The nature of the surface complexes formed on a sample of carbon depends on the composition of the gas phase and on the oxidation kinetics. In 1963 we showed that the interpretations of the phenomena were simplified by the use of very pure graphite. The characterisation of the products has been undertaken in different ways, in particular using a method of thermal degassing under vacuum in successive stages of increasing temperature. After having studied the oxidation of graphite in dry or damp air or oxygen at different temperatures, we extended our field of investigation to cover the behaviour of graphite oxidised radiolytically. The active oxygen is formed by radiolysis of CO₂ under 40 bars pressure, at 350°C temperature and in a flux of about 0.6 mg⁻¹. In addition we studied the effect on carbon degassing of small quantities of methane added to the CO₂.

Graphite irradiated in CO₂ - Since the CO₂ used in the irradiation loops contains more than 20 ppm of water, we compared this oxidation with the corrosion of graphite in damp air: the overall quantities of CO + CO₂ and H₂ + CH₄ obtained by desorption up to 1700°C differ little between one type of oxidation and the other.

On the other hand the quantities of gas released at a given temperature are quite different; the amount of carbon monoxide given off is smaller in the case of the radiolytically oxidised products at about 600°C whereas it is distinctly larger at a higher degassing temperature. In addition the quantity of CO₂, which is very small (a few per cent) after thermal oxidation, reaches about 50% after radiolytic oxidation.

The hydrogen given off from irradiated graphite heated under vacuum is slightly greater in quantity, and begins to be detectable at a considerably higher temperature (1300°C) than after thermal oxidation (1000°C).

Graphite irradiated in CO₂ with addition of CH₄ - Depending on certain parameters, in particular flux, temperature, dimensions and texture of the sample, methane concentration, we observed variations in weight of a positive or negative variety.

a) Examination of samples showing a weight loss after irradiation - Between 0 and 0.3% weight loss the CO + CO₂ desorption curves are very similar, and comparable to those obtained without methane.

Hydrogenated compounds (H₂ + traces of CH₄) differ little according to the degree of corrosion, and start to appear at a lower temperature than those obtained after irradiation in pure CO₂. At 1000°C, 30 to 40% of the hydrogen is desorbed in the former case, whereas in the latter no appreciable quantity is produced below 1300°C. Above 1500°C the amounts of gas obtained become entirely comparable.

b) Examination of samples showing a weight gain after irradiation

The first thing we should note is the appearance of a very large quantity of gas on degassing, the amount being greater in proportion to the weight gained by the carbon.

* Time of irradiation 500 heures (weight loss ∼ 1% in pure CO₂)
This process takes place mainly in two temperature zones, the first from 600 to 1000°C and the other in the vicinity of 1500°C. These two zones lie in the same temperature regions as those defined in the preceding cases but are distinctly broader.

The volumes of carbon oxides (CO + CO₂) are appreciably larger than those of hydrogenated compounds (H₂ + traces of CH₄) over the whole degassing temperature range; here again CO₂ constitutes about 30% of the oxides, and is given off almost completely below 1000°C.

From these first results we feel it is possible to formulate some hypotheses concerning the nature of the surface complexes formed in the various cases:

1) The groups formed from radiolytic oxidation by CO₂ containing traces of moisture have the formula CₓHᵧOz but are different in composition from those formed by thermal oxidation; they are more stable under the action of temperature.

2) In the presence of small concentrations of methane, when no weight increase is observed in the carbon after irradiation, the desorption kinetics are very similar to those obtained without methane; a small amount of hydrogen given off at low temperature is the only indication of the possible existence of a new compound, relatively unstable thermally.

3) The weight increase of carbon is correlative to the existence of two substantial gas liberation peaks. The first only occurs in the presence of methane and seems to be due to the decomposition of this gas, but the presence of oxygenated compounds at the same temperature suggests an interaction with the CO or CO₂ during radiolysis. After thermal oxidation in the presence of moisture the hydrogen and CO are given off at a temperature slightly below the second peak, which leads us to think that the water could have some connection with its formation. However the presence of a much larger quantity of hydrogen can indicate a more complex mechanism.

The experiments under irradiation were installed in the reactor Siloé by the "Section de Préparation et d'Exploitation des Irradiations".