Methane Impurity Production in the Fusion Reactor

Author
Peter T. Dawson
The Canadian Fusion Fuels Technology Project represents part of Canada's overall effort in fusion development. The focus for CFFTP is tritium and tritium technology. The project is funded by the governments of Canada and Ontario, and by Ontario Hydro.

The Project is managed by Ontario Hydro.

CFFTP will sponsor research, development and studies to extend existing experience and capability gained in handling tritium as part of the CANDU fission program. It is planned that this work will be in full collaboration and serve the needs of international fusion programs.
METHANE IMPURITY PRODUCTION
IN THE FUSION REACTOR ENVIRONMENT

CFFTP-G-85038

November, 1984

by Peter T. Dawson
Professor of Chemistry,
McMaster Institute for Energy Studies, McMaster University,
Hamilton, Ontario, Canada L8S 4M1

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Program Manager, CFFTP
2700 Lakeshore Road West
Mississauga, Ontario
L5J 1K5
Prepared by:

P. T. Dawson
Professor of Chemistry
McMaster Institute for Energy Studies
McMaster University

Reviewed by:

K. Y. Wong
Manager - Technology Safety
Canadian Fusion Fuels Technology Project

Approved by:

T. S. Drolet
Program Manager
Canadian Fusion Fuels Technology Project
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1. INTRODUCTION.

1.1. The nature of the problem.

Nuclear fusion, whereby nuclei fuse together to form products of lower total mass and liberate energy, provides the energy source in the Sun and is the most abundant source of energy in the Universe. The D/T reaction is a typical fusion reaction,

\[ D + T \rightarrow ^4\text{He} + n + 17.6 \text{ MeV}. \]

The energy produced is \( > 10^6 \) times greater than from an equivalent mass of fossil fuel, and the fuel required is available from sea-water in limitless quantities as D and Li from which T can be obtained in a breeder reaction,

\[ ^7\text{Li} + n \rightarrow T + ^4\text{He} + n'. \]

Fusion requires temperatures of the order of \( 10^6 \) °C in order to give the nuclei sufficient kinetic energy to overcome the strong repulsion between them since they are both positively charged. In order to attain the required temperature it will be essential to minimise the energy losses from the plasma. Impurities are a major cause of plasma cooling. Ionization of impurity species in the plasma leads to a subsequent decay and emission of radiation. Impurities with large atomic number, \( Z \), such as Mo used in limiters to protect reactor walls, will not be completely stripped of their electrons even at the centre of the plasma. Consequently such impurities must be eliminated and such limiters have been replaced by lower \( Z \) materials such as graphite and TiC. However low \( Z \) impurities will be incompletely stripped at the edge of the plasma and can seriously contribute to plasma cooling by radiation. The most common low \( Z \) contaminants to be considered are water and methane produced by reaction of hydrogen isotopes with oxygen and carbon. This review focusses on the methane production problem. We will be concerned with the sources of carbon in the reactor and also with the reactivity of carbon with hydrogen molecules, atoms and ions and the synergistic effects which can arise from coincident fluxes of electrons and photons and the effects of radiation-induced damage of the materials involved. While the reactor first wall will provide the most hostile environment for methane production, most of the reactions discussed can occur in breeder blankets and also in other tritium facilities such as fuel handling, purification and storage facilities. The material damage in these cases will arise from neutron irradiation and tritium radioactive decay,
1.2. Simple evidence for methane production outside the first wall, and methods to obviate the methane problem.

Coffin and Walthers studied the production of CH$_4$ from graphite samples provided by a pump manufacturer when exposed to T$_2$ gas at 0.8 atm. for 137 days. The results obtained are shown in Table 1.

Table 1: Methane production from T$_2$ exposed to graphite and stainless steel.

<table>
<thead>
<tr>
<th>GAS COMPOSITION</th>
<th>INITIAL</th>
<th>AFTER 137 DAYS EXPOSED TO</th>
<th>GRAPHITE</th>
<th>STAINLESS STEEL</th>
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<tr>
<td>T$_2$</td>
<td>95.6%</td>
<td>86.9%</td>
<td>90.6%</td>
<td></td>
</tr>
<tr>
<td>D$_2$</td>
<td>4.2%</td>
<td>3.6%</td>
<td>3.7%</td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.2%</td>
<td>4.7%</td>
<td>1.4%</td>
<td></td>
</tr>
<tr>
<td>$^3$He</td>
<td>---</td>
<td>3.7%</td>
<td>3.9%</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>---</td>
<td>1.1%</td>
<td>0.4%</td>
<td></td>
</tr>
</tbody>
</table>

It can be seen that not only is there significant production of methane on exposure of the graphite to T$_2$ but also that this occurs on interaction with the stainless steel container by itself. This is in agreement with the earlier experiments of Morris, however he observed that on exposure of stainless steel to deuterium gas there was no methane formation. Similarly, Coffin and Walthers found no methane production on exposure of graphite to D$_2$ at these pressures for 137 days. Clearly the isotopes of hydrogen do not behave in an identical manner and the radioactive decay process is necessary for methane production. Electron bombardment and defect creation by formation of $^3$He could both contribute to the acceleration of the methane formation reaction.

1.2.1. Effect of surface treatment on methane production. Morris investigated the effect of various organic solvent washes, machining and vacuum baking on the CH$_4$ production from T$_2$ interaction with 304 stainless steel. The most effective procedure for reducing the yield was machining away a significant layer, 0.025 cm., of the tube surface. Figure 1 shows the growth of methane impurity in two commercial 304SS and aluminum containers observed by Gill. A reduction in the amount of methane impurity by one to two orders of magnitude was achieved.
by various surface treatments of the steel or aluminum, or by storing the tritium in borosilicate glass, Figure 2. Dry polishing is more effective than electropolishing, consistent with the observation that freshly machined stainless steel is less contaminated with carbonaceous material than an electropolished surface 5. Since much of the piping used in tritium-handling facilities will be of small diameter, Gill and co-workers 6 have suggested the use of a chemical flow polishing technique for minimising contamination problems in such components.

It is perhaps worth noting that the methane production curves are asymptotic to a zero evolution rate after an exposure of 100 days or more. Thus the source of carbon for methane production is presumably only a carbonaceous surface contamination and not a more unlimited source such as carbon alloying components in the steel itself. The containers are self-cleaning and, if further organic contamination can be avoided, for tritium storage the methane problem should disappear. However this is unlikely to be the case for walls at elevated temperature subject to H atom and ion bombardment and radiation damage.

1.3. The methane problem at the first wall and cleaning techniques.

A stainless steel sample which had been subjected to two months of discharges in PLT was analysed by Auger electron spectroscopy (AES) and the results are shown in Figure 3 7. This AES profile shows gross surface carbon contamination over a depth of 20 nm. While this sample was exposed to some CH₄ discharges, it is reported 8 that similar carbon build-up also occurs in pure hydrogen discharges. The removal of such potential sources for plasma impurities has led to a considerable effort directed towards the cleaning of the first wall.

1.3.1. First wall cleaning techniques. Techniques used for cleaning the first wall have been reviewed by McCracken and Stott 9 and by Dylla 10 and include,

(a) chemical or physical pretreatment,
(b) vacuum baking,
(c) pulse discharge cleaning,
(d) glow discharge cleaning,
(e) gettering or wall coating.

As already seen in the discussion of the carbon contamination of storage vessel surfaces, both physical and chemical cleaning techniques are extremely useful for removing gross
contaminating films. However vacuum baking would only be effective if performed at temperatures high enough to permit diffusion of the carbon into the bulk of the sample. This will require baking at temperatures of 500°C for stainless steel and 700°C for Inconel. This is unlikely to be an efficient procedure and the buried carbon may subsequently be resurrected! Pulse discharge cleaning uses the tokomak coil system to initiate a series of low-level discharges at high repetition rate, whereas DC glow discharge uses a centrally located anode and the grounded vessel components serve as the cathode. This technique has the advantage over pulse discharge cleaning that more of the vessel components will be bombarded. RF discharges can also be used. Chemical sputtering using H₂ as an active sputter gas is found to be preferable to physical sputtering using He or Ar because it avoids the possible complications of inert gas outgassing subsequently contaminating the plasma. An example of glow discharge cleaning of PDX is shown in Figure 4. The integrated production of CH₄ over the first 100 hours cleaning was 3500 torr l, which corresponds to the removal of over 100 equivalent monolayers averaged over the 200 m² surface area of the vessel. Impurity control by gettering, i.e. continuous or intermittent deposition of a film, e.g. Ti, which actively chemisorbs impurities has been used in many tokamaks. A major problem with impurity control by gettering is the large quantity of tritium which will be absorbed. The problems will be severe for long pulse devices. Chromium has been suggested as an alternative to titanium because there should be negligible bulk uptake of hydrogen, thereby reducing the tritium inventory.

1.4. Sources of carbon for methane production.

We can identify four main sources of carbon which could act as reactants for the formation of methane.

(a) Carbon (graphite) components, e.g. limiters.

(b) Gross surface contamination by carbonaceous deposits.

(c) As a bulk alloy element, e.g. TiC or stainless steels containing several % C.

(d) Bulk carbon impurity.

Poor cleaning techniques can leave material surfaces grossly contaminated and the methane generation which can arise has been discussed in section 1.2. Furthermore it is clear that such sources of methane can be eliminated by suitable cleaning techniques. No further direct reference will be made to this problem. However carbon is a ubiquitous bulk impurity at the 100 ppm
level and can provide a significant and long-term carbon source for methane production, and furthermore one which will be extremely difficult to eliminate. Potentially the most serious source of methane will be from carbon, carbides and carbon steels and a large part of this review will survey our understanding of the efficiency of methane formation from such materials.

1.5. Reaction sites.

The reaction between carbon and hydrogen to form methane can take place either within the bulk of a material or on the surface. The former is referred to as hydrogen attack, leads to the formation of methane bubbles within the material, and is a significant problem in high pressure vessels in the petroleum industry. This aspect will be discussed in section 2.2, and it is unlikely to be a serious problem at the pressures and temperatures used in fusion and breeder reactors or tritium-handling facilities. Methane production at the surface of a material is a much more efficient process which can be aided by all the subtleties of heterogeneous catalysis. Bulk carbon can supply the surface by diffusion and moreover even when the bulk concentration of carbon is small the equilibrium surface concentration can be very high as a result of surface segregation.

1.6. Factors influencing the surface segregation of carbon.

Before considering the intrinsic reactivity of carbon at the surface it is important to consider the factors which will influence the segregated surface concentration. There are three important aspects to consider in the present application, namely temperature, competitive segregation and radiation effects.

1.6.1. Temperature. The supply of carbon to the surface by diffusion will be at a rate determined by the diffusion coefficient,

$$D = D_0 \exp \left( -\frac{E^*}{RT} \right),$$

where $E^*$ is an activation energy for diffusion, which can be typically ca 30 kcal. mole.$^{-1}$. Consequently at ambient temperatures diffusion can be too slow to supply carbon at a significant rate. However, high temperatures are also in conducive to carbon segregation. A simple ideal bond-breaking model for surface segregation leads to the following equation relating the surface and bulk mole fractions of carbon, $x_s$ and $x_b$ respectively,
\[
\frac{x \delta}{(1 - x \delta)} = \frac{x \delta}{(1 - x \delta)} \exp \left(-\frac{\Delta H_S}{RT}\right),
\]

where \(\Delta H_S\) is the enthalpy of segregation. Clearly at higher temperatures the surface concentration will diminish and finally approach the bulk concentration. Therefore we can anticipate a temperature at which the surface concentration of carbon will be a maximum, limited by kinetics at lower temperatures and by thermodynamics at higher temperatures.

1.6.2. Competitive segregation. Most alloys also contain significant concentrations of other impurity elements such as sulphur, phosphorous and oxygen. Segregation of such elements can be competitive with that of carbon and reduce both the carbon concentration and thereby the methane formation rate. Since the activation energies for diffusion for S and P for example are greater than that for C, such competitive segregation can be expected to occur at higher temperatures and will also contribute to a diminishing of the surface carbon concentration. The poisoning or promoting action of elements such as S and P on the catalytic efficiency of the methane production reaction is also of some interest and this aspect will be discussed in the section 6 of this review.

1.6.3. Radiation effects. Radiation increases the concentration of defects in a material which enhances diffusion rates and can lead to segregation effects being observed at lower temperatures than expected. In addition to this radiation-enhanced diffusion, radiation-induced segregation has been observed. The defect flux to the surface which acts as a sink for their anihilation can carry carbon atoms with them and thus the potential exists for the creation of 'super-equilibrium' carbon concentrations at the surface. These radiation induced effects must be seriously considered in the fusion reactor environment.

1.7. Synopsis.

In the remainder of this review we will consider in some detail our current knowledge of the reactions producing methane. Most of the work to date has used carbon (graphite) itself, carbides or alloys as the source of carbon. In turn we will consider the reactivity of such materials to hydrogen molecules, hydrogen atoms and hydrogen ions with some consideration of the evidence for synergistic effects involving simultaneous electron, photon and ion bombardment. The review will conclude with a discussion of the relevant results from catalytic research on the methanation reaction.
Figure 1. The growth of methane impurity in tritium gas stored in two commercial containers.

Figure 2. The growth of methane impurity in tritium gas stored in eight improved containers, including the effect of surface treatment.
Figure 3. AES depth profile of a stainless steel sample which had been exposed to ca $4 \times 10^3$ high power discharges in PLT.

Figure 4. The partial pressures of residual CH$_4$ (at 16 amu) and CO + C$_2$H$_4$ (at 28 amu) produced within the PDX torus during H$_2$ glow discharge conditioning of the vacuum vessel. The time integrated removal corresponds to the removal of more than 100 equivalent monolayers of carbon.$^{11}$
2. METHANE PRODUCTION BY REACTION OF CARBON WITH HYDROGEN MOLECULES: DECARBURIZATION OF ALLOYS.

In view of the many proposals to use graphite as a first wall material, the efficiency of the reaction of graphite with molecular hydrogen is of concern. Further the removal of carbon from stainless steel and other carbon containing alloys, decarburization, is significant for the utilization of such alloys in all phases of tritium handling technology.

2.1. Interaction of molecular hydrogen with elemental carbon.

It has been long established that the chemisorption of hydrogen on carbon is slow and activated. Thus Kingman found an immeasurable adsorption rate on charcoal below 200°C, and over the temperature range 340 to 395°C the activation energy for chemisorption was 30 kcal./mole. Values for chemisorption activation energy in the range 22 to 35.2 kcal./mole on graphite and 14.5 to 22 kcal./mole on diamond were observed by Barrer. Bansal et al. have suggested that the substrates used in these early studies were not well cleaned. They have investigated the chemisorption of hydrogen on cleaned graphite in the pressure range 0.02 to 0.5 torr and at temperatures between 80 and 600°C. At temperatures below 80°C the chemisorption rate was too slow to be measured and above 600°C the hydrogen reacted with the graphite to produce detectable amounts of methane. The results were displayed in the form of the Elovich equation,

\[
\frac{d\theta}{dt} = a \exp (-\alpha \theta),
\]

which includes a coverage, \( \theta \), dependent activation energy term in the adsorption rate, \( \frac{d\theta}{dt} \). This plot shows several breaks which are interpreted as resulting from surface heterogeneity. Four types of surface sites are identified with chemisorption activation energies equal to 5.7, 8.3, 18.4 and 30.4 kcal/mole. It seems reasonable to assume that the activation energy would be a sensitive function of the C-C spacing on the graphite surface. Sherman and Eyring have given theoretical estimates for the dependence of activation energy on C-C distance which agree well with the experimentally determined values. Brennan and Fletcher have studied the atomization of hydrogen on a carbon filament. In the range of temperature and pressure used, 7.10^{-3} to 4.10^{-5} torr and 1700 to 2000K, the rate was first order in the hydrogen pressure.
The sticking probability for molecular hydrogen was $6.10^{-4}$ at 2000K and the activation energy for the process was found to be 56.3 kcal/mole, much greater than the earlier values and close to one-half the dissociation energy for hydrogen.

At moderate pressures, the rate of formation of methane by reaction of molecular hydrogen with carbon is only large enough to study at very high temperatures. Clarke and Fox have studied this reaction at pressures between 0.01 and 1 atm. and temperatures between 2000 and 3400°C. At lower temperatures and higher pressures the rate is proportional to the first power of the hydrogen pressure, $P_{H_2}$, and to the square root of the $H_2$ dissociation constant, $K$. This has been interpreted as being the result of a surface reaction mechanism in which $H$ atoms, in gas phase concentration equal to $(P_{H_2}K)^{0.5}$, react with surface $CH_2$ species in equilibrium with gas phase $H_2$ via a Freudlich isotherm, dependent on $P_{H_2}^{0.5}$, $K$. Thus, overall the rate becomes proportional to $P_{H_2}K^{0.5}$. The reaction of atomic hydrogen with graphite will be discussed in detail in the next section. At high temperature and low pressure the rate becomes proportional to the sublimation rate of graphite and occurs in the gas phase.

The reactivity of carbon deposited from methane and carbon monoxide on a silica supported Ni catalyst has been studied by Gilliland and Harriott. The reaction was investigated at 1 atm. pressure and temperatures in the range 425 to 760°C. The reactivity, CH$_4$ produced per C atom remaining per minute, varied widely and fell with extent of reaction. This was attributed to the varying amounts of hydrogen remaining in the deposited carbon. The apparent activation energy for CH$_4$ production was found to be 36 kcal/mole. The catalytic enhancement of the methane production rate must be considered in such systems and this will be studied in depth in the section 6 of this review.

The interaction of hydrogen at high pressure, 1 to 30 atm., with carbon char at temperatures in the range 815 to 925°C has been investigated by Zielke and Gorin. The order of the reaction in the hydrogen pressure was found to lie between 1 and 2, and the apparent activation energy for the reaction increased with conversion from ca. 17 to 50 kcal/mole. At pressures of several atmospheres and temperatures in excess of 1600K, Rogers and Sesonske find that the reaction becomes independent of the hydrogen pressure.

We can conclude that methane production rates from carbon and $H_2$ should be negligible at the temperatures and pressures relevant to the fusion reactor and related tritium handling.
facilities. However it may still be necessary to consider the enhancement of the rate of methane production by molecular hydrogen where the surface is also exposed to H atom, H ion and electron bombardment. This topic will be addressed in subsequent sections.

2.2. Carburization and decarburization of alloys.

At temperatures in excess of 500K hydrogen can react with the carbides in steel to produce methane. This reaction can take place either at the surface of the alloy, following diffusion of carbon, or in the interior of the alloy, by diffusion of hydrogen. The former is called decarburization, while the latter is referred to as hydrogen attack. In addition to producing methane, both processes can radically modify the physical properties of the steel and under extreme conditions, such as those obtaining in hydrogen pressure vessels, this can lead to failure of the steel. Experience in the oil refining industry has led to empirical curves, Nelson curves, which delineate the conditions under which damage to steels can be expected. From these curves it is clear that for temperatures below 600°C, steels should be structurally reliable up to 7 atm. pressure. However whether the methane production rate is negligible under such conditions is another question. Hydrogen attack is preceded by an induction period during which no change in properties can be detected. During this induction period the methane pressure is thought to build up in sub-microscopic voids and is balanced by the surface tension, limiting the growth rate of the void. However, at a critical size the void starts to grow rapidly by lattice vacancy condensation.

The kinetics and mechanism of the reactions which occur during the carburization and decarburization of α-iron and γ-iron have been carefully investigated by Grabke and co-workers using resistance and gravimetric techniques. Data for the decarburization rate of α-Fe as a function of H₂ pressure at 650 and 745°C are shown in Figure 5. The slope of this double logarithmic plot indicates that the order of the decarburization reaction is 3/2 in hydrogen. Similar results were obtained for γ-Fe. Thus, for the reaction,

\[ C(\text{in } \alpha- \text{ or } \gamma-\text{Fe}) + 2 \text{H}_2(\text{g}) = \text{CH}_4(\text{g}), \]

the net rate of carbon removal, or methane formation, is given by,
\[ \frac{d P(CH_4)}{dt} = k' P(H_2)^i C(C) - k P(CH_4) P(H_2)^o s, \]

between 500 and 800°C for \( \alpha \)-Fe and between 800 and 1040°C for \( \gamma \)-Fe, where \( [C] \) is the concentration of carbon dissolved in the Fe. The temperature dependence of the rate constants \( k' \) and \( k \) for the forward and back reactions are shown in Figure 6 for \( \alpha \)-Fe. The rate constants \( k' \) and \( k \) for \( \alpha \)- and \( \gamma \)-Fe are,

\[
\begin{align*}
    k'_{\alpha-Fe} &= 5.3 \cdot 10^{-3} \exp (-13.6/RT) \text{ cm. s}^{-1} \text{ atm}^{-i.5}, \\
    k_{\alpha-Fe} &= 1.3 \cdot 10^{3} \exp (-51/RT) \text{ mol cm}^{-2} \text{ s}^{-1} \text{ atm}^{-0.5}, \\
    k'_{\gamma-Fe} &= 2.6 \cdot 10^{-2} \exp (-25.3/RT) \text{ cm. s}^{-1} \text{ atm}^{-i.5}, \\
    k_{\gamma-Fe} &= 4.6 \cdot 10^{-3} \exp (-55/RT) \text{ mol cm}^{-2} \text{ s}^{-1} \text{ atm}^{-0.5},
\end{align*}
\]

where the activation energies for reaction are given in kcal. mol\(^{-1}\).

The rate law observed can be well interpreted by a straightforward mechanism,

\[
\begin{align*}
    H_2(g) &= 2 H(a), \quad \text{(i)} \\
    C(\text{soln}) &= C(a), \quad \text{(ii)} \\
    C(a) + H(a) &= CH(a), \quad \text{(iii)} \\
    CH(a) + H(a) &= CH_2(a), \quad \text{(iv)} \\
    CH_2(a) + H(a) &\overset{\ddagger}{=} CH_3(a), \quad \text{(v)} \\
    CH_3(a) + H(a) &= CH_4(a), \quad \text{(vi)} \\
    CH_4(a) &= CH_4(g), \quad \text{(vii)}
\end{align*}
\]

where all steps are assumed to fast and at equilibrium except reaction (v) which is taken to be rate limiting, in order to obtain agreement with the empirical rate law. Thus the net rate of the forward reaction can be expressed as,

\[ R_v = k_v B(CH_2) B(H) - k'_v B(CH_3), \]

where \( k_v \) and \( k'_v \) represent the forward and back rate constants for elementary reaction step (v) and the \( B \) values are surface concentrations. The surface concentrations of \( H, CH_2 \), and \( CH_3 \) will be,
$\theta(H) = (K_1 P(H_2))^{0.5}$,

$\theta(CH_2) = K_{1u} K_{1u1} \theta(C) \theta(H)^2$,

$\theta(CH_3) = P(CH_4)/\theta(H) K_{v1} K_{v11}$,

where the $K$ values are the pseudo-equilibrium constants. The observed rate law follows directly by substitution,

$$R_v = k_v K_{v11} K_{1u} \theta(C) (K_1 P(H_2))^{1.5} - (K_{v1} K_{v11} K_1^{0.5}) P(CH_4) P(H_2)^{0.5},$$

if the surface concentration of carbon is assumed to be proportional to the bulk concentration (or activity),

$$\theta(C) = K_{11} [C].$$

viz,

$$R_v = k' [C] P(H_2)^{1.5} - k P(CH_4) P(H_2)^{0.5}.$$
Figure 5. A double logarithmic plot of the decarburization rate of \(\alpha\)-iron as a function of the hydrogen pressure. The slope of these plots indicate that the order of the decarburization reaction is 1.5 in the hydrogen pressure.$^{24}$

Figure 6. Temperature dependence of the rate constants for decarburization, \(K'\), and carburization, \(K\), of \(\alpha\)-iron.$^{24}$
Figure 7. Decarburization of austenite in dry hydrogen at 0.96 atm.  

Figure 8. The decarburization rate of austenite plotted as a function of the three-halves power of the hydrogen pressure.  

Figure 9. The effect of less than 1% water vapour on the decarburization rate of austenite in hydrogen at 1150°C.
3. METHANE FORMATION FROM THE REACTION OF HYDROGEN ATOMS WITH GRAPHITE AND OTHER CARBON-CONTAINING COMPOUNDS AND ALLOYS.

3.1. Introduction.

The rate of the reaction between molecular hydrogen, \( \text{H}_2 \), and carbon is only significant at extremely high temperatures and pressures, as outlined in the preceding section. Dissociation of the hydrogen molecules into atomic hydrogen has been found to enhance the reactivity for a multitude of chemical processes and this is found to be the case for the erosion of elemental carbon to produce methane and other hydrocarbons. Typical techniques for generating atomic hydrogen include,

(i) dissociation and desorption from a refractory surface at elevated temperature, e.g. an incandescent tungsten filament\(^ {28} \).

(ii) Passing molecular hydrogen through a radiofrequency, or microwave, electrical discharge; thus Wood and Wise were able to obtain H atom concentrations in the range \( 10^{13} \) to \( 10^{15} \) atoms cm\(^{-3} \) at an \( \text{H}_2 \) pressure in the vicinity of 1 torr, independent of the total \( \text{H}_2 \) pressure, by varying the rf power\(^ {29} \). The interpretation of results obtained using discharge H atom sources may be complicated by the presence of excited species, ions, electrons and photons which can give rise to synergistic effects as will be discussed in section 4.

(iii) In the above examples the hydrogen atoms, together with some molecules and ions, bombard from the gas phase. A quite different approach is to study the gas phase species produced by hydrogen atoms diffusing from the bulk. The H atom source in this case is molecular hydrogen gas to which the reverse surface of the sample is exposed\(^ {30} \).

Proposals to use carbon as a limiter and first wall material has led to considerable effort being devoted to reaction studies of the H atom - graphite reaction, although there have been limited investigations of some carbides and carbon in alloys (SS). We will first review the data available concerning the efficiency of the reaction with graphite, particularly its temperature dependence, and summarise the mechanisms proposed for this reaction. Synergistic effects, the possibility of an enhancement in reaction rate by exposing the sample to electrons, photons
or ions in addition to H atoms, is an extremely important topic which will be addressed in section 4.

3.2. Temperature dependence of the efficiency of the graphite/H atom reaction.

Results for the reaction rate as a function of temperature are shown in Figures 10 to 16. Figure 10 shows the rate constants determined by Wood and Wise\textsuperscript{23} for the erosion of graphite by H atoms at temperatures in the range 455 to 1250K, clearly demonstrating the existence of a temperature of maximum reactivity. The reaction rate is a maximum at ca. 785K and at this temperature we can calculate from the data given in the paper that the erosion rate is \(1.9 \times 10^{-16}\) C atoms cm\(^{-2}\) s\(^{-1}\) at a total H\(_2\) pressure of 1 torr and an H atom concentration of \(5.3 \times 10^{14}\) cm\(^{-3}\). This corresponds to five atomic layers eroded per second for the basal plane.

The results of Rosner and Allendorf\textsuperscript{31} were obtained at very similar H atom pressures to those used by Wood and Wise and are in excellent agreement. As can be seen in Figure 11 the reaction probability passes through a maximum of \(6.1 \times 10^{-4}\) at a temperature of 800K. We calculate a reaction probability from the data of Wood and Wise of \(5.7 \times 10^{-4}\) at 785K; the agreement is excellent. As we will discuss later, the calculation of such reaction probabilities for high H atom fluxes and potentially complex reaction mechanisms is a dubious procedure. However, this does not detract from the excellent agreement between these data obtained under similar experimental conditions.

Coulon and Bonnetain\textsuperscript{32} also observed a maximum in the steady state rate of methane production with increasing pressure using comparable H atom and total H\(_2\) pressures to those used by Wood and Wise. Their results are shown in Figure 12. The reaction rate and the temperature at which the rate attains its maximum value, 850\(\pm\)75K, are dependent on the degree of etching of the surface. The maximum rate recorded in Figure 12 is \(2.10^{15}\) CH\(_4\) molecules cm\(^{-2}\) s\(^{-1}\), or about one order of magnitude less than observed by Wood and Wise.

More recently, Webb et al.\textsuperscript{33} have reported measurements on the graphite/H atom reaction at 10\(^{-2}\) to 10\(^{-1}\) torr with a total H\(_2\) pressure of ca. 1 torr. The temperature dependence of the reaction probability is shown in Figure 13. Although the basal plane data shows a maximum reactivity at 1050-1100K, which is considerably higher than the earlier results, the reactivity of prism planes increases with temperature but shows no decrease up to almost 1200K. The
magnitude of the reaction rate is in good agreement with the earlier data.

In contrast to these investigations, the following studies were all performed at much lower \( \text{H}_2 \) pressures and H atom fluxes. Gould \(^{34}\) performed experiments at pressures which were about four orders of magnitude lower than those described above. The \( \text{CH}_4 \) evolution rate data all followed a pattern whereby the rate rapidly increased to a maximum, then fell to a steady state value at a rate which increased with temperature and the H atom flux (Figure 18). The variation of both the peak and the steady state evolution rates with temperature is shown in Figure 14: Both of these \( \text{CH}_4 \) evolution rates pass through a maximum, shallow in the steady state case, in the vicinity of 650K, and the maximum rate is seen to be about four orders of magnitude lower than the higher pressure results, consistent with the lower atomic flux.

Balooch and Olander\(^{35}\) studied the reaction between H atoms and graphite using a modulated beam. The temperature dependence of the reaction probability for methane formation is shown in Figure 15. These differ from previous results in the absence of any increase in reaction rate with increase in temperature, which is to the left in this diagram. However the rate does decrease with temperature above 700K, which is in agreement with the earlier results, as is the magnitude of the reaction probability.

Recently, Stangeby et. al.\(^{36}\) have performed similar experiments to those of Gould \(^{34}\) and have confirmed the existence of a short time peak reaction rate which decays to a steady state value in ca. 100 s (Figure 20). Their results for the temperature dependence of the activated and steady state rates are shown in Figure 16 (dotted lines). While the activated yield shows a maximum and is in good agreement with the results of Gould and other workers, the steady state or "deactivated" rates show only a decrease with increasing temperature similar to the data of Balooch and Olander \(^{35}\) and not that of Gould \(^{34}\).

3.3. Mechanism.

Wood and Wise \(^{29}\) found that their data were satisfactorily interpreted by the empirical rate equation,

\[
\text{RATE} = k \left[ \text{H}_2 \right] \left[ \text{H} \right]^{0.5},
\]

where \([\text{H}_2]\) and \([\text{H}]\) represent the \( \text{H}_2 \) and H atom partial pressures respectively. It is proposed that under the conditions of the experiment the surface will be largely saturated with H atoms.
Approach of an H atom to the surface will usually result in recombination, except at edge atoms which hold two rather than one H atom: In this case the H atom is considered to react to form a C_n-CH_3 species which can either lose H_2 to revert to its original structure or react with an impacting H_2 molecule via a Rideal-Eley mechanism to produce methane,

\[ C_n-CH_3 + H_2 \rightarrow C_n-CH + CH_4. \]

Assuming that the C_n-CH_3 species attains a steady state during the reaction leads to the observed first order H_2 pressure and half order H atom pressure dependence of the CH_4 production rate. The increase in rate over the temperature range 455 to 715 occurs because the process is activated and Wood and Wise calculate an activation energy of 5.6 kcal mole\(^{-1}\) over this temperature range. This can be compared with the value of 5.0 kcal mole\(^{-1}\) determined by Rye \(^{37}\) over the temperature range 330 to 570K. They attribute the decrease in rate above 800K to the thermodynamic instability of CH_4: The standard free energy of formation of methane becomes positive for T > 830K.

Coulon and Bonnetain \(^{32}\) find the reaction rate to be first order in atomic hydrogen below the temperature at which the rate attains a maximum value, but increases up to second order above this temperature. Also the rate is independent of the H_2 pressure below 973K and 1 torr but shows some dependence above this temperature and pressure. The mechanism proposed involves a competition between H atom recombination,

\[ CH(a) + H(g) \rightarrow C(a) + H_2(g), \]

and reaction,

\[ CH(a) + H(g) \rightarrow CH_2(a), \]

leading ultimately to methane formation.

Gould \(^{34}\) measured the dependence of the CH_4 formation rate on H atom concentration and found it to be first order at 640K.

The modulated atomic hydrogen beam technique used by Balooch and Olander \(^{35}\) leads to new information concerning the mechanism. The variation in reaction probability and phase lag with beam intensity requires an overall order of reaction greater than unity. The very slow change in phase lag with modulation frequency suggests that bulk (hydrogen) diffusion is an important step in the reaction mechanism. The mechanism proposed is as follows,
The slow step in the reaction is assumed to be the penultimate one in which CH\textsubscript{3}(a) is formed, and the last step is fast. It should be mentioned that another reaction branch is observed in which acetylene is formed by combination of two CH(a) species, but this is only observed above 1000K where the methane formation rate is negligible. This model accounts for the decrease in CH\textsubscript{4} formation rate above 800K by an increase in the H atom recombination rate which reduces the surface concentration of H atoms: In this aspect it is identical to the earlier interpretations \cite{29,32}. The authors have analysed their data to determine the kinetic constants for this model, and Balooch \cite{38} has subsequently published a simpler quasi-equilibrium analysis. They have also deduced the appropriate rate law in terms of these constants for the steady state reaction rate at higher pressures where the graphite will be saturated with hydrogen and bulk diffusion can be neglected. The methane production rate for the above mechanism is,

\[
\frac{d[CH_4]}{dt} = K_1 K_2 K_3 \theta_H^2,
\]

where \( K_1 \) and \( K_2 \) are the pseudo equilibrium constants for the addition of the first and second H atom to produce CH(a) and CH\textsubscript{2}(a) respectively, and \( K_3 \) is the rate constant for the following, rate-limiting step: \( \theta_H \) is the surface H atom concentration which is calculated by steady state analysis using the measured H atom, and an assumed H\textsubscript{2} molecule, sticking probability. This model is shown to be consistent with gasification data at H\textsubscript{2} pressures which are six orders of magnitude higher. Significantly, the best fit was obtained by assuming zero sticking probability for molecular hydrogen even at very high pressure. Balooch and Olander could not obtain agreement between their experimental data and the model of Wood and Wise \cite{29}, although they seem to have made a two order of magnitude error in evaluating the reaction probability implied by Wood and Wise’s results.
The procedure of calculating reaction probabilities as the number of CH$_4$ molecules produced per impacting H atom for widely different reaction conditions (e.g., Figure 16) is questionable. Thus if the rate law of Wood and Wise is valid and the rate is first order in H$_2$ and half order in H then the reaction probability calculated without consideration of the H$_2$ pressure is a meaningless quantity. However, most calculated values of the reaction probability fall in the range $10^{-4}$ to $10^{-3}$, in amazing agreement given the well documented dependence of the activity on the structure and history of the sample and the large errors anticipated from such difficult measurements. The misleading character of the reaction probability, CH$_4$/H, is apparent when we take account of the possibility of surface saturation at high H atom flux. Under these circumstances any increase in flux will have no effect on the rate. Surface saturation satisfactorily explains the different reaction probability profiles with increasing temperature: Why in some studies the rate increases before it decreases at high temperature whereas in others only a decrease in rate with temperature is observed. It is significant that the former are primarily high flux studies whereas the later are all low flux studies. For a high flux at low temperature the surface will be saturated with H atoms and can remain so as the temperature is increased. Consequently the rate of CH$_4$ production will increase because of the temperature dependence of the formation reactions, undiminished by any decrease in surface H atom concentration. In contrast, at very low H atom flux the surface concentration of H atoms will be very small and will decrease with increasing temperature, compensating for the increase in $k_3$ and leading to a relatively constant or slowly decreasing reaction probability with increasing temperature. The point is nicely illustrated by the calculations presented by Roth based on the kinetic model of Balooch and Olander. Figure 17 shows the experimental data at low and high H atom fluxes compared with calculated values for the reaction probability at various H atom fluxes in the range $10^{15}$ to $10^{19}$ cm$^{-2}$ s$^{-1}$ assuming a saturation value of $10^{13}$ H atoms cm$^{-2}$. The effect of saturation on the reaction rate profile is well reproduced.

3.4. Transient and Hysteresis Effects.

Transient effects in the CH$_4$ production rate have been observed by several authors. Figures 18, 19 and 20 illustrate the effect which has been observed at both low and high H atom fluxes. The initial higher, or peak, reaction rate has received several
explanations. Gould interprets the decay in rate as being a result of the formation of a stable surface species which blocks CH₄ production. Heating the sample to temperatures greater than 1500K reactivated the sample, but heating to 1200K or lower was not effective as a reactivation procedure.

Coulon and Bonnetain point out the strong similarity between the transients observed in the CH₄ formation rate and the H atom recombination rate. They also observe an interesting hysteresis in the transient phenomenon. Figure 21: The transient is only observed when descending from higher sample temperatures. They conclude that high temperature treatment creates a labile carbon surface by residual gas attack. This surface has a higher activity for both H atom recombination and CH₄ formation but is removed by reaction with atomic hydrogen.

Stangeby et al. find a maximum in the reaction probability only for carbon which has been activated by a high temperature (1200K) treatment for one minute. The steady state rates decrease monotonically with increasing temperature. This implies that the explanation for the increasing reactivity with temperature for the high H atom flux experiments as being caused by an intrinsic increase in rate constant at constant H atom coverage is suspect. However it would appear that the data reported in these experiments are the steady state values and not transient peak values. In any case it seems likely that in the fusion reactor environment defect creation by particle bombardment may make the activated values the appropriate ones.

Following on from the hysteresis observations of Coulon and Bonnetain, Balooch and Olander have also found a hysteresis in the reaction probability at low H atom flux in beam experiments. In Figure 22, the upper curve representing a higher activity was followed when the temperature is increased from 400 to 800K and the reaction profile retraces this curve if the temperature is now decreased from 800 to 400K. However, if the sample is heated at ca. 2000K the lower activity curve is followed at descending temperatures from 800 to 400K. Surprisingly, the "activated" sample has a lower activity!

More work is clearly required at both high and low H atom fluxes in order to reach a definitive interpretation of these phenomena. The role played by diffusion of bulk hydrogen certainly demands further examination.
3.5. Product distribution.

While the focus of this review is on CH₄ production, it is worthwhile to point out that other products result from the reaction of H atoms with carbon. We have already pointed out that in the beam studies of Balooch and Olander 35 there exists a clear demarcation between CH₄ production below 800K and C₂H₂ production above 1000K, with nothing detected at intermediate temperatures.

In the early work of Wood and Wise 29, hydrocarbon product analysis at the temperature of maximum carbon erosion rate revealed 91% CH₄, the remainder being unidentified C₃ to C₈ fragments. By using low energy, in situ mass spectrometry, Rye 37 was able to identify 11 additional products with a majority being cyclic compounds consistent with the graphite structure. Experimental artefacts prevented the analysis of the C₃ region of the spectrum. The relative yields and activation energies of formation for 10 products are given in Table 2.

Table 2: Product distribution and activation energies for formation of several hydrocarbons in the reaction of carbon with atomic hydrogen.37

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>PARTIAL PRESSURE (%)</th>
<th>ACTIVATION ENERGY kcal. mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>74.0</td>
<td>5.3 ± 1.9</td>
</tr>
<tr>
<td>Ethane</td>
<td>20.0</td>
<td>6.9 ± 2.1</td>
</tr>
<tr>
<td>Butene</td>
<td>4.5</td>
<td>6.1 ± 1.1</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>0.82</td>
<td>8.0 ± 3.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.12</td>
<td>5.6 ± 2.0</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>0.36</td>
<td>6.4 ± 2.0</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.16</td>
<td>8.0 ± 2.6</td>
</tr>
<tr>
<td>Methylbenzene</td>
<td>0.11</td>
<td>8.3 ± 3.8</td>
</tr>
<tr>
<td>Methylcyclohexene</td>
<td>0.17</td>
<td>5.0 ± 2.9</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.063</td>
<td>10.0 ± 2.0</td>
</tr>
</tbody>
</table>

3.6. The reaction of carbides and carbon-containing alloys with atomic hydrogen.

VepreK, Haque and Oswald 42 compared the chemical erosion of boron and silicon carbides with that of various carbons. Boron carbide was subject to an H plasma at temperatures which initially rose to 1100°C and thereafter were held in the range 600 to 700°C. The surface was depleted of carbon to produce a passive layer of boron which was unreactive under the conditions
used. However this layer spalled easily which may prove problematic in a fusion reactor. Silicon carbide was similarly unreactive and in this case no surface changes could be detected.

Flaskamp et al.\textsuperscript{30} have presented some very interesting results on the formation of CH\textsubscript{4} by hydrogen atoms diffusing from the bulk of the sample. The stainless steel sample containing 1000 ppm carbon formed part of a closed cell which was exposed on one side to H\textsubscript{2} gas and hydrocarbon species which desorbed from the opposite side were monitored. In the temperature range from 920 to 1470K the desorbing species included CH\textsubscript{4}, CH\textsubscript{3}, CH\textsubscript{2}, C\textsubscript{3}H\textsubscript{4}, C\textsubscript{4}H\textsubscript{6}, and C. The first four species were formed at a rate of approximately 10\textsuperscript{13} cm\textsuperscript{2} s\textsuperscript{-1} which was only slightly temperature dependent. This corresponds to ca. 10\textsuperscript{-2} times the rate of molecular H\textsubscript{2} desorption by recombination. It should be noted that this high CH\textsubscript{4} desorption rate is many orders of magnitude higher than the thermodynamic equilibrium value corresponding to the H\textsubscript{2} flux. Since implantation and permeation of deuterium and tritium will occur in fusion reactors, these results, if correct, are particularly significant.

The decarburization of stainless steel by bombardment with H atoms incident from the gas phase has been studied by Krishnan et al.\textsuperscript{43} Approximately 10% of the 1 torr hydrogen gas incident on the 4340 stainless steel sample (0.4 wt. % C) was atomic hydrogen. At 673K there was no detectable effect, but at 873K a reduction in hardness suggests that the SS has started to lose surface carbon although the bulk analysis technique used could not measure any loss. However at 1173K decarburization was rapid, following parabolic kinetics as can be seen in Figure 23. After 420 min the carbon content had fallen from 0.4 to 0.05%. The solid line in Figure 23 is calculated from the diffusion data for C in SS assuming that this is rate determining. The reactivity of carbon in SS is clearly much greater at 1173K than is that of the carbon atoms in graphite. This increased reactivity of carbon on metal surfaces is a point which will be discussed in detail in section 6 describing the relevant results of methanation catalysis research.
Figure 10. The dependence of the rate of carbon removal on temperature of the graphite and the pressure of hydrogen, after Wood and Wise.\textsuperscript{29}

\[ \text{RATE} = k[H_2][H]^{0.5} \]

\[ k = \frac{\text{RATE}}{[H_2][H]^{0.5}} \text{ (mole/m² cm²/mo)} \]

\[ \frac{1}{T} (\text{°K}) \times 10^3 \]

Figure 11. The temperature dependence of the reaction probability of isotropic graphite by H and O atoms; after Rosner and Allendorf.\textsuperscript{31}
Figure 12. Variation in the rate of methane formation from graphite by reaction with H atoms as a function of temperature for samples etched to different extents; after Coulon and Bonnetain.\textsuperscript{32}

Figure 13. Temperature dependence of the apparent reaction probability for various graphite materials. (a) and (a') pyrolytic graphite in prism orientation, large and small samples respectively, (b) and (b') similar results for the basal plane, (c) isotropic polycrystalline ATJ graphite.\textsuperscript{33}

Figure 14. Peak (triangles) and steady state (circles) methane evolution rates for $1.4 \times 10^{15}$ H atoms cm$^{-2}$ s$^{-1}$ impacting on graphite at different temperatures; after Gould.\textsuperscript{34} (see also Fig. 18)
Figure 15. Temperature dependence of the apparent reaction probabilities for formation of methane and acetylene from graphite impacted with a beam of H atoms (triangles and circles represent duplicate experiments); after Balooch and Olander.35

Figure 16. Methane yield per H atom determined by Stangeby et al.36 (dotted lines) for papyex which had been thermally activated (A) or deactivated (B). The other data are from Vietze et al.50 (C & D); Gould34 (E & F); Balooch and Olander35 (I & J); in each case for activated and deactivated graphite respectively. The high pressure data of Wood and Wise28, (L) Rosner and Allendorf31 and (M) Coulon and Bonnetain32 are also included.
Figure 17. Comparison of the temperature dependence of the reaction probability for methane formation with different H atom fluxes compared with a kinetic model assuming $10^{13}$ H atoms cm$^{-2}$ at saturation, after Roth. Data of (a) Balooch and Olander; (b) Rosner and Alsendorf; (c) Wood and Wise.

Figure 18. Methane evolution curve by reaction of H atoms with graphite at 790K showing peak and steady state evolution rates; after Gould.
Figure 19. Transient phenomena observed in the formation of methane from graphite at various temperatures and a total pressure of 0.5 torr.\(^\text{32}\)

Figure 20. Typical time profile of the CH\(_3\) signal showing a high initial (activated) yield which decays to a lower steady state (deactivated) yield for a papyex sample at 850K subject to \(10^{15}\) H atoms cm\(^{-2}\) s\(^{-1}\) after thermal reactivation at 1200K for 1 minute.\(^\text{36}\)

Figure 21. Hysteresis in the methane formation rate observed by Coulon and Bonnetain on cycling the temperature of the graphite at a hydrogen pressure of 0.5 torr.\(^\text{32}\)
Figure 22. Hysteresis in the reaction probability for methane formation observed by Balooch and Olander.\textsuperscript{35}

Figure 23. Parabolic plot of percent carbon removed in the decarburization of 4340 steel at 1173K by H atoms generated by a microwave discharge in a flowing molecular hydrogen gas stream at 1 torr pressure. The calculated values were obtained on the assumption that diffusion of carbon in the steel was rate limiting.\textsuperscript{43}
4. SYNERGISTIC EFFECTS IN THE REACTION OF ATOMIC HYDROGEN WITH CARBON AND CARBON-CONTAINING MATERIALS.

The walls of a fusion reactor and related tritium breeder or handling facilities will be subject to many particle fluxes in addition to H atoms and ions. Consequently there is considerable interest in the possibility of synergistic effects whereby electron, ion, neutron and photon bombardment enhance the rate of carbon erosion by H atoms.

4.1. Effect of electron bombardment on the formation of methane by atomic hydrogen.

Evidence for a large enhancement in the reactivity of graphite with atomic hydrogen to produce methane was first presented by Ashby and Rye \(^1\). They observed a 20-fold increase in CH\(_4\) partial pressure when electron bombardment was superimposed on the H atom flux. This work was continued, and extended to TiC and TiB\(_2\), in a study of the effect of varying the sample temperature and electron energy \(^45\),\(^46\). For graphite it was found that the methane yield enhancement, \(\epsilon\), was highly dependent on the immediate past history of the sample. The methane yield enhancement is defined as,

\[
\epsilon = \frac{(N - N_0)}{n_e},
\]

where \(N\) and \(N_0\) are the number of CH\(_4\) molecules produced per second with and without electron bombardment respectively, and \(n_e\) is the number of electrons striking the sample per second. Initial values of \(\epsilon\) were higher by as much as an order of magnitude because of the build up of surface hydrogen before electron bombardment \(^45\). After higher temperature treatments \(^46\) pronounced and irreversible decays in both the thermal CH\(_4\) production rates and the yield enhancement were observed. This effect could be understood as being a result of either the removal of highly active sites present on the fresh surface or by depletion of bulk hydrogen by high temperature conditioning. The steady state values of \(\epsilon\) were observed to increase with electron energy, more so at higher sample temperature (Figure 24 \(^46\)), and also with temperature at constant electron energy. The yield enhancements at temperatures below 600K were close to \(10^{-2}\), increasing only slightly with electron energy. These values are claimed to be too high to be accounted for by an electron stimulated desorption (ESD) process \(^46\): However, while ion yields by ESD are typically \(^47\) \(< 10^{-5}\) ions per electron, the ratio of ions to neutrals...
desorbed is typically < 10^{-2} and so the total yield can approach the values observed in these studies. At higher temperatures \(4^c\), the yield enhancements are much more energy dependent, increasing to 10^{-1}. This behaviour is qualitatively similar to that observed for hydrogen atoms and ions in the absence of electron bombardment: Much higher CH\(_4\) production rates are observed for temperatures from 700 to 810K than at lower temperatures. The methane production rates under combined electron and H atom attack were comparable with those observed for H\(^+\) ion bombardment (see section 5) i.e. one or two orders of magnitude greater than H atoms alone. For TiC at 315K the yield enhancement was 6 \times 10^{-3} for electron energies above 80eV comparable to the value observed for graphite \(^{45}\). The fluences used in these experiments were too low to reveal any possible effects from depletion of the surface of carbon.

Haasz et al. \(^{48,49}\) found no enhancement in the CH\(_4\) yield by simultaneous electron and H atom bombardment in a well-baked system with walls cleaned by electron and H atom bombardment. The yield enhancement was undetectable, less than 10^{-5} CH\(_4\) per electron, using 0.1 mA cm.\(^{-2}\) of 1 keV electrons and sample temperatures in the range 700 to 1100K. Spurious synergistic effects were observed only when the vacuum system walls were not thoroughly outgassed \(^{48}\). Since carbon and carbides are usually prepared by processes involving hydrocarbons they are likely to contain hydrogen and hydrocarbons which can give rise to CH\(_4\) under electron impact alone: Thus electron bombardment gave large methane signals, ca. 8 \times 10^{-3} CH\(_4\)/e, before baking. An additional source of CH\(_4\) when using a 'back-fill' technique to produce atomic hydrogen is the adsorption of CH\(_4\) produced on other surfaces in the system which adsorbs on the sample surface and then desorbs by ESD, giving a spurious 'synergistic' effect \(^{49}\). Experiments involving a sequential H atom bombardment to a fluence of 10^{18} cm.\(^{-2}\) produced an unmeasurable CH\(_4\) signal on subsequent electron bombardment. However this may be a result of insignificant H atom loading of the sample \(^{49}\). Vietzke, Flaskamp and Phillipps \(^{50}\) detected only a small influence of simultaneous electron bombardment on the production of hydrocarbons by the interaction of H atoms and graphite. They employed a beam source producing an H atom flux at the target of 1.6x10^{15} cm.\(^{-2}\) s\(^{-1}\) and a smaller flux of H\(_2\) molecules, and sample temperatures in the range 300 to 800K.

Ashby \(^{51,52}\) has recently carried out further research into the origin of the electron bombardment enhancement of the reactivity of graphite with hydrogen observed in their work. In Figure 25 the dependence of the electron yield enhancement, \(\epsilon\), on electron energy at 925K
is compared with the secondary electron yield variation with primary electron energy. The excellent agreement suggests that it is low energy (<20 eV) electrons which are producing the enhancement in reaction rate. Results to be described in the following section on UV photon enhancement of this reaction strongly support this interpretation and point to π → π, valence to conduction band, transitions of graphite centred at 4.8 eV as being responsible. Electron energy loss techniques show that this excitation can arise from electron bombardment and the electron and photon enhancements have an identical temperature dependence (Figure 26). The argument that the electron enhancement is due to ESD of adsorbed CH₄ is countered by a calculation of the CH₄ coverage and, making the assumption that the desorption probability per electron is equal to the probability that the electron will strike a CH₄ molecule, i.e. the fraction of surface covered, the desorption probability is calculated as 10⁻¹². This is nine orders of magnitude lower than the minimum value of the electron yield enhancement. Two potential problems with this argument are the assumption that the electronic excitation in the ESD process is localized and the value assumed for the CH₄ binding energy. However there is a fair margin for error in this model calculation.

Clearly electron enhancement of the H atom reaction with graphite is a contentious issue. Some facts seem clear. High temperature sample treatment reduces the electron enhancement, even to the point where it becomes undetectable. This is probably due to depletion of the sample of hydrogen because when the H atom supply is adequate electron enhancement can readily be observed. It should be stressed that the conclusion that an effect does not occur because it cannot be observed is only valid if the experiment was performed under the optimum conditions for it to be observed. The reduction of data to a yield per particle, e.g. CH₄/H atom, which was criticised in the preceding section also can be misleading in this context. Thus if the thermal rate is sufficiently high that the H atom flux limits the reaction rate then the effect of electron bombardment will indeed be negligible. Furthermore, the higher the electron flux the more negligible will be the yield enhancement per particle. The data in Figure 25 were obtained at a sufficiently low electron flux that the increase in yield was a linear function of the electron flux, viz. the yield enhancement, ε, is independent of electron flux and the H atom supply is adequate. In the fusion reactor the supply of hydrogen is unlikely to be a limiting factor and the synergistic effect of electron bombardment on the methane production by H atom bombardment will need to be taken into consideration.
4.2. Photon enhancement of the reaction of graphite with atomic hydrogen.

An enhancement of the methane production rate from the reaction between graphite and atomic hydrogen has been observed on bombardment by UV photons. The results shown in Figure 27 are for a photon flux of ca. $10^{19}$ s$^{-1}$ with wavelengths less than 300 nm. Photon bombardment provides an additional 10 to 20% to the thermal rate. The UV source was a high pressure Hg arc lamp which covers a range of wavelengths. The dependence of the photoenhancement on wavelength was determined by using filters to vary the wavelength distribution in the incident photon flux. The photoenhancement was found to correlate well with the intensity of the 260 nm. light. This corresponds to the 4.8 eV tr-valence to tr-conduction band transition in graphite. The intensity of the source at 207 nm. was too low to investigate the possibility that 6.0 eV $\sigma$ to $\pi$ transitions would also enhance the reaction rate. The identical temperature dependence of the electron and photon yield enhancement (Figure 26) referred to earlier suggests that both result from a common mechanism, namely the electronic excitation of graphite. While the UV photon flux in the fusion reactor may be small, these studies have provided considerable insight into the electron enhancement of CH$_4$ production.

4.3. Ion bombardment enhancement of the methane yield from the carbon - atomic hydrogen reaction.

For our present purposes we will exclude hydrogen ion bombardment from our discussion. This extremely important topic will be addressed in the following section where it will be seen that H$^+$ ion can be more effective than H atom bombardment by two orders of magnitude. Our interest here is whether radiation modification can produce a similar enhancement in the reactivity towards atomic hydrogen of graphite and other carbon-containing materials.

Veprek and Webb et al. have investigated the effect of MeV He$^+$ ion bombardment on the efficiency of the H atom reaction with graphite. The samples were irradiated in a Van de Graaf accelerator providing a momentum separated 2 MeV He$^+$ beam to a dose of $10^{17}$ to $10^{18}$ cm$^{-2}$. This irradiation caused twinning flaking and faulting in the surface layer due to a build up of lattice stress in the damaged area. All samples showed an increase in reactivity to H atoms which approached one order of magnitude, although the degree of enhancement depended on the initial activity. It is suggested that since the enhanced activity is comparable for all samples that this is due to an overall erosion rate being limited by supply from the
gas phase. The activity is enhanced over a depth of approximately 27 μm which is considerably greater than the 3.6 μm projected range of 2 MeV α-particles in graphite. It is suggested that the lattice stress created by irradiation is relaxed by the formation of extended defects which can spread into the bulk to a depth far exceeding the range of the primary ions. It is conjectured that the activity of irradiated samples would approach that of energetic H⁺ ions if the difference between the sticking probability of H atoms and the trapping probability of H⁺ ions were taken into account.

Vietzke et al. [50] have investigated the effect of 5 keV Ar⁺ ion bombardment on the graphite/H atom reaction. Simultaneous bombardment with Ar⁺ and H atoms gave a dramatic increase in erosion rate of up to two orders of magnitude. The temperature dependence of the reaction probability under simultaneous bombardment is shown in Figure 28. The probability is highly temperature dependent with a pronounced maximum in the vicinity of 800K, and the largest contribution is from CH₃ production, mass 15. C₂ compounds, mass 26, are also produced both with and without Ar⁺ bombardment. Hydrocarbon formation was not observed with simultaneous Ar⁺ and H₂ molecule bombardment, implying that the enhancement is not due to dissociation of molecular hydrogen at the surface. Sequential Ar⁺ and H atom attack only enhanced the activity by much smaller factors up to about 2. Since ion bombardment alone does not lead to a drastic increase in reactivity it is proposed that radiation induced interstitials or vacant sites on the surface react directly with H atoms to form CH, CH₂, or C₂H species before they can be annealed. These species form the reactive precursors for subsequent reaction with H atoms. Once formed these precursors are quite stable since they survive several minutes annealing at 1200K.

Synergistic effects are observed when graphite is subject to ion bombardment. How important they will be in fusion reactors is a question which will only be answered by further research.
Figure 24. Methane yield enhancement versus incident electron energy for atomic hydrogen reacting with Papyex graphite at various temperatures.\textsuperscript{46}

Figure 25. Comparison of the secondary electron yield (solid line) with the methane electron yield enhancement (data points) as a function of primary electron energy.\textsuperscript{52}

Figure 26. Comparison of the quantum yield and electron yield enhancement of the reaction between graphite and H atoms at different temperatures.\textsuperscript{51}
Figure 27. Methane production rate from graphite with and without UV radiation. The photon enhancement data represent additional methane produced over the methane production represented by the thermal data.\textsuperscript{53}

Figure 28. Temperature dependence of the reaction probability, molecules produced per incident H atom, for CH\textsubscript{4} (mass 16) and CH\textsubscript{3} (+CH\textsubscript{4}) (mass 15), and C\textsubscript{2}-compounds (mass 26) by simultaneous H atom and Ar\textsuperscript{+} ion bombardment of graphite.\textsuperscript{50}
5. CHEMICAL SPUTTERING: METHANE FORMATION BY HYDROGEN ION BOMBARDMENT.

The characteristic features which separate chemical from physical sputtering have been reviewed by Roth. Chemical sputtering is defined as that sputtering process whereby volatile molecules are formed between the target atoms and the bombarding ions. Thus the formation of methane by reaction between \( \text{H}^+ \) ions and a graphite or carbide target provides an excellent example of chemical sputtering since methane is a stable molecule which will have an extremely low binding energy to the surface. The range of sample temperatures and ion energies where chemical sputtering and other erosion processes are likely to dominate are summarised in Figure 29, where the physical parameters chosen are those relevant to the \( \text{H}^+/\text{C} \) system. Chemical sputtering will be an activated process and will thus require some minimum temperature. However at too high a temperature the implanted ions will desorb and the contribution of chemical sputtering will become negligible. At a high enough temperature sample evaporation will take place. Physical sputtering, i.e. sputtering by atomic collisions which transfer enough energy to overcome the surface binding energy, will be present at all temperatures for ions with energies above the threshold energy. Consequently chemical and physical sputtering will occur simultaneously. Implantation of the incident particles can chemically transform the target material and thereby increase or decrease its sputter rate: This is referred to as chemically enhanced, or reduced, physical sputtering. Significantly, the range of ion energies and temperatures shown in Figure 29 for chemical sputtering coincides with those relevant in a controlled thermonuclear reactor.

In the first part of this section the focus will be on graphite since this is the target material which has been most investigated. The observations on carbide-materials will be presented at the end of this section.

5.1. Magnitude and temperature dependence of the efficiency of the graphite / \( \text{H}^+ \) ion reaction.

In contrast to the temperature dependence of the H atom / graphite reaction rate where the profile at low temperatures is controversial, there seems to be complete agreement concerning the \( \text{H}^+ \) ion temperature profile. As implied by Figure 29, the methane production rate is low at room temperature, increases to a maximum of 0.1 \( \text{CH}_4 \)/ion in the vicinity of 800K and decreases
again to low values at higher temperatures. Typical results are shown in Figures 30, 31, 32, 33 and 34. Clearly the chemical sputtering with H* ions is much more effective than the H atom reaction, being about two orders of magnitude greater under the optimum conditions for both processes.

5.2. Mechanism for chemical sputtering of graphite by H* ions.

The mechanism described by Erents et al.55,60 is based on the models used to explain the atomic hydrogen - graphite kinetics and has been very successful. Bombardment with H* ions will implant H over a penetration depth which will increase with ion energy. As the dose increases the amount of implanted H will increase but so will the surface concentration. Surface H atoms can recombine to desorb as molecular hydrogen,

\[ \text{H(s) + H(s) \rightarrow H}_2(g) \].

As the surface concentration of hydrogen increases the rate of release will also increase until a steady state is attained when the release and implantation rates become equal. The experimental observation that the CD₄ production rate mimics the D₂ release rate, i.e. builds up slowly, leads to the conclusion that the methane formation occurs only as the H atoms diffuse out and not by reaction between carbon and the incident ions. However the methane production rate is not simply directly proportional to the release rate of hydrogen. This is a direct conclusion which can be drawn from experiments conducted over the temperature range 400 to 1200K where the steady state hydrogen release rate is constant but the methane production rate is strongly peaked at 800K. Thus the rate of methane formation, R, will be some function of both the surface hydrogen concentration, nₛ, and the rate constant for the reaction with carbon to produce methane, k,

\[ R = f(nₛ) \cdot k, \tag{1} \]

where,

\[ k = \nu \exp(-Q/RT). \tag{2} \]

The surface hydrogen atom concentration will increase by the flux of atoms arriving from the bulk, J, and it will decrease by virtue of losses by ion impact desorption, recombination and hydrocarbon production. If the last contribution is small and can be neglected, then the rate of change of surface hydrogen atom concentration will be,
\[
\frac{dn_s}{dt} = J - J_0 \sigma n_s - v_2 \exp(-Q_2/RT) (n_s)^m.
\]  

The term \( J_0 \sigma n_s \) is the ion impact desorption rate for an incident ion flux, \( J_0 \), and a desorption cross-section, \( \sigma \). The rate of thermal desorption is given by the final term in which \( v_2 \) is the frequency factor, \( Q_2 \) is the activation energy for desorption and \( m \) is the order of the reaction. For a steady state, \( dn_s/dt = 0 \), and assuming that \( m = 1 \) the surface hydrogen concentration is calculated as,

\[
n_s = \frac{J_0}{[J_0 \sigma + v_2 \exp(-Q_2/RT)]}.
\]

The assumption that \( m = 1 \) is questionable since the thermal desorption process is bimolecular and would be expected to be second order: However a second order analysis leads to equations of the same form but with greater complexity.

The most straightforward assumption for the form of \( f(n_s) \) is that the methane production rate depends directly on the surface hydrogen concentration, i.e. \( f(n_s) = n_s \). In this case,

\[
R = \left[ J_0 v_1 \exp(-Q_1/RT) \right] / \left[ J_0 \sigma + v_2 \exp(-Q_2/RT) \right],
\]

from which the temperature at which the rate becomes a maximum is determined, by the requirement that \( dR/dT = 0 \), which gives,

\[
T_m = \left( \frac{Q_2}{R} \right) \ln \left[ \frac{v_2(Q_2 - Q_1)}{(J_0 \sigma Q_1)} \right]^{-1}. \tag{6}
\]

This model predicts a reaction rate which increases to a maximum with increasing temperature and decreases at still higher temperatures, if \( Q_2 \) is much greater than \( Q_1 \). Thus, at low temperature, the second term in the denominator of equation \( 5 \) can be neglected compared with the first and \( R \) will increase with \( T \). Thus for \( T < T_m \),

\[
R = (v_1/\sigma) \exp(-Q_1/RT). \tag{7}
\]

However, at high temperature \( v_2 \exp(-Q_2/RT) \) can become much greater than \( J_0 \sigma \) and the rate will decrease. Thus for \( T > T_m \),

\[
R = (J_0 v_1 / v_2) \exp \left[ (Q_2 - Q_1)/RT \right], \tag{8}
\]

which decreases with increasing \( T \) as long as the requirement that \( Q_2 > Q_1 \) is met.

The fit between the model and experiment is quite good as can be seen from Figure 30, where the value of \( Q_2 \) was determined from the peak maximum position as 54.6 kcal. mole\(^{-1}\).
and $Q_a$ was estimated to be 38 kcal. mole$^{-1}$. Subsequent experiments over a wider range of ion energies indicated that the best overall fit could be obtained using $Q_2 = 47$ kcal. mole$^{-1}$ and $Q_4 = 25$ kcal. mole$^{-1}$.

5.3. Ion flux dependence.

Smith and Meyer have pointed out that the Erents, Braganza and McCracken model can account for the variation in $T_m$ and CH$_4$ yield found by different workers. In Table 3 the values of $T_m$, calculated from equation (6), and $Y_m = R_m/J_0$, calculated using equation (5), are tabulated for the results of six experimental groups. The values chosen for the kinetic parameters were $Q_2 = 49$ and $Q_4 = 38$ kcal. mole$^{-1}$, $v_2 = 10^{13}$ s$^{-1}$, $v_4 = 1.56 \times 10^9$ s$^{-1}$, and $\sigma = 10^{-16}$ cm$^2$.

Table 3: Comparison of theoretical values of $T_m$ and $Y_m$ with six independent sets of experimental data, after Smith and Meyer.

<table>
<thead>
<tr>
<th>REFERENCE</th>
<th>ION ENERGY (keV)</th>
<th>$J_0$ (cm$^{-2}$s$^{-1}$)</th>
<th>$T_m$(°C)</th>
<th>$Y_m$ (CH$_4$/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Theory</td>
<td>Expt.</td>
</tr>
<tr>
<td>Sone et al.</td>
<td>1</td>
<td>2</td>
<td>478</td>
<td>460</td>
</tr>
<tr>
<td>Smith et al.</td>
<td>5</td>
<td>16</td>
<td>530</td>
<td>530</td>
</tr>
<tr>
<td>Busharov et al.</td>
<td>10</td>
<td>20</td>
<td>536</td>
<td>-</td>
</tr>
<tr>
<td>Feinberg et al.</td>
<td>0.58,0.88</td>
<td>12,0.6</td>
<td>522</td>
<td>510</td>
</tr>
<tr>
<td>Erents et al.</td>
<td>20</td>
<td>42</td>
<td>556</td>
<td>590</td>
</tr>
<tr>
<td>Roth et al.</td>
<td>6</td>
<td>400</td>
<td>624</td>
<td>630</td>
</tr>
</tbody>
</table>

The excellent agreement between the experimental and calculated results led Smith and Meyer to conclude that the principal cause for the discrepancy between the results was the widely different dose rates involved. Beam energies varied from 0.58 to 20 keV in these experiments and this would affect $T_m$ and $Y_m$ primarily through the ion impact desorption cross-section, $\sigma$. The success of the comparison assuming a constant value of $\sigma$ was taken to imply that the variation in $\sigma$ is small. However, as will be discussed in the following section, it is found that $\sigma$ is a strong function of ion energy.

5.4. Ion energy dependence.

The interaction of deuterons in the energy range 5 to 30 keV with carbon has been investigated by Braganza, Erents and McCracken. After deuteron implantation, a H$^+$ ion beam of the same energy was used to displace the deuterium and the release rate was monitored.
If the release rate is proportional to the number of deuterium atoms present, \( n \), and the \( \text{H}^+ \) ion flux, \( J_0 \),

\[
\frac{dn}{dt} = -J_0 \sigma n
\]

then,

\[
\frac{dn}{dt} = -J_0 \sigma n_0 \exp(-J_0 \sigma t). 
\]

The resulting values obtained for \( \sigma \) are shown in Figure 35 and it can be seen that \( \sigma \) varies by more than an order of magnitude over this energy range.

The experimental results for the \( \text{CD}_4 \) production rate at four different ion energies are shown in Figure 36. It can be seen that the peak methane production rate shifts to lower temperatures and the absolute yield increases in magnitude as the incident energy increases. The theoretical curves shown in Figure 36 were calculated using equation (5) with the experimentally determined values for \( \sigma \). The peak temperatures, \( T_m \), are accurately predicted and the absolute magnitudes are within a factor of two. The same parameters were found to give a good fit to the data obtained by Roth et al. at lower beam energies (0.67 to 3 keV). The values of \( \sigma \) deduced from these measurements are also included in Figure 35. Also shown in this figure is the correlation with the energy deposited in the surface layer suggested by Roth et al.

The results shown in Figure 34 (cited earlier) show that the peak maximum temperature for \( \text{CH}_4 \) production, \( T_m \), is independent of ion energy. According to equation (5), this implies that \( J_0 \sigma \) is constant for these experiments. This is possible, since \( J_0 \sigma \) did decrease with decreasing ion energy, and therefore with increasing \( \sigma \), in these experiments. However, Yamada et al. point out that surface erosion by ion bombardment can change the reactivity of the surface and thereby change the activation energies for reaction and recombination, \( Q_1 \) and \( Q_2 \). This may account for the maximum chemical sputtering yield observed at 1 keV, (Figure 37).

5.5. Sample dependence of the ion yield.

While different forms of graphite are observed to have different physical sputtering yields, the chemical sputtering yields are found to be sample independent. Thus Yamada et al. found comparable \( \text{CH}_4 \) production rates, and temperature and energy dependences, for isotropic carbon, glassy carbon, and two kinds of pyrolytic carbon, and concluded that radiation
damage of the surface led to similar surfaces being created on all carbons.

5.6. Hysteresis effects.

Different methane yields per ion have been observed for increasing and decreasing sample temperature similar to those seen for the H atom reaction \(^{35}\). Figure 39 shows the data of Sone et al.\(^{61}\) in which higher yields are seen for increasing sample temperatures (open circles) compared with those measured for decreasing temperature (solid points). Similar hysteresis effects have been reported by Roth \(^{39}\) as shown in Figure 38. The magnitude of the hysteresis loop increases with the accumulated fluence before yield measurement at each temperature and also is larger for faster temperature changes. It seems likely that since the concentration of implanted hydrogen decreases with increasing temperature that super-saturation occurs on increasing the temperature leading to a higher \(\text{CH}_4\) production rate. Similarly on decreasing the temperature the saturation concentration will require time to build up leading to lower rates. Yamada et al.\(^{59}\) have shown that pre-bombardment at room temperature leads to an enhanced \(\text{CH}_4\) production rate at 525°C which only reaches steady state values for this temperature after a dose of \(10^{18}\) H\(^+\) ions per cm\(^2\) (Figure 40).

5.7. Effect of H\(^+\) ion bombardment of carbides.

Hydrogen ion bombardment of carbides also produces methane by chemical sputtering but it is usually observed that the yield decreases with sputter time presumably as a result of depletion of the surface region of carbon. The results obtained by Braganza, McCracken and Erents \(^{62}\) for SiC and B\(_4\)C are compared with those for carbon in Figure 41. A maximum in the \(\text{CH}_4\) production rate with increasing temperature occurs for all three materials. The maximum yields were \(0.55 \times 10^{-2}\) and \(1.3 \times 10^{-2}\) for B\(_4\)C and SiC respectively, significantly less than observed for graphite, \(4.5 \times 10^{-2}\). These yields parallel the carbon atom densities in the three materials. The yield from SiC was observed to fall off exponentially with time, probably as a result of depopulation of the surface of carbon. Annealing for 4 minutes at 1500K completely recovered the initial yield. Surprisingly Auger electron spectroscopy revealed little difference in surface carbon concentration between annealed and unannealed SiC samples. It should be noted that VepreK et al.\(^{42}\) found no significant erosion of either SiC or B\(_4\)C in an H plasma and Roth et al.\(^{56}\) measured sputter yields for porous SiC which were ca. \(2 \times 10^{-2}\), independent
of temperature. Pontau and Wilson observed extremely low CH₄ production rates, \( \ll 10^{-2} \) CH₄/ion, for a C-SiC alloy at all temperatures in the range 300 to 1000K.

Several recent studies have looked at TiC under H⁺ ion bombardment since this has been proposed as a promising first wall material. Yamada et al. found that the CH₄ yields were an order of magnitude less than for graphite at 500°C and as can be seen from Figure 42, the yields were relatively independent of both temperature and the fabrication technique used for the TiC. A reasonable explanation for the small temperature dependence invokes the replenishment of the depleted carbon layer at the surface by enhanced diffusion of carbon at higher temperatures, thereby offsetting the decrease in CH₄ production rate observed for graphite. A similar enhancement of the surface carbon concentration by chemisorption of carbonaceous impurities on the Ti-rich surface is suggested at low temperatures. A decay in CH₄ yield with time similar to that observed for SiC has been observed by Pontau and Wilson, Figure 43, and by Yamada et al. Hysteresis effects on temperature cycling were observed, similar to those observed for graphite.

Recently Sukenobu and Gomay have studied CH₄ formation and surface modifications produced by H⁺ ion bombardment of TiC coatings. The temperature dependence of the CH₄ yield at 3 and 1 keV are shown in Figure 44, for fluences of 3.2 and 2 x 10¹⁸ ions cm⁻² respectively. Prebombardment effects were avoided by annealing at 1000°C for 30 minutes before each measurement. In contrast to the maximum observed for graphite, and the relatively constant yield observed by Yamada et al. for TiC, the yield is observed to pass through a minimum with increasing temperature. Surface analysis by Auger electron spectroscopy shows that the surface is depleted in carbon at room temperature but not at 590°C, consistent with the greater CH₄ production at room temperature. If the TiC is annealed after irradiation with 1 keV H⁺ at room temperature then the C/Ti ratio increases, and as can be seen from Figure 45 the increase is greater the higher the annealing temperature. It is concluded that enhanced diffusion and surface segregation of carbon is responsible. This explains the increase in CH₄ yield at high temperatures. It is not clear why the yield decreases with increasing temperature up to 590°C. At both room temperature and at 590°C the carbon depletion of the surface is greater the lower the H⁺ ion energy in the range 0.5 to 3 keV which suggests that chemical sputtering of TiC is more effective than physical sputtering at low energies. Finally, the C/Ti ratio is higher at 590°C during sputtering than on annealing in the absence of the ion beam. This is
evidence for radiation enhanced diffusion of carbon in TiC.

While considerably more work needs to be carried out to remove many of the ambiguities present in the results obtained so far, the future for carbide-materials in the first wall seems much more promising than that for carbon itself.
Figure 29. Schematic representation of the ranges of ion energy and sample temperature for various erosion processes such as physical and chemical sputtering and evaporation using the physical parameters relevant to the C/H\textsuperscript{+} system; from Roth\textsuperscript{39}.

Figure 30. Experimental results for the steady state CH\textsubscript{4} formation rate during bombardment of pyrocarbon with 20 keV H\textsuperscript{+} ions (circles and dashed line). The solid line represents the theoretical calculation using eqn.5 with Q\textsubscript{1}=38 and Q\textsubscript{2}=54.6 kcal/mole, \( \sigma = 10^{-16} \text{cm}^2 \) and \( J_0 = 10^{25} \text{cm}^{-2} \text{s}^{-1} \). From Erents et al.\textsuperscript{55}
Figure 31. Temperature dependence of the sputtering yield of pyrolytic graphite with different energy hydrogen ions.

Figure 32. Temperature dependence of the sputtering yield of several graphite samples subject to H⁺ ion bombardment.

Figure 33. Temperature dependence of the CH₄ production rate observed on sputtering a carbon coating on platinum with 5 keV H₂ ions with a dose rate of 1.6x10¹⁵ cm⁻² s⁻¹. The chemical sputtering yield is plotted and was obtained by subtracting the physical sputtering contribution from the total yield.
Figure 34. Temperature dependence of the CH₄ production rate by hydrogen ion bombardment of the basal plane of pyrolytic graphite.₅⁹

Figure 35. Cross-sections for ion-induced release of deuterium from carbon calculated from their own data and that of Roth et al.₅₆ by Braganza et al.₆⁰

Figure 36. Steady state methane production rates on bombardment of pyrolytic graphite with D⁺ ions of different energies. The data points and dashed line represent the experimental data and the solid lines are the result of a theoretical calculation using eqn.[5].₆₀
Figure 37. Energy dependence of the chemical sputtering yield of the basal plane of a pyrolytic graphite target.  

Figure 38. Variation of the CH₄ production rate with temperature on bombarding graphite with 2 keV H⁺ ions. Arrows indicate the direction of the temperature change.  

Figure 39. Hysteresis in the chemical sputtering yield of pyrolytic graphite by 1 keV H⁺ ions.
Figure 40. Dose dependence of the methane formation rate by bombardment with 1 keV H\(^+\) ions at 525°C.
(a) Prebombarded with 9.10\(^{-17}\) cm\(^{-2}\) 1keV H\(^+\) at room temperature.
(b) Sample heated to 700°C after (a)
(c) No prebombardment.\(^{59}\)

Figure 41. Temperature dependence of the CD\(_{4}\) production rate from 20 KeV D\(^+\) bombardment of B\(_4\)C and SiC, compared with that observed for graphite.\(^{62}\)

Figure 42. Steady state CH\(_{4}\) production rates at different temperatures for various TiC samples bombarded with 3 keV H\(_3\) ions.\(^{64}\)
Figure 43. Methane produced per incident H during the bombardment of TiC with 10 keV H$_3^+$ ions with a flux of $10^{15}$cm$^{-2}$s$^{-1}$, after Pontau and Wilson.63

Figure 44. Temperature dependence of the CH$_4$ yield from TiC during hydrogen ion bombardment.65

Figure 45. Variation in the atomic ratio of carbon to titanium determined by AES during the heating of TiC after 1 keV hydrogen ion bombardment at room temperature.65
6. METHANATION AND FISCHER-TROPSCHE CATALYSIS RESEARCH AND ITS SIGNIFICANCE FOR CH₄ IMPURITY GENERATION.

The importance of hydrocarbons in a different branch of energy science, namely the petroleum industry, has led to a considerable body of research into the production of synthetic fuels to replace non-renewable oil stocks. Some of this research has relevance to the methane production problem in the fusion reactor environment.

6.1. Terminology.

There are two main catalytic processes involved in the manufacture of synthetic fuels using carbon monoxide, CO, and hydrogen, H₂, as a feedstock. These are the methanation reaction and the Fischer-Tropsch synthesis. In the methanation reaction, CO and H₂ react to produce methane and water according to either the following stoichiometry,

\[ CO + 3H₂ = CH₄ + H₂O, \]  \hspace{1cm} (1)

or,

\[ 2CO + 2H₂ = CH₄ + CO₂, \]  \hspace{1cm} (2)

the two reactions being coupled through the water gas shift reaction,

\[ H₂O + CO = H₂ + CO₂; \]  \hspace{1cm} (3)

The particular stoichiometry obtained will depend on the catalyst and the reaction conditions. In the Fischer-Tropsch synthesis, polymerisation to form higher hydrocarbons and oxygenated organic species also occurs. A serious question concerning the application of such data will be the relevance of results on the hydrogenation of carbon monoxide to the problem of hydrogenation of carbon. This will be discussed in the following sub-section.

6.2. Relevance of CO/H₂ studies to the C/H₂ reaction.

Carbon monoxide is a ubiquitous impurity in UHV environments and presumably also in all gas handling systems, therefore the CO/H₂ reaction has some direct application to the CH₄ production problem. However, CO is likely to be a small fraction of the total carbon inventory in the fusion reactor and tritium handling facilities. Furthermore, CH₄ is unlikely to be a more
serious contaminant than CO. However, if the CO/H₂ reaction proceeds through a surface carbide intermediate,

\[
\text{CO(g)} + \text{H}_2(\text{g}) \rightarrow \text{C(a)} + \text{H}_2\text{O(g)}, \quad (4)
\]

rather than an oxygen containing surface species,

\[
\text{CO(a)} + x\text{H(a)} \rightarrow \text{COH}_x(a), \quad (5)
\]

then the research on the methanation reaction will have much more significance for the methane problem. It is typical for catalytic research that both types of intermediate have their proponents. Fortunately, the carbidic-intermediate mechanism appears to be gaining increasing support. The evidence in favour of this mechanism will be reviewed in the following sub-section

6.3. Evidence for a carbidic intermediate mechanism in the methanation reaction.

Isotopic substitution has proved to be a very powerful technique in these mechanistic studies. Araki and Ponec \(^{71}\) deposited \(^{13}\text{C}(a)\) on the surface of a clean Ni film by the CO disproportionation reaction,

\[
2^{13}\text{CO} \rightarrow ^{13}\text{C(a)} + ^{13}\text{CO}_2(\text{g}), \quad (6)
\]

at 300°C for 30 minutes. After pumping for 60 minutes at 300°C to remove undissociated CO the film was exposed to a reaction mixture of \(^{12}\text{CO}\) and H₂ at 250°C. The first product to appear was \(^{13}\text{CH}_4\), an induction period of 20 minutes preceded the appearance of \(^{12}\text{CH}_4\) and \(^{12}\text{CO}_2\). This demonstrates that C(a) is used for methanation rather than CO coming from the gas phase.

Wentrcek, Wood and Wise \(^{67}\) used the disproportionation reaction (6) to deposit carbon on the surface of a supported Ni/Al₂O₃ catalyst at 553K using a pulse microreactor. For each measured CO pulse into the reactor, the quantity of CO and CO₂ leaving the reactor was measured. In this way, from the stoichiometry of reaction (6) the amount of C(a) and CO(a) could be determined. The amount of CH₄ produced by a H₂ pulse was then measured and found to correlate accurately with the total amount of C(a), there being no correlation with CO(a). These observations demonstrate that CH₄ is formed via a C(a) intermediate, rather than a "COH"-type species, and that at this temperature the C(a) can be quantitively converted to CH₄. As will be discussed more fully later, heating the C(a) to 723K deactivates it.
Rabo, Risch and Poutsma used a pulse reactor technique to investigate the CO/H\textsubscript{2} reaction by sequentially pulsing CO and then H\textsubscript{2} onto the catalyst. For SiO\textsubscript{2}-supported Ni, Co, and Ru if the catalyst was maintained at 300°C during both the CO and the H\textsubscript{2} pulses a surface carbon species was formed which readily hydrogenated to CH\textsubscript{4}. At room temperature the adsorption of CO is non-dissociative and the adsorbed CO is inert to H\textsubscript{2}. However, if the M-C species formed by a pulse of CO at 200 to 300°C is pulsed with hydrogen at room temperature it does react to form methane and higher hydrocarbons. In contrast, the adsorption of CO on Pd at 300°C was non-dissociative and the chemisorbed CO was less reactive to H\textsubscript{2} than the M-C species formed on Ni, Co, and Ru.

Biloen, Helle and Sachtler have carried out similar experiments to those described above, incorporating \textsuperscript{13}C by \textsuperscript{13}CO disproportionation at 250°C and monitoring the amount of \textsuperscript{13}C on the surface by the amount of \textsuperscript{13}CO\textsubscript{2} produced, then the surface was exposed to \textsuperscript{12}CO/H\textsubscript{2} to initiate hydrogenation. However, these experiments were performed at a high pressure of 0.5 atmospheres as a batch rather than a flow reaction. Under these conditions, methane and higher hydrocarbons were formed, i.e. Fischer-Tropsch synthesis. The observed incorporation of \textsuperscript{13}C into both methane and higher hydrocarbons led to the conclusion that oxygen-free species CH\textsubscript{x} (x = 0 to 3) are possible intermediates in methanation and that they are capable of being incorporated into growing hydrocarbon chains. It is suggested that CO dissociates in a fast step to give carbodic intermediates, from which both methane and higher hydrocarbons are produced. This work was carried out on supported Ni/SiO\textsubscript{2}, but preliminary results reported for Co/SiO\textsubscript{2} and Ru/SiO\textsubscript{2} displayed the same features. In a later paper Sachtler et al. report the results of experiments on UHV deposited Co and Ru metal films using the low pressure (< 1 torr) pulse reactor technique previously applied to Ni. It was confirmed that incorporation of predeposited \textsuperscript{13}C into \textsuperscript{13}CH\textsubscript{4} takes place on Co and Ru as well as Ni. However, for Co the rate of formation of \textsuperscript{13}CH\textsubscript{4} and \textsuperscript{12}CH\textsubscript{4} were comparable whereas for Ru, \textsuperscript{12}CH\textsubscript{4} formation was faster. The authors prefer to interpret these differences as arising from increasing rates of deactivation of the adsorbed carbon in the sequence Ni < Co < Ru, rather than by the existence of different intermediates on different metals (e.g. oxygen-containing species such as RuCHOH). It is pointed out that kinetic pulse experiments carried out at the lower temperature of 200°C, rather than 300°C, show less difference between Ru and Ni. Deactivation of adsorbed carbon is a well established phenomenon as will be discussed more fully in section 6.5. Nijs and Jacobs
have shown \(^7\) that a supported Ru surface fully precovered with \(^{13}\text{C}\) reacts with \(^{12}\text{CO}/\text{H}_2\) under Fischer-Tropsch conditions at 200°C to incorporate the \(^{13}\text{C}\) into methane but not higher hydrocarbons. Surface carbon is easily hydrogenated to methane but does not initiate chain growth.

A different approach to the unravelling of the mechanism of the methanation and Fischer-Tropsch reactions has been attempted by Brady and Petitt \(^7\), by studying the catalytic decomposition of diazomethane, \(\text{CH}_2\text{N}_2\), on metal surfaces. On Ni, Pd, Fe, Co, Ru, and Cu surfaces at 25 - 200°C diazomethane reacts to form exclusively ethylene, \(\text{C}_2\text{H}_4\), and nitrogen. However, in the presence of \(\text{H}_2\) on Fe, Co, and Ru, linear alkanes and mono-olefins with chain lengths in the range \(\text{C}_1 - \text{C}_{18}\) are formed, typical of the Fischer-Tropsch synthesis. On Ni and Pd, diazomethane and hydrogen react to form not only methane but some higher hydrocarbons as well. This is to be compared with the observation that using a \(\text{CO}/\text{H}_2\) feed Ni and Pd produce exclusively \(\text{CH}_4\) at 1 atm, but that at higher pressures (68 atm) higher hydrocarbons are also formed with a distribution much like that observed with \(\text{CH}_2\text{N}_2/\text{H}_2\) at 1 atm. Interestingly, with Cu the only hydrocarbon produced is ethylene, \(\text{C}_2\text{H}_4\), just as in the absence of \(\text{H}_2\). Apparently this reflects the inability of Cu to dissociate hydrogen. This work \(^7\) shows that methane, and higher hydrocarbon, formation does not require an oxygen-containing intermediate and can proceed via carbidic (=CH\(_2\)) species. Experiments \(^7\) on the change in molecular weight distribution caused by the addition of \(\text{CH}_2\text{N}_2\) to the feed during a \(\text{CO}/\text{H}_2\) reaction and also an examination of the \(^{13}\text{C}\) distribution in the propene formed from \(^{13}\text{CO} + \text{H}_2 + ^{12}\text{CH}_2\text{N}_2\) lead to the conclusion that mechanisms involving oxygen-containing intermediates are incorrect.

Goodman and co-workers \(^7\) have studied the methanation reaction on single crystal metal surfaces which could be characterised in UHV by Auger electron spectroscopy and transferred without contamination to a separate reaction cell to investigate the kinetics of the methanation reaction at pressures in the range 1 to 1500 torr. Following the reaction the single crystal could be transferred back into UHV for surface analysis. Disproportionation of \(\text{CO}\) at 600K on a Ni(100) surface which had been cleaned by oxidation-reduction cycles produced an Auger spectrum with no detectable oxygen, only a ‘carbidic’ carbon peak which could be removed by heating in 100 torr of hydrogen \(^7\). A subsequent kinetic study of the buildup of carbidic carbon and its removal in \(\text{H}_2\) \(^7\), showed that the kinetic parameters associated with carbide formation and removal are comparable with those observed for a \(\text{CO}/\text{H}_2\) reaction mixture.
formation and its reduction is likely to be a major route to methane production from CO/H\textsubscript{2} mixtures on Ni surfaces.

Happel and co-workers \cite{77,78,79} have used transient multiple isotope tracing techniques to study the kinetics of the CO/H\textsubscript{2} methanation reaction over supported Ni catalysts. Using \textsuperscript{13}C as a tracer \cite{77} it was shown that hydrogenation of adsorbed CH\textsubscript{X} intermediates was an important step in the methanation mechanism. In experiments using deuterium as a tracer,\cite{78} this conclusion was confirmed and it was shown that the order of abundance of CH(a) species at 210 and 230\textdegree C was CH(a) > C(a) >> CH\textsubscript{2}(a) = CH\textsubscript{3}(a). It appears that the hydrogenation of CH(a) controls the rate of methanation. These observations were confirmed by later \textsuperscript{13}C tracing studies \cite{79}.

Cant and Bell \cite{80} also used transient response isotopic tracing together with in situ infra-red spectroscopy in studies on the methanation reaction over ruthenium. The rate at which non-oxygenated carbon underwent hydrogenation was faster than the rate at which adsorbed CO was hydrogenated, supporting the hypothesis that non-oxygenated carbon is an intermediate in CO hydrogenation.

Biloen et al.\cite{81} performed a stepwise switch from a \textsuperscript{12}CO/H\textsubscript{2} feed to \textsuperscript{13}CO/H\textsubscript{2} and thereby monitored the transient kinetic behaviour. The detailed relaxation behaviour was suggestive of intermediates which were 'carbidic' in nature. The same order of magnitude surface coverage of the carbidic intermediates was determined as observed by Goodman \cite{76} and by Happel et al.\cite{77}.

Lest it be assumed that all recent studies lead to the conclusion that non-oxygen containing carbidic intermediates are unquestionably the active species in methanation, the results of Murakami and co-workers \cite{82,83} are of interest. Using a supported Ni catalyst at 473K in flowing H\textsubscript{2},\cite{82} a pulse of CO was introduced into the gas stream and the subsequent production of CH\textsubscript{4} and H\textsubscript{2}O was monitored. It was observed that CH\textsubscript{4} and H\textsubscript{2}O were produced at the same rate. It was concluded that the rate determining step in methanation is C-O bond dissociation in CO(a) or COH\textsubscript{X}(a): Probably the latter in view of the observed inverse H/D isotope effect. It was also observed by infra-red spectroscopy,\cite{83} that the rate of disappearance of adsorbed CO on supported Pd and Ni was identical with the rate constant for methane formation, implying CO dissociation is rate limiting. While this is a reasonable interpretation of these results,
We conclude that the mechanism of the methanation reaction of CO/H\textsubscript{2} involves a rapid dissociation of CO to form a carbidic intermediate which hydrogenates to form CH\textsubscript{4}. Thus, apart from such considerations as the competition of CO for surface sites, it is reasonable to expect considerable relevance of the extensive methanation data to the problem of surface carbon hydrogenation to methane.

6.4. Factors affecting the reactivity.

Among the multitude of factors which can affect the activity of a catalyst we can list the following,

(a) the electronic structure of the metal,
(b) the geometrical structure of the metal,
(c) alloying,
(d) the presence of poisons and promoters,
(e) nature of the carbon overlayer.

The nature of the carbon overlayer is extremely important, and will be determined by such operating parameters as pressure and composition of the CO/H\textsubscript{2} reactant mixture, and the temperature of the catalyst. The large volume of information on this topic warrants a detailed discussion which will be presented in section 6.5.

(a) The metals investigated are all to the right side of the transition series, and can be divided into the following categories\textsuperscript{73}:

(i) methanation catalysts, i.e. those which produce methane and less significant quantities of higher hydrocarbons. These include nickel and palladium.

(ii) Fischer-Tropsch catalysts such as iron, cobalt, and ruthenium which produce a wide range of hydrocarbons including linear alkanes and mono-olefins with some non-linear isomers. The molecular weight distribution can cover an extremely wide range from methane to polythene. The detailed distribution depends on the reaction conditions: However many systems obey the Shultz-Flory distribution, 

\[ C(n+1)/C(n) = \alpha, \quad \alpha \leq 1, \]

where \( C(n) \) and \( C(n+1) \) are the molar concentrations of hydrocarbons.
with \( n \) and \( n+1 \) carbon atoms in the chain. Thus methane is invariably a dominant product. The separation of metals into methanation and Fischer-Tropsch catalysts is arbitrary and may in fact be confusing: Thus, for example, data are reported for Ni with \( \alpha = 0.33 \pm 0.7 \).

(iii) Inactive metals such as copper.

(b) Geometrical structure can have a major effect on catalytic activity and catalytic reactions can be divided into structure-sensitive and structure-insensitive reactions. Research in this area requires very careful studies on single crystal surfaces and there is little information available for the methanation reaction. Data of Kelley and Goodman on the methanation rate over Ni(100) and Ni(111) single crystal surfaces are summarised in Figure 46 and are compared with those observed for supported high area Ni catalysts. The rates expressed on a per surface site basis (turnover numbers) are all comparable, indicating that, at least for Ni, the methanation reaction is structure insensitive.

(c) Alloying of an active metal, Ni, with an inactive metal, Cu, has been investigated by Ponec and co-workers. It was found that the addition of 10 atomic percent Cu was sufficient to decrease the methanation rate by an order of magnitude. The specific rate constants were only changed slightly: It was the maximum carbon surface coverage which was most drastically reduced. This is probably a result of the reduction in the size of the Ni clusters below that required for dissociation of CO and formation of adsorbed carbon. The role played by surface segregation in this system is not discussed. The studies of van Barneveld and Ponec show that while alloying Ni with Cu decreases the activity for total hydrocarbon synthesis, the selectivity for higher hydrocarbon formation is increased.

(d) Poisons and promoters can have profound effects on the rates of catalytic processes. Figure 47 shows the results of Goodman on the effect of sulphur on the methane production rate of a Ni(100) catalyst. The pronounced non-linear shape of this curve should be noted: Only a 10% covering with sulphur is sufficient to reduce the methanation rate by more than an order of magnitude. One sulphur atom is capable of deactivating ten Ni atoms. This is interpreted as a long-range electronic effect rather than an ensemble effect because it depends on the electronegativity of the poison. Thus phosphorus atoms were found to poison only four nearest neighbour Ni atoms and therefore a 10-atom Ni ensemble is not required for methanation. Bonzel and Krebs have studied the Fischer-Tropsch synthesis on potassium promoted iron
catalysts. It was found that K enhances the rate of carbon deposition and thereby decreases the rate of methane formation. We have the ironic situation that S poisons a catalyst by decreasing the C surface concentration on Ni, yet K acts as a promoter to increase the surface concentration of carbon on Fe, but this also decreases the methane formation rate. Clearly the nature of the adsorbed carbon is all important: This will be discussed more fully in the next sub-section.

6.5. Different forms of adsorbed carbon in the methanation reaction.

It is well established that there are different states of adsorbed carbon on metals and that they have widely different reactivities. A useful introduction to this subject is provided by the work of McCarty and Wise in which they used the temperature-programmed reaction spectroscopy technique to study the reaction between surface carbon on Ni-Al2O3 with hydrogen. Four types of surface carbon were observed to form on a Ni methanation catalyst by exposure to CO at 500 to 600K. In decreasing order of reactivity towards hydrogen they are:

(a) chemisorbed carbon atoms (ω)
(b) bulk nickel carbide, Ni3C (β)
(c) amorphous carbon (α)
(d) crystalline elemental carbon

The ω-phase and the initial monolayers of Ni3C are much more reactive than the elemental forms to reaction with H2 at 100 kPa. The ω- and β-forms populate the surface at 550K in a ratio of 2:1 as revealed by the thermal reaction spectra shown in Figure 48. The maximum CH4 evolution rate occurs for the ω-carbon at 470K, whereas the β-carbon reaction rate does not reach a maximum until 880K. At low coverage a very reactive ω'-state was formed which produced methane even at 300K. The ω- and β-carbon states were stable up to 600K, but at higher temperatures a slow conversion to graphite was observed. In separate experiments the reactivity towards H2 of surface carbon produced by decomposition of ethylene at 575K was investigated, Figure 49. In addition to the ω- and β-states, a state labelled γ-carbon was observed. Since the β- and γ-states both correspond to many monolayers of carbon and their peak maxima shift to higher temperatures with increased coverage they were both identified with bulk phases, speculated to be Ni3C and amorphous carbon respectively. At 665K the ω- and β-carbon states slowly transform to a less reactive form, crystalline graphite, which required
temperatures in excess of 800K for reaction with hydrogen to produce methane.

Conversion of active carbon to an inactive form was observed on Ni/Al$_2$O$_3$ at 723K by Wentrcek et al.\textsuperscript{67} Similarly, Rabo et al.\textsuperscript{68} showed that the Ni-C adlayer formed by dissociation of CO, was reactive to H$_2$ in the temperature range 25 to 300°C, but was inactivated by heating to 500°C.

More direct evidence as to the different surface states of carbon is provided by spectroscopic characterization of the surface before and after reaction at high pressure. This approach has been adopted by Goodman and co-workers,\textsuperscript{75,84} using Auger electron spectroscopy (AES) for surface analysis. A Ni(100) single crystal sample was cleaned by oxidation-reduction cycles, the cleanliness being established by AES, and carbon was then deposited on the surface by the CO disproportionation reaction. When this reaction was carried out at 600K the adsorbed carbon gave a carbon Auger peak as shown in Figure 50(c) and this could be removed by heating in 100 torr of hydrogen. However, when the CO disproportionation reaction was carried out at 700K, the carbon Auger peak shape was quite different, Figure 50(a), and this carbon Auger peak was not attenuated by heating in 100 torr of H$_2$ at 650K for a prolonged period. The reactive and non-reactive carbon adlayers are designated 'carbidic' and 'graphitic' by comparison with the carbon AES peak shapes obtained \textsuperscript{90} from single crystal graphite, Figure 50(b), and from nickel carbide, Figure 50(d). A more detailed picture of the carbon build up on a Ni(100) surface on exposure to CO at 24 torr at various temperatures and flashing to 600K to remove residual CO is given in Figure 51.\textsuperscript{76} Whenever the C/Ni$_{248}$ peak height ratio exceeded 0.28 the carbon peak shape became graphitic (Figure 50a) whereas below this value the peak shape was carbidic (Figure 50c).

The reactivity of carbon on polycrystalline surfaces of Pt and Rh has been investigated by van Langeveld et al.\textsuperscript{94} using Auger electron spectroscopy. Two classes of carbon were identified: (A) amorphous and graphitic carbon; and (B) molecular fragments of the adsorbed CH$_4$ or CO and carbidic carbon. Type (A) is very unreactive towards hydrogen whereas type (B) reacts quickly, e.g. completely removed from Rh by 0.5 mbar H$_2$ at 300K. Type (B) transformed into unreactive type (A) on heating.

From transient isotope labelling experiments Biloen et al.\textsuperscript{81} and Happel et al.\textsuperscript{77,78,79} have shown that during steady state reaction only a small portion of the surface carbon layer
can be considered to be active intermediates. For example, Biloen et al.\textsuperscript{81} calculate that for a total pressure of CO/H\textsubscript{2} of 3 atm. at 215°C the upper limit for the fraction of the surface covered with active intermediates on Ni/SiO\textsubscript{2} is 0.08. Similar low values are observed on Co and Ru/Al\textsubscript{2}O\textsubscript{3}. However when such catalytic surfaces are titrated with H\textsubscript{2} in the absence of CO very large amounts of methane are produced. For Ni this amounted to 46 monolayers in exceptional cases. Clearly there exists a large pool of potentially reactive carbon of which a very small fraction is active during steady state catalysis. This picture is further supported by the assymetry in half-lives for the changes \textsuperscript{12}CO $\rightarrow$ \textsuperscript{13}CO $\rightarrow$ \textsuperscript{12}CO on an aged catalyst\textsuperscript{81}.

The first research group to use a high pressure reactor in conjunction with a UHV surface analytical facility was that of Somorjai. Dwyer and Somorjai\textsuperscript{92} studied methanation on a polycrystalline Fe foil at 300°C in a 3/1 H\textsubscript{2}/CO mixture at 6 atm. The surface was characterised by AES before and after the reaction. The products were C\textsubscript{1} - C\textsubscript{5} hydrocarbons with CH\textsubscript{4} representing 85% of the total. The initial methanation rate was 1.7 molecules per site per second with an activation energy of 23±2 Kcal. mole\textsuperscript{-1}. The AES spectra shown in Figure 52 reveal the presence of surface carbon but no oxygen. The methanation rate falls with reaction time until after 4 hours it is only 0.38. As can be seen from Figure 52 at this time the carbonaceous overlayer has become so thick that it completely obscures the Fe signal for which the analysis depth is at least 2 nm. The hydrogenation of this carbonaceous multilayer was studied in the absence of CO and the methane evolution curve is shown in Figure 53. The initial rate was identical to that observed immediately prior to termination of the CO/H\textsubscript{2} reaction. AES spectra confirmed that carbon was being removed from the surface multilayer but complete removal was not possible even after 24 hours. The thick carbon multilayer produced CH\textsubscript{4} exclusively but after this hydrogen reduction the ability to synthesize higher hydrocarbons from CO/H\textsubscript{2} was restored. There are two surprising aspects of this work: One is the relatively small fivefold decrease in methanation rate on formation of a thick layer: Second is the carbon AES peak shape observed throughout the reaction (Figure 52) is definitely not carbidic, if the (unstated) resolution of the AES analysis is sufficient to make discussion of peak shape meaningful. This is in contrast with the results observed on Ni surfaces at the same temperature\textsuperscript{75,84} (Figure 50c) but like the graphitic adlayer observed at the higher temperature of 700K (Figure 50a). The graphitic layer on Ni was unreactive to H\textsubscript{2} at 650K in contrast to that on Fe at 300°C. While the H\textsubscript{2} pressures were quite different in these studies, the implication seems to be
that Fe is a much better catalyst for hydrogenation of graphite than Ni. This may be significant for the use of steels in the fusion reactor.

Carbonaceous deposits on Fe(110) following methanation at 1 atm. with a much higher $H_2/CO$ ratio of 20/1 and temperatures in the range 525 to 655K have been investigated by AES and C 1s X-ray photoelectron spectroscopy. Three phases were identified after reaction by their AES and XPS spectra shown in Figures 54 and 55, viz:–

(I) A CH$_x$ phase characterized by a C 1s binding energy of 283.9 eV. It is claimed that this layer is largely CH$_x$.

(II) A carbidic carbon-hydrogen phase with a binding energy of 284.2 eV.

(III) Graphitic carbon with a C 1s binding energy in the range 284.7 to 285.0 eV depending on the amount of intercalated hydrogen.

Phases I and II could be completely removed by hydrogenation at 630K for 60 minutes whereas the graphitic phase III was quite inert.

Galwey studied the hydrogenation of bulk nickel carbide itself in the temperature range 250 - 300°C,

$$\text{Ni}_3\text{C} + 2\text{H}_2 \rightarrow 3\text{Ni} + \text{CH}_4.$$  

The major product was methane and its production rate was found to be directly proportional to the total amount of Ni$_3$C and to the H$_2$ pressure in the range 15 to 60 torr. However at the lower temperature of 100°C, in 50 torr of H$_2$ the rate of reaction was so slow that product could barely be detected after one hour. Since the carbidic methanation intermediate on the surface of a Ni catalyst reacts under these conditions, many authors have pointed out that this 'surface carbide' must have different properties from bulk Ni$_3$C. After outgassing Ni$_3$C at 460°C for two hours no hydrogenation reaction was observed even at 290°C in 50 torr of H$_2$. This is consistent with the known thermal decomposition reaction of Ni$_3$C,

$$\text{Ni}_3\text{C} \rightarrow 3\text{Ni} + \text{C},$$

which occurs autocatalytically on heating at temperatures above 300°C with an induction period which is 100 minutes at 355°C. As has been pointed out many times already, the elemental carbon produced will be relatively inert towards hydrogenation.
6.6. Mechanism for the methanation reaction.

It cannot be claimed that the mechanism of the methanation reaction is established beyond doubt. However the weight of recent research seems to point to a carbidic reaction intermediate. By way of a summary and to provide a focus we will present this mechanism and limit further discussion to it.

\[
\begin{align*}
\text{H}_2(g) & \stackrel{\$}{\rightarrow} 2\text{H(a)} \\
\text{CO(g)} & \stackrel{\$}{\rightarrow} \text{CO(a)} \\
\text{CO(a)} & \stackrel{\$}{\rightarrow} \text{C(a)} + \text{O(a)} \\
\text{H}_2(g) + \text{O(a)} & \stackrel{\$}{\rightarrow} \text{H}_2\text{O(g)} \\
\text{CO(g)} + \text{O(a)} & \stackrel{\$}{\rightarrow} \text{CO}_2(g) \\
\text{C(a)} & \stackrel{\$}{\rightarrow} \text{C}^\exists(a) \\
\text{C(a)} + \text{H(a)} & \stackrel{\$}{\rightarrow} \text{CH(a)} \\
\text{CH(a)} + \text{H(a)} & \rightarrow \text{CH}_2(a) \\
\text{CH}_2(a) + \text{H(a)} & \rightarrow \text{CH}_3(a) \\
\text{CH}_3(a) + \text{H(a)} & \rightarrow \text{CH}_4(a) \\
\text{CH}_4(a) & \rightarrow \text{CH}_4(g)
\end{align*}
\]

In this mechanism CH\(_x\)(a) (\(x = 0 - 3\)) represents an adsorbed carbidic intermediate and C\(^\exists\)(a) represents the pool of less active carbon which can react by transformation back into carbidic carbon. Dissociative chemisorption of H\(_2\) and CO are considered to be fast and the chemisorbed oxygen atoms are rapidly removed by reaction with CO to form CO\(_2\) gas and, or, H\(_2\) to form water, accounting for the absence of any oxygen on the surface at steady state. Most proponents of the ‘carbidic’ mechanism consider that one of the surface reaction steps involving addition of hydrogen to a CH\(_x\) species is rate limiting. Thus Bell and co-workers\(^8\)\(^9\),\(^9\) consider that the final addition of a hydrogen atom to adsorbed CH\(_3\) is rate limiting, which is an assumption which they claim is supported by the existence of an inverse isotope effect. However this assumption would suggest that the dominant active surface species at steady state would be CH\(_3\)(a) whereas the results of Happel et al.\(^7\)\(^8\) indicate that the most abundant species is CH\(_a\)(a).
This result can be taken to mean that the addition of a hydrogen atom to CH(a) is rate limiting, and in the mechanism outlined above this view has been adopted leading to all preceding steps being written as quasi-equilibria. Van Ho and Harriott have measured the rates of hydrogenation of adsorbed carbon, i.e., carbon gasification, methanation, and carbon deposition (in the absence of hydrogen). Figure 56 gives some of their results which show that the rate of carbon gasification is greater than the methanation rate from which they conclude that these steps cannot be rate limiting. Conversely, the methanation rate exceeds that of carbon deposition from CO and therefore such a disproportionation step cannot be a step in the mechanism. They suggest that hydrogen assisted dissociation, 

\[ \text{CO(a)} + 2\text{H(a)} \rightarrow \text{C(a)} + \text{H}_2\text{O(g)} \]

may be the slow step in the reaction. It should be pointed out that in methanation CO competes with H₂ for surface sites, as revealed by the negative reaction order in CO pressure for methanation, and this may account for the faster carbon gasification rate in the absence of CO. Furthermore while it seems reasonable to argue that H₂ assists the dissociation of CO, it is not clear why it must remain rate limiting. Goodman and co-workers quote the following turnover numbers (reactions per surface site per second) for a nickel surface at 450K: For methanation in 4/1 H₂/CO mixture at 120 torr, 3.10⁻⁴ (Figure 46); for carbide formation in pure CO at 24 torr, 2.10⁻⁴ (Figure 51); and for carbide hydrogenation in pure hydrogen at 100 torr, 2.10⁻⁴ (Figure 57). Thus these data suggest that the rate of the methanation reaction is determined by a balance of carbide formation and removal, neither step being rate limiting in the usual sense.

6.7. Conclusions.

The large and growing volume of research data on the kinetics and mechanism of the methanation catalytic reaction clearly have application to the problem of CH₄ production in the fusion reactor and tritium facilities environment. The presence of large quantities of CO competing for adsorption sites with hydrogen will have to be considered, but the methanation data will provide an excellent starting reference for any studies on the hydrogenation of surface carbon.

The range of metallic systems investigated is understandably restricted to those with
potential application as methanation or Fischer-Tropsch catalysts. Fortunately this includes both iron and nickel which may provide models for the important austenitic stainless steels. However a large number of the attractive first wall materials such as titanium, vanadium, chromium and their alloys have not been investigated. These systems should be a focal point for future studies on the hydrogenation of surface carbon.
Figure 46. A comparison of the rate of methane synthesis from 96 torr H$_2$ and 24 torr CO over single crystal nickel catalysts with (100) and (111) orientations, with those observed over supported Ni/Al$_2$O$_3$ catalysts, after Goodman.

Figure 47. Methanation rate for 120 torr total pressure, H$_2$/CO-4/1, over a Ni(100) catalyst at 600K as a function of sulphur coverage.
Figure 48. Temperature programmed surface reaction with H₂ following carbon deposition by exposure of Ni/Al₂O₃ to CO at 550K. The relative carbon deposits were (a) 0.48; (b) 1.19 and (c) 3.14; after McCarty and Wise.²⁹

Figure 49. Temperature programmed surface reaction of H₂ with carbon deposited by ethylene decomposition at 575K. The relative carbon deposits were (a) 0.45; (b) 1.4; (c) 3.7 and (d) 11.1.²⁹
Figure 50. Comparison of the carbon AES signals on Ni(100) crystal surfaces with those observed from single crystal graphite and nickel carbide. (a) Following 1000s heating at 700K in 24 torr CO;\textsuperscript{75} (b) Single crystal graphite;\textsuperscript{90} (c) Following 1000s heating at 600K in 24 torr CO;\textsuperscript{75} and (d) Nickel carbide;\textsuperscript{90} after Goodman et al.\textsuperscript{75}

Figure 51. The carbon build-up as monitored by AES on a Ni(100) single crystal surface by reaction with 24 torr pure CO. The ordinate values have been normalized to the Ni\textsubscript{844} Auger transition intensity.\textsuperscript{76}
Figure 52. Auger spectra of a polycrystalline iron foil before, after 30 minutes, and after 4 hours of reaction at 300°C in a 3/1 H$_2$/CO mixture at a total pressure of 6 atm.\textsuperscript{92}

Figure 53. Methane produced by direct hydrogenation of the carbon multilayer deposit generated as shown in Figure 52.\textsuperscript{92}
Figure 54. Carbon Auger spectra of the three carbonaceous surface phases formed on Fe(110) by reaction with a 20/1 H₂/CO mixture at 1 bar: (I) 15 s at 565 K; (II) 15 s at 615 K, and (III) 90 min. at 615 K, after Bonzel and Krebs.⁹³

Figure 55. C is X-ray photoelectron spectra observed for three carbonaceous surface phases formed after H₂/CO reactions at 1 bar: (I) H₂/CO 100, 10 min. at 525 K; (II) H₂/CO 20, 10 min. at 565 K; and (III) H₂/CO 20, 10 min. at 655 K. The total carbon concentration increases from phase I to phase III.⁹³
Figure 56. Comparison of the methanation rate with those for carbon deposition and carbon gasification for a 2% Ni/SiO$_2$ supported catalyst, after van Ho and Harriott.\textsuperscript{97}

Figure 57. Carbide removal by reaction with 100 torr H$_2$. Before the reaction at each temperature the Ni(100) surface was precarbided by exposure to 24 torr CO at 600K (see Figure 51). The dashed line indicates the carbide level following a methanation reaction at 120 torr using 4/1 H$_2$/CO ratio.\textsuperscript{76}
7. CONCLUSIONS.

Methane impurity production poses a serious problem for the development of a successful fusion reactor. The impact of this problem on the several components of the reactor facility, - first wall, breeder blanket, tritium handling, purification and storage, - will be quite different in magnitude.

The production of methane in the fueling facility can be minimised without serious design constraints on the gas handling, storage and purification equipment. Techniques exist for cleaning the components and any further work will be directed towards the development of suitable and economic engineering techniques to clean the fuel handling components and prevent further contamination. Particular attention will need to be paid to the optimum location for methane-removal in the fuel clean-up cycle. Significant problems may occur in the release of tritium from metal tritides, used either for storage or purification, because the high temperatures involved may lead to efficient methane production. Consequently further research on the formation of methane from carbon segregating from suitable tritide-formers such as titanium would be desirable. Such studies would also be relevant to the use of titanium and chromium, for example, as getters for gas clean-up.

The more hostile environment provided by the reactor first wall and the breeder blanket, and also the direct impact of the methane produced within the first wall, means that much greater attention must be paid to identifying and minimising the processes leading to methane formation in these facilities. Further research is clearly needed on the production of methane from alternative limiter materials to graphite, for example low Z alloys and refractory carbides and nitrides of the low Z metals titanium, vanadium and chromium. Studies on the impact of carbon in steels as a reservoir for the continuous generation of methane are appropriate in view of the understandable reluctance of the engineering community to use untried novel structural materials. Much more work needs to be carried out on the segregation of carbon under the combined influence of heating and radiation, and into the efficiency of such surfaces for catalysing the reaction of such segregated carbon with tritium to form methane. First wall, breeder blanket and fuel handling facilities will all require effective engineering practices to ensure that an installation once cleaned from sources for methane production does not become recontaminated. During the development and early history of a commercial fusion reactor, the need for frequent extensive maintenance, repair and redesign, will make this requirement very
difficult indeed, and may delay the successful conclusion to the fusion programme if not given appropriate emphasis. Consequently the development of satisfactory 'in situ' methane clean-up techniques and production inhibitors, e.g. self-segregating renewable poisons to catalytic formation, may be advisable.
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