CLM - P 451

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METHANE FORMATION DURING THE INTERACTION OF ENERGETIC PROTONS AND DEUTERONS WITH CARBON

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ABSTRACT

Methane production has been investigated as a function of temperature during ion bombardment, and during post-irradiation thermal release of implanted hydrogen in pyrocarbon. The reaction is shown to be directly correlated with the release of trapped hydrogen rather than an ion/surface interaction. During bombardment, methane production is not observed below target temperatures of 450K. The methane yield reaches a maximum of 9% of the hydrogen release rate at 850K after which it falls to < 0.2% at 1200K. No residual gas effects on hydrocarbon production have been observed even at pressures up to 10^{-5} torr.

Following bombardment, methane is formed during heating of the carbon at temperatures in excess of 800K. A peak in methane production is observed at 1000K, whilst the peak in hydrogen release occurs at 1200K. An analytical model for the temperature dependence of methane production during bombardment is presented, and this agrees well with the experimental results.

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1. INTRODUCTION

There is a considerable body of literature on the interaction of carbon with hydrogen, particularly as a plasma[1-5]. In these investigations the formation of methane and, at higher temperatures, acetylene has been observed. In many of them a maximum was observed in the rate of production of methane as a function of temperature at $\sim$ 800K. The importance of these reactions has recently been recognised in the field of thermonuclear fusion and in other energy technologies such as coal gasification. This has stimulated a number of recent investigations of the interaction of ion beams[2,3] and atomic beams[4] with carbon surfaces. Busharov et al[2] using a 10 keV H^+ beam found that the sputtering coefficient decreased in the temperature range 800°C to 1400°C and was constant in the range 400-800°C. Other investigators[3] have seen a maximum in the total sputtering coefficient at $\sim$ 600°C with incident ions in the energy range 1 to 5 keV. Balooch and Olander[4], using an atomic hydrogen beam, have on the other hand seen no maximum, but a steadily decreasing production of methane as the temperature increases. In order to examine the interaction in more detail we have undertaken

an investigation of the rate of production of methane during ion bombardment using a mass spectrometric technique.

2. EXPERIMENT

The ion beam apparatus used in the present work has been described in detail in an earlier publication, McCracken et al[6]. Principal features include magnetic beam selection to avoid possibility of impurities, and a differentially pumped system which enables background pressures of $\leq 1 \times 10^{-9}$ torr (H_2, CH_4 and CO) to be maintained in the target chamber. Targets such as Ni and Mo quickly saturate with hydrogen during bombardment, when all the incident proton beam is re-emitted. Under these conditions a maximum partial pressure of $2\text{-}3 \times 10^{-8}$ torr of hydrogen is recorded in the continuously pumped target chamber. A quadrupole mass spectrometer is used to make measurements of both H_2 (mass 2) and CH_4 (masses 15 and 16) re-emission. Detection of atomic species (e.g. H,D) would not be expected and was not observed, since the quadrupole was situated out of line of sight of the target.

Calibration of the mass spectrometer for hydrogen, methane and acetylene was made prior to the series of experiments on pyrocarbon. This was done using a gas handling plant and a sintered leak of known conductance. The hydrogen calibration was checked using the ion beam as a gas source, under target saturation conditions.

The target consisted of a small strip of pyrocarbon, 10 mm long x 1 mm x 0.5 mm, with its plane of deposition normal to the incident proton beam. A 0.025 mm diameter Pt/Pt-Rh. thermocouple was fixed into a small hole in the carbon using an electron beam welder. The couple was used via a control system to ramp the target temperature up to 1700K for gas release measurements, and hold the temperature constant during bombardments.

A slightly different arrangement to that used in earlier work is now used to achieve a reasonably uniform beam current density over the bombarded area. The central region of the 3-4 mm diameter beam is used for target bombardment, whilst the beam edges are allowed to spill onto a zirconium surface, which acts as a trap for the incident protons[7]. The zirconium can be rotated into the beam line via a rotary feed-through, as can a molybdenum target which quickly saturates and has the opposite effect of re-emitting all the beams. These facilities are used to check hydrogen background levels and quadrupole calibration during bombardments.

3. RESULTS

The generation of methane represents a chemical erosion over and above that

normally associated with ion bombardment, i.e. physical sputtering. The experiments have been planned to examine the extent of this process as a function of target temperature. It will be shown that the trapped hydrogen (rather than the incident beam) plays an important role in methane formation, hence it is useful to examine the form of hydrogen re-emission with ion dose during bombardment. Such curves are illustrated in Figure 1 for a variety of carbon temperatures up to 1163K. In all measurements in this work, 20 keV ions (H^+ or D^+) were used.

A sample-hold system on the quadrupole mass spectrometer enabled the methane production rate to be monitored simultaneously with the hydrogen re-emission rate during bombardment. Results from the measurement, Figure 2, are shown for a deuterium beam incident on pyrocarbon at 850K. The data have been normalised to the 100% D_2 re-emission level to show that the CD_4 production follows closely the D_2 release. In fact, in terms of number of molecules of each gas being formed, CD_4 is about 9% of the D_2 at the optimum temperature for methane production. No reduction in the D_2 level during methane production was observed, hence no normalisation was found to be required for D_2 re-emission data.

In Figure 3 is plotted the envelope of results from a series of experiments at different target temperatures, in which the equilibrium gas release rates of both methane and deuterium were measured. A sharp peak a little above 800K (deutero-methane) and at 850K (methane) is observed in the hydrocarbon production rate. Very little acetylene formation was observed in the temperature range of the present measurements. Methane production falls to $\leq$ 0.2% beam level (the minimum detectable level) at temperatures below $\sim$ 450K and above $\sim$ 1200K. The characteristic fall off in D_2 re-emission above 1200K observed earlier[8], and attributed to inward diffusion of deuterium, is again observed in this figure. It is observed that some 90% of the total implanted deuterium is released as D_2 during a thermal desorption.

Post-bombardment thermal release of gas trapped in the solid during low temperature bombardment has also been investigated. At the end of bombardment the gas release of both methane and hydrogen stop immediately, the peak heights decaying in the time determined by the vacuum time constant. The target is then heated up linearly with time and the methane and hydrogen release rates monitored simultaneously. The results are shown in Figure 4. It is observed that the deuterium shows a maximum due to the thermal release from the implanted region followed by the depletion of the gas from the solid. The deutero-methane shows a similar behaviour but the maximum production rate occurs at a lower temperature and is, in fact, $\sim$ 33% of the maximum deuterium production rate. It follows that the rate of methane formation is not directly proportional simply to the release rate of hydrogen. It is also noteworthy that the peak in the methane formation rate is some 200K higher than that occurring during bombardment.

From the results of Figure 4 we see that no thermal re-emission takes place

at temperatures $\lesssim$ 850K. However in Figure 1 it is clear that at low temperatures, e.g. 373K, re-emission is occurring at doses $\gtrsim 6 \times 10^{17}$ ions cm^{-2}. This release during bombardment is temperature dependent. Beam heating was considered, but shown to be unimportant even at the highest current densities used. Thus the mechanism of gas sputtering or ion induced re-emission must be responsible. This mechanism has previously been studied in detail for Ar^+ and He^+ ions in tungsten[9,10].

4. DISCUSSION

An examination of the experimental results leads to the clear conclusion that the methane formation occurs by the interaction of the trapped atoms with the surface as they diffuse out rather than the incident energetic ions. A similar suggestion has been made by Busharov et al[2]. This conclusion is most obvious from the results of Figure 2 where it is observed that methane production only starts when the deuterium is released rather than when bombardment begins at t = o. The next question is to ask why the methane formation rate has a maximum? A qualitative argument has been put forward that it is the result of the increasing chemical reaction rate and a decreasing hydrogen residence time on the surface[11]. Very recently a detailed model has been proposed by Balooch and Olander[4] taking into account these factors. It shows clearly that since both the chemical reaction rate and the residence time are exponential functions of temperature the formation will also be exponential, i.e. there will be no peak. They show that the methane production rate decreases with increasing temperature in very good agreement with their experimental results using thermal hydrogen atoms.

In order to explain the peak observed in the presence of ion interactions we propose the following model as a development of that suggested by Balooch and Olander. The rate for formation of methane $\mathcal{R}$ is given by:

$$\mathcal{R} = f\ (n_s)\quad F(T) \tag{1}$$

where $F(T) = A \exp(-Q_1/RT)$, $f(n_s)$ is a function of surface concentration of hydrogen atoms n_s, and A and Q_1 are the constants of the chemical reaction rate $F(T)$. The surface concentration is given by:

$$\frac{dn_s}{dt} = J - J_o\, \sigma\, n_s - \frac{n_s}{\tau} \tag{2}$$

where J is the rate of arrival of hydrogen atoms from the bulk to the surface, J_o is the arrival rate of the incident ions and τ is the surface lifetime, $\tau = \tau_o \exp(Q_2/RT)$. In equation (2) the third term is the rate of thermal desorption of hydrogen atoms. We have neglected the other terms in their earlier analysis[4]

leading to depletion of the n_s, due to methane and acetylene formation, on the grounds that they are small. The second term is the new term included to take into account depletion of the surface concentration due to desorption induced by the incident ions. The cross-section σ for this process is known to be large, $\sim 10^{-16}$ (11).

To obtain the temperature dependence let us assume the steady state situation where $dn_s/dt = 0$ and $J = J_o$. Hence:

$$n_s = J_o \Big/ \{J_o \sigma + \tau_o^{-1} \exp(-Q_2/RT)\} \qquad (3)$$

Now taking the simplest case and assuming that $\mathcal{R}$ is directly proportional to n_s we obtain

$$\mathcal{R} = J_o A \exp(-Q_1/RT) \Big/ \{J_o \sigma + \tau_o^{-1} \exp(-Q_2/RT)\} \qquad (4)$$

which can be shown to have a maximum at T_m

$$T_m = \frac{Q_2}{R} \left[\ln \frac{(Q2/Q1 - 1)}{(J_o \sigma \tau_o)} \right]^{-1} \qquad (5)$$

Experimentally $J_o = 10^{15} cm^{-2} s^{-1}$, $\sigma \sim 10^{-16} cm^2$, and $\tau_o = 10^{-13}$ was assumed. A good fit to the experimental curve is obtained using Q_1 = 38kcals/mole, Q_2 = 54.6kcals/mole, Figure 5. Q_2 is determined by the position of the peak. Q_1 being within the logarithmic term is not very sensitive, and the estimated value is only very approximate. A value of 2×10^{-3} for the constant A was used to achieve normalisation to the maximum observed CH_4 yield. This does not, of course, affect the shape of the curve.

From equation (4) it is seen that at high temperatures the formation rate of methane is limited by thermal desorption of H_2 and as the temperature increases the formation rate $\mathcal{R}$ decreases. As the temperature decreases the chemical reaction rate F(T) decreases. However, if no beam desorption takes place the lifetime increases at a greater rate than the reaction rate decreases, $(Q_2 > Q_1)$. Thus the formation rate $\mathcal{R}$ of the methane increases at lower temperature. If there is also beam desorption then at some temperature the beam desorption rate $J_o \sigma$ becomes comparable with the thermal desorption term τ; the longer lifetime does not occur and the methane production is dominated by the chemical rate of reaction F(T) which decreases as temperature decreases. An interesting consequence of this model is that the position of the peak will vary with the desorption cross section σ and hence with beam energy, as observed by Roth et al.(3) However, as

there is yet no reliable experimental data for σ as a function of energy, no quantitative comparison can be made. The value of n_s, (10^{16}cm^{-2}) deduced from equation (3) at low temperature is not unreasonable when one considers that one carbon atom can possibly accomodate several hydrogen atoms in the near-surface region.

Considering the results shown in Figure 3 it is seen that the deutero-methane peak occurs at a lower temperature than the hydrogen methane. This could be explained by a slight difference in the activation energy for desorption which is the principal parameter determining the position of the peak. In Figure 4 the appearance of the peak at much higher temperature is due to the time dependence of the flux to the surface, i.e. J in equation (2) is varying with time. This emphasises the dependence of $\mathcal{R}$ on the surface concentration n_s.

It is obvious that this model is oversimplified and, in particular, it is likely that the formation rate is a higher order function of the surface concentration n_s. Further development of the model taking into account time dependence and dependence on ion beam energy is required.

5. CONCLUSIONS

The experimental results show the methane production rate during H^+ bombardment of carbon to be determined primarily by the equilibrium concentration of hydrogen atoms on the carbon surface. A model has been put forward which explains the observed peak in the methane production rate with temperature. It also explains the difference between the case of ion bombardment and the interaction of a thermal atomic beam as being due to the effect of ion induced desorption.

Previous investigations where a peak has been observed have in general used r.f. discharges. In these cases some desorption due to either ions or electrons would be expected, and this may well explain the disagreement with the temperature dependence observed using thermal atoms. The temperature at which the peak occurs varies considerably, and this would be consistent with the variations in discharge conditions.

The existence of a peak follows from the supposition of one temperature independent process (beam desorption) and one temperature dependent process (thermal desorption). The position of the peak is determined by the parameters governing thermal and beam desorption. Thus an alteration of the surface structure or the presence of impurities may have a marked effect on methane production. Secondly, the current density and the cross section for desorption also change

the position of the peak and its absolute magnitude. Thus the situation in a fusion reactor with a large ion energy distribution and a large flux of neutrons and other radiation will be quite different from that in a laboratory experiment. In general the increased radiation will be expected to lower the hydrogen atom concentration and hence the formation rate of methane.

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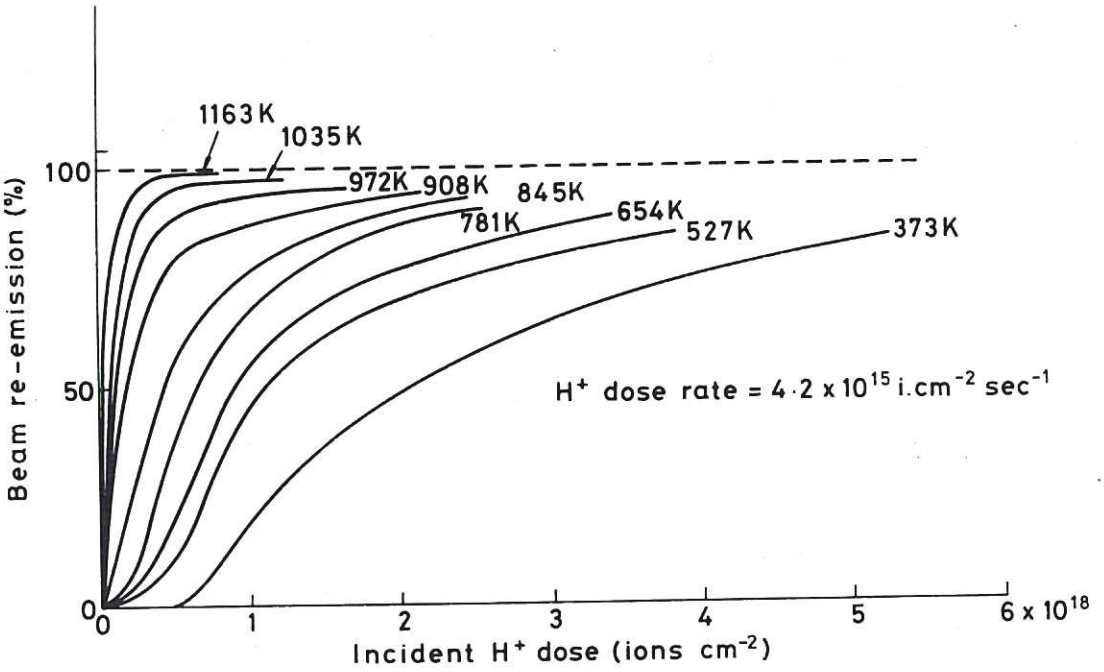

Fig.1 Re-emission of H_2 from pyrocarbon during 20 keV H^+ bombardment, at different target temperatures.

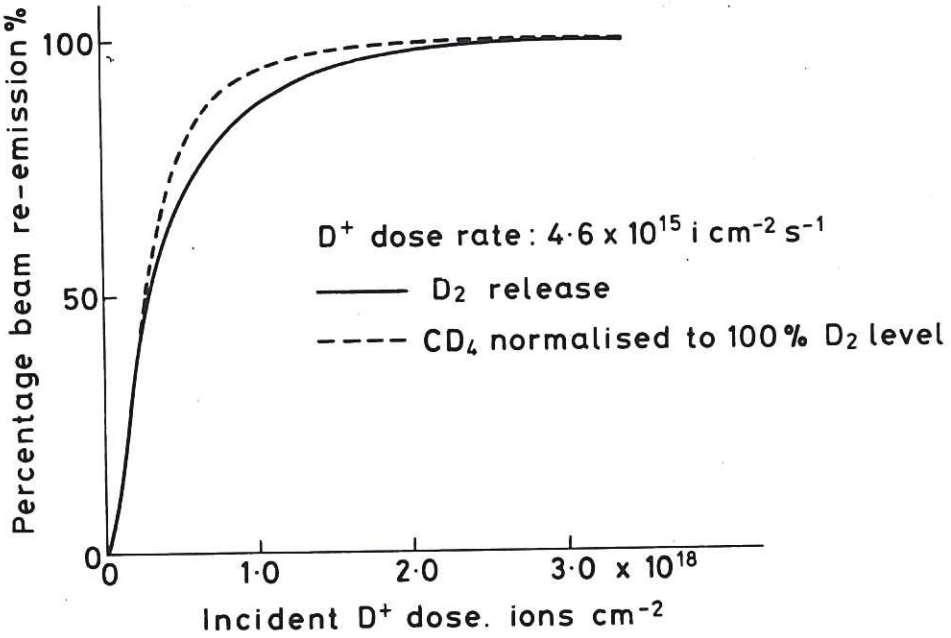

Fig.2 Methane formation, and deuterium re-emission during 20 keV D^+ → pyrocarbon at 850K.

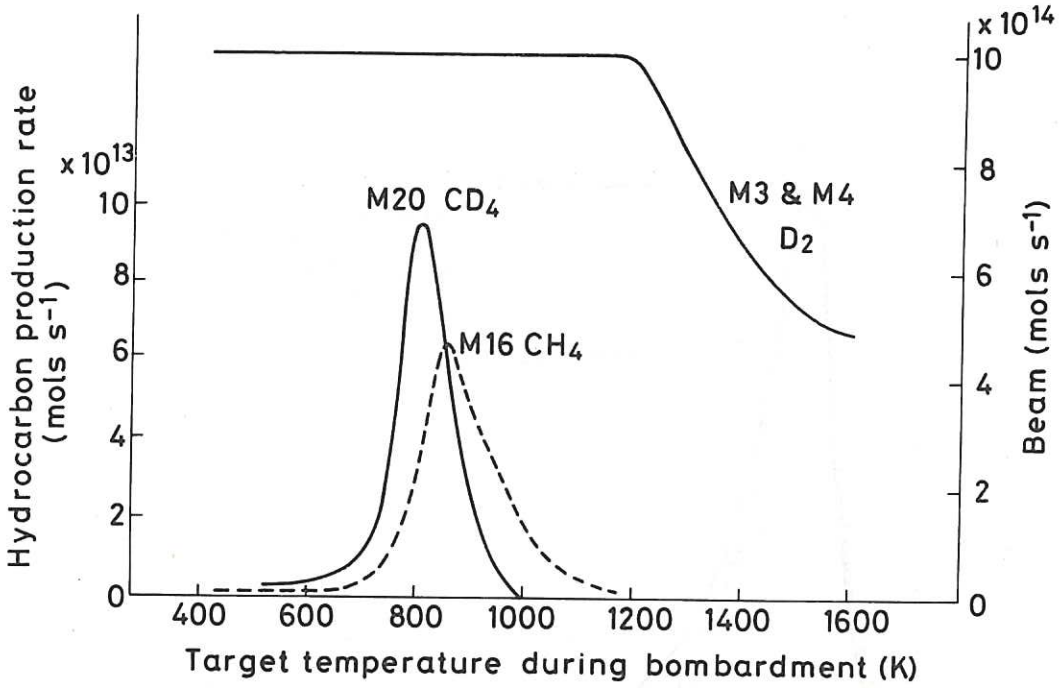

Fig.3 Equilibrium gas release rates as a function of target temperature during H^+ and D^+ → pyrocarbon.

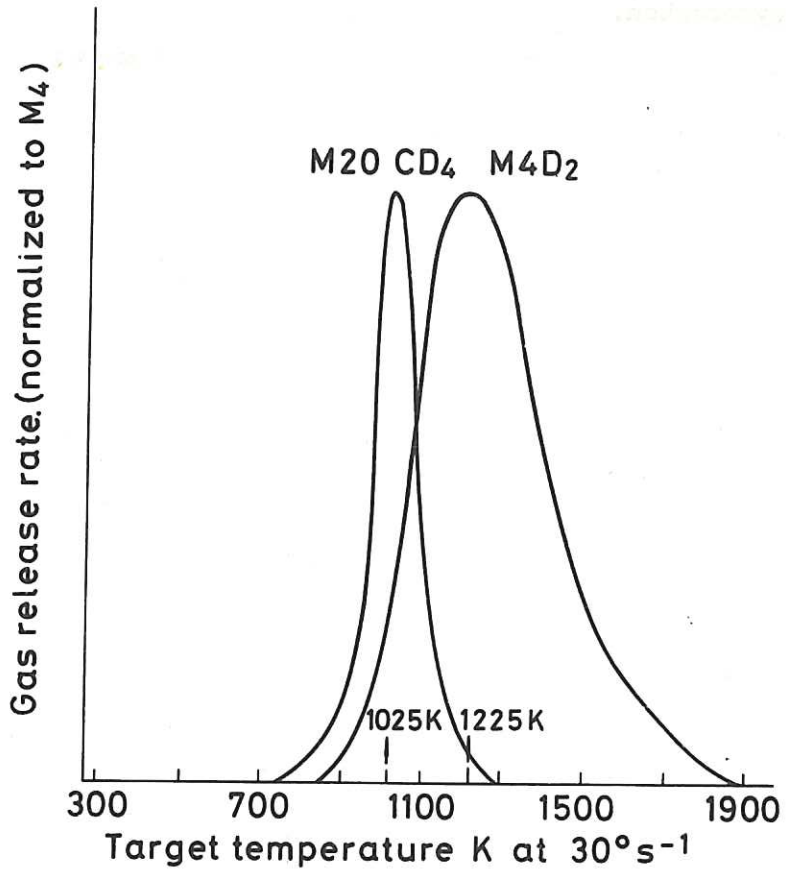

Fig.4 Thermal release of deuterium and methane from pyrocarbon.

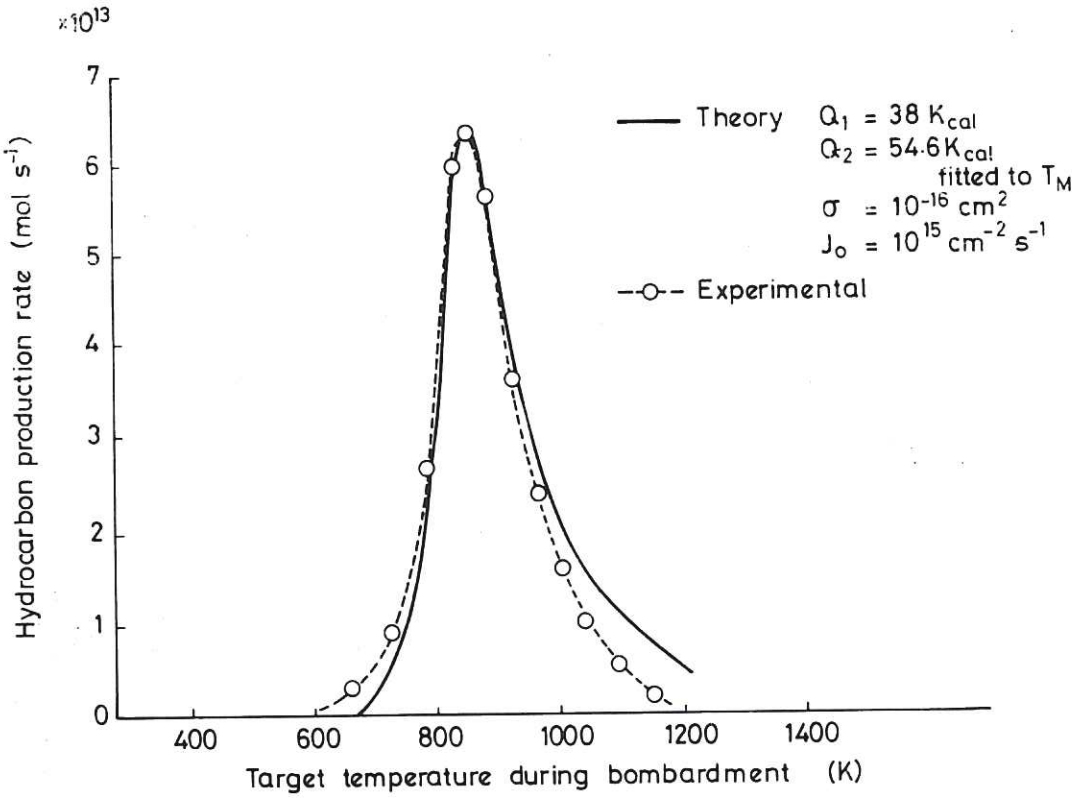

Fig.5 Theoretical and experimental equilibrium methane formation rates during H^+ → pyrocarbon.

CLM-P 451