product</u>	<u>Appearance Potential (volts)</u>				<u>Suggested Process</u>	<u>Relative Abundance</u>
	<u>Hagstrum</u>	<u>Hagstrum & Tate</u>	<u>38</u>	<u>Lozier</u> ³⁹		
(1) C ⁺	20.9 ± 0.2	20.9		20.9	CO → C ⁺ (² P)+O ^{-x} (2.2)	5.5
(2)	22.8 ± 0.2	22.8		22.8	CO → C ⁺ (² P)+O ^x (¹ D)	
(3) O ⁺	23.2 ± 0.3	23.3		-	CO → C(³ P)+O ⁺ (⁴ S)	3
(4) O ⁻	9.6 ± 0.2	9.5		9.5	CO → C(³ P)+O ^{-x} (2.2)	
(5)	21.1 ± 0.2	20.9		20.9	CO → C ⁺ (² P)+O ^{-x} (2.2)	
(6) CO ⁺	14.1 ± 0.2	14.1		14.00 ³⁶	CO → CO ⁺	100

The fifth column of Table IV contains the processes thought by Hagstrum to best represent the appearance potential data. The O^{-x}(2.2) refers to a negative ion possessing 2.2 volts of excitation energy. Hagstrum also found that the only ion formed with kinetic energy was the O⁺ ion of process (3), the most abundant of which possessed 1.5 volts of kinetic energy. Earlier work by Hagstrum and Tate had given an additional appearance potential, that of the CO⁺⁺ ion occurring at 42.5 volts, while the relative abundances of the CO⁺, C⁺, O⁺ and CO⁺⁺ ions were found by Hayakawa and Suguiwa⁵ to be 100, 5.5, 3 and 0.2

The excellent agreement obtained by Hagstrum with earlier appearance potential measurements made it

possible for him to calculate a series of values for the dissociation energy of CO and so arrive at a unique value for this quantity. This part of his work will be left until the section dealing with the determination of this energy.

The observation of higher excited states of the CO^+ ion has been reported by Weissler et alia¹⁴ using a photo-ionization method. The appearance potentials for these ions being given as 16.6, 20.1 and 25.7 volts, in good agreement with spectroscopic measurements.

2. Heat of Dissociation of CO. $D(\text{CO})$: $D(\text{CO})$ is a particularly important quantity because of its relation with the heat of sublimation of carbon, $L(\text{C})$, and through it to the heats of formation and bond energies of every carbon containing molecule. The relation between $L(\text{C})$ and $D(\text{CO})$ is obtained from a well known thermochemical cycle which yields:

$$L(\text{C}) = D(\text{CO}) - 3.721 \text{ ev (85.78 Kcal)}$$

No general agreement on a unique value for $D(\text{CO})$ has yet been reached and at present there are still four values receiving support from different workers. The values under consideration for $D(\text{CO})$

are 9.14, 9.61, 9.85 and 11.11 volts, the corresponding values of $I(C)$ being 125.0, 135.8, 141.3 and 170.4 Kcal/mole respectively.

The methods used in the determination of $D(CO)$ can be grouped under three main headings (a) electron impact studies (b) spectroscopic measurements and (c) carbon vapour pressure measurements.

(a) The work of Hagstrum³⁷ described in the previous section represents probably the best electron impact results for $D(CO)$. Hagstrum, from the appearance potentials summarised in Table IV, calculated a series of values for the dissociation energy of CO assuming all possible excitations of the products. Comparison of the different series showed that the only single value of $D(CO)$ satisfying the demands of the appearance potential data was 9.61 volts, agreeing well with an earlier spectroscopic value obtained by Hagstrum³⁴. However this unique figure of 9.61 volts was deduced assuming that the $O^{-\text{II}}(2.2)$ ion had an excitation energy equal to the electron affinity of the oxygen atom, which was generally accepted at that time to be 2.2 volts. Recent measurements by Branscomb and Smith⁴⁰ have however indicated that in fact the electron

affinity of atomic oxygen may be as low as 1.48 volts, in which case an excited O^- ion at 2.2 volts must be unstable and would not be observed. The conclusion is that until the controversy over the electron affinity of atomic oxygen is resolved, the electron impact value for $D(CO) = 9.61$ volts must remain in doubt.

Attempts have been made to determine $L(C)$ from measurements of appearance potentials for CH^+ and C^+ ions from several small molecules, but this leads to values of $L(C)$ ranging from 100 to 240 Kcal/mole and must therefore be considered unreliable. Lindholm⁴¹ using monochromatic ions to bombard CO and then analysing the fragments with a spectrometer was able to deduce a value of 9.605 volts for $D(CO)$, a result in remarkable agreement with that of Hagstrum. Evidence of a lower limit to $D(CO)$ was provided by Kenty et alia who noted the failure of metastable Xe atoms to dissociate CO in collisions of the second kind and took this to mean that $D(CO)$ was not less than 9.4 volts.

(b) Spectroscopic studies have yielded many values for $D(CO)$ ranging from 6.92 up to 11.11 volts. The bulk of the spectroscopic evidence comes from reported observations of what are known as predissociations. These

are slight fluctuations in the intensity of the vibrational or rotational structure of various CO spectral band systems. True predissociation often enables an upper limit to the dissociation energy to be fixed. However abnormalities in the intensity distributions may be due to phenomena other than predissociations and great care has to be taken in interpreting such effects.

The value of $D(\text{CO}) = 6.92$ volts was deduced by Schmid and Gero⁴² from data interpreted as evidence of predissociation. However the objections that this value produces an impossibly low figure for $L(\text{C})$ and also grossly violates certain rules in spectroscopy has led to it being largely discarded. Herzberg⁴³ using a different interpretation of the same data arrives at a value for $D(\text{CO})$ of 9.14 volts. The main objection to this value is that it also violates a certain rule in spectroscopy, although support is provided by the studies of Faltings et alia⁴⁴ on the photo-dissociation of CO. However the interpretation of this work has been strongly criticised by Gaydon and Penney⁴⁵.

Probably the most acceptable spectroscopic value for $D(\text{CO})$ is 11.11 volts. It appears to be generally agreed that the predissociation data indicates

a true dissociation limit occurring at 11.11 volts. The controversy arises over the degree of excitation to be assigned to the atomic products of the dissociation at this limit, the true value of $D(CO)$ being 11.11 volts minus the atomic excitation energy. Gaydon⁴⁶ provides strong evidence for supposing that the figure of 11.11 volts represents the true dissociation energy of CO. He points out that it does not cause the violation of rules in spectroscopy that lower values cause and also cites the support lent by most of the recent values for the latent heat of sublimation of carbon. However the value proposed by Gaydon definitely does not agree with Hagstrum's recent electron impact data.

(c) Attempts have been made to measure $L(C)$ directly from the vapour pressure of carbon. The problem is difficult experimentally because of the very high temperatures involved and the fact that gaseous carbon is not completely monatomic, there are also doubts about the interpretation of the results unless perfect equilibrium is attained.

Brewer et alia⁴⁷, Simpson et alia⁴⁸ and Marshall and Norton⁴⁹ obtained values of around 170 Kcal/mole for

$L(C)$ which yields a value for $D(CO)$ of 11.11 volts, however Goldfinger et alia carrying out similar experiments found $L(C)$ to be about 142 Kcal/mole and favours for $D(CO)$ a value of 9.85 volts, such a value is however barely distinguishable from that of Hagstrum.

Some of the most significant experiments have been the studies of the evaporation of carbon in the ion source of a mass spectrometer, carried out by Chupka and Ingram⁵⁰. The carbon is formed by thermal evaporation of solid carbon, the gas then diffuses into an electron beam where ionization takes place, mass analysis of the ions follows. Comparison of the ion intensities with those from a standard enabled the workers to measure the absolute pressure of the molecular species in the carbon gas. The vapour pressure of carbon atoms at 2400°K was found to be 2×10^{-8} atmospheres which compares well with the value calculated from $L(C) = 170$ Kcal/mole.

Other methods for determining $D(CO)$ do not yield a single value more favourable than any other, although it does appear that either 9.61 volts or 11.11 volts represents the true dissociation energy of CO .

3. Negative Ion Formation: The formation of negative ions in carbon monoxide has been investigated by Wahlin²⁵,

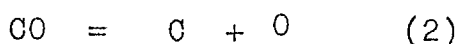
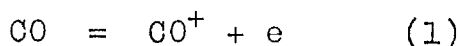
Bradbury and Tatel²⁶, Tate and Lozier⁵¹, Lazier and more recently by Rosenbaum and Neuert.²⁷ All concur in the conclusion that the carbon monoxide molecule has negligible electron affinity. No negative ions are formed in it until actual dissociation of the CO occurs. The electron impact studies of Hagstrum discussed earlier revealed that O^- ions are formed at electron energies of 9.6 volts and 20.9 volts. It is perhaps interesting to record that although Hagstrum studied CO extensively and carefully he found no evidence for the formation of a C^- ion, similar studies in a CO discharge by Smith and Branscomb⁴⁰ revealed little or no trace of this ion.

4. Overall effect of radiation upon CO: Cameron and Ramsey⁵² and Lind and Bardwell⁵³ found, in contrast to their experiments with CO_2 , that CO was very sensitive to γ -radiation. They observed that the CO was readily decomposed with the subsequent formation of CO_2 and a carbon-rich solid. The nature of this solid was found to vary with the conditions in which it was formed, being particularly dependent upon temperature. Observations by early workers that the pressure changes produced by the irradiation of the CO could not be

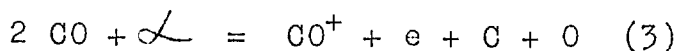
reconciled with the equation $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ was taken to indicate that the solid was not pure carbon. The present concept is that the solid is some form of carbon suboxide polymer of complex and variable composition. In most of the experiments carried out at temperatures below 100°C the solid was seen to have a brown or yellow colour and usually settled to the bottom of the irradiation vessel as though nucleation in the gas had occurred. Cameron and Ramsey described two solids, a black one, possibly carbon, which settled and a brownish yellow film which was evenly distributed over the walls of the vessel. On heating these solids in vacuum, CO_2 and CO were produced leaving behind a residue of carbon. Lind and Bardwell reported that if the gases were pumped off and the vessel filled with CO_2 which was then re-irradiated, the solids disappeared and CO was formed. CO irradiation at higher temperatures ($350\text{--}500^\circ\text{C}$) produced black deposits which possibly indicates a higher proportion of carbon. The state of knowledge of these solids is at present incomplete.

Hirschfelder and Taylor³⁰ using the data

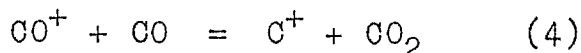
available at that time were able to account for the effect of radiation on CO. They considered that the $\mathcal{L}$ -particle and its fast secondary electrons were principally engaged in the reactions:



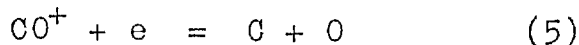
these occurring with about equal probability, the primary processes thus being represented by the equation:



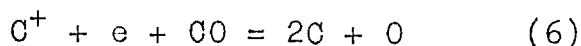
The subsequent fate of the CO^+ ion was decided as follows, it was considered that a certain fraction w of the CO^+ ions underwent the ion exchange reaction:



while the remaining fraction $(1-w)$ underwent the neutralization process:

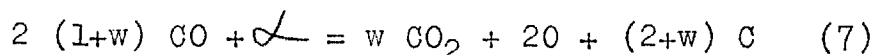


the fate of the C^+ ion of reaction (4) being decided by a further neutralization process, viz:



the simultaneous collision with a CO molecule indicated in equation (6) was considered necessary

because the energy produced by the direct neutralization of the C^+ ion to yield a carbon atom only would have to be released in the form of radiation and such processes were known to have a small probability. The resultant expression for the effect of radiation upon CO is thus:



4 Hirschfelder and Taylor considered the excess carbon to be the origin of the carbon suboxides found in the experimental observations and felt there was a possibility that some carbon atoms may reach the vessel wall to form solid carbon, a conclusion consistent with Cameron and Ramsey's observations of two solids. Since the oxygen can oxidise either the carbon suboxide or the solid carbon it is impossible to predict the ratio of the products obtained, but the analysis showed that about two molecules of CO will disappear per ion pair formed. Lind and Bardwell deduced an initial ion pair yield of about three which is supported by the work of Woodley.

(C) Radiation induced reactions in the system
CO₂/CO/C:

From the studies made on the radiolysis of CO₂ it was reasonably easy to predict the effect of introducing solid carbon into a system in which CO₂ was being irradiated. By analogy with the reports on the effect of mercury, phosphorus and nitrogen dioxide it was expected that the carbon would be oxidised with the formation of CO until a steady state condition was reached.

A thorough review of the present position regarding the reaction between carbon dioxide and carbon under the influence of radiation has recently been presented by Wright.³³ Since the problem is directly concerned with the compatibility of CO₂ and carbon under nuclear reactor conditions many experiments have been performed in-pile. Of importance in the in-pile experiments is the energy absorbed by the CO₂ and the carbon in the reactor rather than the incident radiation. It is known that two components of reactor radiation can transfer energy - gamma rays and fast (i.e. non-thermal) neutrons. Gamma rays can ionize directly

but their main effect is to produce fast secondary electrons which cause many more ionizations and excitations. Fast neutrons however transfer energy by elastic collisions producing energetic recoil ions which then cause further ionizations and excitations, and in solids cause atomic displacements.

In the CO₂/graphite system encountered in the reactor, energy can be absorbed in three regions (a) the solid carbon (b) the bulk gas and (c) the gas in the pores of the carbon. Calorimetric measurements made in the core of B.E.P.O., the experimental reactor at Harwell, have however shown that the same energy is absorbed per unit mass for all three regions, for the same thermal neutron flux. These measurements showed that the rates of energy absorption in carbon, carbon dioxide, carbon monoxide and oxygen, independent of their chemical form, were all of the order of 2.83 milli-watts per gram at a thermal neutron flux of 10^{12} neutrons per sq.cm.per sec. 81% of this energy being due to gamma radiation and 19% to fast neutron scattering.

There were two distinct possibilities as to the cause of the radiation induced reaction between CO_2 and carbon, (1) that the radiation was producing "active sites" on the carbon possessing sufficient energy to enable them to react with CO_2 , or (2) that the radiation was producing in the CO_2 active species, for example atomic oxygen, capable of reacting with the carbon. Since in any practical reactor system the mass of graphite greatly exceeds the mass of gas under irradiation, it was at first thought that the radiation would exert a much greater influence on the reaction through the energy absorbed in the graphite than through that absorbed by the gaseous reactant. It was expected that carbon atoms displaced from their normal lattice positions by irradiation of the graphite and the resultant distorted lattice would be more reactive than the normal graphite, also carbon atoms recoiling from fast neutron collisions would cause local excitations which might stimulate chemical reaction. However all the observations on the radiation induced reaction between carbon dioxide

and carbon indicate that it is the energy absorbed in the gas phase which is the more important, although reactor irradiation of the graphite has been found to enhance subsequent thermal oxidation in air or oxygen.

Some of the fundamental concepts of the radiation induced reaction were established by Davidge and Marsh⁵⁴ who studied the reaction in an all-glass apparatus in B.E.P.O. In their work the gas was circulated by a glass piston pump over the graphite which was contained in a temperature-controlled furnace in the core of the reactor. A large silica bulb was incorporated in the gas system close to the furnace to enable the volume of gas under irradiation to be increased when required. The reaction was followed by analysing gas samples for CO. It was observed that the rate of CO formation was considerably greater when the gas was passed through the large silica bulb before reaching the graphite than when this large volume was downstream of the sample, other variables being kept constant. This clearly demonstrated that it was the absorption of energy in the gas phase that

determined the extent of the subsequent reaction with the graphite. Davidge and Marsh, and other workers, have also observed that the CO concentration could be brought to a steady state value of between 0.3 and 1.4 volume % which was considerably above the maximum thermodynamic value for the conditions in the absence of radiation of 0.06%. The rate was found to depend linearly on radiation intensity and was approximately independent of temperature in the range 25°C - 350°C, it did however depend on pressure, gas flow and ratio of gas to graphite in a complex manner.

Copestake and Corney⁵⁵ have recently carried out an extensive series of experiments in which sealed silica bulbs containing a known pressure of CO₂ and a carbon sample were irradiated. Irradiations were carried out in B.E.P.O. at 80°C and 500°C and in DLD0 at 30°C, the latter providing a pure gamma radiation source. The knowledge that reactor radiation could still cause gas evolution from carbon irradiated in vacuum at temperatures of 80°C after previous degassing treatment at much higher temperatures led Copestake and

Corney to study the effect in the presence of CO_2 . They found that the amount of gas evolved by radiation was not sufficient to obscure the changes in gas composition produced by the radiation induced reaction between CO_2 and carbon. In one set of experiments a variety of different carbons were irradiated in CO_2 to see if the nature of the carbon influenced CO production. The results of such experiments were expressed in terms of the number of molecules of CO produced per 100 ev of total energy absorbed in the CO_2 , denoted by G_{CO} , a selection of these results are given in Table V.

Table V					
CO_2 press m.m.	Wt of Carbon (gm)	Nature of Carbon	Thermal neutron dose (n.v.t. x 10)	% CO	G_{CO}
(a)					
406	3.05	Pile grade A graphite	1.68	0.68	0.32
480	3.05	Ungraphitised carbon	3.53	2.2	0.48
391	3.18	Regraphitised graphite	1.78	0.71	0.32
352	5.99	CH_4 impregnated graphite	2.56	1.22	0.39
(b)					
607	3.27	Ungraphitised cellulose carbon	2.75	0.33	0.092
558	1.83	Pile grade A graphite	2.75	0.30	0.083
604	1.71	Graphitised cellulose carbon	3.05	0.31	0.078

These results showed that apparently the nature of the carbon had little effect on the CO production. Further experiments by Copestake and Corney showed that the rate of CO production decreased with increase in the total radiation dose and there were indications that the CO concentration was approaching a steady value. It was also found that the radiation yield of CO decreased with increase of the initial CO₂ filling pressure, other conditions being constant, the precise relationship appearing to depend strongly upon the geometry of the system. The effect of variations in weight and shape of the carbon specimens gave results difficult to correlate. The G_{CO} values obtained for irradiation in a pure gamma source tended to be lower than for the corresponding B.E.P.O. irradiations, the precise significance of this difference is, however, uncertain in view of the differences in dosimetry and energy spectra. The report of a reaction in a pure gamma source is contrary to the finding of Woodley (1954) who reported very little reaction between CO₂ and graphite after 105 days in a gamma source at

30°C in sealed tubes. Irradiations at 500°C indicated that the radiation induced reaction had only a small temperature coefficient. The irradiation at pile temperature of quartz bulbs containing CO resulted in the formation of CO₂ and a brown solid which adhered to the walls of the bulb. Wide variations in the amount of CO₂ produced occurred in the presence and absence of a graphite sample. Heating the quartz vessel, after pumping off the excess gases, produced more CO₂ and CO with the brown solid turning black, suggesting that decomposition of the initially brown polymer was occurring. The results are identical with earlier studies on the radiolysis of CO.

The question of whether carbon transport still occurs in the CO₂/CO/C system under irradiation when steady state conditions obtain has been studied, in a preliminary manner only at present, by Dominey⁵⁶. Using ¹⁴C in the solid phase he has shown that radiation induced transport of carbon to the gas phase continues even in static systems with CO concentrations of about 50%, well above the steady state value.

Most of the results obtained from studies of the radiation induced reaction are capable of a qualitative interpretation in terms of the competition between the gas phase species CO or carbon suboxides and the solid carbon for the oxidising O atoms or O_3 molecules produced from the irradiated CO_2 . Changes in gas pressure, gas to graphite ratio and geometrical arrangement would affect the access of these oxidising species to the carbon surface. Account has also to be taken of the reactions occurring within the pores of the carbon as well as on the geometrical surface, for although there is considerably less gas in the pores, the proximity to the carbon of the active species formed by irradiation makes the pore reaction important.

Attempts to establish a precise relationship between carbon loss and CO formation have been restricted by the difficulty of obtaining measurable weight losses in small experimental systems and of making the larger engineering systems sufficiently leak-tight to achieve a material balance. The difficulty of distinguishing weight

loss due to carbon removal from that due to changes in surface oxide on the specimen is also met with. A full quantitative treatment of the radiation induced reaction between CO_2 and carbon is made difficult by the complex character of the transport of the oxidising species to the carbon and the nature of the heterogeneous step once they have arrived.

Cowen and Lind⁵⁷ have recently presented a report on laboratory studies carried out on the reaction between graphite and CO_2 activated in a discharge tube. In these experiments the gas was maintained at pressures of about 3 m.m. and activation was by means of an electrodeless discharge induced from a high frequency generator. Studies of the emission spectrum of the gas in the discharge were made and the following species were definitely identified, CO_2 , CO^+ , O^+ , C and C^+ while at a later date positive identification of neutral atomic oxygen was made. CO and CO_2^+ were tentatively identified but no firm conclusions over O_2^+ and O_2 could be reached, ozone was excluded from the

search as there was no satisfactory evidence for an emission spectrum from this relatively unstable molecule. The spectroscopic studies could not identify the species responsible for the carbon removal. Experiments in an applied electric field suggested that they were uncharged which restricted the choice to ozone or atomic oxygen, the temperature was considered too low for significant attack by molecular oxygen. The effect on the graphite oxidation rate of additives to the gas was studied and for CO, CCl₄ and CFCl₃ significant reductions in attack occurred. More extensive work on CO showed that if the addition of the gas was made beyond the discharge but prior to the gas reaching the graphite then it was ineffective in reducing the attack. The application of certain metals, in particular copper, to the geometric surface of the graphite caused an appreciable decrease in the attack by the activated CO₂. It was found that a phosphate treatment of the graphite was ineffective in reducing the reactivity of the graphite. The results of this work are strongly paralleled by studies in-pile, with the exception of the metal

treatment. One of the disadvantages of this method is ignorance of the energy input to the activated gas. More work is needed in this field before it is possible to relate the results to in-pile conditions.

PRELIMINARY EXPERIMENTS AND RESULTS

(A) Experiments with a high voltage discharge tube:

1. Apparatus and Procedure: The essential feature of this apparatus was the reaction vessel which was a high voltage discharge tube through which CO_2 flowed, this is shown in fig.1. In one set of experiments the carbon was deposited onto a glass rod by means of a smoky flame and inserted into the central column, while in another set the carbon was in the form of a long thin filament. With the CO_2 flowing, a high alternating potential (~ 2000 volts, $50^\circ/\text{s}$) was applied by means of a transformer between the two aluminium electrodes, thus causing a discharge in the gas. The resulting excited and ionised species produced in the CO_2 were made to flow past the deposit or filament and observations were made on the effect this had on the carbon. CO_2 pressures of between 0.4 and 1.4 m.m. of Hg were used, the pressure being given by a butyl phthalate manometer. The discharge tube was cooled by means of a number of jets of air.

2. Results: These experiments showed clearly that the carbon was being attacked by the products from the discharge in the CO_2 . The experiments in which a carbon filament was used revealed that the portion of the filament actually in the discharge suffered considerably more attack than parts immediately outside. In one experiment with a CO_2 pressure of 0.4 m.m. of Hg. a loss of carbon of 5.5 mgrms was recorded after an exposure of 60 minutes. The effect of the attack was most apparent visually with a carbon deposit supported on a glass rod, here it was observed that at points high up the central column, i.e., far removed from the discharge, no attack occurred.

The large number of species capable of being produced in the discharge made it desirable to obtain some control over the energy input to the gas and led to the development of apparatus employing thermionic electrons of controlled energy.

(B) Experiments using electrons of controlled energy:

1. Apparatus: The apparatus in fig.2 represented the first attempt to use electrons of con-

trolled energy to promote a reaction between CO_2 and carbon. The essential features were an electron emitting thermionic filament surrounded by a spiral nickel grid which was held at a positive potential with respect to the filament. The electrodes were attached to stainless steel rods soldered into glass-to-metal seals which in turn were soldered into a stainless steel disc. This disc contained a trapezoidal groove near its edge which contained a neoprene rubber O-ring supplied by Edwards High Vacuum Ltd. The O-ring finally rested on a ground glass flange at the top of the reaction vessel.

2. Procedure and Results:

(i) Flow experiments. Preliminary experiments were carried out with this system in which CO_2 at a pressure of the order of 5μ was allowed to flow through the reaction vessel. The emitting filament was heated to about 900°C and an accelerating potential of about 40 volts was applied to the grid. The carbon in these experiments consisted of a film of soot supported on a small glass slide suspended in the reaction vessel adjacent to the grid. Under these conditions removal of the carbon

FIG. 1. DISCHARGE
TUBE

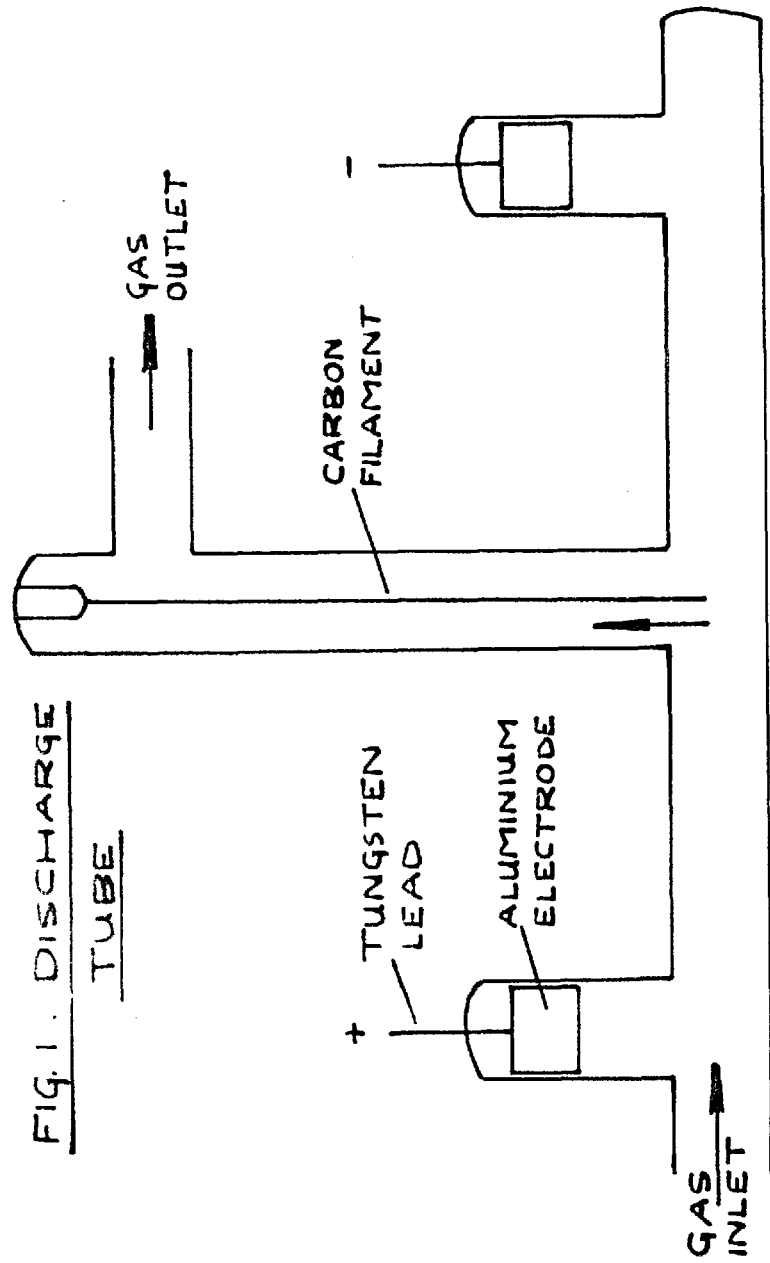
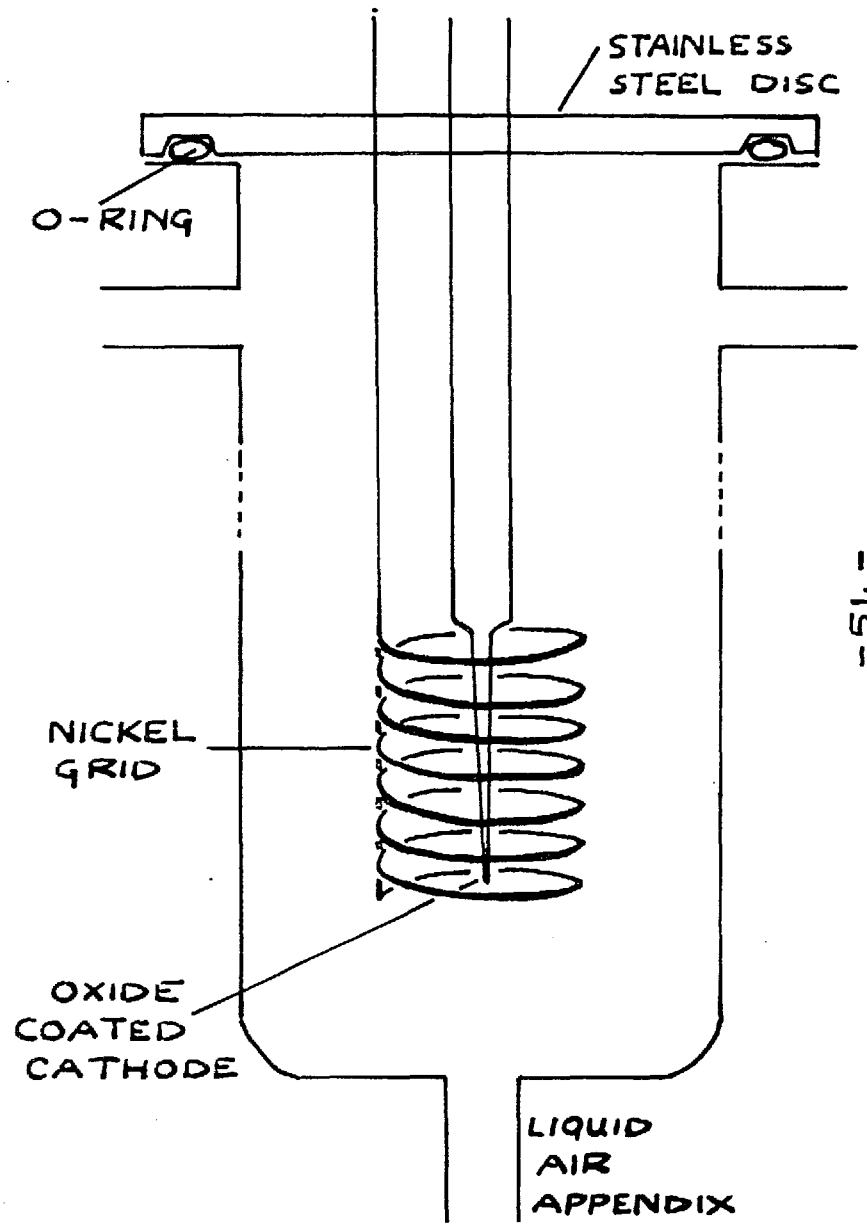


FIG. 2. PRELIMINARY CONTROLLED
ELECTRON APPARATUS



film was observed, periods of 3 to 5 hours being needed for a visible effect to be produced. A similar experiment with the filament on but with no accelerating potential revealed no such attack, even though the CO_2 was allowed to flow for a considerably longer time.

The accelerated electrons were apparently activating the CO_2 so as to make it capable of attacking carbon.

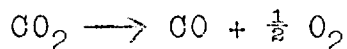
(ii) Static experiments. In view of the slow rate of removal of the carbon film a further set of experiments were undertaken in which a static charge of CO_2 was exposed to electron bombardment for short periods of time both in the presence and absence of a carbon film. The resulting gases were analysed but no direct measurement of any change in the carbon film was made since the amount of CO_2 used was too small to produce a measurable weight loss of carbon.

In these static experiments a measured pressure of CO_2 was established in the reaction vessel and a known electron current was drawn from the thermionic filament for a known time with a

measured positive potential applied to the grid. The final total pressure was recorded, after which the pressure of non-condensable gas was found by immersing the appendix on the reaction vessel in liquid oxygen, the fall in pressure indicating the final pressure of CO_2 . The duration of the reactions was varied from 5 to 300 secs., and initial CO_2 pressures of 40-75 μ were used, the applied grid voltage was kept roughly constant at + 20 to + 24 volts.

The experiments showed clearly that, as expected, the CO_2 was being decomposed when carbon was present. But they also showed that the CO_2 appeared to decompose equally readily in the absence of carbon.

In the absence of carbon it was thought that an overall reaction likely to occur as a result of electron bombardment would be:



In some reactions therefore the presence of free oxygen was investigated by glowing a platinum filament in the reaction products to cause recombination of O_2 and CO , with the appendix

on the reaction vessel immersed in liquid air. No change in pressure was in fact observed and it was concluded that O_2 was absent. It was therefore considered likely that in the absence of carbon the excited CO_2 was decomposing by reaction with either the thermionic filament or the mercury vapour present in the reaction vessel, either process leading to the removal of atomic oxygen and formation of CO. The results of work with the new apparatus, to be described in detail later, made it clear that the reaction of excited CO_2 with the filament was the explanation of the decomposition of CO_2 in the absence of carbon. With carbon present it therefore seemed probable that the excited CO_2 could react both with the filament and/or the carbon. In the absence of an accelerating potential on the grid no reaction of the CO_2 with the filament and/or the carbon occurred.

The results also showed that both in the presence and absence of carbon the percentage reduction in the amount of CO_2 present, for a fixed value of the emission current, did not bear

a simple relationship with time but rather tended to some form of steady state value. The results of experiments with and without carbon are given in Table 1. Each row of figures in this table corresponds to a single Run with a static charge of CO_2 . The first column gives the initial pressure of the static charge of CO_2 in the reaction vessel; this is followed by the time for which the CO_2 is subjected to the electron bombardment. The third column records the average emission current in the grid - filament circuit during the Run. In the fourth column is the final total pressure of gas present in the reaction vessel at the end of the Run, while column 5 contains the non-condensable gas pressure (assumed to be CO) with the CO_2 condensed in the appendix on the reaction vessel. The difference between these two pressures gives the final CO_2 pressure in column 6. The last column contains the percentage reduction in the amount of CO_2 present for a fixed average emission current of 50 ma.

Similar experiments were also carried out in the presence of carbon filaments which could be heated electrically. A comparison of the rate and manner of decomposition of the CO_2 when the filament was at 20°C and when it was heated to 2000°C showed them not to be substantially different.

Difficulties were encountered in maintaining the system vacuum tight and the cause of the trouble was eventually traced to the O-ring seal. In spite of re-machining of the groove and attention to all the recommendations of the suppliers the device could never be relied on to remain vacuum tight. This, together with the unknown effect of the O-ring and the metal disc on the progress of the reactions occurring in the system, led to the apparatus being entirely reconstructed. This reconstruction involved improvements in the preparation and storage of the CO_2 , design of a new electrode system which both increased the efficiency of the carbon removal process and widened the scope of the experiments, provisions for removal of mercury vapour from the system and the

replacement of the metal disc and O-ring by a greased cone and socket arrangement.

The new apparatus in its final form and the experiments performed with it are described in the next section.

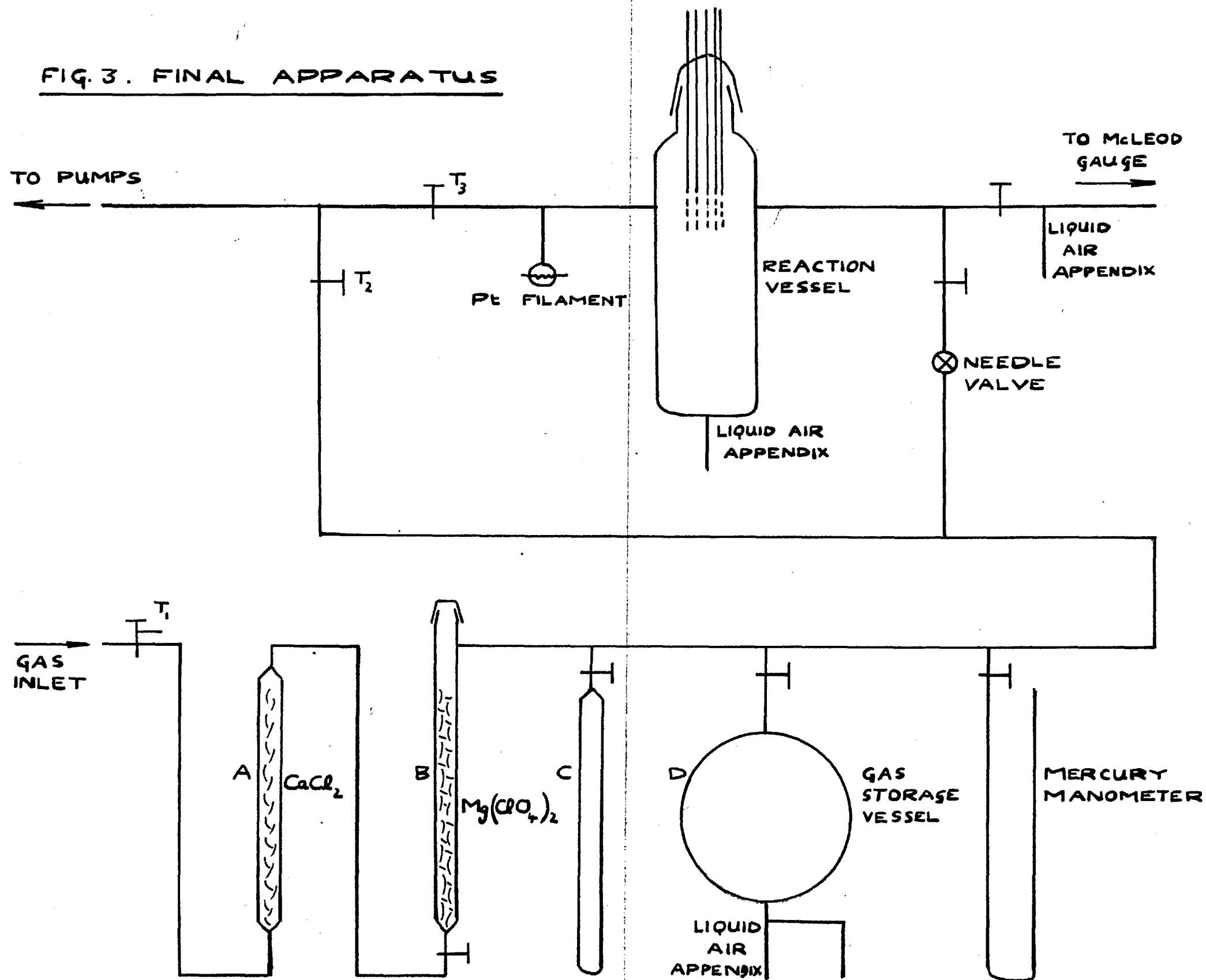
FINAL EXPERIMENTS AND RESULTS

(A) Experiments using electrons of controlled energy:

1. General description of final apparatus: The apparatus was constructed of Pyrex glass and consisted of two sections, a low pressure section in which the reactions were carried out and a section in which the gas was prepared and stored. A diagram indicating the general lay-out of the apparatus is reproduced in Fig. 3.

In the storage section were two drying tubes; A contained calcium chloride (CaCl_2) and B magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$). The gas was introduced via tap T_1 , passed through the two drying tubes and the distillation section and was stored in the large bulb D. Beneath D were two small tubes, one of which contained a small amount of magnesium perchlorate to keep the gas dry while being stored and the other served as a liquid air appendix. Also included in the section was a long narrow tube C used in the distillation of the CO_2 and a mercury manometer which enabled a check on the gas pressure in the section to be made. The different parts of the storage section were connected by capillary tubing.

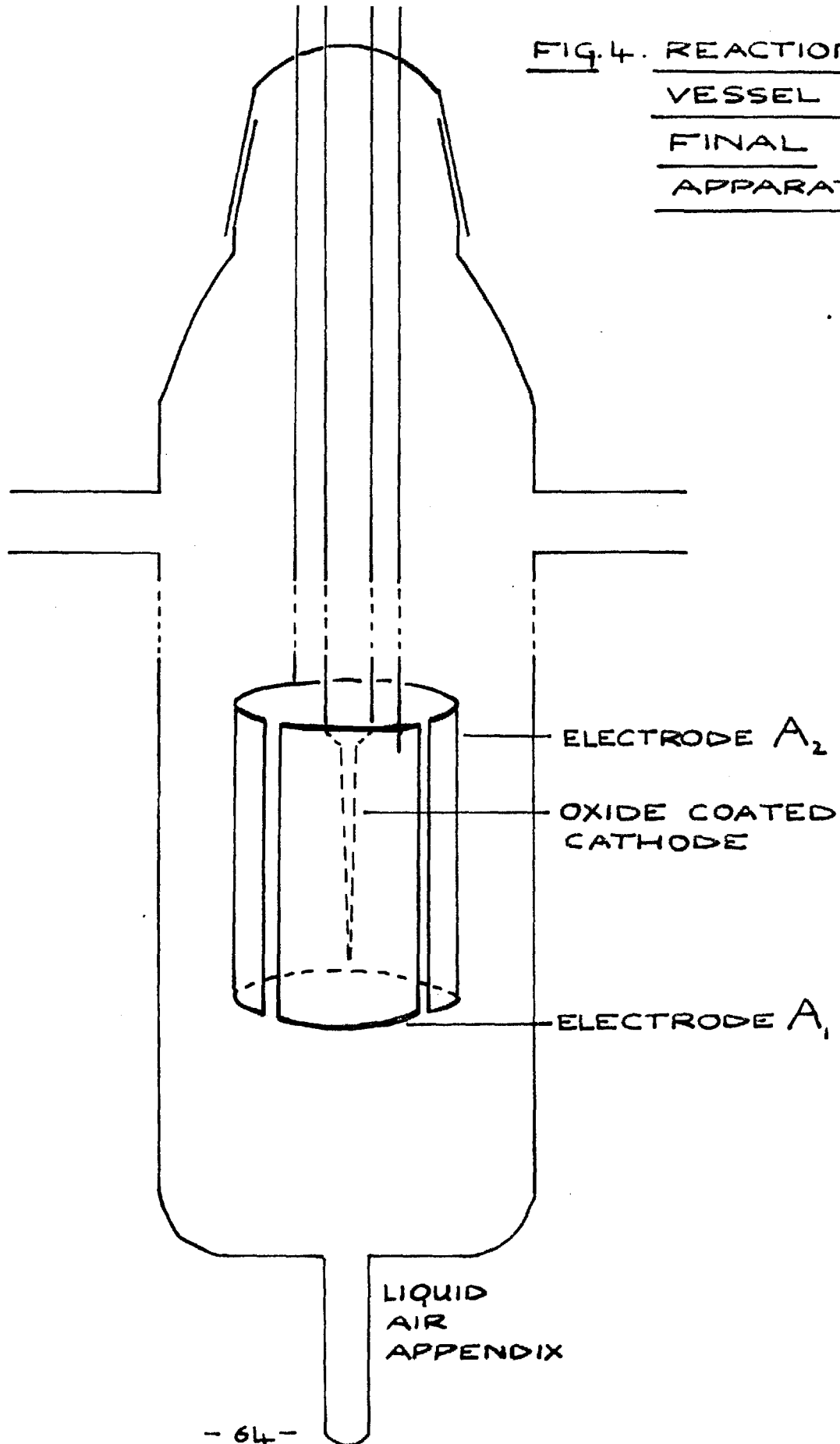
FIG. 3. FINAL APPARATUS



The CO₂ was provided from a commercial cylinder; it was fractionated by alternately freezing it out in tube C and bulb D using liquid oxygen and pumping away the top and bottom parts. This was done a number of times and the prepared gas was finally stored in bulb D. The CO was also provided from a commercial cylinder; it was dried by tubes A and B and then stored in the bulb D. When being used the appendix on the bulb D was immersed in liquid oxygen to retain any condensible impurities such as CO₂.

The low pressure section consisted of a McLeod gauge, a small platinum filament and the reaction vessel; a liquid air trap was also included between the McLeod gauge and the reaction vessel so as to enable experiments to be carried out in the absence of mercury vapour. The McLeod gauge was of the bench-type supplied by Edwards High Vacuum and was provided with a graduated scale capable of reading the gas pressure directly down to 1×10^{-5} m.m. of Hg. The gauge was slightly modified by replacing the fixed reservoir of mercury with a movable one connected by thick walled rubber

FIG. 4. REACTION
VESSEL IN
FINAL
APPARATUS



tubing to the manometer; this enabled the lever of mercury to be more accurately adjusted. Additional air traps were included so as to prevent any air trapped between the mercury and the rubber tubing from being swept over. To prevent mercury being accidentally let over into the reaction vessel a non-return valve was installed just above the Mcleod. The small platinum filament was included in a side arm for use in earlier experiments in which the presence of free oxygen was investigated.

In its final form the reaction vessel is as reproduced in Fig. 4., its dimensions were body length 25 cms and internal diameter 8 cms. Attached to the body of the vessel were a B.45 cone and socket, the socket contained 5 tungsten leads which supported the various electrodes used in the experiments. Beneath the reaction vessel was a small liquid air appendix used in the analysis of the reaction products. The electrodes consisted of a small anode A_1 , a larger electrode A_2 used for supporting the carbon deposit and a cathode C_1 . Electrodes A_1 and A_2 were of metal foil; in a few

earlier experiments this foil was of tungsten but owing to the cost and difficulty of working this metal the majority of the experiments were performed with aluminium electrodes, the results being the same with both metals. The cathode C₁ consisted of a composite oxide coated thermionic filament supplied by the Osram Valve Co., Hammersmith. This filament has as the base metal nickel of purity 99.9% with small traces of silicon and magnesium. Onto this base metal is applied a coating consisting of a mixture of barium, strontium and calcium carbonates in the proportion 50% BaCO₃, 40% SrCO₃ and 10% CaCO₃. These carbonates are then reduced to the corresponding oxides, this is followed by an activation process which causes the reduction of the barium oxide to give an excess of barium atoms in the surface of the coating, it is these excess barium atoms which provide the electron emission. Each electrode was connected by a short stainless steel rod through a terminal to the tungsten lead.

The gas was admitted from the storage section into the low pressure section by means of an Edwards

high vacuum spindle sealed needle valve, type OSIC. This provided a very fine control over the gas flow and with a pressure differential of 1 atmosphere a pressure of as little as 5μ could be maintained in the reaction vessel. The valve was connected to the apparatus by two metal B.14 cones fitted into B.14 glass sockets with picein wax.

The taps T_2 and T_3 enabled either section to be pumped out independently of the other. Evacuation of the apparatus was provided by a mercury vapour diffusion pump, type 2M3A, backed by a "Speedivac" rotary high vacuum pump, model 1SP30, both supplied by Edwards High Vacuum. This combination enabled pressures of less than 1×10^{-5} m.m. of Hg. to be obtained easily prior to the admission of the gas. A liquid air trap was included between the diffusion pump and the reaction vessel so that the effect of mercury vapour backstreaming from the diffusion pump could be minimised.

The presence of adsorbed gases on the walls of the reaction vessel and the metal parts contained therein made it necessary to bake out the vessel.

The heating was provided by means of thermocord connected to a temperature regulator supplied by Electrothermal Engineering Ltd. The cord was wrapped around the vessel which was then enclosed in asbestos cloth to contain the heat. The temperature, which was recorded by a thermocouple, was raised to 300°C for about 30 minutes, the vessel being pumped continuously. Baking was carried out prior to each experiment. In addition, after the apparatus had been baked, the two electrodes A₁ and A₂ were made positive with respect to the cathode and then subjected to electron bombardment for short periods, currents of about 500 milli-amps were quickly established. This procedure ensured that the walls of the reaction vessel, the electrodes and the filament were in the same condition for each experiment prior to the admission of the gas.

The filament heating was provided by a small mains transformer, the potential drop across the ends of the filament being about 3 volts. The accelerating potential applied to the electrons was obtained from a variable resistance connected across a D.C. supply, while the current and voltage measurements were

recorded by AVO-meters, type Mark 8. Vacuum greases were provided by Edwards High Vacuum. Apierzon 'N' being used for the tops and Apierzon 'L' for the cone and socket connections, both these greases have vapour pressures of less than 10^{-6} m.m. Hg. at room temperature. All the mercury used had been distilled three times at low pressure and was guaranteed clean by the supplier. Before the erection of the apparatus all the glass-ware was cleaned, first in chromic acid and then thoroughly washed out with distilled water and dried.

The carbon films were prepared by burning naphthalene in air and depositing the carbon onto thin metal foil (electrode A₂). The metal foil holding the carbon deposit was then placed in a tube furnace and heated to about 500°C. in a continuous flow of nitrogen, after which it was transferred to the reaction vessel. The area of the metal foil onto which the carbon was deposited was 6 cms x 8.5 cms. and the carbon films usually weighed about 6 milli-grams. The weight loss of carbon was determined by weighing the metal foil holding the carbon at the beginning and end of each experiment using a "Nivoc" aperiodic balance, the

accuracy of the weighings being ± 0.10 milli-gms. Care was taken to adopt the same technique for weighing the carbon in each experiment, this was considered important because of the taking up of moisture by the carbon and possible changes in any surface oxide, these being unknown factors which presumably varied with the time of exposure of the carbon to the atmosphere.

An extensive series of experiments was initially carried out with this apparatus using a flow of CO_2 , while later experiments with static charges of gas involved the exposure to electron bombardment of CO_2 , CO and CO_2/CO mixtures; some experiments were also performed with a flow of CO. The details of these experiments together with the results and interpretations are described in the next chapters.

2. Flow experiments with CO_2 .

(i) Weight loss of carbon: A series of experiments was carried out in the presence of carbon with a continuous flow of CO_2 passing through the reaction vessel at pressures of the order of $60 - 70\mu$ and 20μ . The filament was heated to about 900°C . and with the anode A_1 held 25 volts positive with respect to the

FIG.5 (a). CARBON OR BARE METAL FOIL AT A
POSITIVE POTENTIAL W.R.T. FILAMENT.

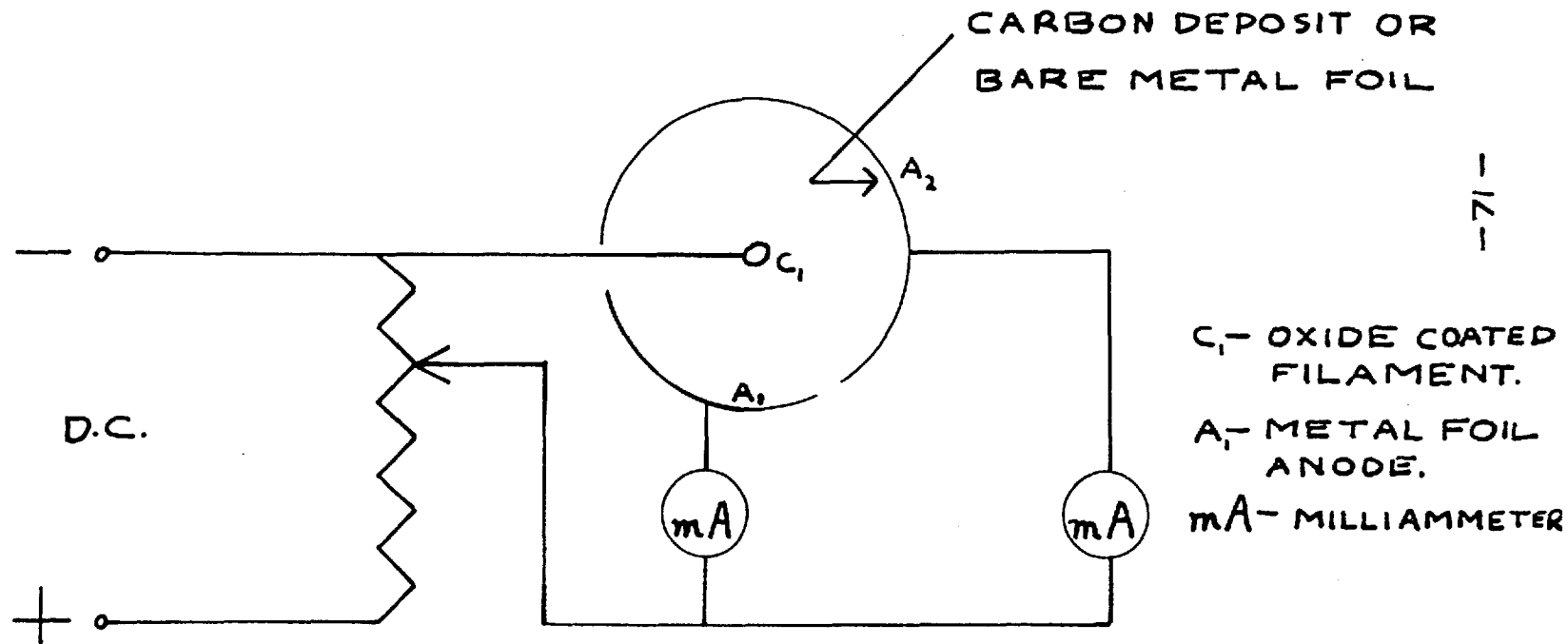


FIG. 5(2). CARBON OR BARE METAL FOIL AT
SAME POTENTIAL AS FILAMENT.

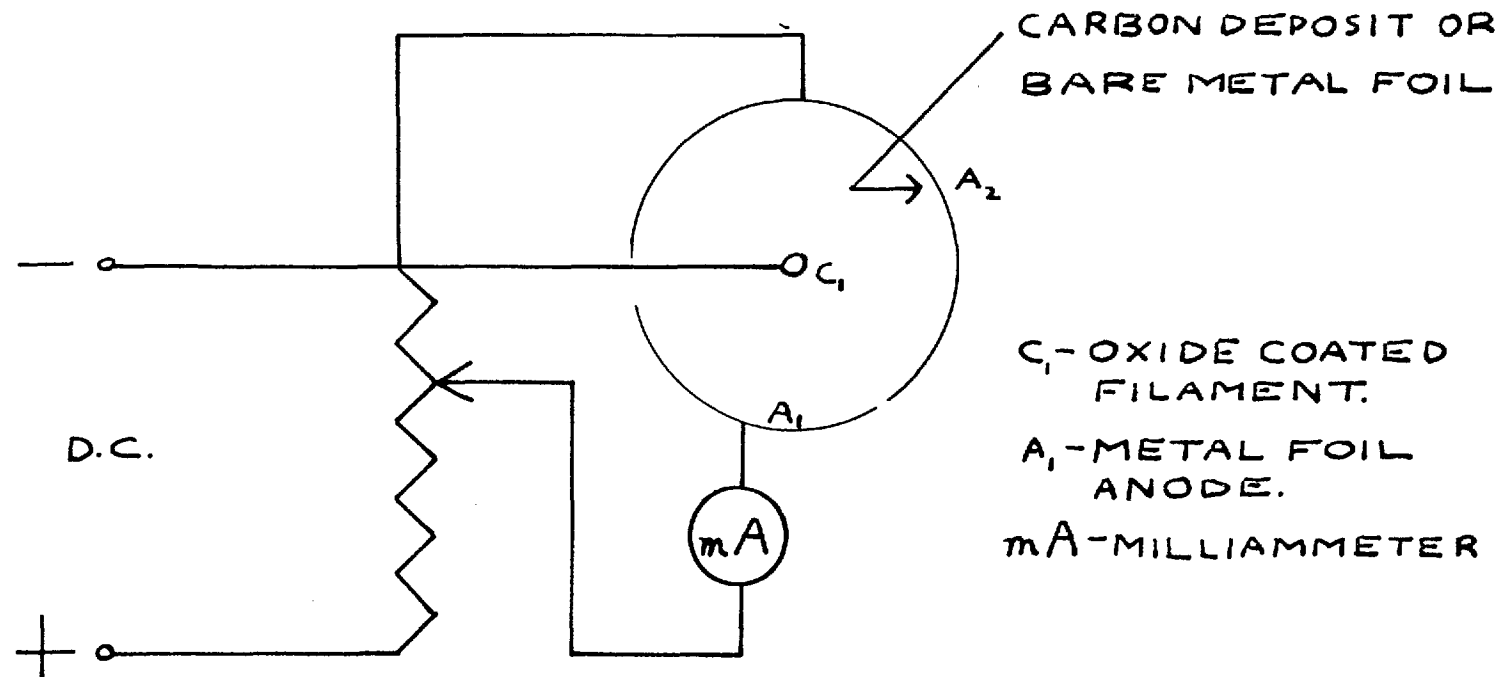
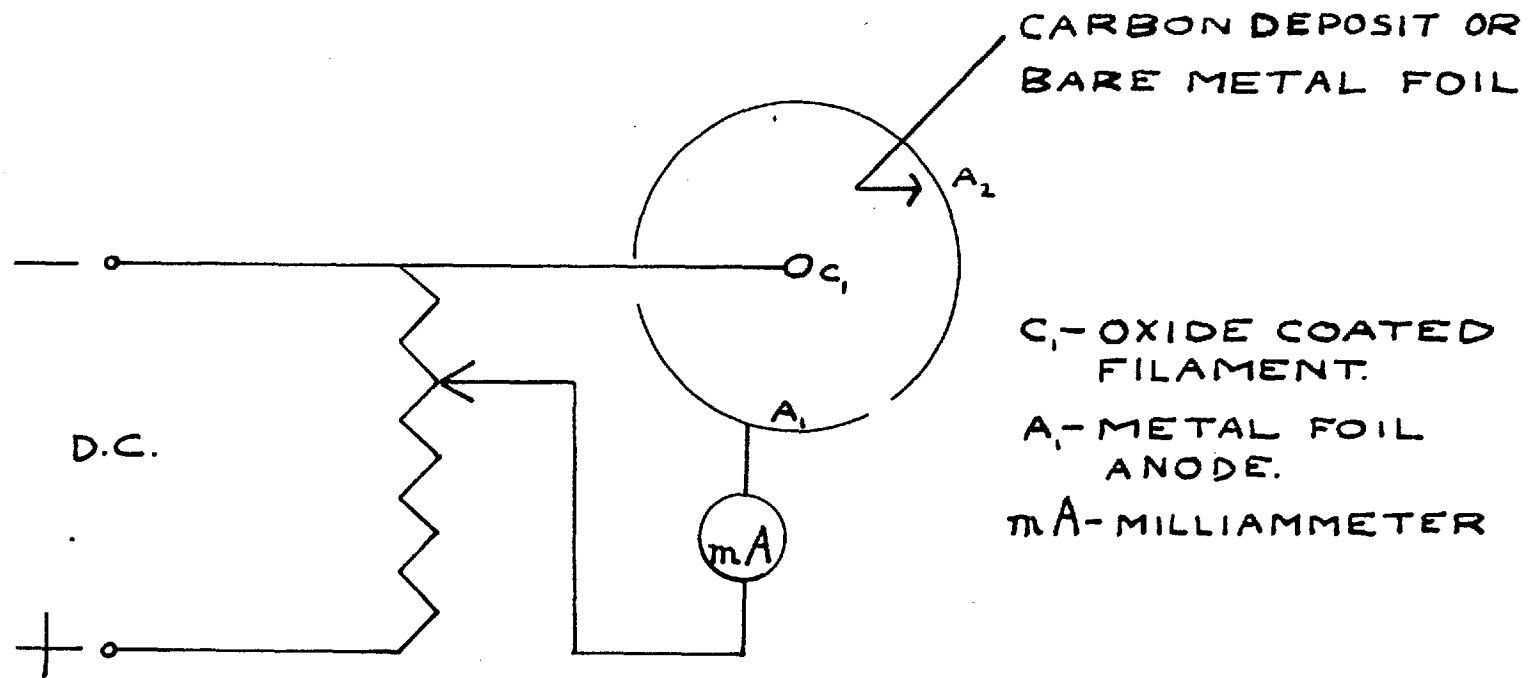


FIG.5 (c). CARBON OR BARE METAL FOIL
SUSPENDED IN REACTION VESSEL.



cathode a discharge was produced in the CO_2 . The experiments were performed with the second and larger electrode A_2 , upon which the carbon was deposited, in one of the following three conditions:-

- (a) at a positive potential of 25 volts with respect to the cathode.
- (b) at the same potential as the cathode.
- (c) merely suspended in the reaction vessel and therefore insulated from the other electrodes.

The electrical circuits corresponding to these three conditions are illustrated in Figs. 5(a) (b) and (c). The purpose of these experiments was to determine whether the active species produced in the CO_2 by the accelerated electrons and which attacked the carbon were neutral, or positive or negative ions.

A typical run will now be described in detail. The CO_2 was first introduced into the reaction vessel and by adjusting the needle valve the required flow pressure was achieved. The electron accelerating potential of 25 volts was applied between the cathode and the anode A_1 with the carbon on the electrode A_2 in one of the three conditions specified. The filament was then switched on and the stop-clock started. During

the time the filament was on readings were taken at suitable intervals of the electron emission current to A_1 , with the carbon in condition (a) the current to A_2 was also recorded. Readings were also taken of the maximum accelerating potential being applied to the electrons, while appropriate checks were made with the Mcleod to ensure that the CO_2 pressure remained appreciably constant. The CO_2 under electron bombardment was allowed to flow for times ranging from 10 to 150 minutes; at the end of a run the CO_2 supply was closed and with the reaction vessel evacuated readings of the emission current continued to be taken for a further 2 or 3 minutes. Any weight loss of carbon occurring was determined by weighing the electrode A_2 containing the deposit at the beginning and end of the run. The appearance of the discharge produced in the CO_2 calls for comment. It took the form of a light blue glow which was most intense in the region between the cathode and the electrodes. It was not possible to tell if the glow was actually on the carbon surface but it was often very close to it. The visible blue glow corresponds to a wavelength of about $5000 \text{ \AA}$ or about 2.5 eV, it is to be noted that a low lying

excited state of atomic oxygen occurs at about 2 volts and suggests that part of the blue glow observed is due to excited oxygen atoms.

The effect of having the carbon in the three different conditions specified in the reaction vessel is illustrated in Tables 2 and 3 and in the graphs shown in Fig. 6(a) (b) and (c). These graphs are of the measured weight loss of carbon (milli-grams) plotted against the corresponding total number of milli-amp. minutes recorded during the experiment. The significance of the total milli-amp. minutes is that it represents the total number of electrons available for impact with the CO_2 during the experiment, although not all the electrons emanate from the filament, as some may be produced by ionization of the CO_2 . The almost complete lack of data for the distribution of energy of electrons in an electric field in a gas makes it impossible to estimate the most probable electron energy, it can only be said that the electrons will possess energies not exceeding 25 volts. Hence a comparison of the weight loss of carbon for a given number of milli-amp. minutes under the three conditions outlined above is intended to indicate whether the

FIG. 6(2). CARBON POSITIVE W.R.T. FILAMENT.

○	WITH MERCURY VAPOUR	}	CO ₂ PRESSURE 60-70μ.
Δ	WITHOUT " "		
x	WITH " "	}	" " 20μ.
•	WITHOUT " "		

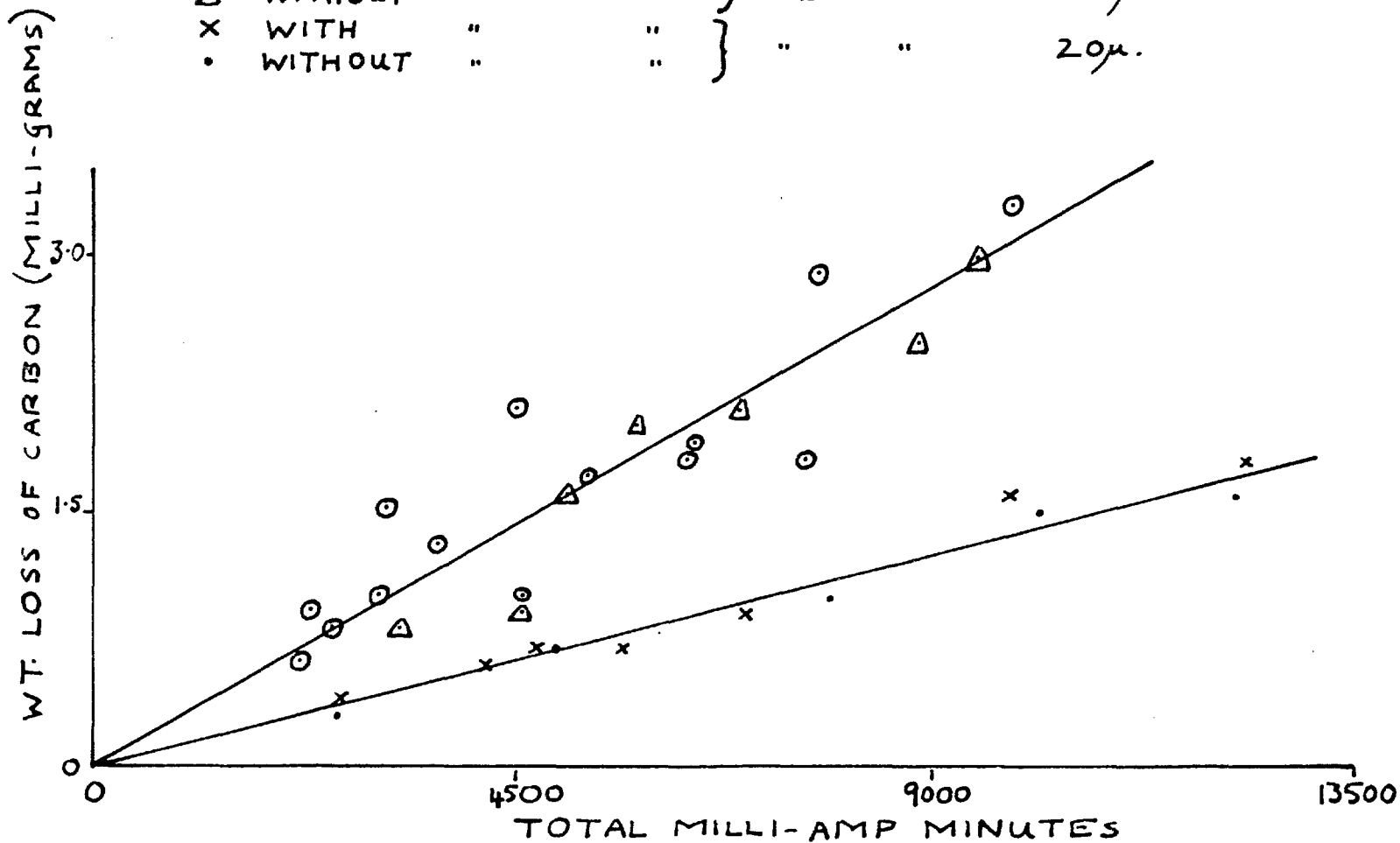


FIG. 6(b). CARBON AT SAME POTENTIAL AS FILAMENT.

○ WITH MERCURY VAPOUR, CO₂ PRESSURE 60-70 μ .
 x " " " " " " 20 μ .

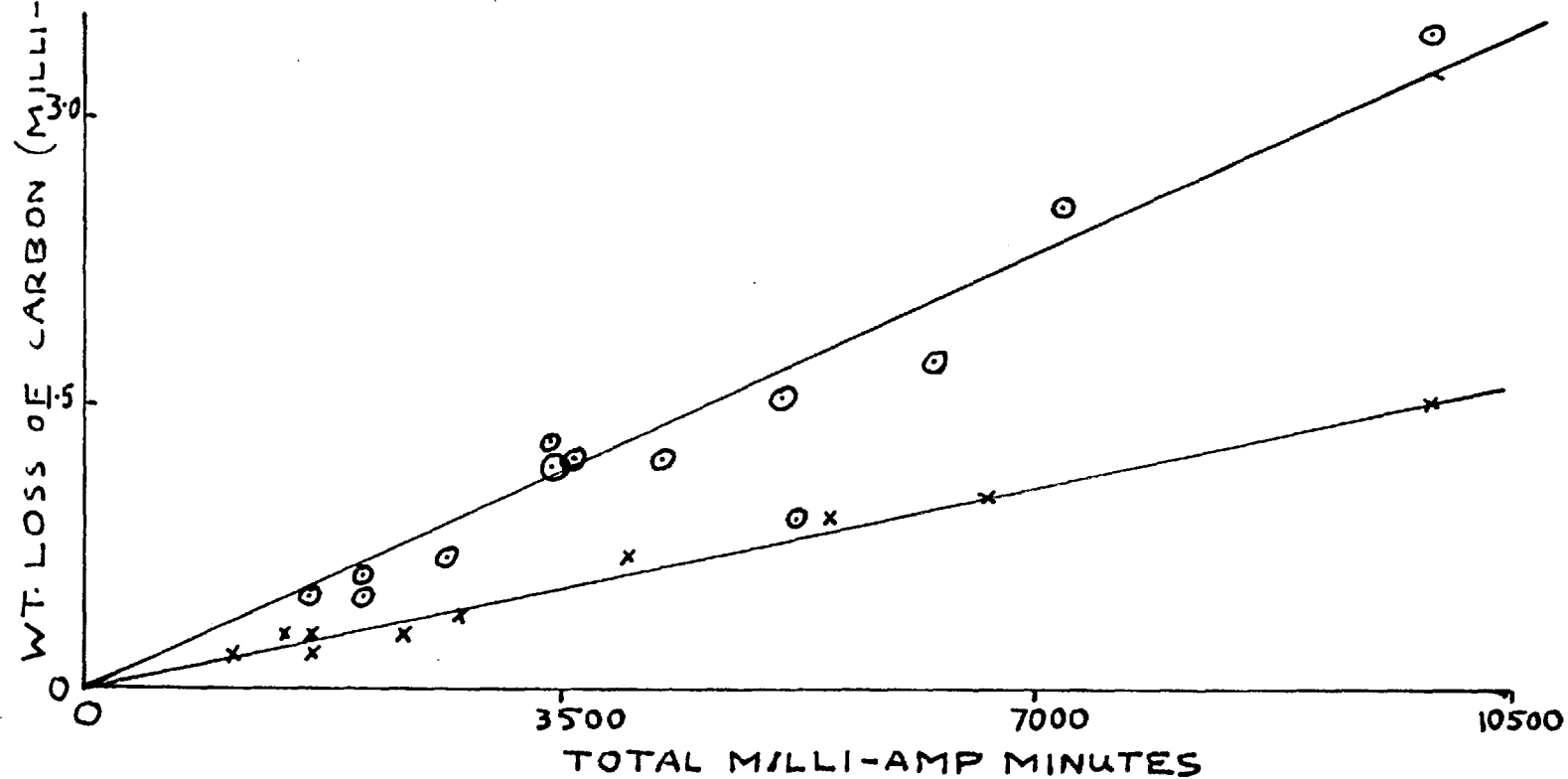
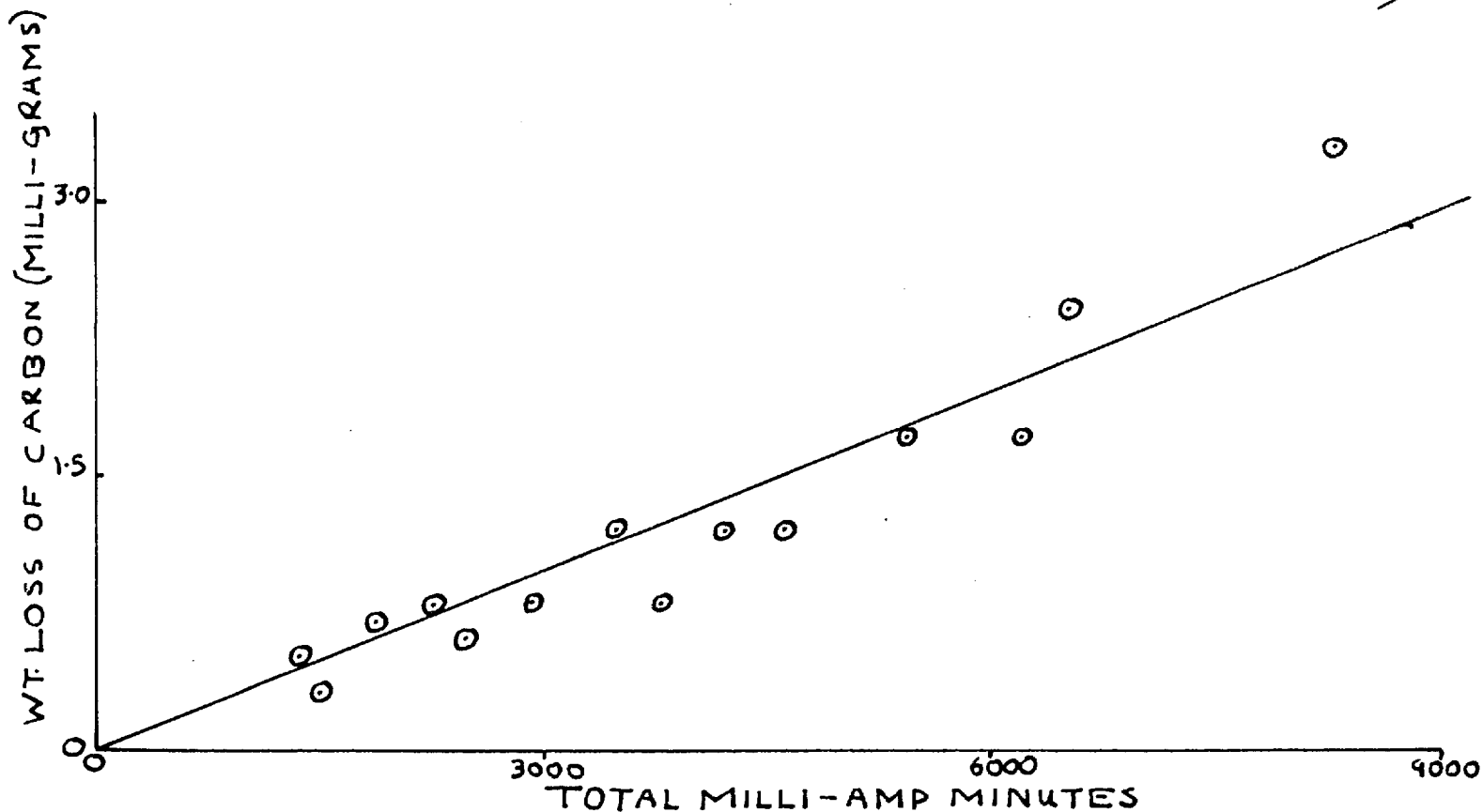


FIG. 6(c). CARBON SUSPENDED IN REACTION VESSEL.

○ WITH MERCURY VAPOUR, CO_2 PRESSURE 60-70 μ .



active species produced in the CO_2 by electrons in the energy range 0 - 25 volts and which attack the carbon are neutral, or charged positively or negatively.

Assuming that if the active species are electrically charged, they are all of the same sign, then the result of case (a), in which the carbon is at a positive potential with respect to the filament would indicate that positive ions are not responsible for the attack, since they would be repelled by the potential on the carbon. This result in itself provides strong evidence for supposing that the active species are in fact neutral, since it is known that the processes involving the formation of negative ions in CO_2 , the other alternative, have a very low probability. However, the possibility does exist that the active species are negative ions, to test this the carbon in case (b) was held at the same potential as the filament and so received no electron current. The electron accelerating potential is being applied between the filament and the small anode A_1 , the active species will hence be formed in the region between the filament and A_1 . If, as appears possible from the results of case (a), the active species are negatively charged they will be

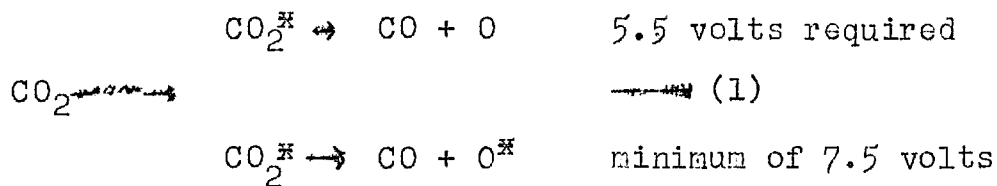
repelled by the carbon and attracted to the anode A_1 on which they would be neutralised and this, it is believed, would cause a reduction in the attack upon the carbon. The results of case (b) show no such reduction and suggest that the species are not negatively charged. Further evidence for the species not being negatively charged is provided by the result of case (c) in which the carbon is suspended in the reaction vessel and so insulated from the other electrodes. The formation of the active species here is similar to that in case (b); however in this case if negatively charged species are responsible for the attack and could furthermore reach the carbon, then the carbon would acquire a negative charge which would prevent the arrival of the similarly charged active species, a cessation in the attack should quickly occur. However the results of case (c) show no such cessation occurring and again suggest that the active species are not negatively charged.

The results obtained with the carbon in the three conditions specified strongly suggests therefore that the species causing the principal attack on the carbon are not electrically charged. The

possibility that the active species produced by the impact of the electrons with the CO₂ may possess some kinetic energy is not considered to affect the results, since this kinetic energy would, if present, be very small.

The identity of the active species cannot be considered fully established by the present results but the general considerations suggest that atomic oxygen is responsible by virtue of the ease with which it could be produced in the CO₂ and the fact that the species has been shown to be neutral.

Assuming that the primary electron collisions occur with the CO₂ only, the most likely steps in primary excitation (without ionization) are believed to be:-



required; the reaction with the carbon occurring as:

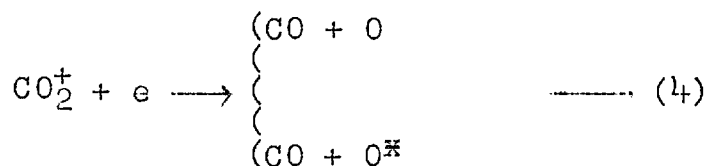


Although the active species has been shown to be neutral the formation of positive ions as an

intermediate process is possible. The positive ion formation is believed most likely to occur via the direct ionization of the CO₂ viz:



The fate of the CO₂⁺ ion is difficult to predict, since, at these relatively low pressures (60 - 70μ and 20μ), electron-ion homogeneous recombination leading to dissociation appears rather unlikely. Such a recombination process would however lead, in a similar manner to reaction (1), to the formation of carbon monoxide and neutral or excited atomic oxygen viz;



This process, if occurring, would help to explain the results of the studies on the effect that electrical clearing fields on the carbon has on the subsequent reaction with excited CO₂. It is felt that the fate of the CO₂⁺ ion is partly decided by the geometry of the system, since at low pressures recombination processes are very dependent on the presence of a third body.

Dissociative ionization processes leading to the formation of C^+ , O^+ etc. must be less likely to occur because of the higher energies required (≥ 20 volts); while negative ion formation must, because of the low pressures and nature of the process, have an extremely low probability.

A further primary process occurring at energies of about 16.5 volts is the complete dissociation of the CO_2 molecule into $C + O + O$. The relative importance of this process upon the reactions occurring with the carbon is at present unknown; however within the electron energy range being used this process will most likely have a lower probability of occurring than reaction (1).

A comparison of the results at 60 - 70 μ and 20 μ i.e. at a pressure ratio of about 3:1, shows that the weight losses are not in the ratio of 3:1 but are nearer 2:1. This may be interpreted as indicating that at 20 μ the distribution of electron energies is such as to provide more electrons with energies capable of inducing a reaction between CO_2 and carbon; this would also include the reaction $CO_2 \rightarrow C + O + O$ becoming of more importance.

It is seen from the graphs reproduced in Fig.

6 (a) (b) and (c) that the carbon weight losses increase linearly with total milli-amp. minutes. Since a flow of CO_2 is being used there should be, after an initial period, no further build-up of reaction products to interfere with the transport of the active species to the carbon. A steady condition should be reached whereby a constant fraction of the active species produced will react with the carbon, the remainder being lost by other means; the linearity should therefore not be unexpected. Any scatter observed in the results is considered to be due to variations in the electrode geometry and CO_2 pressure and also unavoidable discrepancies in the weighing technique.

(ii) Protective effect of carbon upon an oxide coated cathode:

A further set of experiments was carried out with the carbon omitted from the system. The conditions were identical to those in the experiments in which the carbon was present and which have been described in the previous part (i). CO_2 flow pressures of 60 - 70 μ and 20 μ were used and the anode A_1 was 25 volts positive with respect to the cathode. The other electrode A_2 , which was now bare, was as before in one of the

following three conditions:-

- (a) at a positive potential of 25 volts with respect to the cathode.
- (b) at the same potential as the cathode.
- (c) suspended in the reaction vessel and therefore insulated from the other electrodes.

The procedure adopted was identical to that used for the experiments described in part (i). The CO₂ flow pressure was first established in the reaction vessel; the accelerating potential was then applied between the anode A₁ and the cathode, and with the other electrode A₂ in one of the conditions specified the filament was switched on and the stop-clock started. Readings were then taken at suitable intervals of the emission current to A₁ (and to A₂ when in condition (a)). At the end of a run, and with the reaction vessel evacuated, readings of the emission current continued to be taken for a further 2 or 3 minutes.

It was quickly discovered that the presence or absence of carbon had a marked effect upon the emission current from an oxide coated cathode. The effect is best illustrated by a comparison of the graphs of electron emission current versus time

taken in the presence and absence of carbon. Typical graphs are shown in Figs. 7, 8 and 9 for CO₂ pressures of about 60 - 70 μ and in Figs. 10 and 11 for CO₂ pressures of about 20 μ . The protective effect due to the presence of the carbon is clearly indicated from the graphs by the marked difference in the behaviour of the emission current with and without carbon. In all cases the average level of emission obtained in the absence of carbon is considerably lower than that obtained with carbon. In many cases the initial currents observed with and without carbon were of the same order, but in the absence of carbon there quickly followed a rapid decay to currents of the order of 20 ma. and less, whereas with carbon present the final current was often of the order of 100 ma.

The result of case (c), in which an insulated carbon deposit is in the reaction vessel, indicates that the protective effect is due only to the presence of the carbon and not due to a change in the current receiving surface as could be concluded simply from the result of case (a).

Many other similar experiments were carried out and the results of these are included in Tables

FIG. 7. CARBON (OR METAL FOIL) AT A
POSITIVE POTENTIAL WITH
RESPECT TO THE FILAMENT.
APPLIED POTENTIAL 25V.
CO₂ PRESSURE 70 μ .

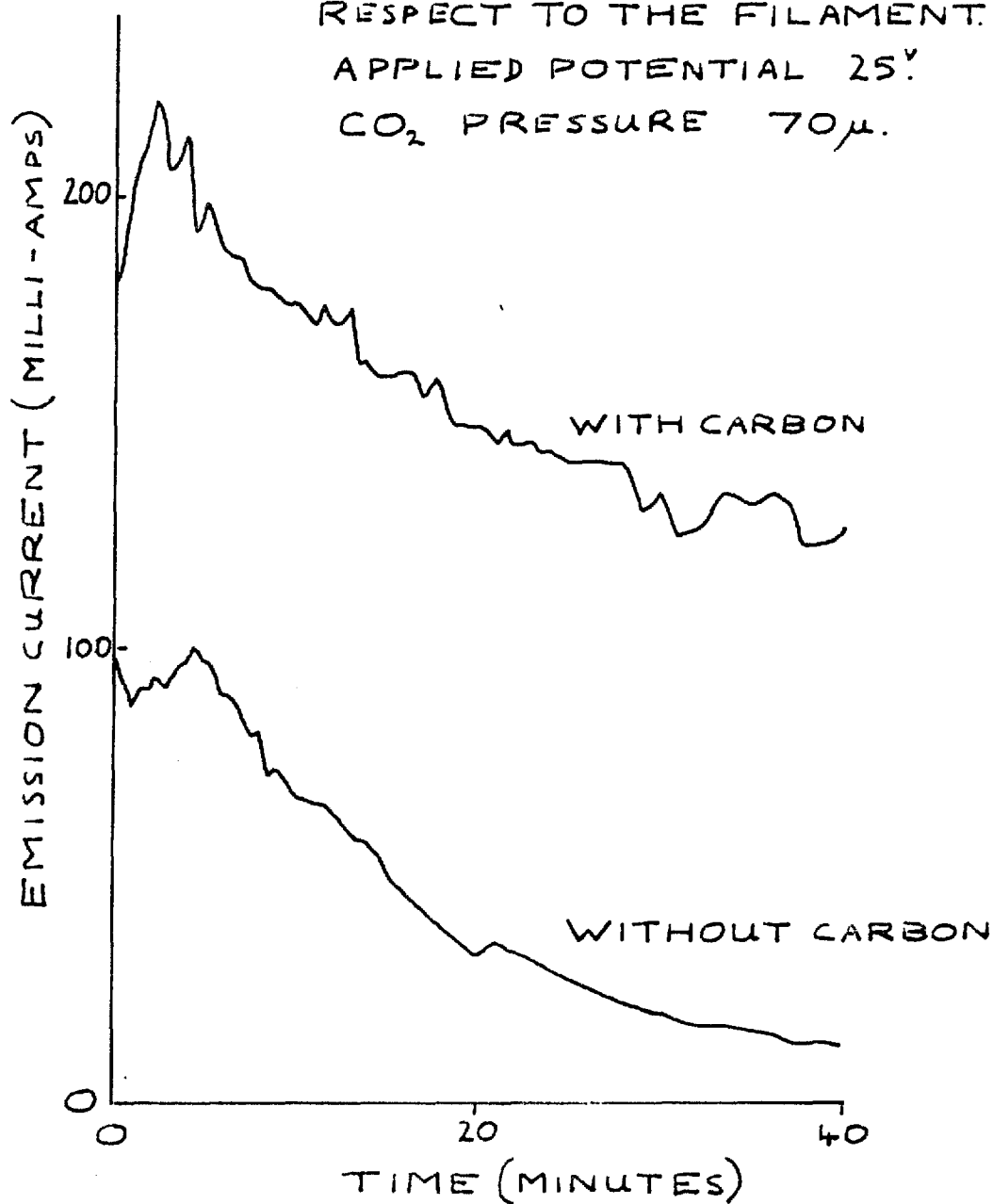


FIG. 8. CARBON (OR METAL FOIL) AT
SAME POTENTIAL AS FILAMENT.
APPLIED POTENTIAL 25%.

CO₂ PRESSURE WITH CARBON 75 μ .
" " WITHOUT " 60 μ .

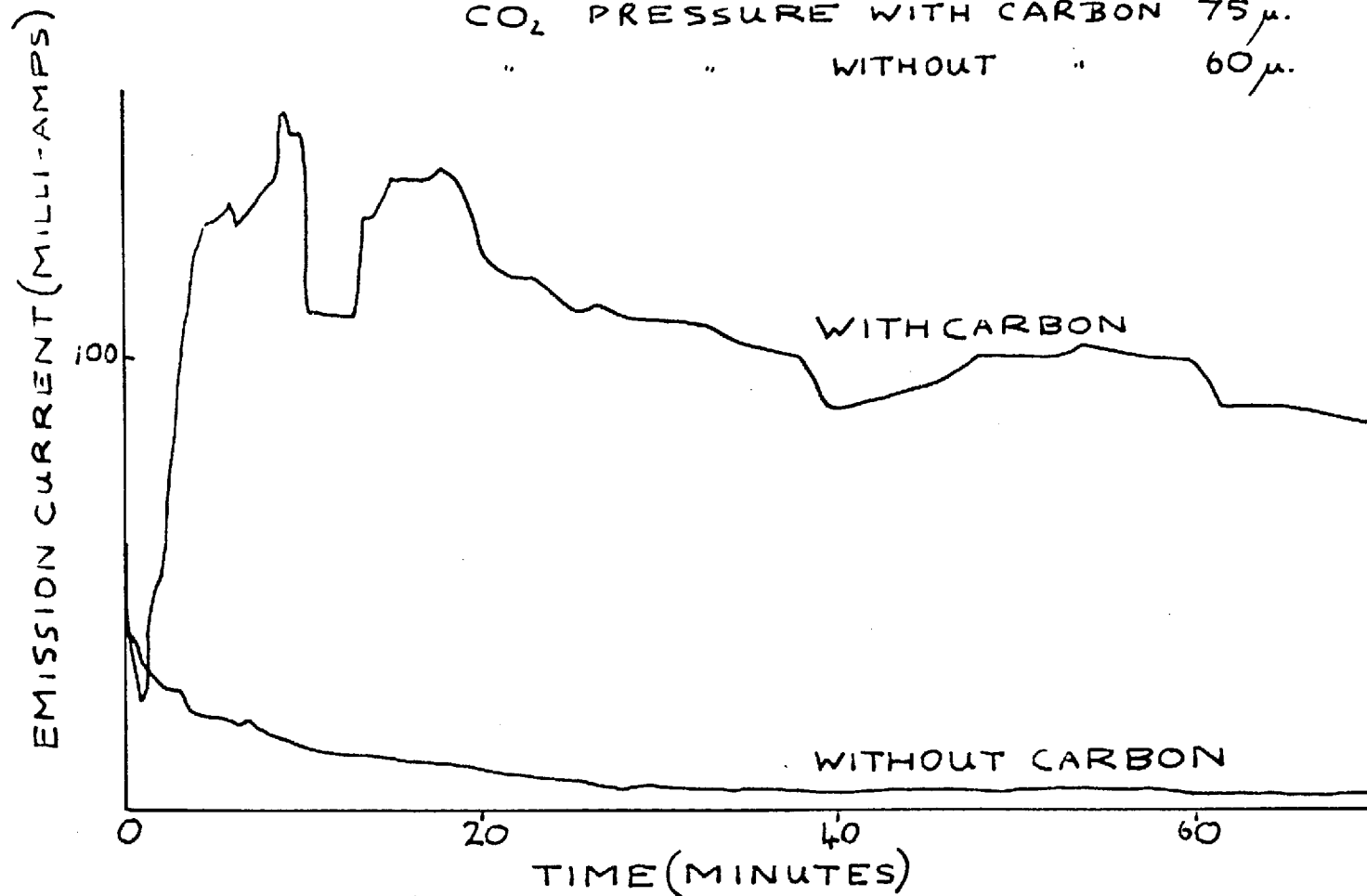


FIG. 9. CARBON (OR METAL FOIL)
SUSPENDED IN REACTION
VESSEL.

APPLIED POTENTIAL 25V

CO₂ PRESSURE WITH CARBON 65 μ .

" " WITHOUT " 73 μ .

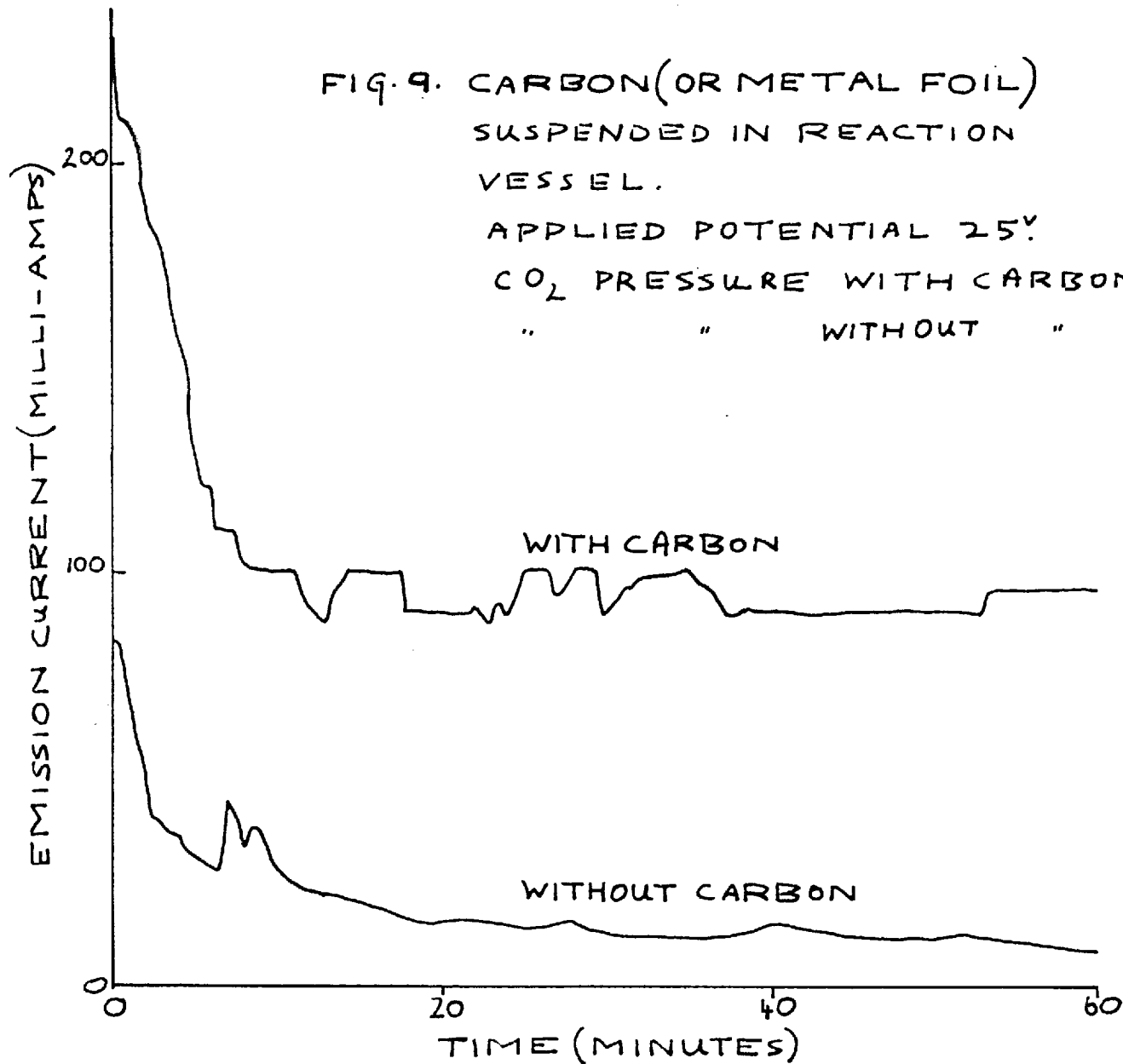
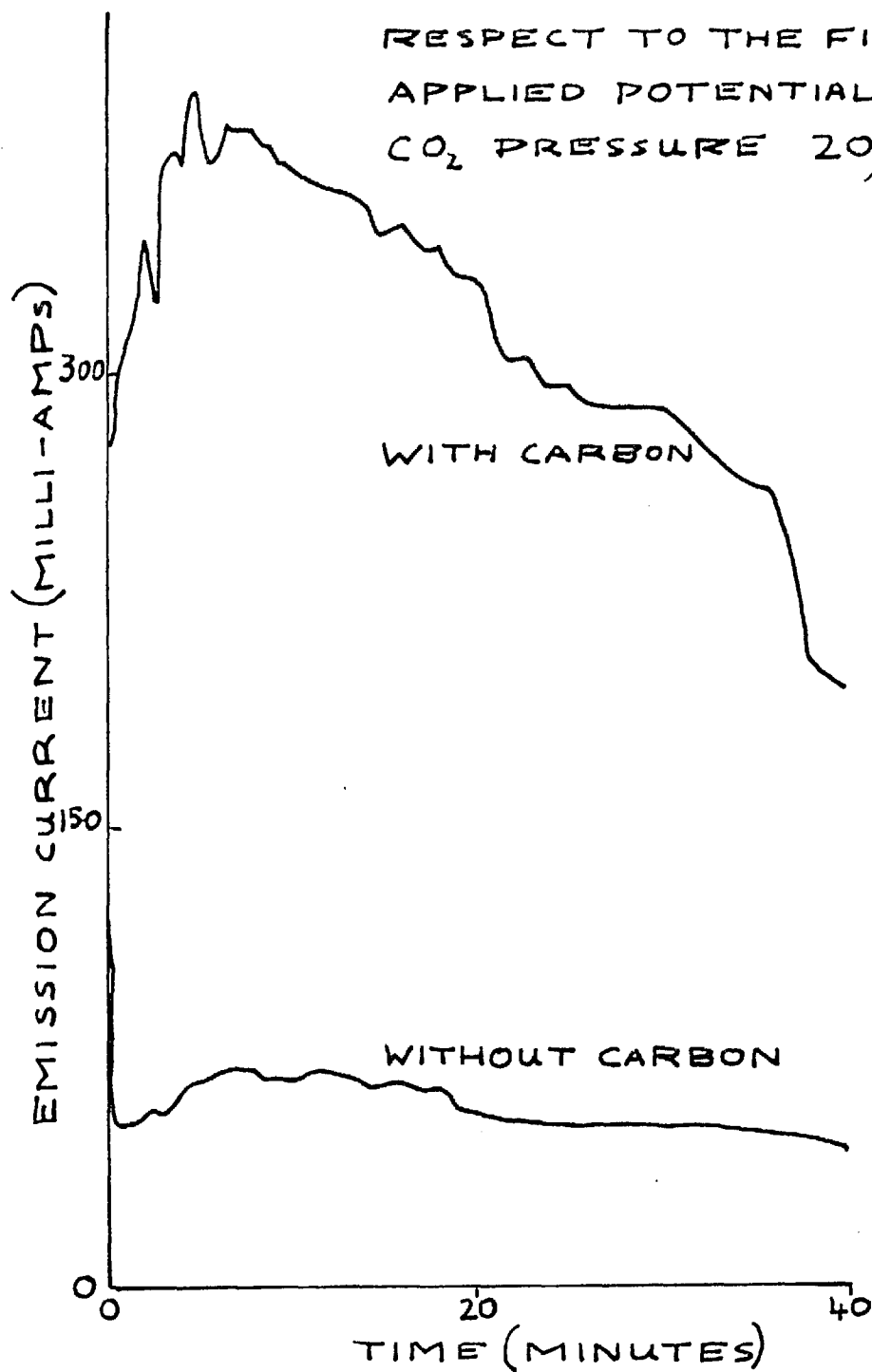


FIG.10. CARBON (OR METAL FOIL) AT A
POSITIVE POTENTIAL WITH
RESPECT TO THE FILAMENT.
APPLIED POTENTIAL 25V.
CO₂ PRESSURE 20 μ .



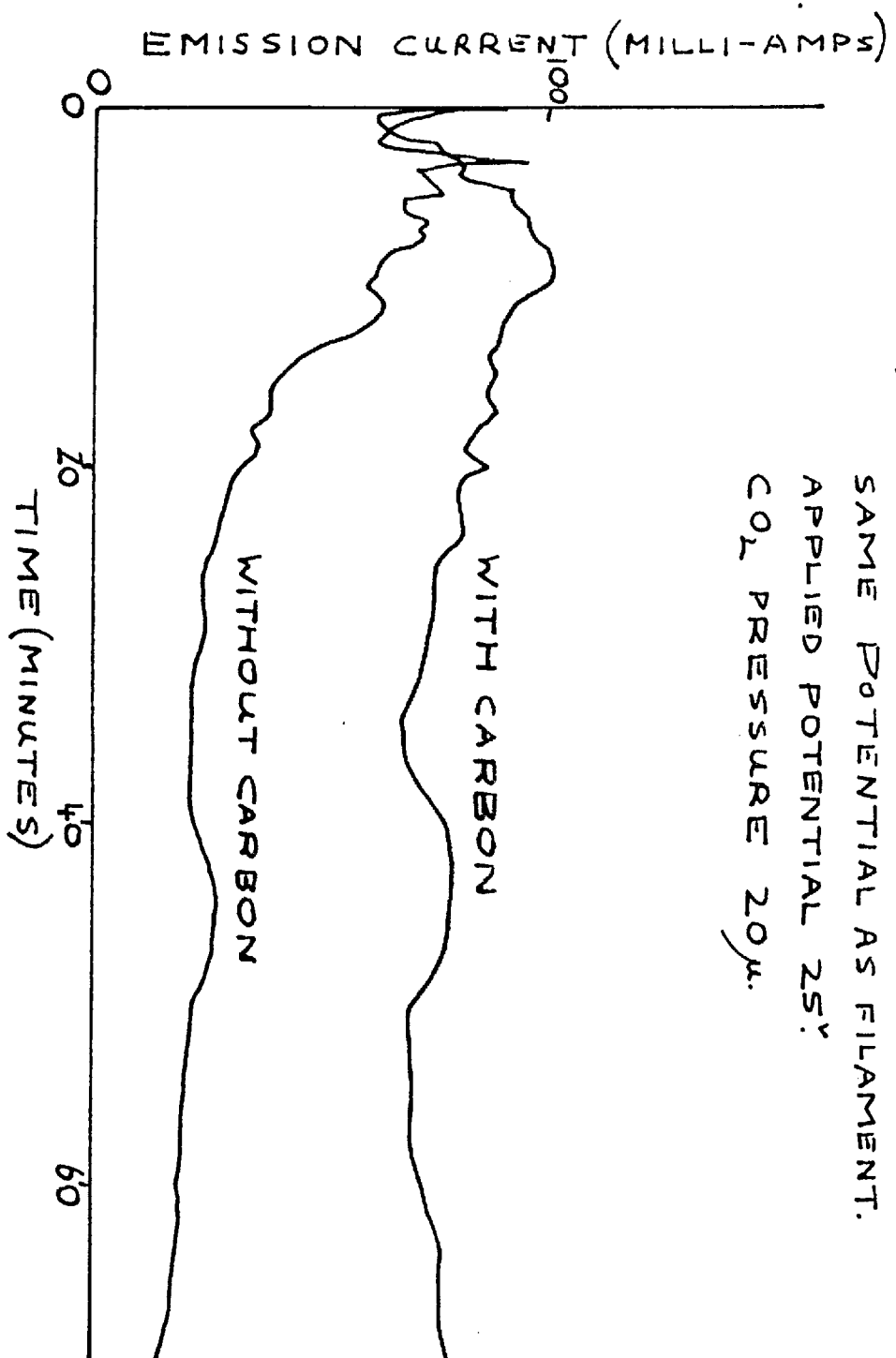


Fig. 11. CARBON (OR METAL FOIL) AT
SAME POTENTIAL AS FILAMENT.
APPLIED POTENTIAL 25V
CO₂ PRESSURE 20μ.

2 and 3 for CO_2 pressure of $60 - 70\mu$ and 20μ respectively. These tables enable a comparison to be made between the average emission current in milliamps obtained in the presence and absence of carbon for experiments of varying duration. The protective effect provided by the carbon is clearly apparent and by comparing the ratios of the average emission current for experiments of the same duration with and without carbon it can be seen that the factor of protection is of the same order for all three conditions examined. Further graphs representing emission current versus time in the presence and absence of carbon under the conditions specified are reproduced in Figs. 26 to 34 incl., for CO_2 pressures of $60 - 70\mu$ and in Figs. 35 to 38 incl., for CO_2 pressures of about 20μ , these are contained in the Appendix.

All the results quoted involved the use of aluminium foil for the electrodes A_1 and A_2 which restricted the pre-heating of the carbon films to temperatures of about 500°C ; however some early work on the protective effect of carbon upon an oxide coated cathode was carried out using tungsten foil

FIG. 12. CARBON (OR METAL FOIL) AT
A POSITIVE POTENTIAL
W.R.T. FILAMENT.
CARBON PRE-HEATED TO
1000°C.
APPLIED POTENTIAL 25V.
CO₂ PRESSURE 61-63μ.

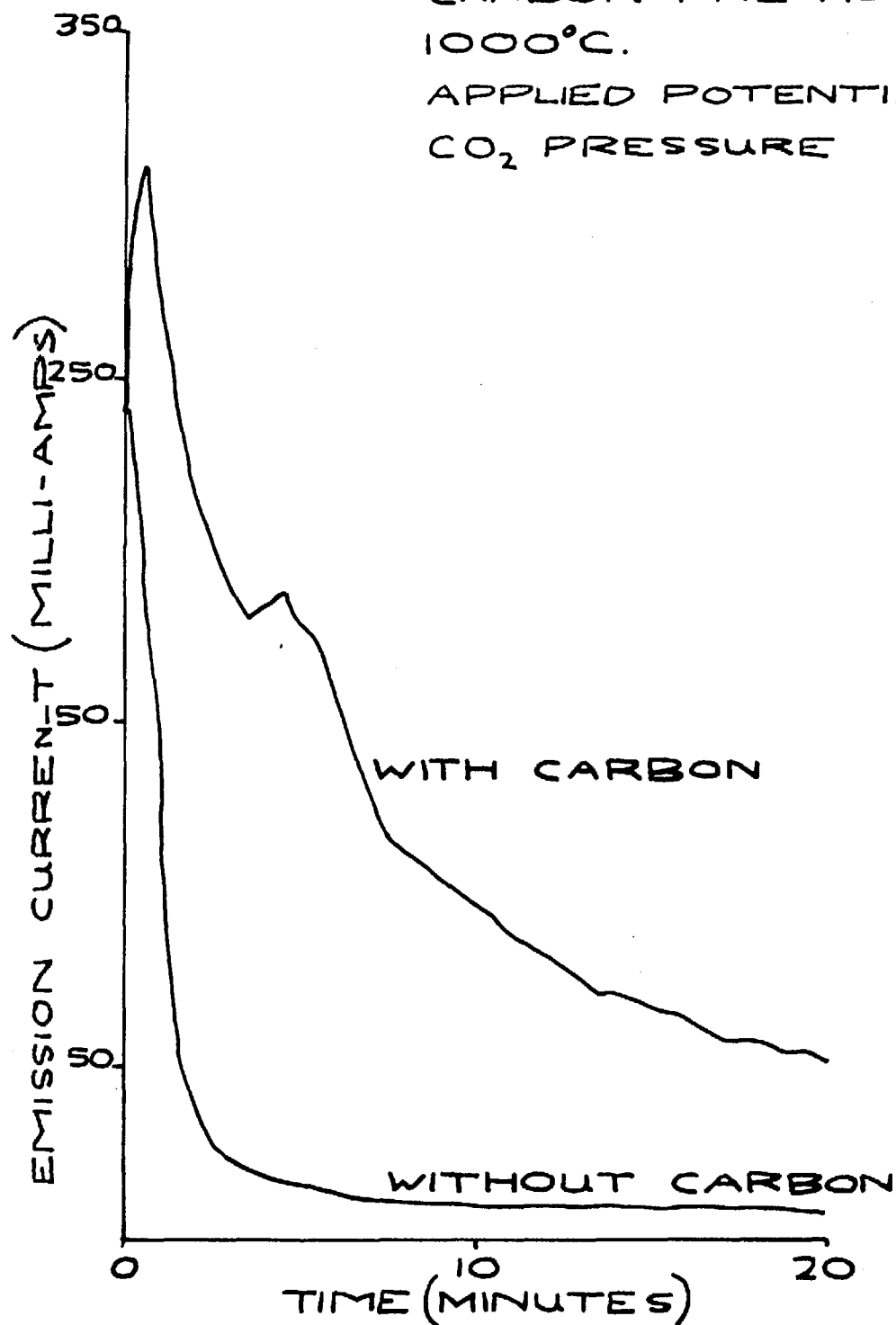


FIG. 13. CARBON (OR METAL FOIL)
AT SAME POTENTIAL AS
FILAMENT.
CARBON PRE-HEATED
TO 1000°C .
APPLIED POTENTIAL 25.
 CO_2 PRESSURE $61-65\mu$

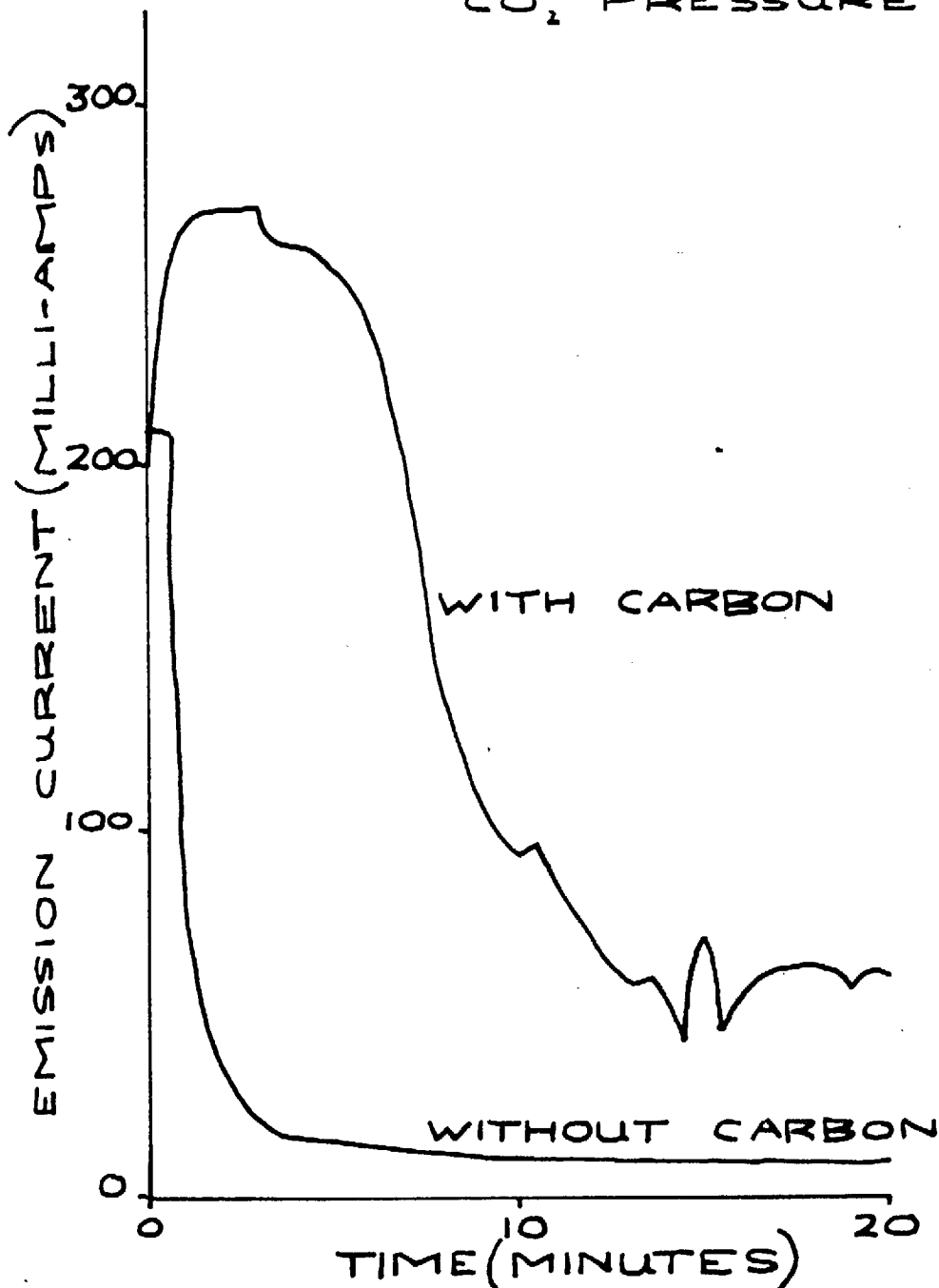
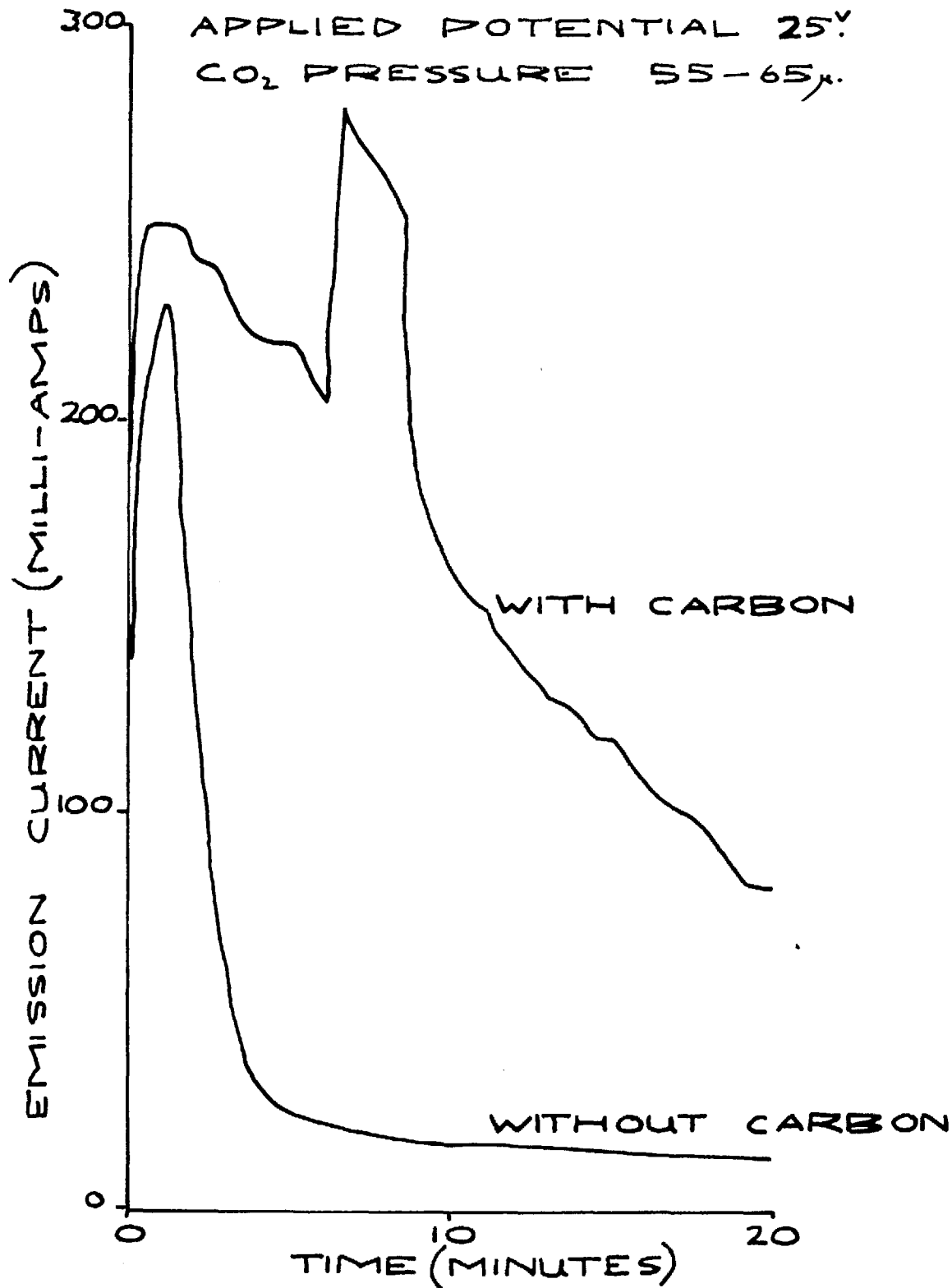


FIG. 14. CARBON (OR METAL FOIL)
SUSPENDED IN REACTION VESSEL.
CARBON PRE-HEATED TO 1000°C .
APPLIED POTENTIAL $25^{\vee}$.
 CO_2 PRESSURE $55-65\mu$.



which enabled pre-heating of the carbon to be carried out at temperatures of about 1000°C. The results of these experiments showed the protection to be identical with the subsequent experiments using aluminium. Graphs representing the emission current versus time in the presence and absence of carbon using tungsten foil are reproduced in Figs. 12, 13 and 14.

The interpretation of this protective effect is that the accelerated electrons are producing in the CO₂ active species capable of attacking both the carbon and the filament. With carbon in the reaction vessel there is a consequent reduction in the attack upon the filament due to the removal by the carbon of a large fraction of the active species. Assuming that similar collision processes are occurring in the CO₂ in the presence and absence of carbon and that the probability of accommodation on the bare metal foil (in the absence of carbon) is the same as on carbon, it would appear from the results that the active species are de-activated by reaction with the carbon but not with the bare metal foil. Hence in the absence of carbon a higher proportion of active species are available for attack

upon the filament.

It was found that the level of emission was usually higher for case (a) in which the carbon (or bare metal foil) was held at a positive potential with respect to the cathode. This, it is believed, may be due in part to the position of the carbon in relation to the region in which the active species are formed. Since in case (a) the carbon is acting as an anode it will be receiving a major portion of the electron current and hence most of the active species will be formed adjacent to the carbon and have a greater chance of collision with it followed by de-activation. In cases (b) and (c), however, the formation of the active species occurs between the filament and the small metal anode A_1 and in order to reach the carbon these species will have to by-pass the filament, thus the chance of a collision with the filament is increased.

The recovery of the emission observed by heating the filament in vacuo suggests the following sequence of events: reaction of the excited CO_2 with the filament resulting in the formation of BaO due to oxygen combining with the metallic barium

which is present in the surface of the filament and which is believed to be responsible for the electron emission. Subsequent heating in vacuo results in a reduction of the BaO by the substrate metal (which in this case is nickel together with small traces of silicon and magnesium), with regeneration of barium metal and recovery of the emission.

Wagener in his book "The Oxide Coated Cathode" quotes the results of Hermann & Krieg's work on the influence of gases and vapours on the emission from an oxide coated cathode (Ann. Phys. 4, 441 (1949)). Their results for CO₂ are similar to those obtained in the present work, although the conditions were somewhat different. They found also that the poisoning effect of the ionised gas was no greater than that of the corresponding molecule.

It is of special interest that reaction of the active species with the carbon in the cold appears to occur more readily than with the metallic barium on the surface of the filament at 1000°C.

These observations explain the facts observed in the preliminary static experiments, where CO₂

was decomposed both in the presence and absence of carbon. In the absence of carbon the decomposition products $\text{CO} + \text{O}$ are prevented from recombining by the subsequent reaction of the oxygen with the filament.

(iii) Effect of mercury vapour:

The experiments described above were performed in the presence of mercury vapour which at room temperature has a vapour pressure of the order of 1.5μ . The effect of its removal from the gas phase on the carbon weight loss was studied.

The mercury vapour was removed using petroleum ether-cardice cold traps between the McLeod and the reaction vessel, and the reaction vessel and the diffusion pump. The temperature of such a trap is about -80°C at which the vapour pressure of mercury is about $3 \times 10^{-6}\mu$. However the presence of a mercury manometer in the upstream section means that some mercury vapour will be swept through the needle valve with the CO_2 . It appears likely that the effective reduction in the concentration of the mercury vapour was by a factor

of about 10^3 or 10^4 . The experiments were carried out with the carbon film, supported on electrode A_2 , at the same positive potential of 25 volts with respect to the cathode as electrode A_1 , and with CO_2 pressures of $60 - 70\mu$ and 20μ . The procedure adopted was identical to that used in the experiments described in part (i).

The role of excited mercury atoms as activators for many chemical reactions is well known. It appeared possible that the mercury atoms could produce active species by absorbing energy and transferring it to the CO_2 or would remove active species by acting as a "sink" for the oxygen atoms.

The effect of mercury vapour was investigated by comparing weight losses of carbon for a given number of milli-amp. minutes in the presence and absence of mercury vapour.

The results obtained with mercury vapour absent from the reaction vessel are given in Table. 4.; while a comparison of these results with those obtained in the presence of mercury vapour is provided by the graphs reproduced in Fig. 6 (a).

which is of carbon weight loss versus milli-amp. minutes at CO₂ pressures of 60 - 70 μ and 20 μ in the presence and absence of mercury vapour.

It can be seen that the mercury vapour plays an unimportant role in the reactions occurring in the CO₂ in the present system. The graphs show that the weight losses are independent of the presence or absence of mercury vapour, being of the same order in both cases. Evidence for the ineffectual role of mercury atoms in the CO₂/carbon reaction is further provided by the behaviour of the emission current with time. Typical graphs of emission current versus time obtained when mercury vapour is absent are reproduced in Figs. 15 and 16 for CO₂ pressures of 60 - 70 μ and Figs. 17 and 18 for pressures of 20 μ . These clearly show that the emission current follows the same pattern of behaviour as when mercury is present and suggests, by analogy with the effect noticed when carbon was absent, that mercury is unimportant in the present system.

(iv) Effect of electron bombardment:

The effect of prolonged electron bombardment upon

FIG. 15. CARBON AT A POSITIVE
POTENTIAL W.R.T. FILAMENT.
WITHOUT MERCURY VAPOUR.
APPLIED POTENTIAL 25V.
CO₂ PRESSURE 70 μ .

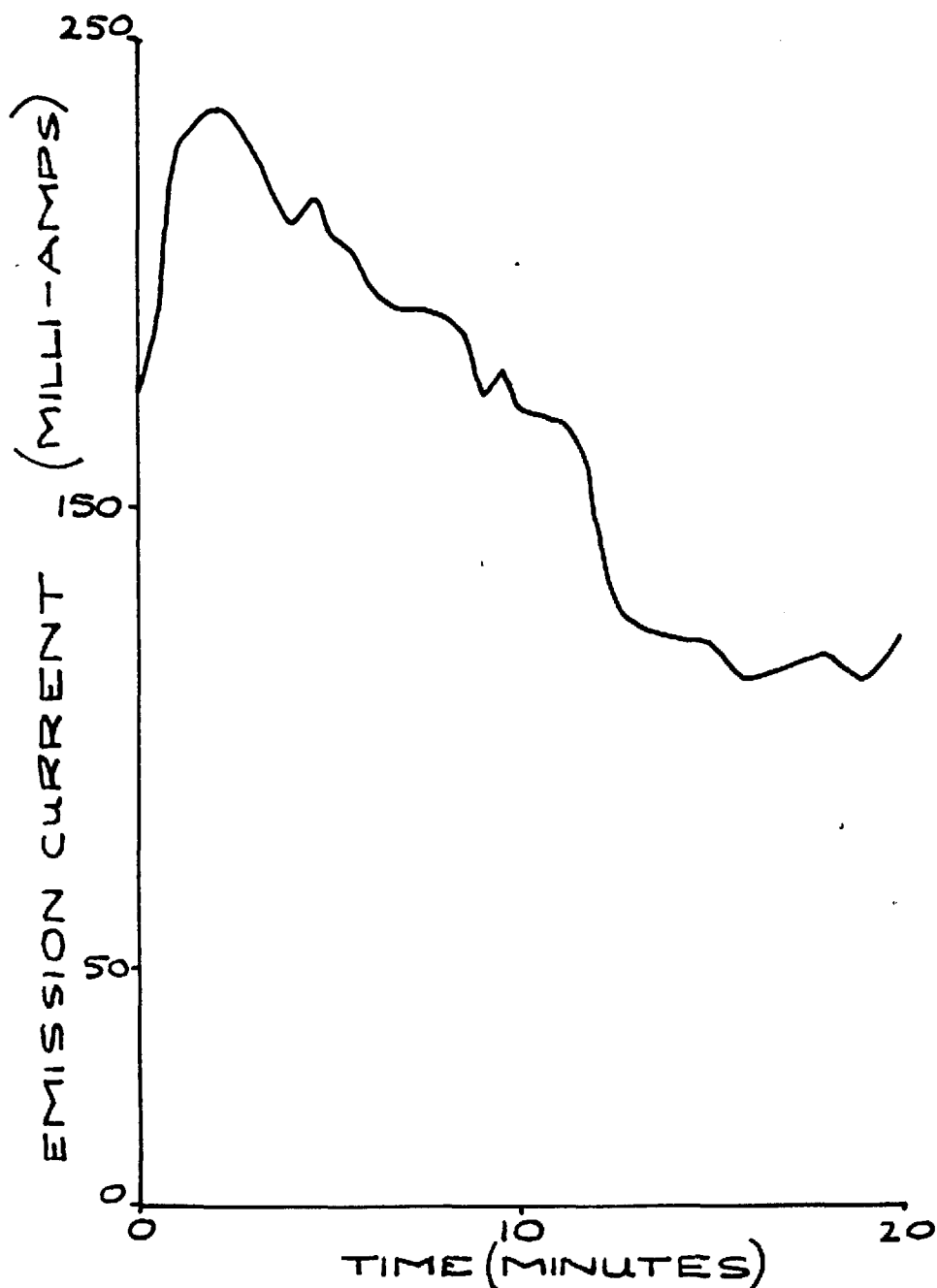


FIG. 16. CARBON AT A POSITIVE
POTENTIAL W.R.T. FILAMENT.
WITHOUT MERCURY VAPOUR.
APPLIED POTENTIAL 25V.
CO₂ PRESSURE 61 μ .

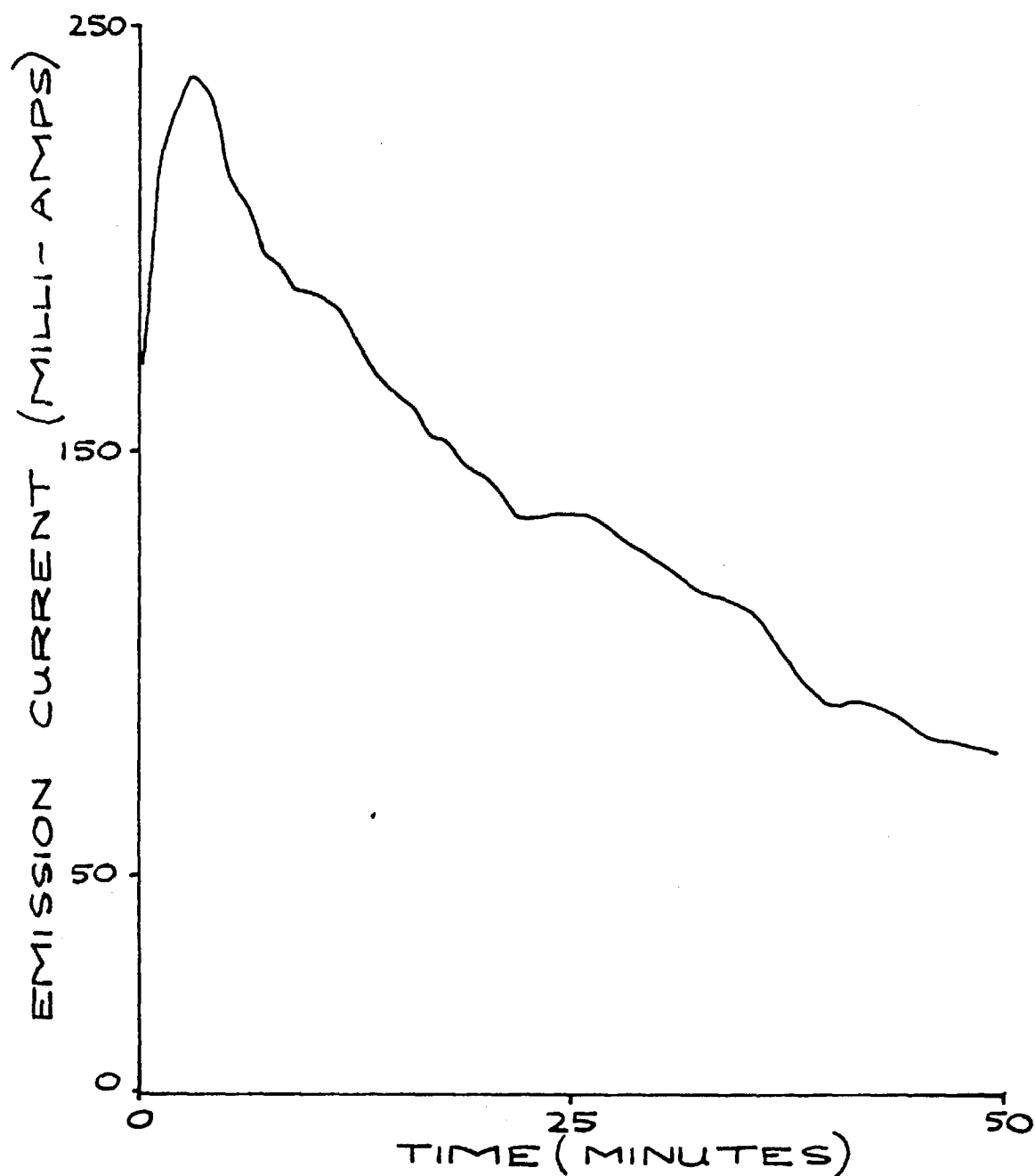
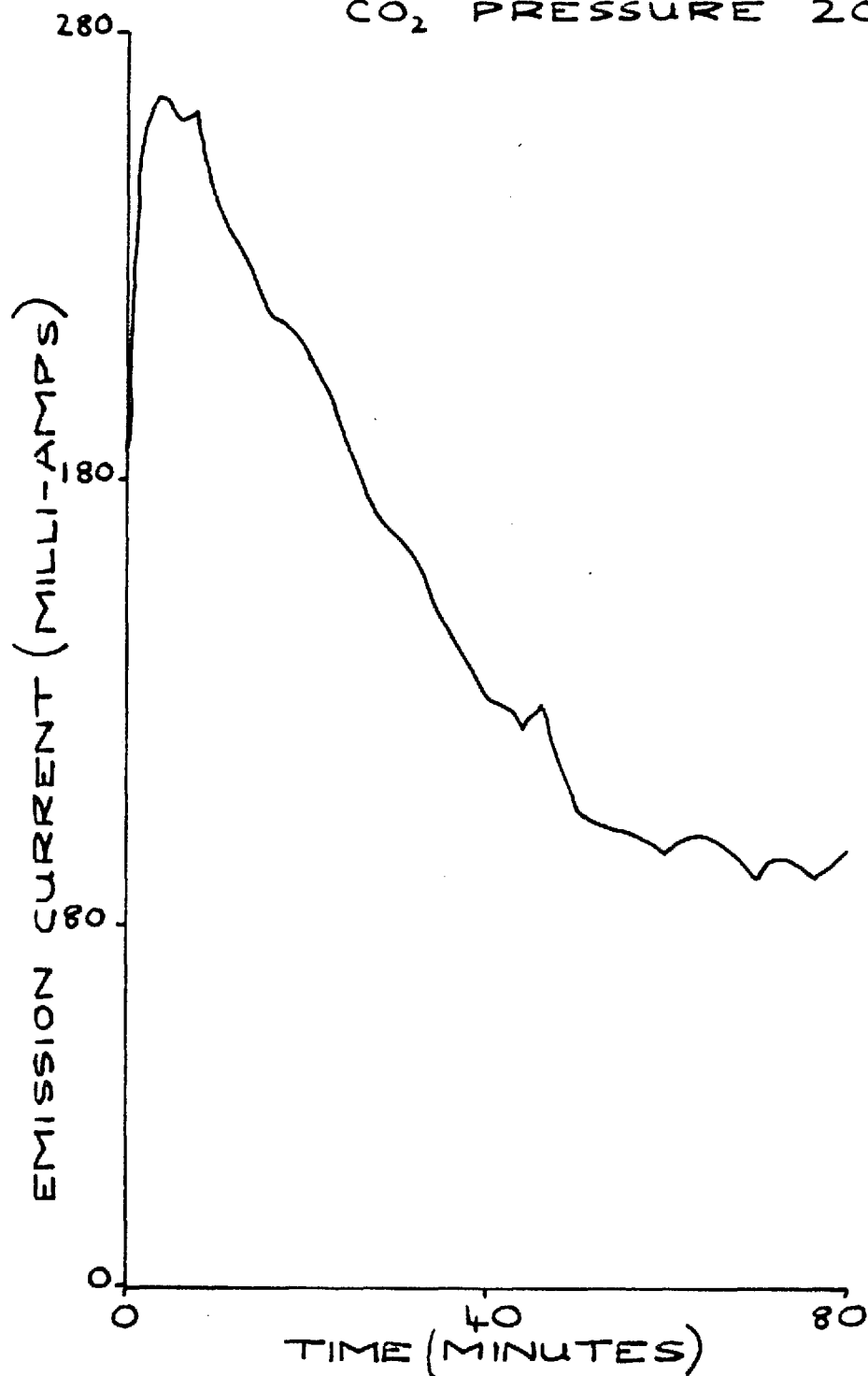


FIG. 17. CARBON AT A POSITIVE
POTENTIAL W.R.T. FILAMENT.
WITHOUT MERCURY VAPOUR.
APPLIED POTENTIAL 25V.
CO₂ PRESSURE 20 μ .



FIG. 18. CARBON POSITIVE WITH
RESPECT TO FILAMENT.
WITHOUT MERCURY VAPOUR.
APPLIED POTENTIAL 25V
CO₂ PRESSURE 20 μ .



the carbon in the absence of CO_2 was studied by carrying out experiments under vacuum with the carbon film held 25 volts positive with respect to the cathode. It was found that no weight loss of carbon occurred even after a 30 minute exposure resulting in the production of almost 13000 milli-amp. minutes. Any carbon weight loss observed in the presence of CO_2 was evidently due only to an attack by active species produced in the CO_2 by the accelerated electrons. It was also found that if the carbon deposit which had been bombarded with electrons under vacuum was then exposed to CO_2 in the presence of accelerated electrons, the resulting weight loss was of the same order of magnitude as that observed when using a fresh carbon deposit, other conditions being constant. The surface of the carbon film was apparently unaffected by the electron bombardment; the effect may however be somewhat different using electrons of considerably higher energy, due to the heating of the carbon for example.

(v) Experiments with 15 volt electrons:

It has been observed that the effect on the emission from an oxide coated cathode of a flow of CO_2 exposed

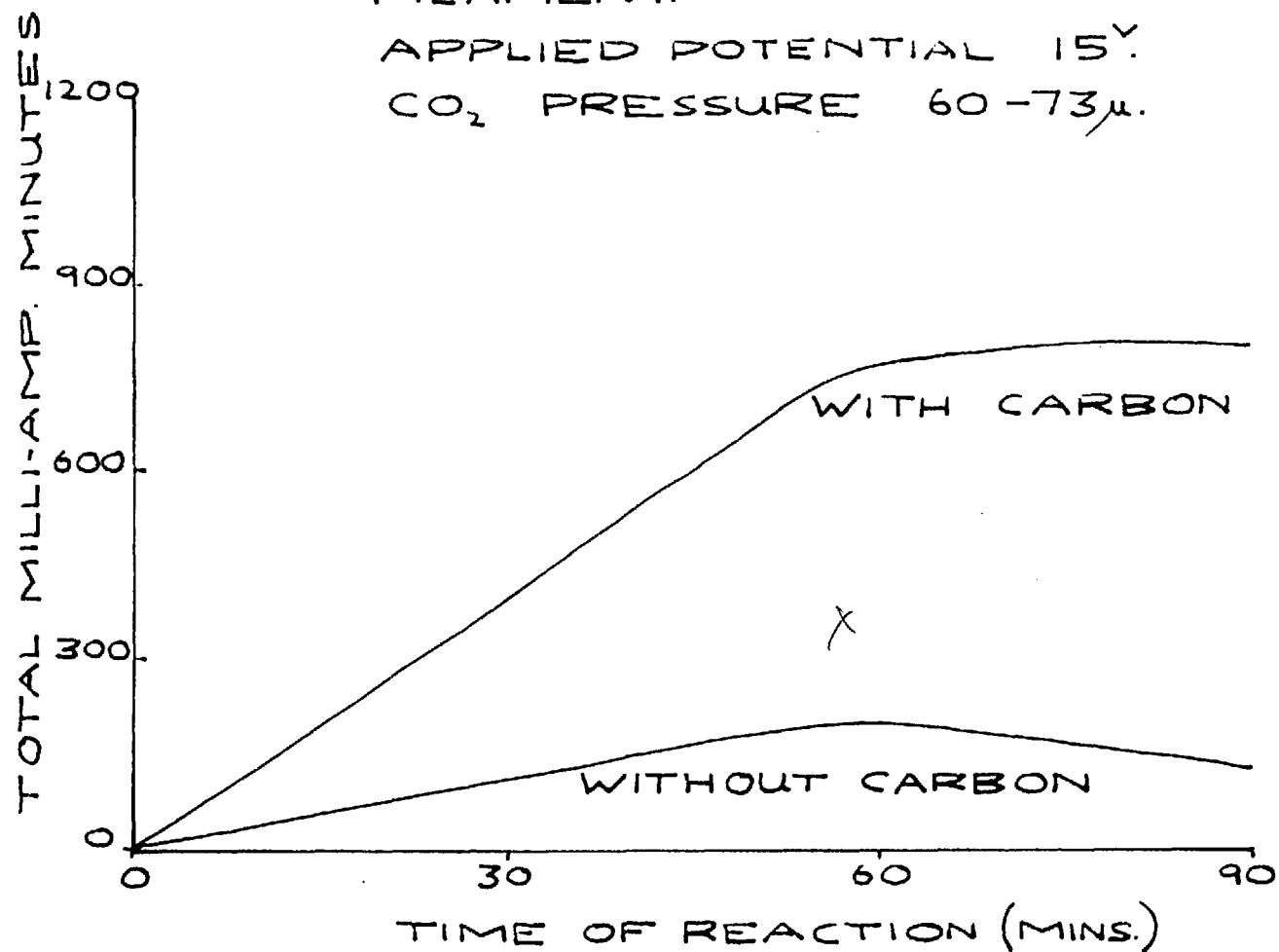
to electrons possessing energies not exceeding 25 volts depends on the presence or absence of carbon. This may provide a means of studying the radiation induced reaction between CO_2 and carbon under conditions where measurements of a weight loss of carbon and/or gas analysis of the reaction products could not be used.

Experiments have therefore been carried out in the presence and absence of carbon with a flow of CO_2 at pressures of 60 - 70 μ exposed to electrons possessing energies not exceeding 15 volts. The electrode A_1 and the carbon (or bare metal foil) were held 15 volts positive with respect to the cathode. The procedure was as before, with the CO_2 flowing the filament was switched on and the stop-clock started. Readings of the emission current to the two anodes were taken at suitable intervals. Losses in weight of carbon under these conditions were too small to measure because of the low emission currents obtained at this electron potential.

The results of these experiments are given in Table. 5 it can be seen that the average emission current obtained in the presence of carbon was in all cases greater than that obtained when carbon was absent,

FIG. 19. CARBON (OR METAL FOIL) AT A
POSITIVE POTENTIAL W.R.T.
FILAMENT.

APPLIED POTENTIAL 15V.
CO₂ PRESSURE 60-73 μ .



other conditions being constant. The difference is perhaps best illustrated by the graphs shown in Fig. 19 which represents the best lines drawn through the points representing the total number of milli-amp. minutes versus time of experiment obtained in the presence and absence of carbon. The maximum number of milli-amp. minutes obtained with carbon is seen to be about 800 while without carbon it is only about 150, these values being reached after about 60 minutes in both cases. It was often found that in the presence of carbon the initial current was of the order of 20 ma., with a subsequent decay to about 7 ma. Whereas without carbon initial currents were usually no higher than about 10 ma., followed by a decay to currents of the order of 1 or 2 ma.

It is suggested that the interpretation of the effect at 25 volts can again be used to explain the present observations, namely that the carbon is removing active species produced in the CO_2 by the accelerated electrons which would otherwise react with the filament. The presence or absence of carbon determines the extent of the reaction with the filament and hence the emission current received.

It is believed that the use of electrons possessing energies not exceeding 15 volts reduces the primary processes occurring in the CO_2 to dissociation into $\text{CO} + \text{O}$ which occurs at a minimum energy of 5.5 volts. The simple ionization of CO_2 is thought not to occur since it is known that the probability of ionization is zero at the ionization potential and the maximum energy the electrons are capable of possessing (<15 volts) must certainly be very close to, if not less than, the ionization potential of CO_2 (13.7 volts).

The effect observed on the emission current due to the presence or absence of carbon and the evidence of processes capable of occurring in the CO_2 under these conditions strongly suggests that atomic oxygen is the primary radiolysis product responsible for the attack upon the carbon. Relating this to the in-pile conditions is dealt with in the summary.

3. Static experiments with CO_2 and CO .

(1) Procedure: In this series, experiments were performed wherein static charges of pure CO_2 , pure CO and a CO_2/CO mixture were exposed to electron

bombardment for measured periods of time. The two electrodes A_1 and A_2 were both held at a positive potential of 25 volts with respect to the cathode. With the discharge on, readings of the electron emission current were recorded at suitable intervals and resulting changes in gas composition were measured. Upon completion of experiments with a particular gas a careful examination of electrodes and leads was made in order to see if any carbon deposition had occurred, this was of particular interest in experiments in which a high percentage of CO was present.

With one exception all the experiments with static charges of pure CO_2 were carried out in the presence of a carbon film. Initial CO_2 pressures of 60 - 90 μ were used while times of exposure to electron bombardment ranged from 5 to 7200 secs. After the discharge was switched off the final total pressure was recorded, after which the pressure of non-condensable gas was found by immersing the appendix on the reaction vessel in liquid air, the fall in pressure indicating the final pressure of CO_2 .

Experiments with static charges of pure CO were performed both with and without carbon. Initial

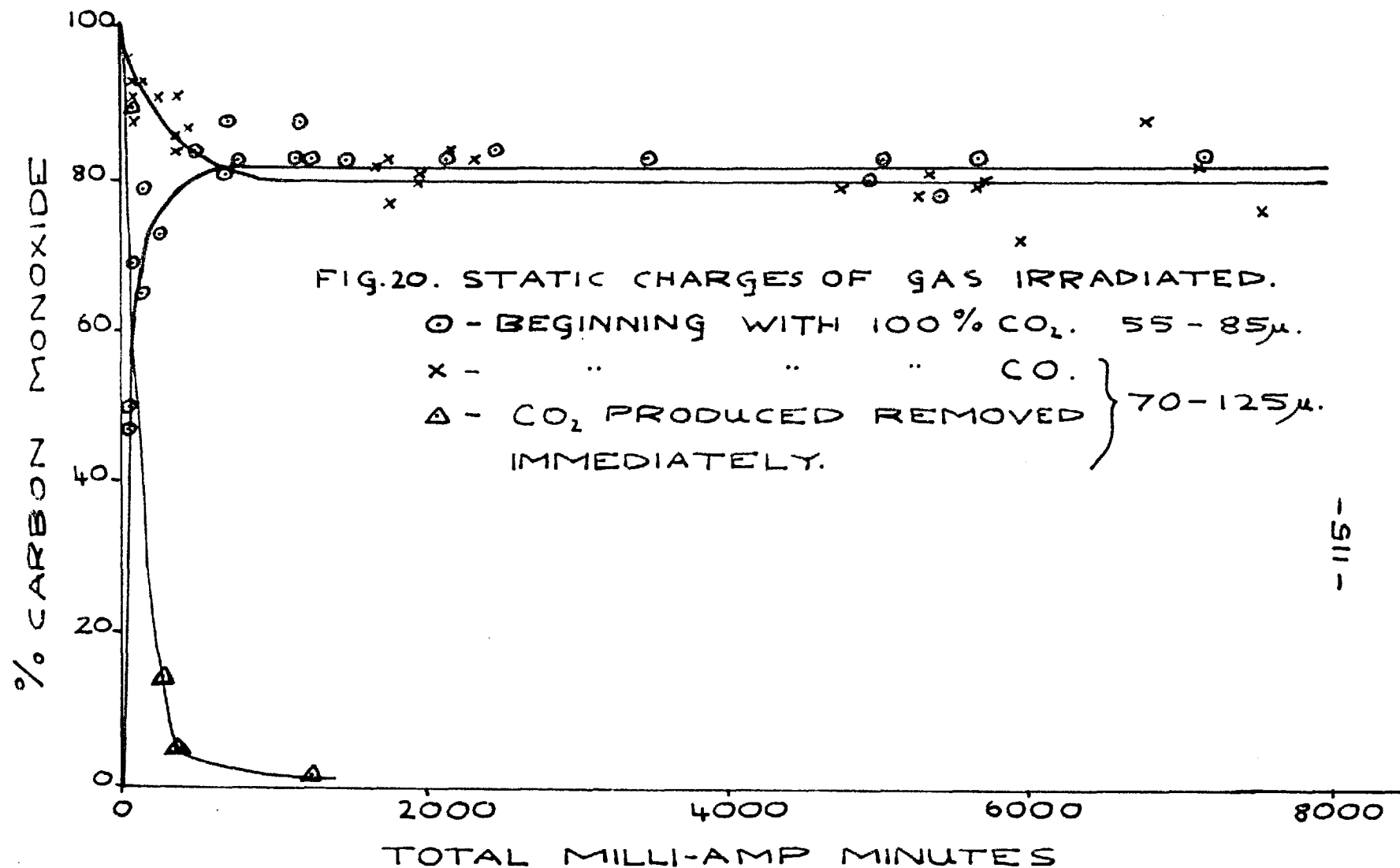
CO pressures from 60 - 125 μ were used with times of exposure from 15 to 3600 secs. The final total pressure and final CO pressure were measured as described above, in this case the difference between the two pressures indicated the amount of CO₂ produced from the radiolysis of the CO. Some additional experiments were carried out in which the CO₂ was removed immediately upon production by having the appendix on the reaction vessel immersed in liquid air throughout the exposure. It was of interest here to see how the decomposition of the CO was affected by the absence of the CO₂.

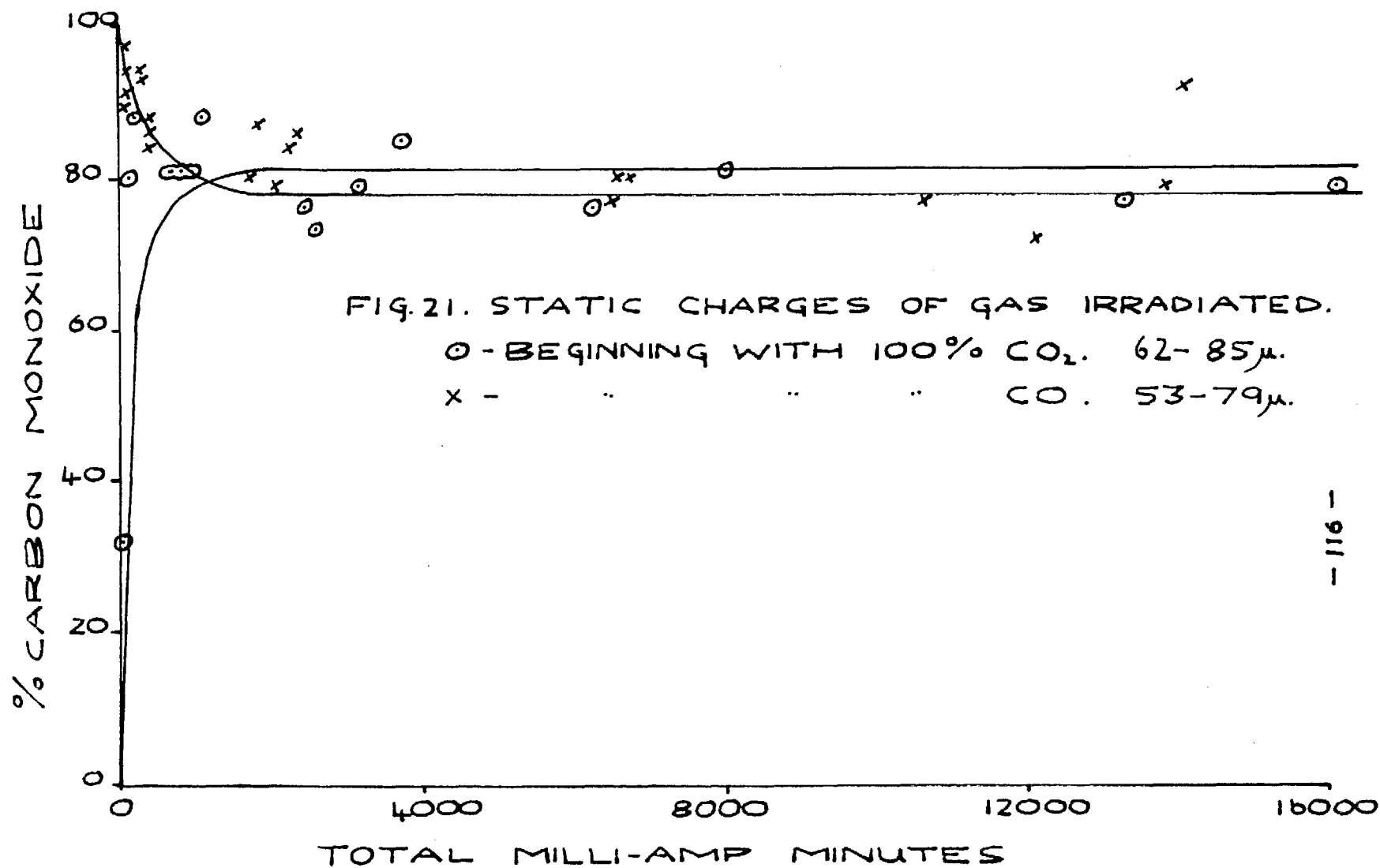
The final static experiments involved exposure to electron bombardment of a mixture of 60% CO₂ and 40% CO in the presence of carbon. Initial CO₂/CO pressures of 60 - 80 μ were used with times of exposure from 5 to 3600 secs. Gas composition changes were measured by noting the final total pressure and the pressure with CO₂ frozen out, the fall in pressure indicating the final CO₂ pressure.

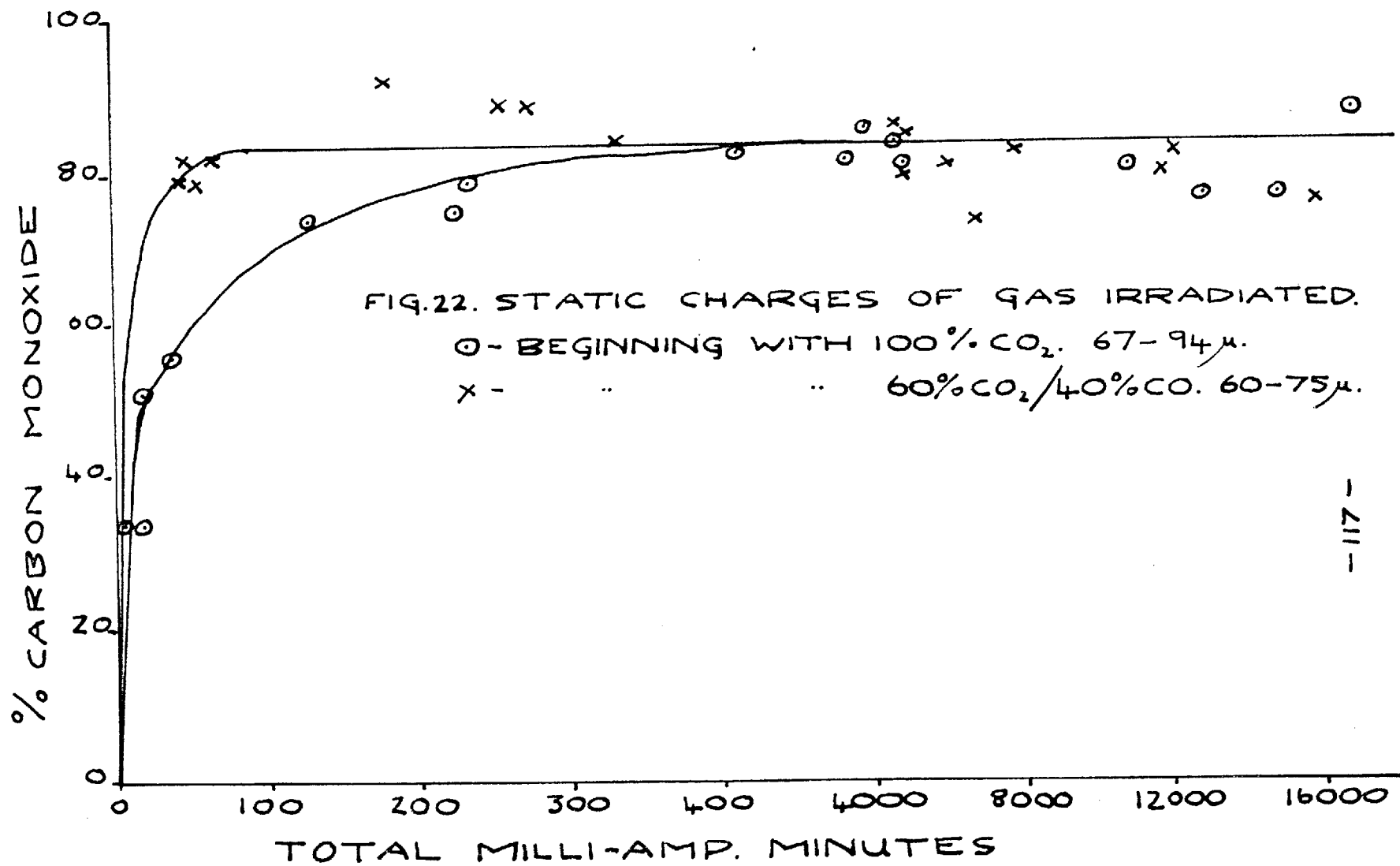
(ii) Results with pure CO₂: The experiments with static charges of pure CO₂ showed, as in the earlier preliminary experiments, that CO₂ was being decomposed

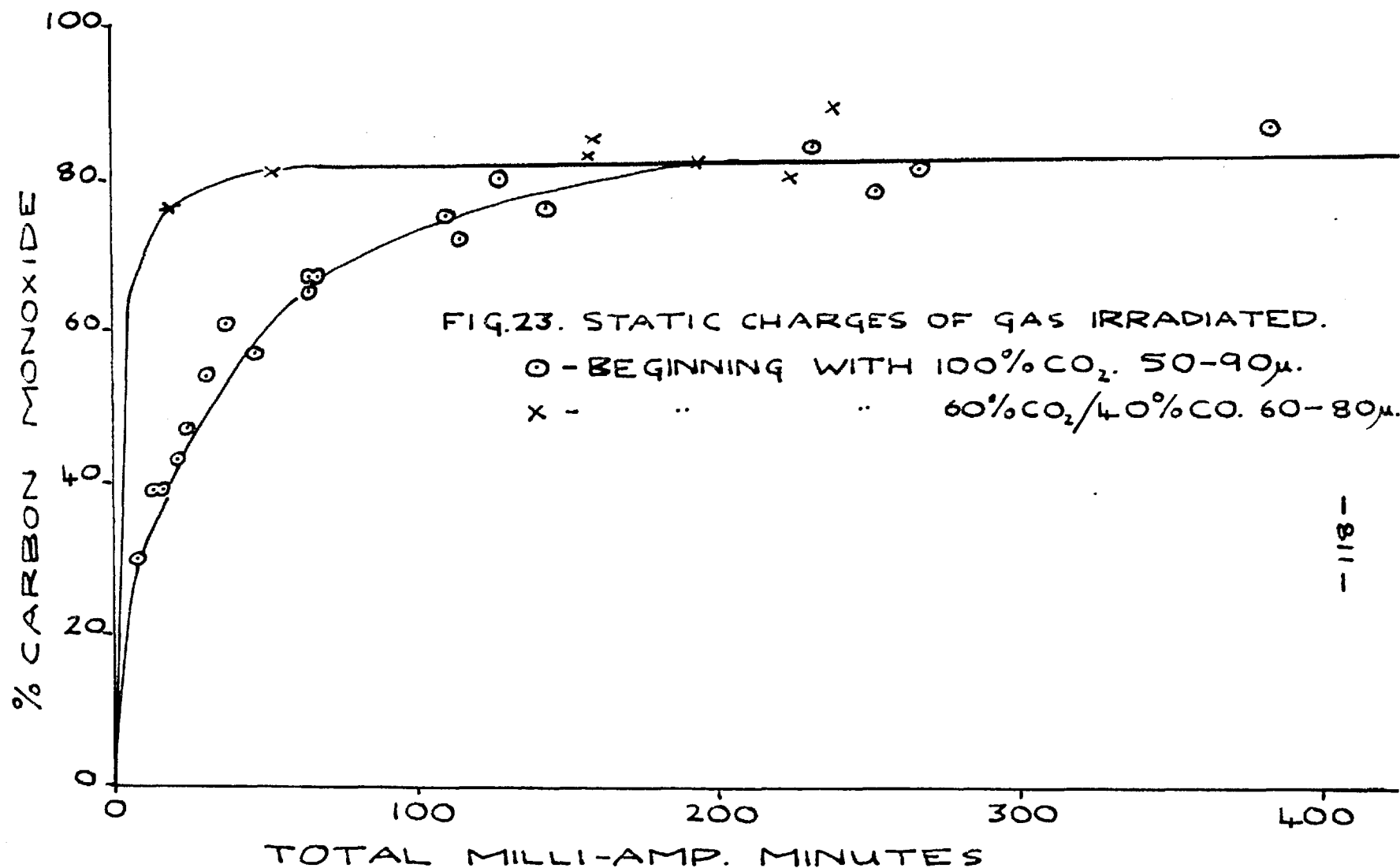
both in the presence and absence of carbon. However it was also observed that with carbon absent the emission current was considerably lower than when carbon was present. It was apparent that a similar effect was occurring as in the CO₂ flow experiments, namely that the carbon was removing a considerable fraction of the active species produced in the CO₂ by the accelerated electrons and which in the absence of carbon would attack the filament and so inhibit the emission. It is suggested therefore that the results of experiments employing a static charge of CO₂ in the presence of carbon refer to events occurring in the CO₂-carbon system, the effect of the filament being of secondary importance.

The results of the experiments using static charges of CO₂ with a carbon film present are given in Tables. 6, 8, 9 and 10 while those obtained without carbon are given in Table. 7. In the tables of results with carbon use in again made of the total number of milli-amp. minutes recorded during the exposure of the static charge of gas. The results showed that









the decomposition of the CO_2 rapidly attained some steady state condition. Expressed in terms of the % of CO formed as measured in the final gaseous mixture versus the corresponding total number of milli-amp. minutes it was found that from 0 to about 100 milli-amp. minutes the % of CO formed increased approximately linearly, while over the range from 100 to 1000 the % of CO gradually approached a steady value which was then maintained up to the highest number of milli-amp. minutes recorded, almost 25,000. The results are perhaps best illustrated by the graphs shown in figs. 20, 21, 22 and 23 which correspond to the results shown in Tables 8, 9, 10 and 6 respectively, the data concerning experiments with CO and CO_2/CO mixtures shown in these graphs will be discussed later. The graphs show clearly that the % of CO formed as referred to the final products of the irradiation of the static charges of CO_2 with electrons quickly attains a steady state value of about 80%. An examination of the carbon film at the end of each complete run showed clearly that removal of carbon was occurring. There were also clear indications from the appearance of the carbon film

and the other electrode and leads that deposition of a carbon-like solid was also taking place, due presumably to a reverse reaction involving CO as suggested by the steady state condition observed. This substance was very black and can be compared with the observations of earlier workers in this field on the radiolysis of CO, which, as described, was found in quite high concentrations in the present experiments.

It has been suggested that in the presence of carbon the results obtained under static conditions refer to the CO₂-carbon reaction, while in the absence of carbon the results are explained in terms of a reaction of the activated CO₂ with the filament. Accepting this to be true it would be expected that in the presence of carbon the total yield of carbon in the gas phase should be greater than in the absence of carbon. A comparison of the results obtained with and without carbon provides evidence that this is so, although the difference is not as great as would be expected.

(iii) Results with pure CO: The results of the experiments with static charges of CO with and without carbon are given in Tables 11 and 12 (a) while

the corresponding graphs representing the % of CO remaining as measured in the final gaseous mixture versus the corresponding total number of milli-amp. minutes are shown in Figs. 20 and 21. It was found, in a similar manner to the CO₂ runs, that between 0 and about 1000 milli-amp. minutes the % of CO remaining decreased gradually to a steady value which was maintained up to values as high as 20,000 milli-amp. minutes. The graphs reveal clearly that the steady value obtained for the % of CO remaining in the final product after starting with pure CO virtually coincides with the steady value obtained for the % of CO formed as referred to the final product after starting with pure CO₂, namely about 80%. The graphs shown in Fig. 20 also include the results of the experiments in which the CO₂ formed from the radiolysis, of the CO was removed immediately upon production (Table. 12 (b)). It can be seen that in this case the destruction of the CO very quickly goes to near-completion; within about 1000 milli-amp. minutes there is practically no CO remaining. Deposits of a carbon-like solid, similar in appearance to that occurring in the CO₂ experiments, were found upon examination of

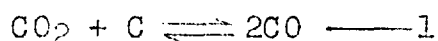
electrodes and leads at the end of a complete run.

(iv) Results with CO₂/CO mixtures: The results of the experiments involving the exposure to accelerated electrons of static mixtures of 60% CO₂ and 40% CO are given in Tables 13 and 14. The corresponding graphs of % of CO formed as measured in the final gaseous mixture versus the corresponding total number of milli-amp. minutes are reproduced in Figs. 22 and 23; included with these graphs are the results of experiments with pure CO₂ (Tables. 10 and 6 respectively). It was found by using CO₂/CO mixtures that the % of CO formed attained a steady value of about 80% after about 100 milli-amp. minutes as compared with the figure of about 1000 required when pure CO₂ was used, this effect is clearly shown in the graphs. This steady value was maintained for values as high as 20,000 milli-amp. minutes. It was again observed that deposition of a carbon-like solid occurred.

(v) Comment: The results obtained using pure CO₂, pure CO and CO₂/CO mixtures indicate that some form of steady state is being attained whereby the formation of CO by the decomposition of CO₂ and subsequent reaction with carbon is balanced by a reverse reaction

involving CO to - reform CO₂ and cause deposition of carbon.

If it is assumed that this radiation - induced steady state condition, observed when starting either with pure CO₂ or pure CO, can be expressed by the chemical equation:



then the ratio of ΔP_{CO} , the amount of CO produced (or destroyed), to ΔP_{CO_2} , the amount of CO₂ destroyed (or produced) should equal 2.

i.e. $\frac{\Delta P_{\text{CO}}}{\Delta P_{\text{CO}_2}} = 2$, if equation 1. represents adequately reactions occurring in the system.

However, it is found that the experiments beginning with pure CO₂ yield values for this ratio always less than 2 with many values lying between 0.8 and 1.4. Whereas the experiments beginning with pure CO yield values always greater than 2, the majority being about 4. A possible explanation for this is that more of the initial gas present (i.e. CO₂ or CO) is being lost than can be accounted for; however in spite of this the relative pressures of CO₂ and CO adjust themselves to yield the same steady state value for the % of CO formed (or remaining) in both

cases. The observed removal from the gas phase of one of the radiolysis products to form a carbon-like deposit capable of adsorbing gas may account for the apparent loss of gas. However losses of gas will probably also be occurring by the well known clean-up phenomena always observed in low pressure hot cathode discharge devices. It is to be noted that the rate of attack upon the carbon in the CO₂-flow experiments is rather less than, but of the same order of magnitude as the initial rate of CO₂ destruction in the CO₂-static experiments. the initial CO₂ pressures being of the same order in both cases.

The results of the experiments with CO₂/CO mixtures, namely that the steady state condition is arrived at more quickly than with pure CO₂, would be expected if a purely chemical equilibrium was being considered. However, in view of the peculiarities noted in the ratio of ΔP_{CO} to ΔP_{CO_2} for the experiments with pure CO₂ and CO it is perhaps interesting that the CO₂/CO system behaves as it does.

Any attempt to analyse the processes occurring in the present static system necessarily involves a knowledge of the amount of energy absorbed by the CO₂.

and the CO. This will depend upon the distribution of the energy of the electrons in the two gases which is not accurately known. However it is felt that the fact that dissociation of the CO₂ molecule requires a minimum energy of 5.5 volts whereas for CO the dissociation energy lies somewhere between 9 and 11 volts is important in determining the relative amounts of energy absorbed by the two gases.

In this connection it is perhaps interesting to record the results of some experiments by Sun and Weissler⁸. They measured the absorption cross-section (σ) of CO₂ and CO in the vacuum ultra-violet under the same pressure conditions (10 - 40 μ of Hg.). The wavelength region studied was 1306 Å - 374 Å which corresponds to an electron voltage range of 9.5 - 33 volts, and is thus of special interest. The results of their experiments are given below.

<u>Carbon Dioxide</u>		<u>Carbon Monoxide</u>	
<u>Wavelength (Å)</u>	<u>Average σ (nb)</u>	<u>Wavelength (Å)</u>	<u>Average σ (nb)</u>
1306	1.6	1306 - 955.3	0
1243.3 - 1183.0	0	923.2	23
1127.8	96	923.0	35
991.5	47	916	48

955.3	74	904.5 - 799.7	14 - 19
923.3	117	796.7	46
922.5	113	790.1 - 554.5	16 - 25
915.9	76	except 763.3	29
799.9	28		
765.1	75		
673.8 - 373.8	30 - 40		

The significance of these results lies in the fact that the rules governing the absorption of light by molecules, namely the Franck-Cordon principle, holds for electron impacts.

4. Flow experiments with CO

(i) A series of experiments was carried out with a continuous flow of CO passing through the reaction vessel at pressures of the order of 60 - 80 μ . The electrodes A₁ and A₂ were both held 25 volts positive with respect to the cathode, experiments being performed both in the presence and absence of carbon. The procedure adopted was similar to that in the corresponding CO₂ experiments. The CO flow pressure was first established in the reaction vessel; the accelerating potential was then applied, the filament was switched on and the stop-clock started. Readings of the emission current were taken at suitable intervals. The weight of the carbon deposit was determined at the beginning

and end of each experiment to determine the extent of any carbon transport.

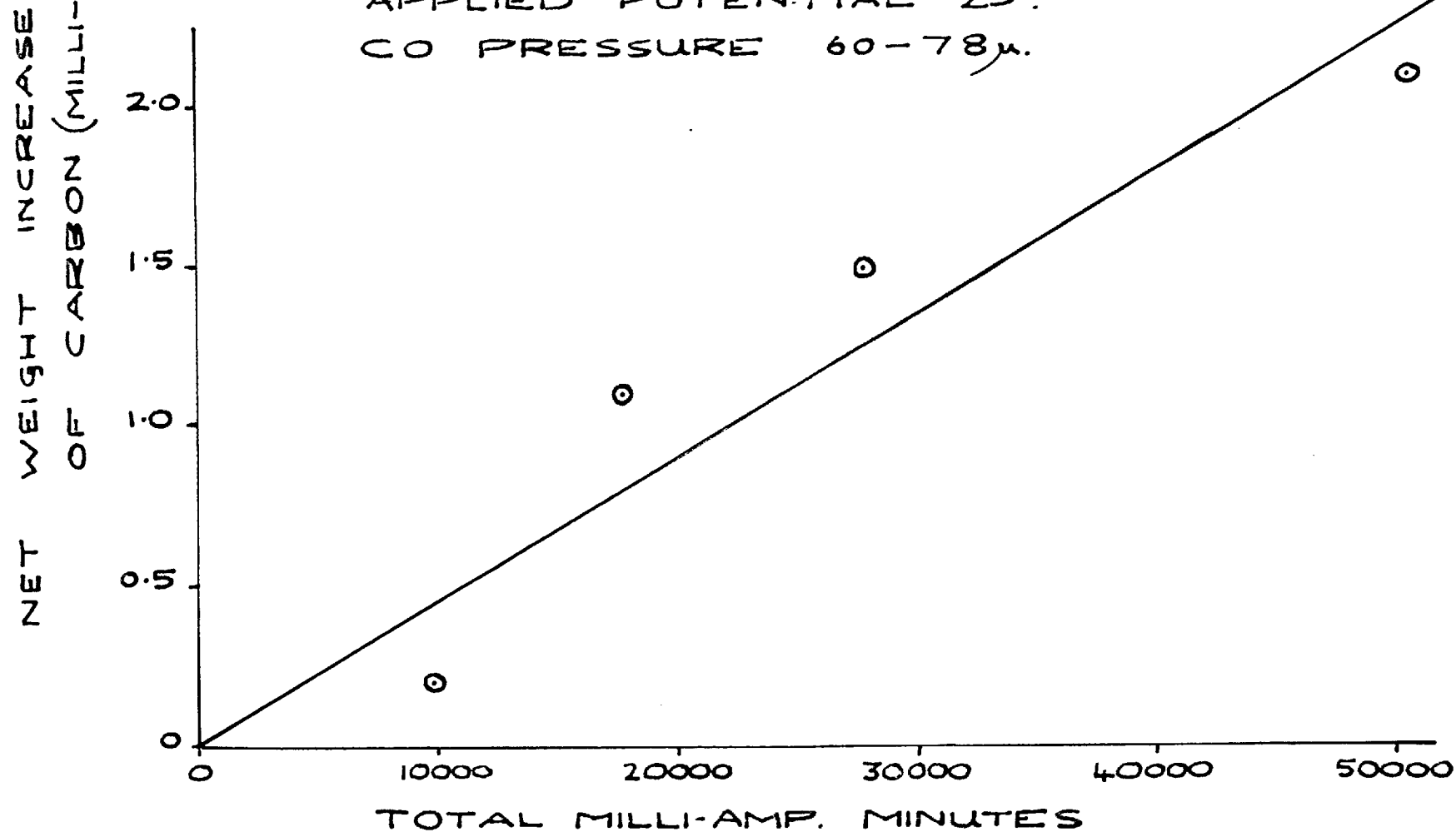
Results: The results of the experiments described above are given in Table. 15. It was found that the emission current was unaffected by the presence or absence of carbon. It appeared likely that if atomic oxygen was being formed by the simple dissociation of the CO molecule and was combining with the filament its return to the gas phase, due to combination with CO, was so rapid as to leave the emission unaffected; this would be more than likely in view of the high concentration of CO present which is a strong reducing agent. The emission currents recorded were high, being about twice the maximum current observed when using a flow of CO₂ with carbon present. It was almost as if the presence of the CO was enhancing the emission, however it seems more likely that the exposure of the filament to CO₂ causes an instantaneous poisoning effect which is only prevented from going to completion by the presence of the carbon.

The result of weighing the carbon deposit revealed that deposition of a carbon like-substance was occurring. The graph representing the net weight

increase of the carbon deposit versus the corresponding total number of milli-amp. minutes is reproduced in Fig. 24. The apparently linear relationship is similar to that observed in the CO_2 flow experiments. However whereas in those experiments, where a weight loss of carbon was being measured, it was found that the production of about 9000 milli-amp. minutes was sufficient to cause a loss of about 3 mgms. of carbon, a similar figure for the present experiments is found to cause a deposition of only about 0.5 mgms. Allowing for the fact that deposition is occurring on other surfaces, although it is felt that this is quite slight, the difference is significant. Assuming that the deposit observed was carbon it was found that the rate of production of this substance in these CO flow experiments was of the same order of magnitude as the initial rate of destruction of CO in the static experiments.

(ii) Further experiments without carbon using the same conditions as above were performed wherein CO was allowed to flow through the system for short intervals of time with the appendix on the reaction vessel immersed in liquid air. The purpose of this was to remove immediately any CO_2 produced from the radiolysis

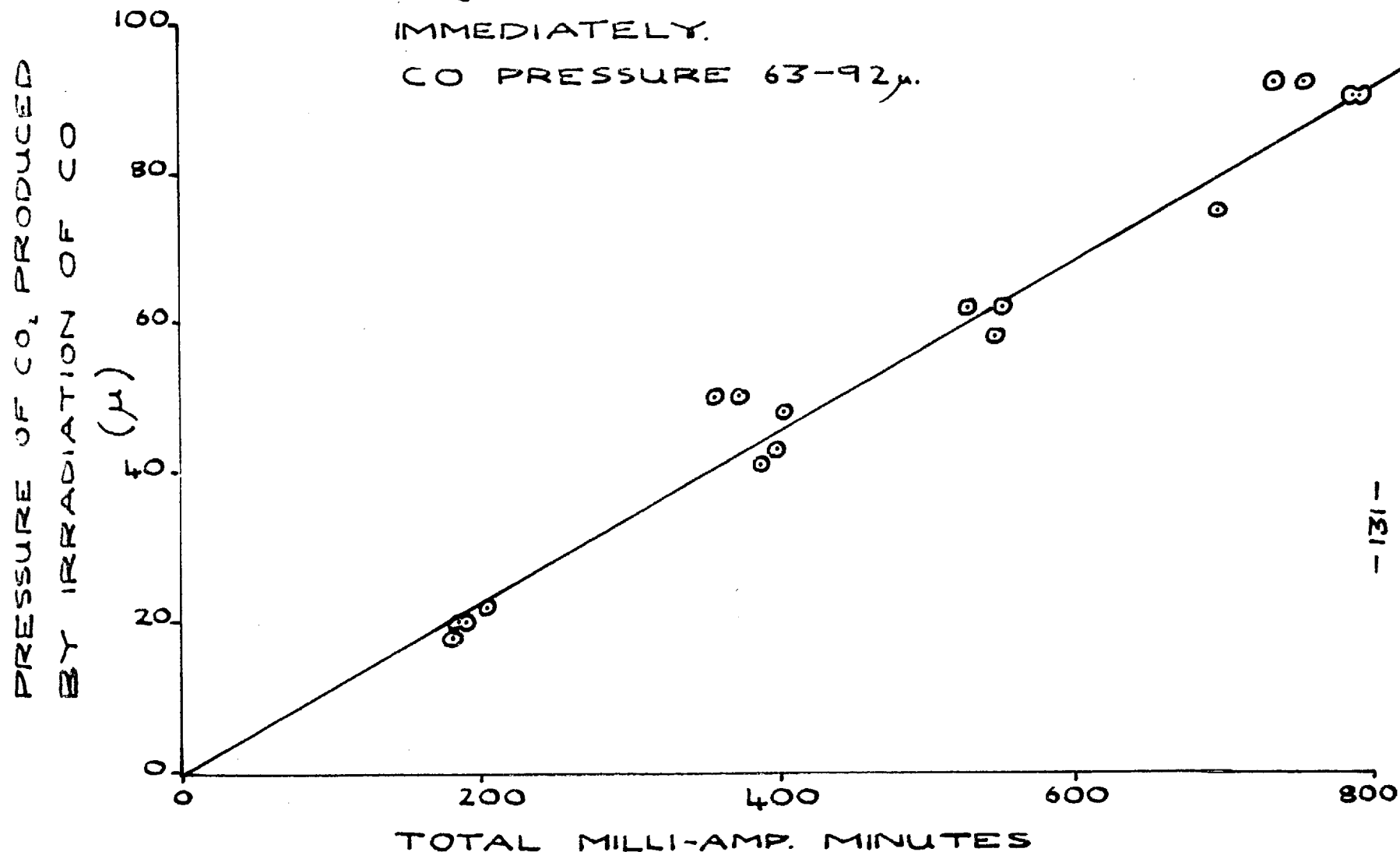
FIG. 24. FLOW OF CO IRRADIATED.
CARBON AT A POSITIVE POTENTIAL
W.R.T. FILAMENT.
APPLIED POTENTIAL 25V.
CO PRESSURE 60-78 μ .



of the CO. At the end of each interval the system was pumped out, closed off from the pumps and the liquid air removed, the amount of CO₂ produced was then measured. As always with the CO flowing readings of the emission current were taken at suitable intervals. These experiments were carried out using the same filament and electrodes. At the end of the complete set of experiments the electrodes were re-weighed to determine the extent of any deposition process and the results compared with the total amount of CO₂ produced.

Results: The results of the experiments just described are given in Table. 16. while they are represented graphically in Fig. 25. This graph is of the CO₂ pressure produced from the CO irradiation versus the corresponding total number of milli-amp. minutes recorded. It can be seen that the CO₂ produced increases, as expected, linearly with the number of milli-amp. minutes. The yield of CO₂ was found to be quite large in these experiments, being about 1μ of CO₂ produced per 8 milli-amp. minutes recorded. The overall effect being similar to that observed in the corresponding static CO experiments.

FIG.25. FLOW OF CO IRRADIATED.
CO₂ PRODUCED REMOVED
IMMEDIATELY.
CO PRESSURE 63-92 μ .



It was again observed that deposition of a carbon-like solid was occurring. Re-weighing the electrodes A₁ and A₂ at the end of the experiment enabled the weight of the major part of this deposit to be estimated. By assuming that the deposit was carbon it was found that the total number of atoms in the deposit was of the same order of magnitude as the total number of CO₂ molecules produced, in accordance with the equation:



In this connection it is to be noted that the rate of production of CO₂ in these CO flow experiments was rather less than, but of the same order as the initial rate of destruction of CO in the static CO experiments in which the CO₂ produced was removed immediately.

GENERAL SUMMARY

1. Results

Experiments have been performed in the presence of carbon in which a flow of CO_2 at pressures of 60 - 70 μ and 20 μ has been exposed for varying lengths of time to accelerated electrons possessing energies not exceeding 25 volts. It has been observed that removal of carbon is occurring; the actual weight loss of carbon increasing linearly with time, other conditions being constant. The weight loss of carbon is also apparently independent of its electrical condition in the system. It has therefore been concluded that active species produced in the CO_2 by the accelerated electrons and which are assumed to be responsible for the attack upon the carbon are not electrically charged. An analysis of the processes capable of occurring in the CO_2 suggests that the active species are oxygen atoms.

Similar experiments to those described above have been carried out in the absence of carbon. A comparison of the behaviour of the emission current with time in the presence and absence of carbon has revealed that the carbon is apparently exerting a

protective effect upon the emission from the oxide coated cathode, the protection being by a factor of about 5. This protection is believed to be due to the removal by the carbon of active species formed in the CO_2 by the accelerated electrons and which in the absence of carbon would attack the filament and so inhibit the emission. It is considered that the attack on the filament occurs by reaction of atomic oxygen with metallic barium which is present in the surface of the filament and which is believed to be responsible for the electron emission.

It has also been found that the nature and extent of the attack upon the carbon are unaffected by the presence or absence of mercury vapour. This must certainly be due in part to the relatively long mean free paths of the active species and the proximity of the carbon to the region in which they are formed. The effect that changes in electrode geometry and/or CO_2 pressure had upon the extent of the carbon attack in the presence and absence of mercury vapour would allow this to be verified.

Exposure of carbon to electron bombardment under vacuum has shown that no removal of carbon occurs

as a result of the impact of the electrons with the surface.

Experiments have been carried out in the presence and absence of carbon wherein a flow of CO_2 at pressures of 60 - 70 μ is exposed to electrons possessing energies not exceeding 15 volts. It has been found that even at these energies the carbon provides protection for the filament. It has been suggested that the carbon is playing a similar role to that proposed in the experiments at 25 volts, namely removal of active species formed in the CO_2 by the accelerated electrons. At these electron energies it would appear that only oxygen atoms could cause this effect.

Experiments have also been carried out in which static charges of CO_2 have been exposed to electrons of energies not exceeding 25 volts in the presence of carbon. It has been found that the % of CO formed as referred to the final gaseous mixture rapidly attains a steady state condition. Similar experiments with static charges of CO and CO_2/CO mixtures gave further evidence of a steady state condition. The deposition of a carbon-like solid observed in all three types of

experiment suggested a reverse reaction involving CO was occurring although the pressure changes observed under steady state conditions could not be reconciled with the simple chemical equation $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$.

Experiments with a flow of CO have again revealed extensive deposition occurring, it was found in one set of experiments that the total deposition occurring, if assumed to be carbon, was of the same order of magnitude as the total CO_2 produced.

Finally it has been found that in spite of the peculiarities of the static systems, the initial rates of reaction in the static experiments could be compared with the rates of reaction in the corresponding flow experiments.

2. General Conclusions:

1. Carbon is rapidly attacked in the cold by CO_2 at low pressures under the influence of low energy electrons.
2. The active species attacking the carbon are not electrically charged.
3. Analysis of the results and conditions suggests that atomic oxygen is the primary radiolysis product responsible for the attack.

4. The CO₂-carbon reaction has been shown to be independent of the presence or absence of mercury vapour.
5. At the electron energies used carbon removal by electron impact at the surface is not occurring.
6. Under static conditions the CO₂-carbon reaction rapidly attains a steady state condition which cannot, however, be reconciled with the simple chemical equation $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$.
7. Deposition of a carbon-like solid has been observed in the static CO₂-carbon experiments and in similar experiments with CO and CO₂/CO mixtures and with a flow of CO.
8. The initial rates of reaction in the static experiments with CO₂ and CO can be compared with the rates of reaction in the corresponding flow experiments.
9. The unusual behaviour of CO₂ under the influence of low energy electrons in the absence of carbon has been shown to be due to the reaction of the active species with the oxide coated cathode.
3. Comparison of low pressure - low energy results with effects in - pile:

A comparison between the results of the present CO₂-flow

experiments and effects liable to be encountered in-pile is made difficult by the widely differing conditions existing in the two systems. In the present system the maximum CO₂-flow pressure lies between 60 and 70μ while the radiation used takes the form of electrons possessing energies not exceeding 25 volts, also the carbon although reactive is of unknown structure. In contrast for a reactor of the Calder Hall type CO₂ pressures of about 7 atmospheres are used while the radiation which is responsible for promoting the CO₂-carbon reaction is of two kinds - fast neutrons and gamma rays. The majority of the fast neutrons possess energies of about 1 Mev but neutron energies as high as 16 Mev have been recorded while the gamma ray spectrum includes energies extending from about 30 kev to about 3 Mev. The relative contributions of these two types of radiation has been found to be about 20% and 80% respectively. The carbon used as a moderator in-pile has extensive pore structure and indeed the reaction occurring in the pores is of considerable importance in assessing the overall behaviour to be expected.

It is felt that some comparison can be made between the present results and those to be expected

in-pile on the basis of events occurring in the gas phase.

Although the significance is uncertain it is perhaps interesting to note that the ratio of the CO₂-flow pressure to the average energy of the quantum of radiation incident upon the CO₂ is of the same order of magnitude for both the reactor and the present low pressure system.

Since the gamma-radiation contributes the major portion of the energy absorbed in the CO₂-carbon system it is felt reasonable to deal mainly with this in comparing the conditions in-pile with those in the present low pressure system. The gamma ray quanta of energy less than 1 Mev absorbed in the gas phase will produce considerable ionization of the CO₂ by the photoelectric and Compton effects. The free electrons ejected as a result of the ionization will often obtain kinetic energies practically equal to the energy of the quanta and will thus be capable of producing further ionization and excitation in the gas. It is known that fast electrons produce 1 ion pair in CO₂ per 34 eV of their energy; a secondary electron possessing, for example, an energy of 100 keV will therefore produce

about 3,000 ion pairs. It can thus be seen that almost all the ionization (and excitation) occurring in the CO_2 is due to the action of the fast secondary electrons rather than to the quanta themselves. This gives perhaps added significance to the fact that the ratio of CO_2 pressure to quantum radiation energy is of the same order for both systems, since now the bulk of the incident radiation takes the same form in both cases, namely electrons. Quanta of energy greater than 1 Mev can be absorbed by a process known as pair production and need not concern us here.

The value of 34 eV quoted as the average energy required to form one ion pair for fast electrons includes the energy lost by exciting collisions. It is known that the excitation of CO_2 occurring at a minimum energy of 5.5 volts leads to the formation of $\text{CO} + \text{O}^{(*)}$, it therefore seems likely that atomic oxygen will be produced in quite large quantities. At the high gas pressures used the fate of the CO_2^+ ion, which is considered to be the most abundant ion formed, will be decided to a considerable extent by electron-ion homogeneous recombination leading to dissociation into $\text{CO} + \text{O}^{(*)}$. Recombination followed simply by the emission of radiation may

also occur; here the radiation emitted will be capable of promoting further processes in the gas phase. Because of the high gas pressures used collisions in the gas phase will probably be more important than wall collisions. It would seem reasonable to suppose that the attack upon the carbon will only be made by active species formed adjacent to the surface, in this respect the reaction occurring in the pores of the carbon will thus be of particular importance.

This analysis suggests that processes and products occurring in the gas phase in-pile are paralleled by events occurring in the present low pressure system. The essential difference between the two systems is in the much greater life-time of the active species produced in the low pressure system; this results from the fact that secondary processes in the gas phase do not occur to anything like the extent they do in-pile. The effect of using a carbon deposit as opposed to the nuclear graphite used in-pile is considered to be mainly one of different reactivities.

The results of the present low pressure work indicate that atomic oxygen is the primary radiolysis

product responsible for the attack upon the carbon. In-
pile this attack will probably be supplemented by the
effect of ozone being formed in a secondary gas phase
process. It would seem likely that the atomic oxygen,
since it is a primary product, would be responsible for
the reaction in the pores while the ozone, since it is
a secondary product, would be concerned with the external
surface reaction. The protective effect of the carbon
observed at 15 volts is taken to indicate that the
CO₂-carbon reaction will readily occur under the
influence of quite low energy radiation. This makes the
problem of finding means of reducing the effect of this
reaction very difficult; the two different approaches
which present themselves are:

- (a) the addition of either something chemically
unreactive to the gas phase which provides a more
acceptable low energy path for the absorption of
the radiation or something which offers a medium
with which the active species may react in
preference to the carbon, or
- (b) treating the carbon so as to increase its
resistance to attack either by reducing the

(b) continued

accessible surface area, reducing the reactivity of the carbon or by applying to the surface a physical barrier to the active species. Any treatment must not however involve the use of materials having anything but a very low capture cross-section for thermalneutrons.

Method (a) is perhaps more promising due to the comparative ease with which additions to the gas phase can be made. Experiments carried out in the reaction vessel in which static charges of CO_2 have been irradiated have shown, in spite of the failure to obtain a good material balance, that the decomposition of the CO_2 rapidly attains a steady state condition. Similar experiments with CO_2/CO mixtures has shown that this steady state condition is attained more quickly than in the corresponding experiments with pure CO_2 . It would appear that the decomposition of the CO_2 is limited by the reverse effect due to the build-up of CO and that the effect of the CO -additive is to increase the rate of removal of oxidising species by means other than the carbon, this can

only be achieved at the expense of the carbon oxidation processes. Whether this removal is occurring in the gas phase is uncertain; this effect together with the inability to obtain a good material balance provokes enquiry on the effect of surfaces other than the carbon, e.g. irradiation vessel walls etc. The experiments with static CO_2/CO mixtures and also with a flow of pure CO showed clearly that deposition of carbon was occurring. This suggests that although the addition of CO to the CO_2 may reduce the attack upon the carbon the deposition process may present problems in the future reactor circuits, particularly if extensive deposition occurs on heat exchanger surfaces. Accepting from the results of the flow experiments that removal of carbon occurs in pure CO_2 and that deposition of carbon occurs in pure CO , the behaviour in CO_2/CO mixtures is still uncertain. It is still not known from the model channel experiments in-pile if under steady state conditions the gas phase removal processes have become so rapid as to prevent any active species reaching the carbon or whether the carbon removal process is being compensated by a reverse deposition process. Such effects would be very

dependent upon the gas pressures used and the geometry of the system. The present low pressure apparatus in which these factors can be more easily varied would seem to provide a means of studying this problem in more detail.

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TABLE. 1.

Preliminary experiments in which static charges of CO₂ were exposed to electron bombardment in presence and absence of carbon. Grid 25 volts positive with respect to cathode. Times of exposure 5-300 secs. CO₂ pressure range 43-70 μ .

With carbon

Initial CO ₂ Pressure (μ)	Time of Reaction (secs.)	Average Emission Current To Grid. (mA)	Final Total Pressure (μ)	Pressure with CO ₂ frozen out (μ)	Final CO ₂ Pressure (μ)	% loss of CO ₂ Per 50mA
70	5	45	71	10	61	14
68	5	50	68	10	58	15
63	15	44	64	11	53	18
61	15	52	70	18	52	15
70	15	73	78	25	53	17
65	60	45	67	17	50	25
63	60	72	78	38	40	25
70	120	45	75	21	54	25
63	120	66	78	40	38	30
59	180	45	66	23	43	30
62	180	66	82	48	34	34
50	300	45	58	25	33	38
57	300	61	87	53	34	33

Without carbon

62	5	62	64	12	52	13
50	15	72	57	17	40	14
62	15	77	68	20	48	15
43	15	80	53	21	32	16
61	15	85	69	25	44	16
46	60	63	52	16	36	17
68	60	67	77	23	54	15
53	60	70	63	24	39	19

TABLE. 1. (Contd.,)

60	90	65	69	22	47	17
52	90	68	65	24	41	15
48	90	52	61	29	32	31
67	120	64	79	25	54	15
54	120	68	67	27	40	18
55	180	51	65	31	34	38
60	180	54	85	50	35	38
61	180	76	69	36	33	29
56	300	73	66	34	32	28

TABLE. 2.

(a) Carbon or bare metal foil 25 volts positive with respect to the cathode. CO₂ pressure range 60 - 70 μ .

With carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-Amp Minutes	Weight Loss of Carbon (m.gms)	CO ₂ Pressure (μ)
161	226	20	4520	2.1	63
162	117	20	2340	.9	65
163	158	20	3160	1.5	70
164	154	20	3080	1.0	65
177	216	30	6480	1.9	62
178	115	40	4600	.5	63
179	160	40	6400	1.8	70
180	154	50	7700	1.8	70
181	230	20	4600	1.0	63
182	130	20	2600	.8	70
183	199	27	5373	1.7	65
193	110	20	2200	.6	65
194	188	20	3760	1.3	68
236	111	70	7770	2.9	63
238	165	60	9900	3.3	63

Without carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-Amp Minutes	CO ₂ Pressure (μ)
159	88	15	1320	69
160	88	10	880	65
184	49	40	1960	70
262	18	70	1260	65
263	27	70	1890	73
298	37	30	1110	72

TABLE. 2. (Contd.,)

(b) Carbon or bare metal foil at same potential as cathode. CO₂ pressure range 60 - 70 μ .

With carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-amp Minutes	Weight Loss of Carbon (mgms)	CO ₂ Pressure (μ)
195	41	40	1640	.5	70
196	53	50	2650	.7	65
197	71	50	3550	1.2	64
198	85	40	3400	1.3	65
199	65	30	1950	.2	63
200	130	40	5200	.9	68
202	66	30	1980	.5	70
203	84	50	4200	1.2	62
204	88	40	3520	1.2	62
205	83	25	2075	.6	67
235	60	150	9900	3.4	72
240	103	70	7210	2.5	75
303	98	64	6272	1.7	60
304	57	90	5130	1.5	65

Without carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-amp Minutes	CO ₂ Pressure (μ)
206	19	30	570	61
207	24	30	720	67
234	9	60	540	60
261	8	150	1200	70
297	16	50	800	76
299	21	40	840	68

TABLE. 2. (Contd.,)

(c) Carbon or bare metal foil suspended in reaction vessel. CO₂ pressure range 60 - 70 μ .

With carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-amp Minutes	Weight Loss of Carbon (mgms)	CO ₂ Pressure (μ)
150	140	30	4200	1.2	64
151	113	20	2260	.8	70
154	64	30	1920	.7	70
156	173	20	3460	1.2	65
158	162	40	6480	2.4	73
165	104	60	6240	1.7	65
172	64	60	3840	.8	70
173	77	20	1540	.3	60
174	63	40	2520	.6	70
175	73	40	2920	.8	67
176	114	40	4560	1.2	65
237	59	140	8260	3.3	67
241	45	30	1350	.5	60
242	57	95	5415	1.7	70

Without carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-amp Minutes	CO ₂ Pressure
149	80	10	800	62
152	31	20	620	70
153	33	20	660	68
155	75	20	1500	62
157	65	15	975	73
259	19	60	1140	63
260	14	100	1400	73

TABLE. 3.

(a) Carbon or bare metal foil 25 volts positive with respect to the cathode. CO₂ pressure range 20 - 23 μ .

With carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-amp Minutes	Weight loss of Carbon (mgms)	CO ₂ Pressure (μ)
211	244	20	4880	.7	20
212	279	15	4185	.6	20
213	265	10	2650	.4	20
214	280	25	7000	.9	20
215	228	25	5700	.7	20
216	310	40	12400	1.8	20
232	278	35	9830	1.6	21

Without carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-amp Minutes	CO ₂ Pressure (μ)
185	83	60	4980	20
186	76	60	4560	20
187	56	40	2240	20
190	66	30	1980	20
210	51	60	3060	20
302	92	50	4600	20

TABLE. 3. (Contd.,)

(b) Carbon or bare metal foil at same potential as cathode CO₂ pressure range 20 - 23 μ .

With carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-amp Minutes	Weight loss of Carbon (mgms)	CO ₂ Pressure (μ)
217	46	50	2300	.3	20
218	67	30	2010	.5	21
220	54	30	1620	.2	23
221	54	30	1620	.3	20
225	52	20	1040	.2	20
226	69	40	2760	.4	21
227	71	20	1420	.3	22
228	79	50	3950	.7	21
229	78	70	5460	.9	21
230	60	110	6600	1.0	20
231	66	150	9900	1.5	20

Without carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-amp Minutes	CO ₂ Pressure (μ)
188	45	40	1800	20
189	46	40	1840	20
208	40	30	1200	20
233	24	110	2640	20
264	20	150	3000	23
265	17	150	2550	21
300	29	40	1160	23
301	26	60	1560	19

TABLE. 4.

(a) Carbon 25 volts positive with respect to cathode,
mercury vapour absent from reaction vessel. CO₂
pressure range 60 - 70 μ .

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-amp Minutes	Weight loss of Carbon (mgms)	CO ₂ Pressure (μ)
243	194	30	5820	2.0	65
244	169	30	5070	1.6	65
245	164	20	3280	.8	70
246	148	60	8880	2.5	70
247	140	50	7000	2.1	61
248	159	60	9540	3.0	68
249	232	20	4640	.9	60

Carbon 25 volts positive with respect to cathode,
mercury vapour absent from reaction vessel. CO₂
pressure range 20 - 22 μ .

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-Amp Minutes	Weight loss of Carbon (mgms)	CO ₂ Pressure (μ)
250	198	40	7920	1.0	20
251	186	55	10230	1.5	20
252	248	20	4960	.7	20
253	153	80	12240	1.6	20
254	264	10	2640	.3	22

TABLE. 5.

(a) Carbon or bare metal foil 15 volts positive with respect to the cathode. CO₂ pressure range 60 - 70 μ .

With carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-Amp Minutes	CO ₂ Pressure (μ)
268	6.8	90	612	63
269	9.6	90	864	63
272	14.1	60	846	66
273	19.8	60	1188	70
275	8.0	60	480	70
277	23.2	30	696	72
292	10.1	30	303	65
291	13.9	45	625	73
294	12.2	30	366	65
295	9.5	30	285	70

Without carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-Amp Minutes	CO ₂ Pressure (μ)
266	.99	90	89	72
267	1.27	90	114	63
270	2.91	60	175	60
271	3.2	60	192	71
274	6.4	60	384	62
276	1.7	30	51	70
278	5.7	30	171	67
290	2.4	30	72	65
293	2.96	30	88	70
296	4.5	45	202	64

TABLE. 6.

Run 305 : Static charges of CO₂ exposed to electron bombardment. Carbon 25 volts positive with respect to cathode. Times of exposure 5 - 300 secs. CO₂ pressure range 50 - 90 μ .

Initial CO ₂ Pressure (μ)	Time of Reaction (secs)	Average Emission Current (nA)	Final Total Pressure (μ)	Pressure with CO ₂ frozen out (μ)	Final CO ₂ Pressure (μ)	Total Milli-amp Minutes	% CO.
76	15	268	90	60	30	67	67
72	15	261	80	54	26	65	67
55	30	250	70	50	14	128	80
71	30	229	90	65	25	115	72
76	60	253	108	84	24	253	78
60	60	268	81	66	15	268	81
55	15	187	60	34	26	47	57
63	30	221	76	57	19	111	75
56	60	232	80	67	13	232	84
66	120	242	92	84	8	484	91
68	120	222	100	87	13	444	87
70	5	159	70	27	43	13	39
63	5	190	63	25	38	16	39
60	10	178	65	35	30	30	54
68	10	150	70	33	37	25	47
85	5	113	87	26	61	9	30
76	10	129	78	34	44	21	43
61	120	192	87	75	12	384	86
75	180	190	115	100	15	570	87
67	180	178	102	86	16	534	84
50	180	185	82	70	12	555	85
51	15	147	52	32	20	37	61
65	30	129	72	47	25	64	65
83	60	144	99	75	24	144	76
88	300	196	135	125	10	980	92
71	300	168	130	115	15	840	88
58	300	130	92	80	12	650	87

TABLE. 7.

Run 306: Static charges of CO₂ exposed to electron bombardment. Without carbon, bare metal foil 25 volts positive with respect to cathode. Times of exposure 5 - 900 secs. CO₂ pressure range 50 - 90 μ .

Initial CO ₂ Pressure (μ)	Time of Reaction (secs)	Average Emission Current (mA)	Final total Pressure (μ)	Pressure with CO ₂ frozen out (μ)	Final CO ₂ Pressure (μ)	Total Milli-amp Minutes	% CO.
75	5	132	70	30	40	11	43
50	5	86	45	17	28	7	38
60	15	88	55	37	18	22	67
56	15	61	50	25	25	15	50
82	30	63	75	40	35	32	53
64	30	43	58	29	29	22	50
54	60	43	50	37	13	43	74
77	60	45	70	40	30	45	57
65	120	44	63	45	18	88	71
53	120	51	51	40	11	102	78
59	180	63	58	47	11	189	81
75	180	46	73	50	23	138	69
91	300	92	93	72	21	460	77
62	300	89	58	47	11	445	81
89	5	17	85	5	80	17	6
56	15	24	50	12	38	6	24
73	30	38	65	20	45	19	31
50	60	47	44	25	19	47	57
77	120	54	70	39	31	108	56
55	180	94	53	45	8	282	85
57	300	68	53	47	6	340	88
72	900	134	71	56	15	2010	79

TABLE. 8.

Run 307: Static charges of CO₂ exposed to electron bombardment. Carbon 25 volts positive with respect to cathode. Times of exposure 5 - 3600 secs. CO₂ pressure range 55 - 85 μ .

Initial CO ₂ Pressure (μ)	Time of Reaction (secs)	Average Emission Current (mA)	Final Total Pressure (μ)	Pressure with CO ₂ , frozen out (μ)	Final CO ₂ Pressure (μ)	Total milli-amp Minutes	% CO ₂
78	5	251	72	34	38	21	47
65	15	243	66	46	20	61	69
81	30	218	87	57	30	109	65
88	60	242	105	77	28	242	73
80	120	241	110	93	17	482	84
55	180	232	87	77	10	696	88
85	300	233	125	110	15	1160	88
65	300	225	76	63	13	1125	83
70	600	213	90	75	15	2130	83
80	900	213	102	85	17	3495	83
80	1800	189	93	77	16	5670	83
82	1800	180	103	81	22	5400	78
67	1800	164	85	68	17	4920	80
69	300	150	90	75	15	750	83
66	60	126	72	57	15	126	79
75	15	83	74	37	37	21	50
69	900	164	93	78	15	2460	84
67	1800	167	88	73	15	5010	83
68	3600	168	82	67	15	10080	82
68	3600	157	85	67	18	9420	79
72	600	148	110	91	19	1480	83
85	2700	159	115	96	19	7155	83
61	480	156	81	67	14	1248	83
77	3600	151	120	102	18	9060	85
61	300	136	74	60	14	680	81

TABLE. 9.

Run 310: Static charges of CO₂ exposed to electron bombardment. Carbon 25 volts positive with respect to cathode. Times of exposure 5 - 7200 secs. CO₂ pressure 62 - 85 μ .

Initial CO ₂ Pressure (μ)	Times of Reaction (secs)	Average Emission Current (mA)	Final Total Pressure (μ)	Pressure with CO ₂ frozen out (μ)	Final CO ₂ Pressure (μ)	Total Milli-amp Minutes	% CO.
77	5	162	63	20	43	14	32
73	60	199	61	54	7	199	88
75	300	219	65	57	8	1095	88
78	900	251	65	55	10	3765	85
62	1800	267	37	30	7	8010	81
85	3600	269	48	38	10	16140	79
70	7200	231	27	23	4	27720	85
63	300	167	69	56	13	835	81
66	900	213	70	55	15	3195	79
68	60	137	76	61	15	137	80
66	1800	204	55	42	13	6240	76
68	300	196	80	65	15	980	81
70	3600	222	66	51	15	13320	77
74	7200	171	55	40	15	20691	73
78	900	161	87	66	21	2415	76
80	7200	203	49	35	14	24360	71
72	900	173	45	33	12	2595	73
79	300	144	90	73	17	720	81

TABLE. 10.

Run 311: Static charges of CO₂ exposed to electron bombardment. Carbon 25 volts positive with respect to cathode. Times of exposure 5 - 3600 secs. CO₂ pressure range 67 - 94 μ .

Initial CO ₂ Pressure (μ)	Time of Reaction (secs)	Average Emission Current (mA)	Final Total Pressure (μ)	Pressure with CO ₂ frozen out (μ)	Final CO ₂ Pressure (μ)	Total Milli-amp Minutes	% CO.
88	5	224	77	26	51	19	34
94	60	227	97	73	24	227	75
88	300	237	80	68	12	1185	85
80	900	319	38	32	6	4785	84
67	3600	282	17	15	2	16920	88
90	15	154	96	54	42	38	56
70	120	207	90	75	15	414	83
70	300	205	94	79	15	1025	84
70	900	261	73	63	10	3915	86
70	3600	247	43	33	10	14820	77
76	15	76	74	38	36	19	51
79	60	129	92	68	24	129	74
80	300	198	112	95	17	990	85
79	900	224	100	82	18	3360	82
73	3600	214	64	49	15	12840	77
75	120	118	97	77	20	236	79
84	3600	181	89	72	17	10860	81
77	15	36	74	25	49	9	34
84	1800	164	102	83	19	4920	81
70	900	153	82	67	15	2295	82

TABLE. 11.

Run 314: Static charges of CO exposed to electron bombardment. Carbon 25 volts positive with respect to cathode. Times of exposure 15 - 1800 secs. CO pressure range 53 - 79 μ .

Initial CO Pressure (μ)	Time of Reaction (secs)	Average Emission Current (μ A)	Final Total Pressure (μ)	Pressure with CO ₂ frozen out (μ)	Final CO ₂ Pressure (μ)	Total Milli-amp Minutes	%CO.
65	15	290	50	47	3	72	94
77	60	295	33	31	2	295	94
79	300	475	7	6	1	2380	86
57	900	453	5	4	1	6795	80
57	15	372	41	40	1	93	97
60	60	356	28	26	2	356	93
60	300	370	15	13	2	1850	87
66	1800	471	12	11	1	14130	92
65	15	454	47	43	4	113	91
57	60	418	28	24	4	418	86
60	300	444	25	21	4	2220	84
68	900	440	20	16	4	6600	80
64	1800	462	14	11	3	13860	79
59	60	416	26	23	3	416	88
61	900	435	22	17	5	6525	77
54	600	383	25	22	3	383	88
66	60	407	44	37	7	407	84
75	300	414	44	35	9	2070	79
65	1800	406	25	18	7	12180	72
53	15	395	37	33	4	99	89
55	60	373	26	22	4	373	85
69	300	346	35	28	7	1730	80
65	180	355	30	23	7	10650	77

TABLE. 12.

Run 324: Static charges of CO exposed to electron bombardment. Without carbon, bare metal foil 25 volts positive with respect to cathode. Times of exposure 15 - 3600 secs. CO pressure range 70 - 125 μ .

(a)

Initial CO Pressure (μ)	Time of Reaction (secs)	Average Emission Current (mA)	Final Total Pressure (μ)	Pressure with CO ₂ frozen out (μ)	Final CO ₂ Pressure (μ)	Total Milli-amp Minutes	% CO.
73	15	70	68	65	3	17	96
160	60	212	47	43	4	212	91
90	900	453	49	43	6	6795	88
95	15	386	81	75	6	96	93
93	60	414	63	55	8	414	87
93	300	465	47	39	8	2325	83
91	900	474	45	37	8	7110	82
86	15	439	68	63	5	110	93
105	900	504	38	29	9	7560	76
75	15	430	54	49	5	107	91
107	15	380	86	80	6	95	93
100	15	392	80	73	7	98	91
75	60	379	42	36	6	379	86
85	60	414	45	39	6	414	86
120	60	379	88	76	12	379	86
115	300	436	74	62	12	2180	84
95	300	392	53	43	10	1960	81
78	300	389	46	37	9	1945	80
95	900	378	61	48	13	5670	79
93	900	380	51	41	10	5700	80
76	900	396	42	30	12	5940	72
85	15	409	62	57	5	102	92
95	15	369	74	65	9	92	88
81	15	382	53	48	5	95	91
125	60	372	88	80	8	372	91
85	60	349	49	41	8	349	84
115	60	327	72	62	10	327	86
118	300	357	75	62	13	1785	83

TABLE. 12 (Contd.,)

76	300	355	47	36	11	1775	77
110	300	338	73	60	13	1690	82
95	900	356	67	54	13	5340	81
110	900	317	71	56	15	4755	79
77	3600	332	52	39	13	19920	75
110	3600	332	63	47	16	19920	75
112	900	352	67	52	15	5280	78

(b) Conditions as in (a) except that appendix on reaction vessel immersed in liquid oxygen, therefore CO₂ removed immediately it is produced and does not interfere with radiolysis of CO.

94	15	337	72	64	8	84	89
88	60	263	35	5	30	263	14
75	300	69	29.5	1.5	28	345	5
70	900	82	31.5	.5	31	1230	1.5

TABLE. 13.

Run 312: Static charges of 60% CO₂/40% CO mixtures exposed to electron bombardment. Carbon 25 volts positive with respect to the cathode. Times of exposure 5 - 3600 secs. CO₂/CO pressure range 60 - 80 μ .

Initial CO ₂ /CO Pressure (μ)	Time of Reaction (secs)	Average Emission Current (mA)	Final Total Pressure (μ)	Pressure with CO ₂ frozen out (μ)	Final CO ₂ Pressure (μ)	Total Milli-amp Minutes	% CO.
66	5	232	59	45	14	19	76
71	60	239	45	40	5	239	89
68	300	314	20	18	2	1570	90
80	900	395	28	23	5	5925	82
65	15	207	62	50	12	52	81
81	300	276	70	57	13	1380	81
60	3600	369	14	12	2	22140	86
62	300	375	52	41	11	1875	79
68	300	268	69	57	12	1340	83
65	60	194	71	58	13	194	82
67	60	225	65	52	13	225	80
66	300	268	60	48	12	1340	80
69	900	275	53	41	12	4125	77
72	3600	276	25	18	7	16560	72
61	1800	256	27	20	7	7680	74
65	300	256	53	42	11	1280	79
66	60	162	61	52	9	160	85
65	60	159	66	55	11	159	83
62	900	230	42	32	10	3450	76
62	3600	212	35	26	9	12720	74
67	300	221	62	49	13	1105	79
60	300	196	53	42	11	980	79
64	1800	164	64	49	15	4920	77
68	1800	165	65	49	16	4950	76
66	300	214	73	58	15	1070	79

TABLE. 14.

Run 313: Static charges of 60% CO₂/40% CO mixtures exposed to electron bombardment. Carbon 25 volts positive with respect to the cathode. Times of exposure 15 - 3600 secs. CO₂/CO pressure range 60 - 75 μ .

Initial CO ₂ /CO Pressure (μ)	Time of Reaction (secs.)	Average Emission Current (mA)	Final Total Pressure (μ)	Pressure with CO ₂ frozen out (μ)	Final CO ₂ Pressure (μ)	Total Milli-amp Minutes	% CO.
65	15	192	55	45	10	48	82
73	60	180	61	56	5	180	92
70	300	222	43	39	4	1110	91
60	900	334	13	11	2	5010	85
62	1800	405	6	5	1	12150	83
70	900	458	23	17	6	6870	74
72	300	307	73	62	11	1535	85
60	60	276	61	54	7	276	89
66	15	262	63	52	11	65	82
65	300	363	62	52	10	1815	84
68	15	225	68	54	14	56	79
66	60	257	73	65	8	257	89
65	300	318	75	66	9	1590	88
65	900	331	61	49	12	4965	80
68	3600	266	42	32	10	15960	76
68	900	405	57	46	11	6075	81
71	1800	395	60	48	12	11850	80
73	60	333	71	60	11	333	84
70	300	345	69	60	9	1725	87
67	900	324	68	56	12	4860	82
69	3600	312	50	42	8	18720	84
61	900	316	65	56	9	4740	86
67	15	183	68	54	14	46	79
75	300	284	82	69	13	1420	84
75	1800	263	70	58	12	7890	83

TABLE. 15.

Carbon or bare metal foil 25 volts positive with respect to the cathode. CO pressure range 60 - 80 μ .

With carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-Amp Minutes	Net weight Increase of Carbon (mgms.)	CO ₂ Pressure (μ)
315	446	22	9812	.2	60
316	442	40	17680	1.1	78
318	406	60	27960	1.5	74
320	423	120	50760	2.1	75

Without carbon

Run No.	Average Emission Current (mA)	Time of Reaction (mins)	Total Milli-amp Minutes	CO ₂ Pressure (μ)
317	455	40	18200	74
319	436	60	26160	72
321	446	120	53520	80
322	403	40	16120	66

TABLE. 16.

Run 323: Flow of CO through system, CO₂ produced removed immediately by liquid oxygen around reaction vessel. Final CO₂ pressure measured. Without carbon, bare metal foil 25 volts positive with respect to cathode. Times of CO flow 30 - 600 secs. CO pressure range 63 - 92 μ .

CO Pressure (μ)	Time of Reaction (sec)	Average Emission Current (mA)	Final CO ₂ Pressure (μ)	Total Milli-amp Minutes
85	600	412	200	4120
80	600	404	200	4040
65	600	375	200	3750
72	300	405	150	2025
83	120	396	90	792
76	120	349	75	698
85	120	0	6	0
87	120	368	92	736
88	60	400	43	400
78	60	372	50	372
67	60	389	41	389
73	30	380	20	190
79	30	378	20	189
75	30	411	22	205
74	120	395	90	790
83	60	358	50	358
82	120	0	5	0
75	30	0	3	0
77	60	402	48	402
74	120	378	92	756
92	30	375	19	187
71	30	364	18	182
63	90	365	58	547
65	90	352	62	528
80	90	367	62	550

APPENDIX

1. Graphs of emission current from an oxide coated cathode versus time in the presence and absence of carbon.

figs.26 to 34 inc. CO_2 flow pressure 60-70 μ

figs.35 to 38 inc. CO_2 flow pressure 20 μ

FIG. 26. CARBON (OR METAL FOIL) AT A
POSITIVE POTENTIAL WITH RESPECT
TO THE FILAMENT.
APPLIED POTENTIAL 25V.
CO₂ PRESSURE 65 μ .

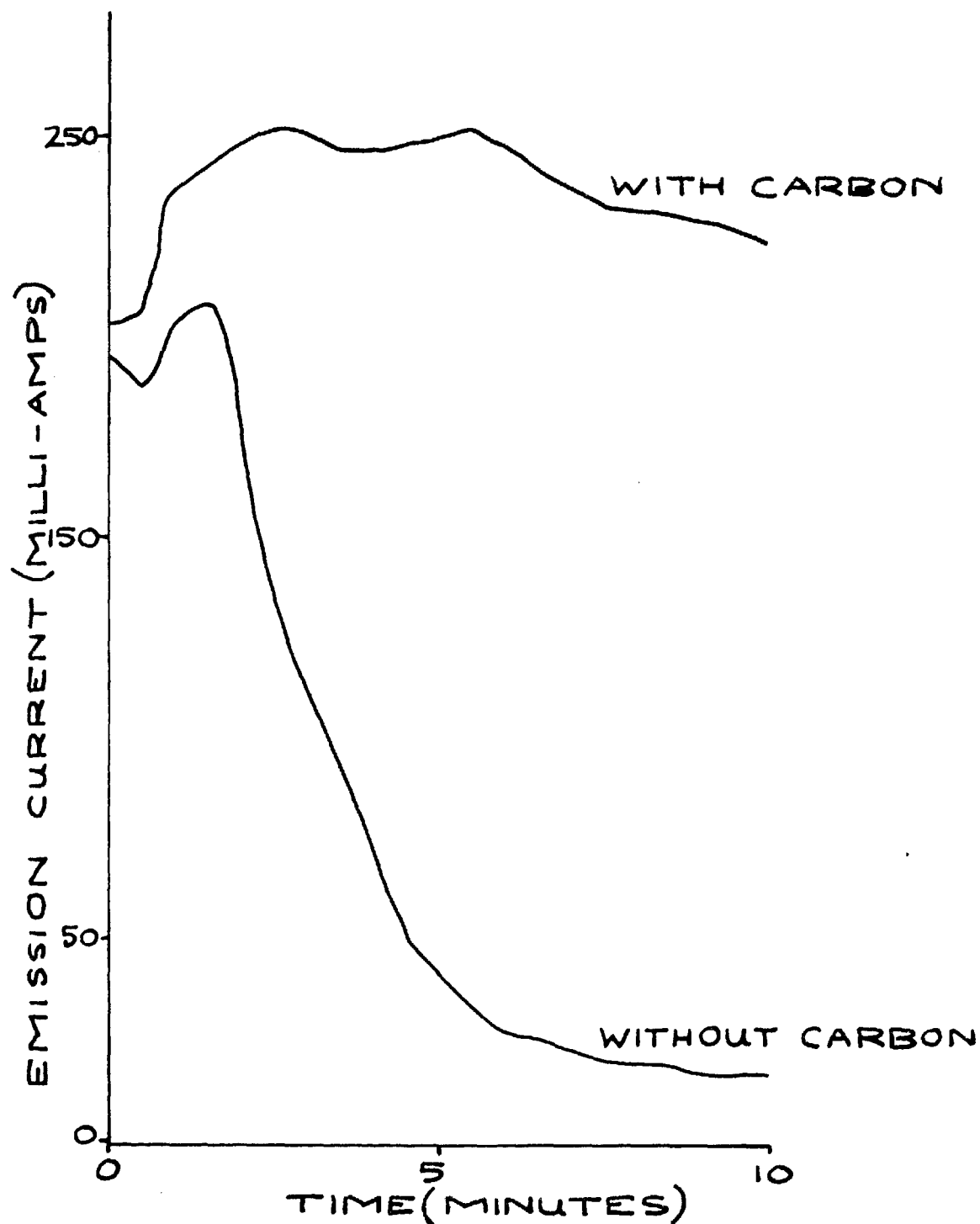


FIG. 27. CARBON (OR METAL FOIL) AT A
POSITIVE POTENTIAL W.R.T.
FILAMENT.

APPLIED POTENTIAL 25V.
CO₂ PRESSURE 62-72 μ .

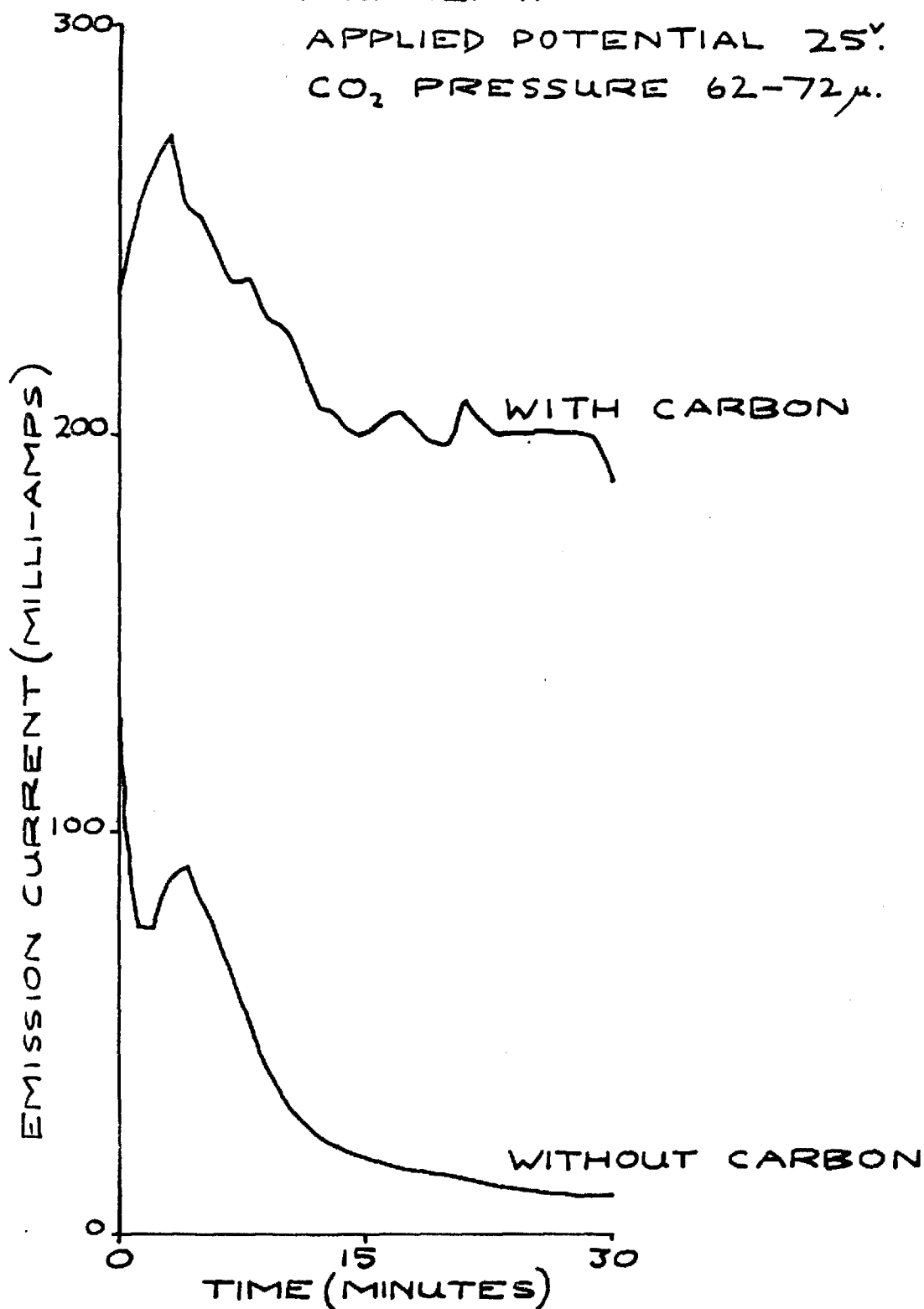


FIG. 28. CARBON (OR METAL FOIL) AT A
POSITIVE POTENTIAL W.R.T.
FILAMENT.

APPLIED POTENTIAL 25 $\sqrt$.

CO₂ PRESSURE 63-73 μ

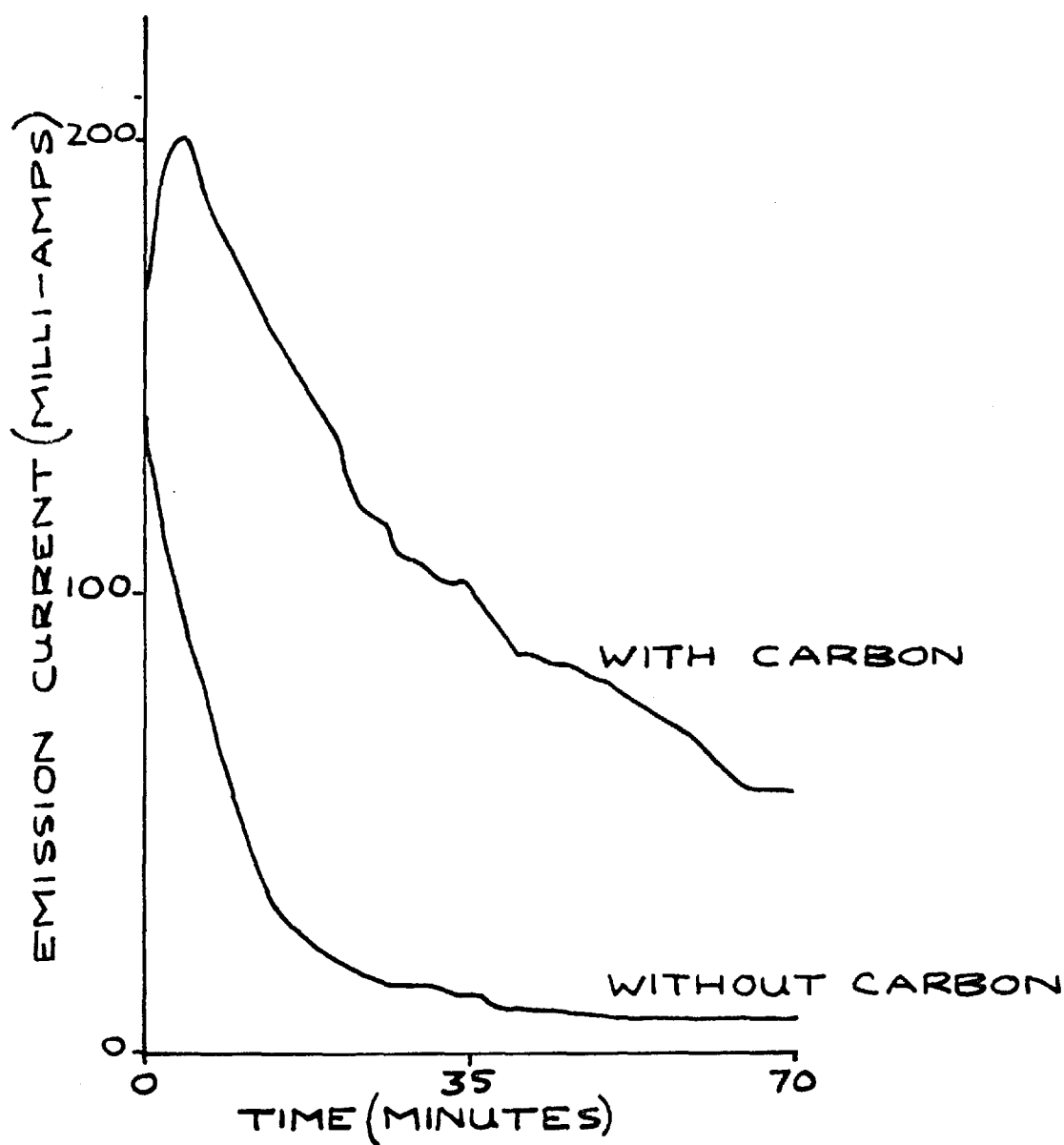


FIG. 29. CARBON (OR METAL FOIL) AT
SAME POTENTIAL AS THE
FILAMENT.

APPLIED POTENTIAL 25^v

CO_2 PRESSURE $63 - 67 \mu$

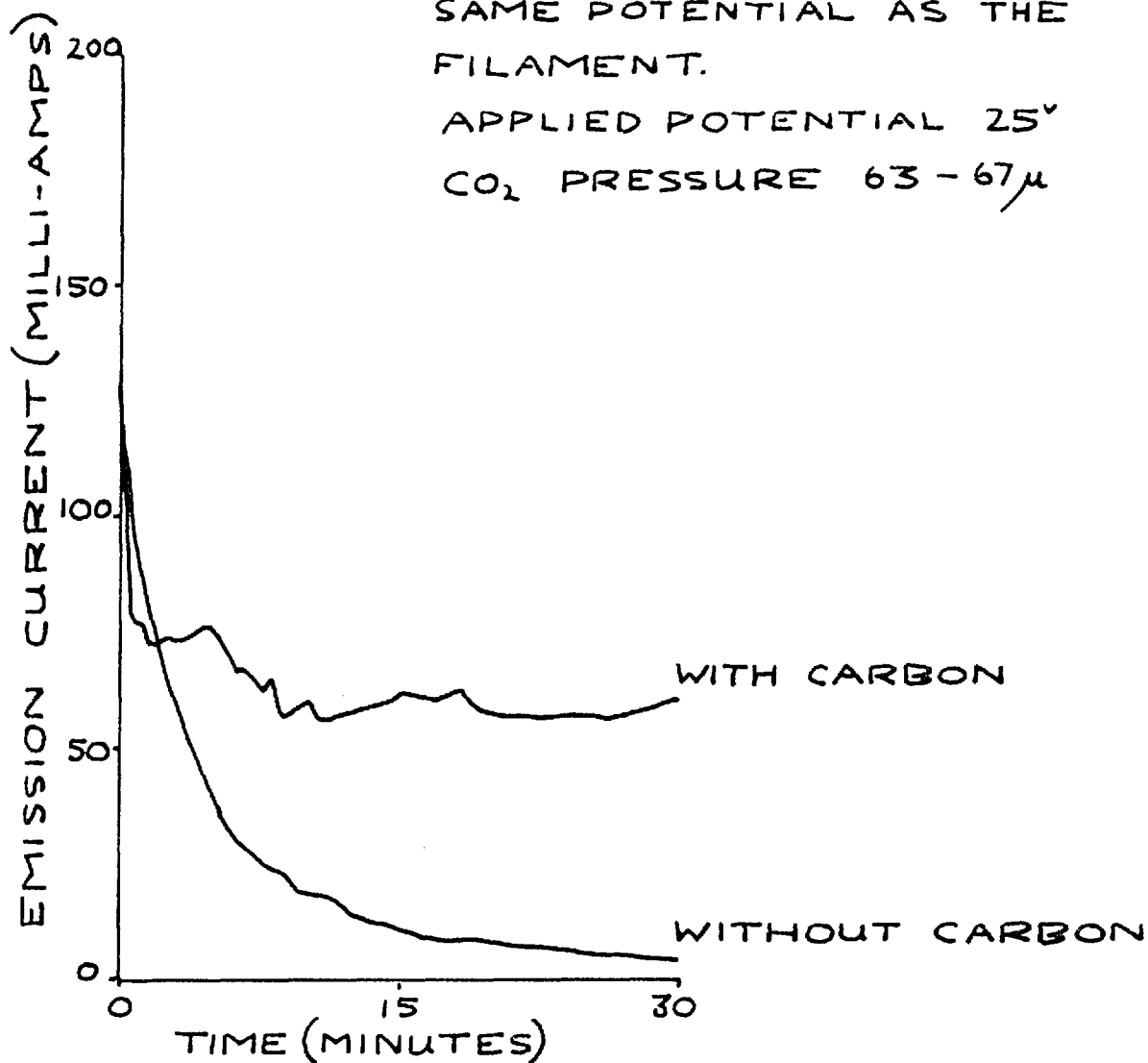


FIG. 30. CARBON (OR METAL FOIL) AT
SAME POTENTIAL AS FILAMENT.
APPLIED POTENTIAL 25V.

CO₂ PRESSURE WITH CARBON 62 μ
" " WITHOUT CARBON 76 μ .

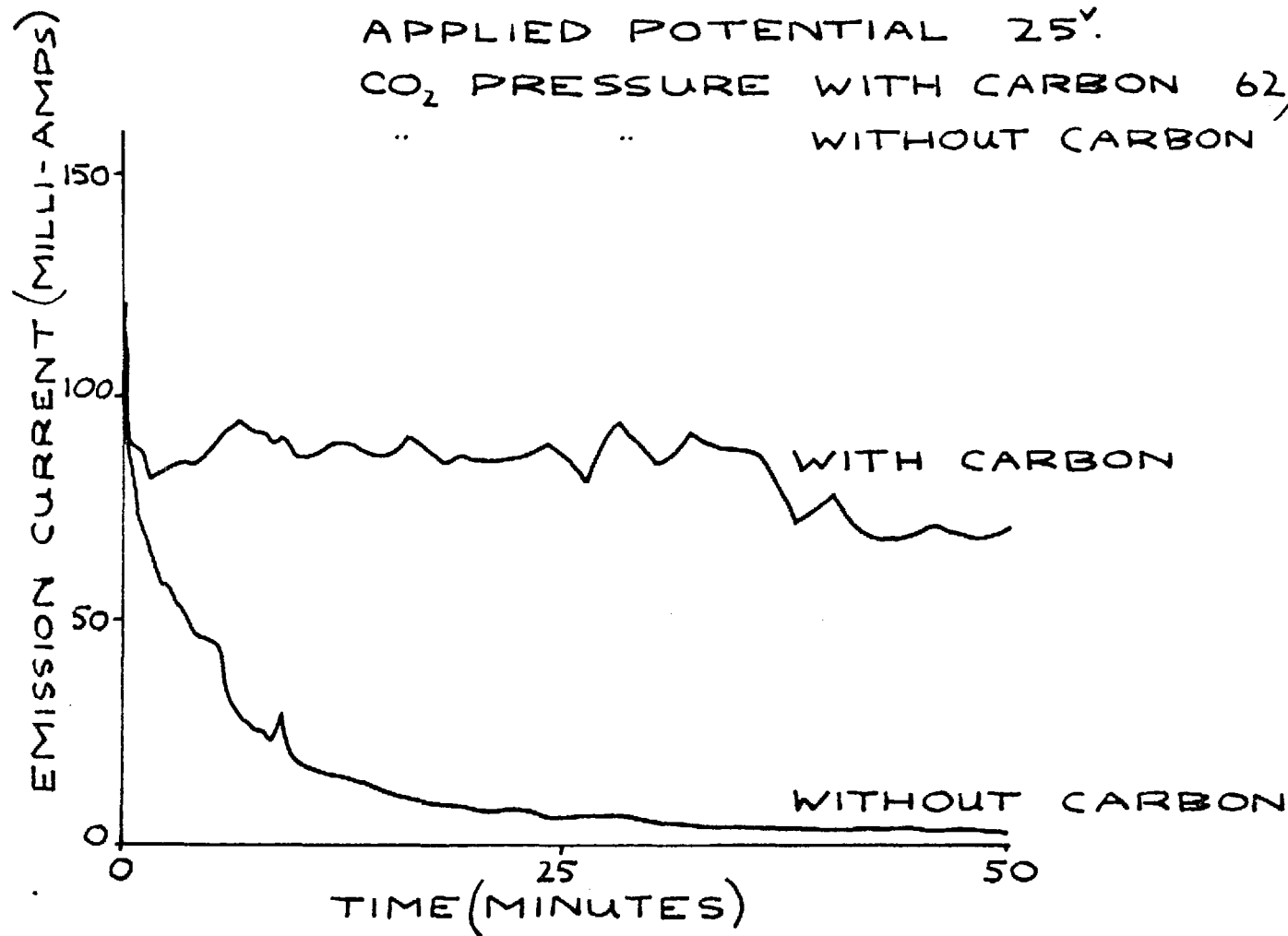


FIG. 31. CARBON (OR METAL FOIL) AT
SAME POTENTIAL AS FILAMENT.
APPLIED POTENTIAL 25^v.
CO₂ PRESSURE 70 μ .

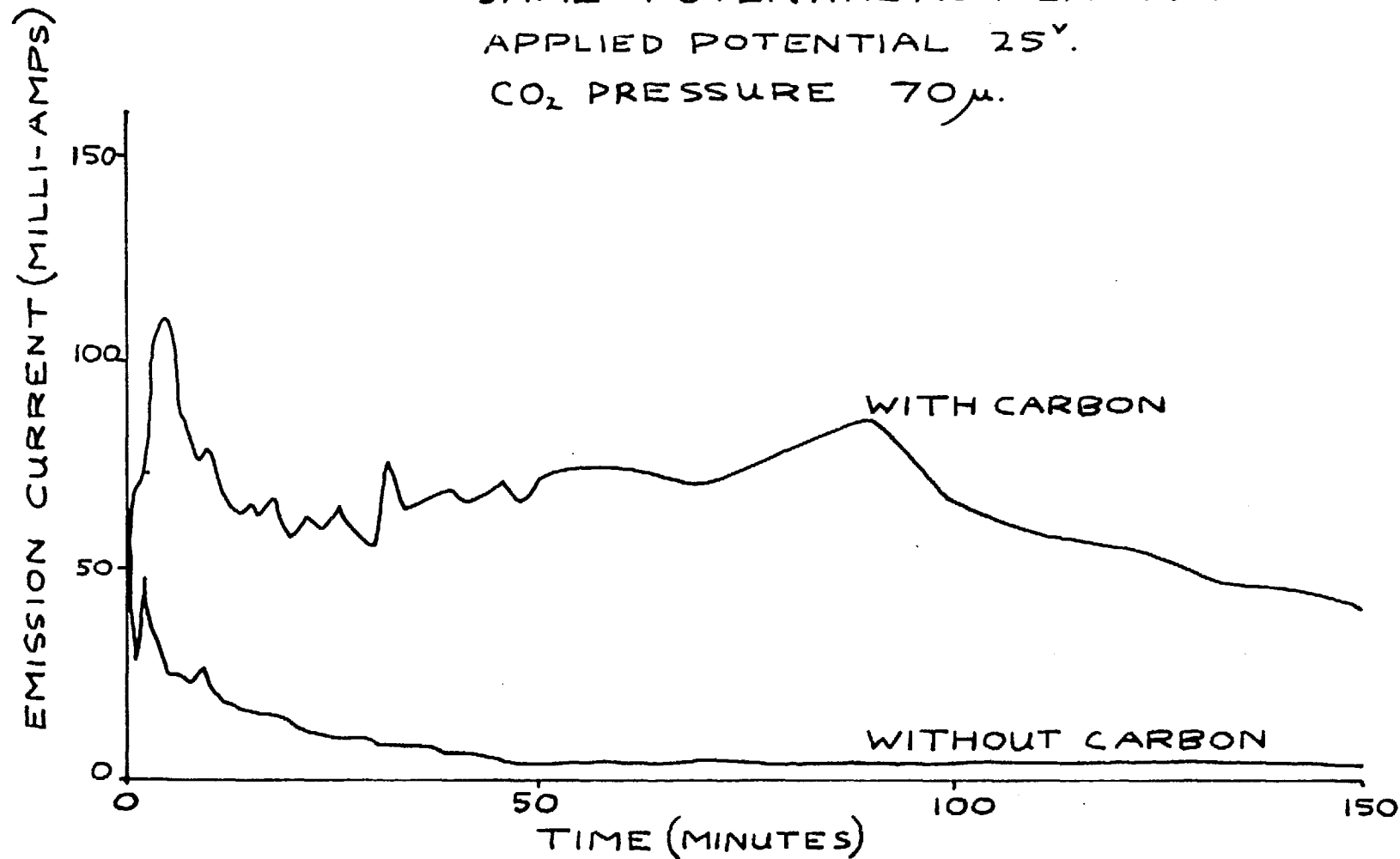


FIG. 32. CARBON (OR METAL FOIL)
SUSPENDED IN REACTION
VESSEL.
APPLIED POTENTIAL: 25V.
CO₂ PRESSURE 65 μ .

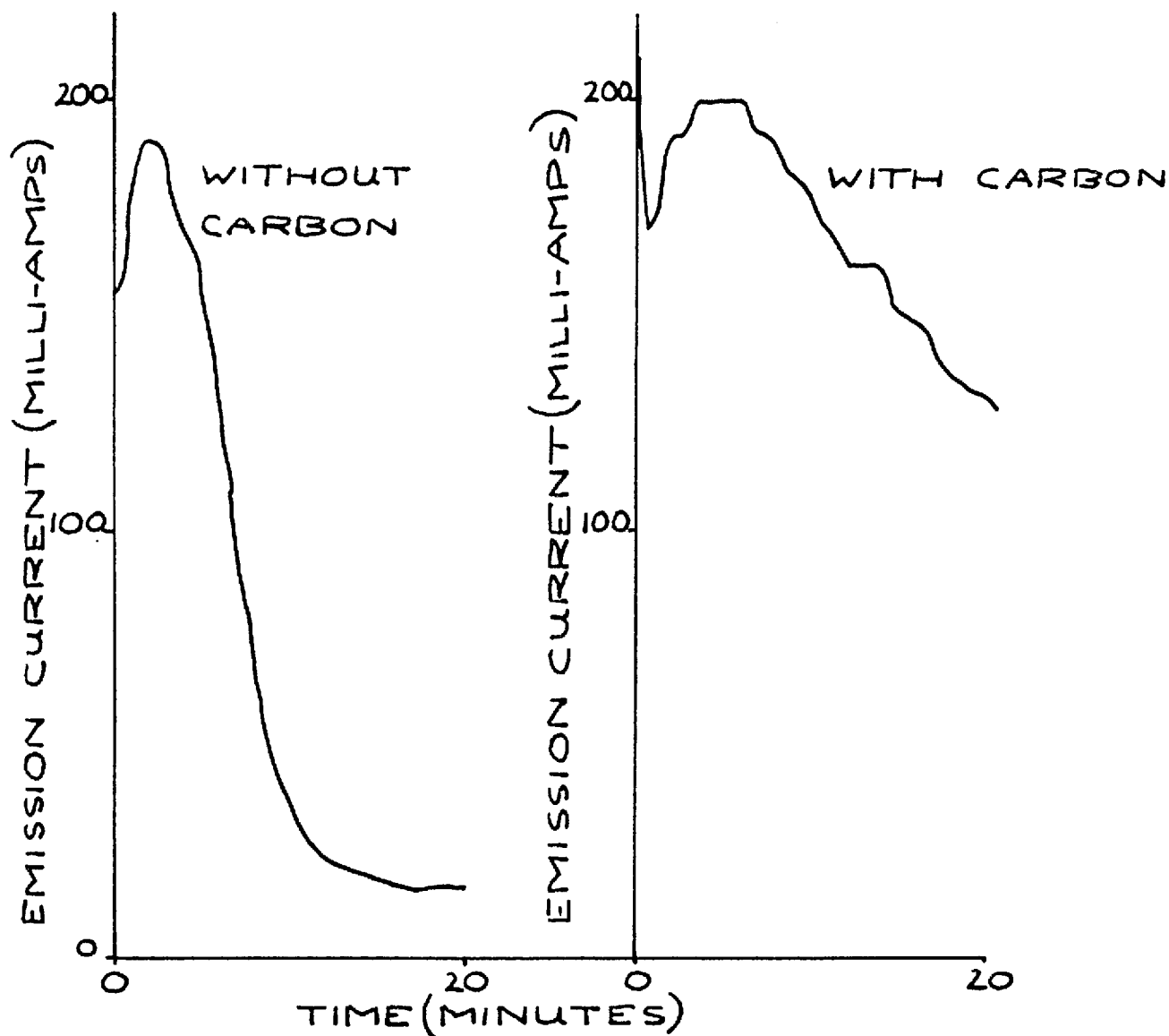


FIG. 33. CARBON (OR METAL FOIL)
SUSPENDED IN REACTION
VESSEL.
APPLIED POTENTIAL 25%
CO₂ PRESSURE 65 μ .

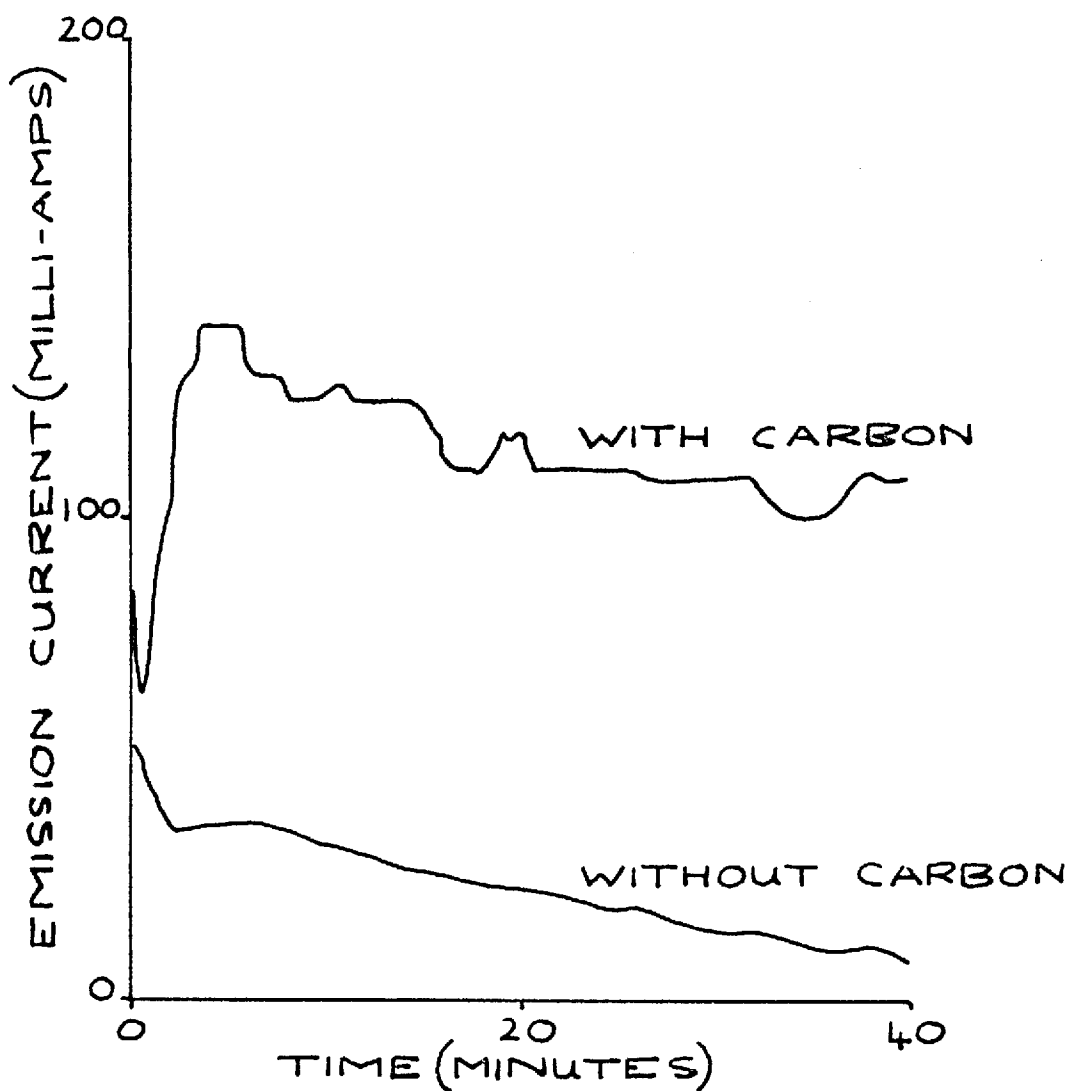


FIG. 34. CARBON (OR METAL FOIL)
SUSPENDED IN REACTION VESSEL.
APPLIED POTENTIAL 25%.
CO₂ PRESSURE 67-73 μ .

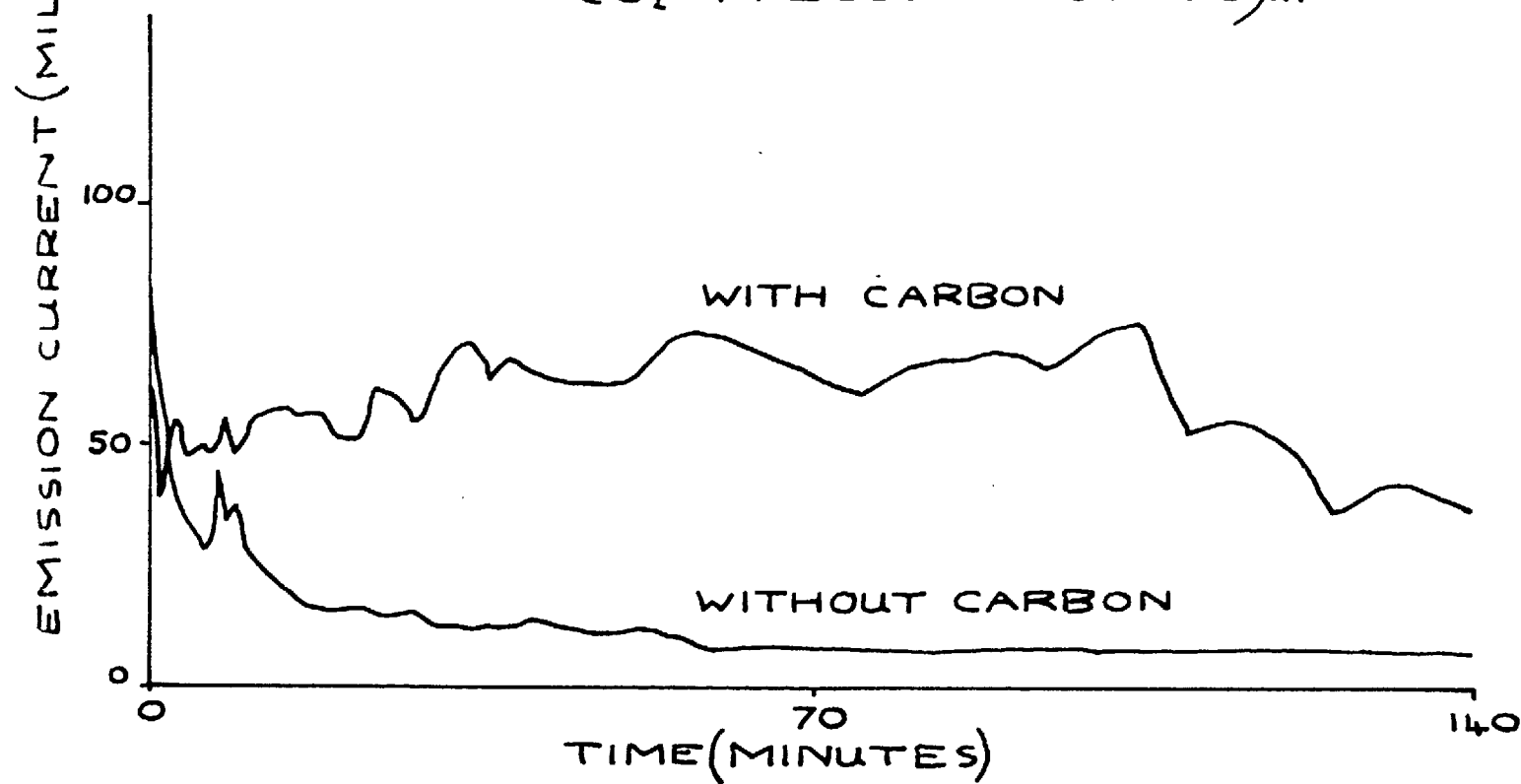


FIG. 35. CARBON (OR METAL FOIL) AT A
POSITIVE POTENTIAL W.R.T.
FILAMENT.

APPLIED POTENTIAL 25^v.

CO₂ PRESSURE 20 μ .

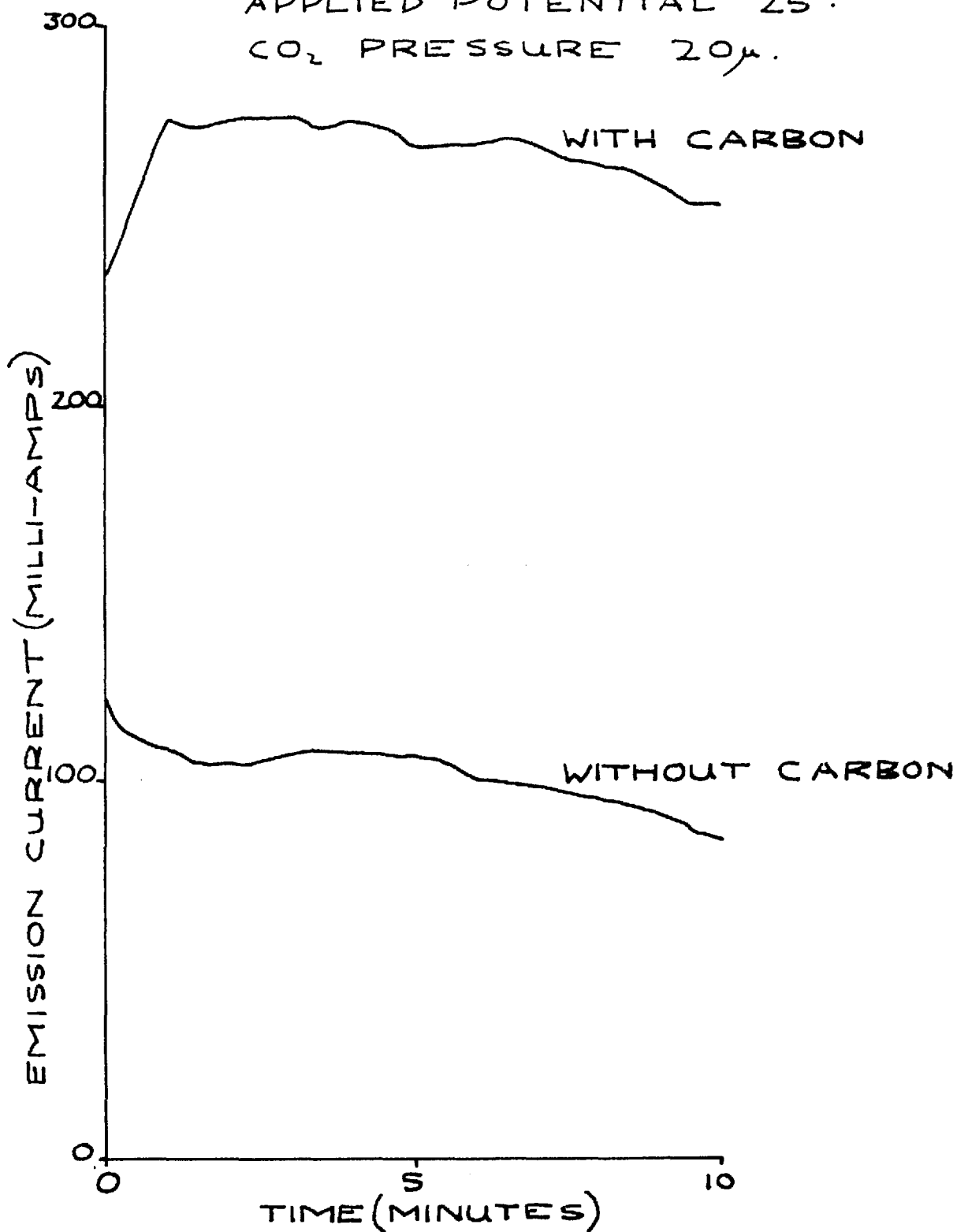


FIG.36. CARBON (OR METAL FOIL) AT
A POSITIVE POTENTIAL W.R.T.
FILAMENT.

APPLIED POTENTIAL 25V.

CO₂ PRESSURE 20 μ .

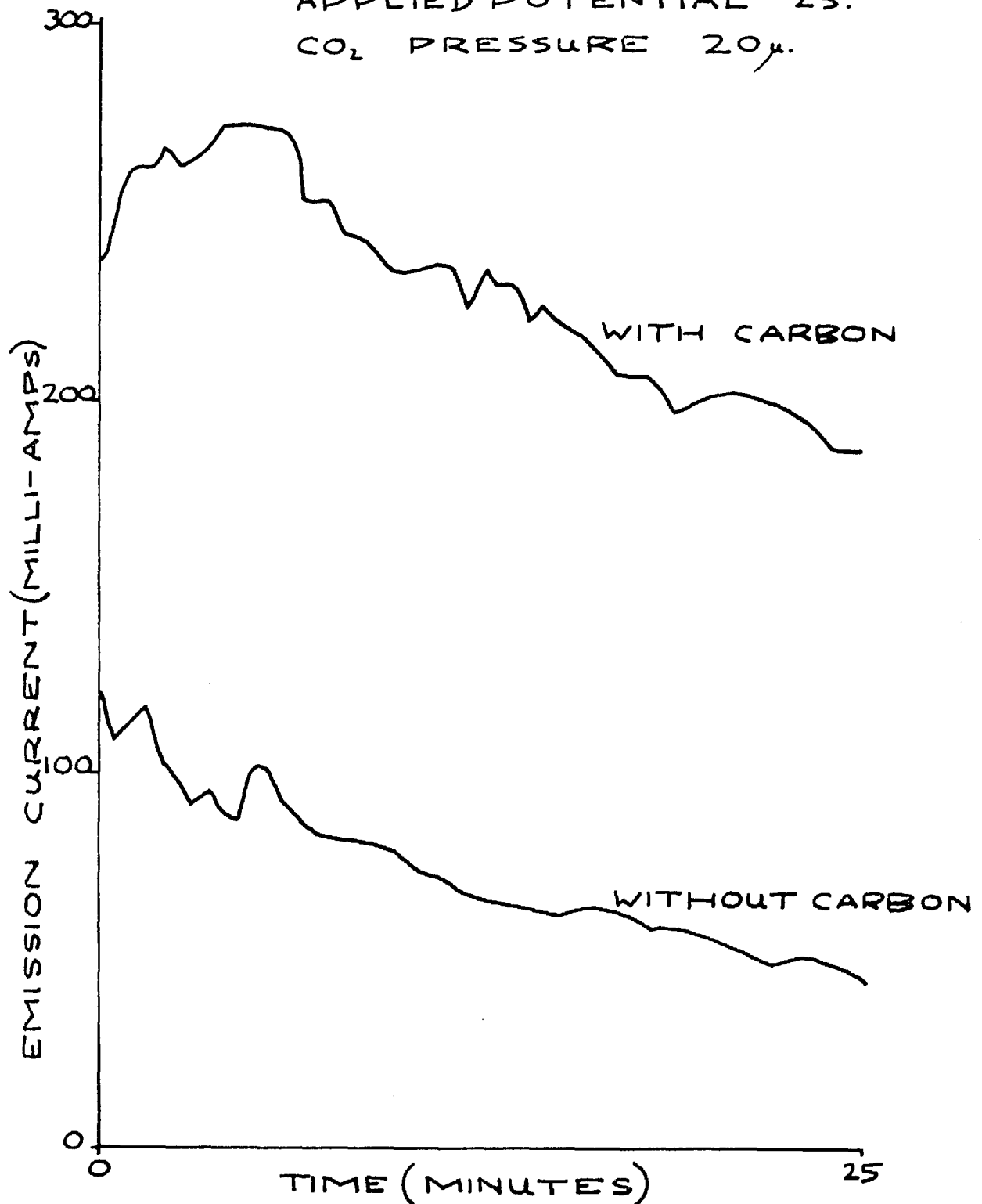


FIG. 37. CARBON (OR METAL FOIL) AT
SAME POTENTIAL AS THE
FILAMENT.
APPLIED POTENTIAL 25V.
CO₂ PRESSURE 21 μ .

