

Estimation of the Probability of Methane Decomposition on Hot Platinum Surface by Thermionic Emission

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ABSTRACT: The electron emission from hot metals, thermionic emission, is sensitive to changes in the metal surface conditions. It provides a continuous response to changes in the surface coverage especially in the early stage of adsorption. The adsorption of gases on the surface generally causes a change in the electron emission. Thus, from changes in the electron emission, the probability of decomposition may be found.

A relation between the hydrocarbon decomposition probability and the initial rate of thermionic emission increase has been found. This was experimentally tested in the case of methane decomposition on hot platinum surface. The simplicity and the sensitivity of this technique make it an attractive one. This paper will describe the use of thermionic emission for the estimation of the decomposition probability of methane on platinum surface.

Clean metal surfaces emit electrons differently to surface with adsorbed layers. Emission may increase or decrease depending on the type of adsorbed species. Therefore thermionic emission is a useful tool in studies of high temperature heterogeneous reactions.

The relation between the thermionic emission current, J , and the metal surface temperature, T , is given by the well-known Richardson equation, (Richardson 1921).

$$J = Ae^{-\phi/KT}$$

In this equation, A is constant, ϕ is the surface work function and K is Boltzmann constant. If $\ln J$ is plotted against $1/T$, the surface work function can be obtained from the slope of the resulting straight line.

Since the work function change, $\Delta\phi$, is our measured quantity rather than the surface coverage, θ , it is necessary to infer θ from $\Delta\phi$. It is an acceptable approximation at low coverage to assume that the coverage varies linearly with the work function (Cultter, Tempkins 1959, Langmuir 1923).

$$\phi \approx \phi_0 + \Delta\phi_{\max} \theta$$

where $\Delta\phi_{\max}$ is the maximum work function change. If the variation of A in the emission equation is unimportant, or if $\ln A$ varies linearly with θ , it is easy to show that

$$\theta = \frac{\ln J - \ln J_{\text{pt}}}{\ln J_c - \ln J_{\text{pt}}}$$

Where J is the current at coverage θ .

J_{pt} is the current for a clean Pt surface.

J_c is the current in the case of a monolayer of carbon.

This approximation of the work function is acceptable at low coverage. At high surface coverage the work function may show a maximum or minimum (Becker 1955, Bonzel 1984). Depolorization occurs as the adatoms become closely packed on the surface. This results in a reduction of the amount by which each adspecies lowers the work function caused by the electric field developed from adjacent adspecies.

Thermionic emission from a metal is infrequently used in surface studies at a realistic pressure. It has, since Langmuir's study of Cs adsorption (Langmuir and Kingdon 1925, Langmuir and Taylor 1932), often been used as a high vacuum, surface sensitive probe (Abdullaev, Tontegode and Yusifov 1979). With few exceptions however, such as high pressure thermionic converters (Kettani 1970), it is seldom used at pressures exceeding 1 Torr, either for fundamental studies or applications. There are only a few ways in which thermionic emission has been exploited. High pressure thermionic converters (Chang 1963) are one example, and the space charge limited gas chromatography detector of Hudson *et al.* (Hudson, King and Brandt 1961), is another. Jerner and Magee (1970) studied the thermionic work function changes in the oxidation of beryllium. The fact that a

small change in the surface coverage produces significant changes in the work function of the surface has led to frequent use of thermionic emission in studies of the adsorption of atoms and molecules on solid surfaces. In this paper, changes in thermionic emission current are used to evaluate the decomposition probability of methane on platinum.

Theory

When a gas molecule impinges on the surface it has a probability of being adsorbed. This probability is known as the sticking coefficient. The adsorption of gases on surface generally causes a change in the electron emission. Thus, from changes in the emission one can infer the existence of adsorption, desorption, and decomposition processes. It is possible to follow the rate at which emission varies and from this to obtain information about the rates of those surface processes at high temperature.

Thermionic emission provides a continuous response to changes of surface conditions. It is sensitive to the early stages of carbon deposition, so the probability of decomposition may be found. To find a relation between the hydrocarbon decomposition probability, σ_{dec} and the initial rate of current increase, $\Delta J/\Delta t$, consider the following:

$$n_o \, d\theta_c/dt = \sigma_{\text{dec}} \, f_h (1-\theta_c)$$

For low coverage, $\theta_c \approx 0$

$$n_o \, d\theta_c/dt = \sigma_{\text{dec}} \, f_h$$

So the probability of decomposition is,

$$\sigma_{\text{dec}} = (n_o / f_h) \, d\theta_c/dt$$

Since

$$J = A \exp (-\phi/kT)$$

Then

$$\begin{aligned} dJ/dt &= -A \exp (-\phi/kT) \, 1/kT \, d\phi/dt \\ &= -(J_o/kT) \, d\phi/dt \end{aligned}$$

But

$$\begin{aligned}\phi &= \phi_0 - \Delta\phi \theta_c \\ d\phi/dt &= -\Delta\phi d\theta_c/dt\end{aligned}$$

So

$$dJ/dt = J_0 (\Delta\phi/kT) d\theta_c/dt$$

Substituting for $d\theta_c/dt$, then the probability of decomposition is

$$\sigma_{dec} = n_0/f_h kT/\Delta\phi \quad 1/J_0 \quad \Delta J/\Delta t$$

Where n_0 is the number of active sites. f_h is the hydrocarbon flux, given by

$$f_h = 1/4 n u$$

$$f_h = 3.513 \times 10^{22} P_h(\text{Torr}) / (MT)^{1/2} \text{ molecules/cm}^2 \text{ sec.}$$

Where P_h is the hydrocarbon pressure in Torr, M is the molecular weight. So the initial rate of current increase due to deposition of carbon, DJ/Dt , will give an estimate of the decomposition probability, σ_{dec} .

Experimental Conditions

The experimental apparatus, as seen in Figure 1, consists of two parts, the thermionic emission reactor and the glass low-pressure fast flow system.

The thermionic emission reactor contains an emitter and collector assembly as seen in Figure 1. The emitter is an electrically heated platinum filament (5 mil-diameter, 2 cm length) mounted on a brass and ceramic frame and positioned 3 mm from a nickel wire collector. It is equipped with thermocouple leads. Collector voltage is supplied by a 9-V battery and emission current is measured by a Keithly Electrometer (Model 610 C).

A 1-mil Pt/Pt 10% Rh thermocouple is welded to the center of the filament. This is done under a microscope by heating the filament to incandescence and contacting it with a thermocouple lead held at a slightly different potential. This method avoids mechanical damage due to spotwelding, provides excellent thermal and electrical contact, and allows accurate placement.

- a) Mercury O ring piston flowmeter
- b) Bubbler for liquid HCs
- c) Stepdown transformer; Variac not shown
- d) Flange for filament assembly
- e) Pt filament
- f) Collector
- g) 9 v battery
- h) Keithley 810C electrometer
- i) Thermocouple gauge

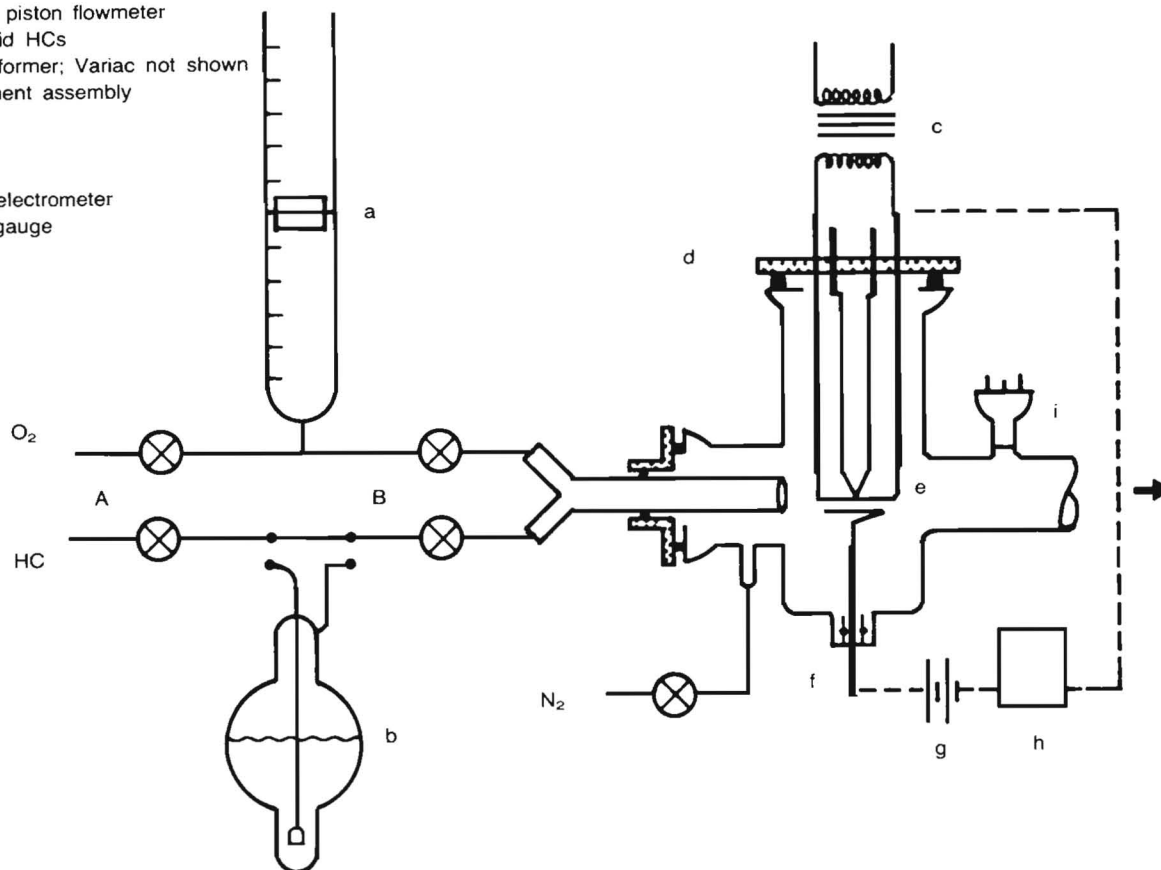


Fig. 1. Fast flow thermionic emission apparatus.

It is convenient to use a thermocouple for measuring the filament temperature rather than voltage (resistance) taps, since a thermocouple needs no calibration. The thermocouple reading is falsified, however, if the filament is heated with direct current. Therefore, we supplied the filament with alternating current from the isolated secondary of a stepdown transformer which was controlled by a Variac. This method of heating introduces a small ripple in the filament temperature which is then impressed on the emission current. By monitoring the output of the Keithly electrometer, we found the peak to peak ripple in the current to be less than 5% of the D.C. level; this corresponds to a temperature variation of only several degrees in 1500°C. The filament thermal response is sufficiently slow to ensure that rapid variations in Joule heating are effectively averaged out. Since the temperature oscillations are small, the thermocouple output could be measured with either a Leeds and Northrup millivolt potentiometer or a Hewlett-Packard 3465 A digital multimeter, both of which responded to the dc component alone.

In later experiments it was found necessary to control the temperature in order to permit sudden changes in reactant pressure. This required a temperature controller in which the thermocouple output was used as feedback to control the A.C. power supply that heated the filament. The use of a thermocouple of A.C. filament power supply is a very novel approach that posed special control problems. An efficient controller of this type was used.

The fast flow system contains the gas inlet and the flow meters. There are three gas inlets, regulated by needle valves, which are connected to the reactor. One supplied an inert carrier gas, usually nitrogen. The two other two allowed oxygen and/or a hydrocarbon to be directed at the incandescent filament. Gas flow rates through each of these inlets were independently measured by constricted mercury O-ring piston flow meters, one of which is shown in Figure 1. (This is a 100 cc buret which bears a machined Lucite cylinder grooved to hold a mercury O-ring). The flowmeter may be used as a reservoir filled with gas at 1 atmosphere via valve A, while valve B remains closed. With A closed and B open to admit gas to the reactor, the piston's rate of descent gives the gas flow rate. By then opening and regulating valve A to freeze the piston, one can perform continuous experiments at constant flow rate.

Total reactor pressures were kept between 10 μ and 1 Torr to minimize space charge and ensure free molecular flow conditions near the filament.

A flow divider as seen in Figure 2 is used to direct the hydrocarbon flow to and from the filament. The flow divider is placed between the flow system and the thermionic emission reactor. The hydrocarbon is supplied through a flexible

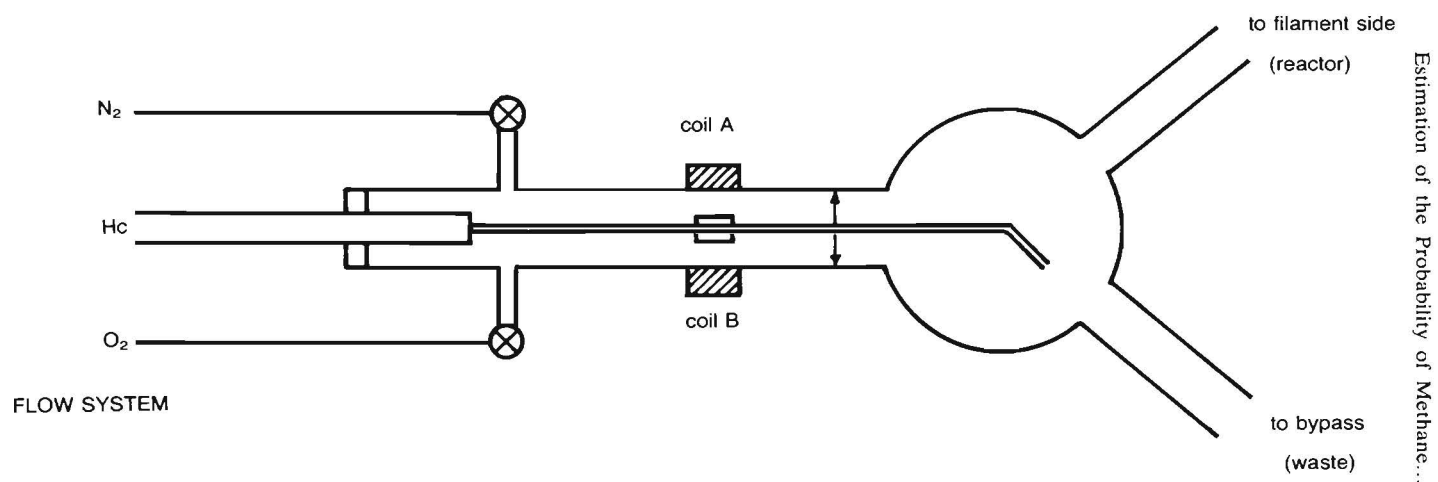


Fig. 2. The hydrocarbon flow divider.

hypodermic needle. The needle carries a small iron slug, and therefore it can be moved easily by coils A and B, which are energized alternately to move the needle from the bypass to the filament side. The current variation, when the hydrocarbon is directed to the filament, is traced by a chart recorder.

This experimental arrangement gives an approach to the study of the initial rate of decomposition of hydrocarbons, and permits the probability of decomposition to be estimated.

Results and Discussion

Hydrocarbon flow can be directed either to the filament or to a bypass. At $t = 0$ the hydrocarbon is directed to the filament, and the current is traced on a chart recorder, so the increase in current may be found as a function of time.

In these experiments the probability of hydrocarbon decomposition is estimated from the current changes, as discussed before, using the following relation:

$$\sigma_{\text{dec}} = n_o / f_h \quad kT / \Delta \phi \quad 1/J_o \quad \Delta J / \Delta t$$

Where

$$n_o = 1.3 \times 10^{15}, \text{ site/cm}^2 \text{ for platinum (Engel and Ertl 1979).}$$

$$f_h = 3.513 \times 10^{22} P_h (\text{Torr}) / (\text{MT})^{1/2}, \text{ molecules/cm}^2 \text{ sec.}$$

P_h is the hydrocarbon pressure in the filament vicinity,

$$P_h = (f_{hc}/f_n) (P_{\text{tot}})$$

Where P_{tot} is the total pressure, and f_{hc}/f_n is the flow ratio of hydrocarbon flow rate to the flow rate of nitrogen.

Table 1 below shows some values of the probability of decomposition as function of temperature for methane decomposing on platinum. Below is a sample calculation.

$$\begin{array}{ll} \text{AT } 1643^\circ\text{K for } P_{\text{tot}} & = 250\mu \\ f_{hc} & = 0.60 \text{ cm}^3/\text{min} \\ f_n & = 1.97 \text{ cm}^3/\text{sec} \end{array}$$

Table 1. Average values of the probability of methane decomposition on platinumProbability of Decomposition, CH₄/Pt

Temp. °K	fhc = 0.60 cm ³ /min		fhc = 0.47 cm ³ /min	
	P _{tot} = 250 μ fn = 1.97 ^{ccs}	P _{tot} = 480 μ fn = 4.05 ^{ccs}	P _{tot} = 330 μ fn = 3.17 ^{ccs}	P _{tot} = 760 μ fn = 6.72 ^{ccs}
1643	2.3×10^{-4}	1.2×10^{-4}	1.7×10^{-4}	1.7×10^{-4}
1677	2.1×10^{-4}	7.6×10^{-5}	1.3×10^{-4}	9.5×10^{-5}
1711	6.0×10^{-5}	4.5×10^{-5}	8.2×10^{-5}	7.2×10^{-5}
1742	4.7×10^{-5}	2.8×10^{-5}	5.7×10^{-5}	3.4×10^{-5}
1765	4.4×10^{-5}	2.5×10^{-5}	4.5×10^{-5}	2.3×10^{-5}

$$\begin{aligned}
 \text{So} \quad P_h &= (0.60/1.97 \times 60)(250) = 1.3\mu \\
 \text{and} \quad f_h &= 7.0 \times 10^{17} \text{ molecules/cm}^2 \text{ sec} \\
 n_o/f_{hc} &= 1.86 \times 10^{-3} \\
 kT/\Delta\phi &= 0.14
 \end{aligned}$$

The current changes from 8.5×10^{-11} to 1.3×10^{-9} Amps. in 16 sec, so

$$(1/J_o) (\Delta J/\Delta t) = 0.89$$

Then

$$\sigma_{dec} = 1.86 \times 10^{-3} \times 0.14 \times 0.89 = 2.3 \times 10^{-4}$$

In these experiments the hydrocarbon pressure was kept at a low level, of the order of microns, so that deposition rates, and concomitant emission variations, were slow enough to be monitored by a chart recorder.

Figure 3 shows a plot of the decreasing probability of decomposition vs. temperature for the second and the third column of Table 1.

If the decomposition probability is independent of the coverage, the current vs. time may be obtained from the following simple model.

$$\begin{aligned}
 n_o \, d\theta/dt &= \sigma_{dec} f_h (1-\theta) \\
 d\theta/dt &= (1-\theta)/t_o
 \end{aligned}$$

Table 2. An estimation of the surface coverage from electron current as function of time

Time sec	J Amp	θ_1 $t_o = 5.35$ s
0	3.9×10^{-9}	0.0
3	0.2×10^{-7}	0.39
5	0.5×10^{-7}	0.60
8	1.0×10^{-7}	0.76
11	1.5×10^{-7}	0.86
14	2.3×10^{-7}	0.96
16	2.7×10^{-7}	1.00

Where

$$t_o = n_o / (\sigma_{dec} f_h)$$

Then the coverage, θ is

$$\theta = 1 - \exp(-t/t_o)$$

Since

$$J = A \exp(\phi/kT) \quad \text{and}$$

$$\phi \approx \phi_o - \Delta\phi \theta$$

So

$$\begin{aligned} J &= A \exp(-\phi/kT) \exp(-\Delta\phi \theta/kT) \\ &= J_o \exp[-\Delta\phi/kT [1 - \exp(-t/t_o)]] \end{aligned}$$

Figure 4 shows a plot of calculated J vs. time as compared to values obtained from the chart recorder.

The surface coverage may be estimated in two ways, first from the values of the decomposition probability as

$$\theta_1 = 1 - \exp(-t/t_o)$$

Where

$$t_o = n_o / (\sigma_{dec} f_h)$$

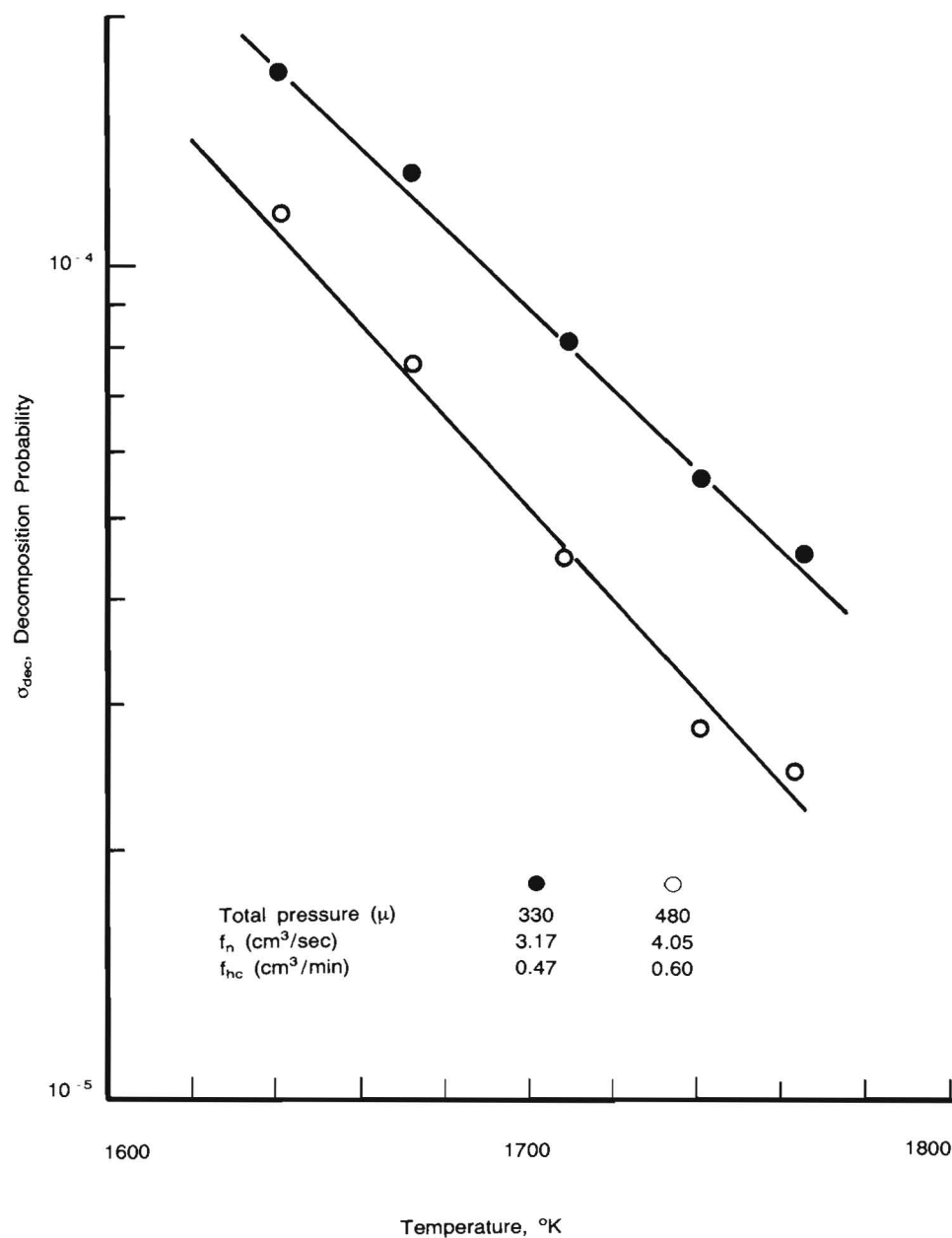


Fig. 3. Plot of hydrocarbon decomposition probability vs. temperature.

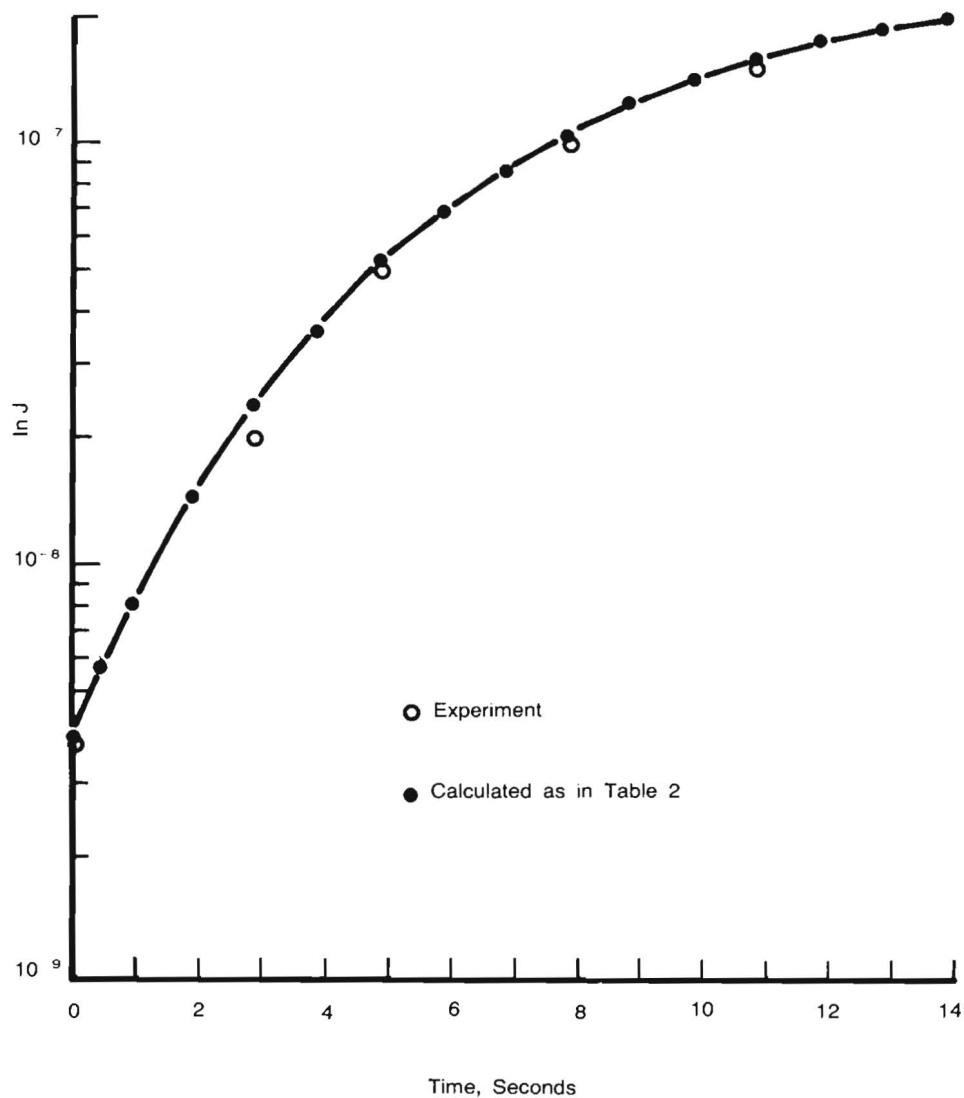


Fig. 4. Emission current vs. time for constant flow of methane on Pt: comparison of theory and experiment.

Also the coverage may be estimated from the current, since the linear approximation of the work function with the coverage is assumed, so

$$\theta_2 = (1n J - 1n J_{Pl}) / (1n J_c - 1n J_{Pl})$$

Table 2 shows an estimation of the coverage as function of time.

Conclusions

Unlike other techniques for surface analysis which require ultra high vacuum as complex instrumentation, thermionic emission can give useful information for the study of some high temperature heterogeneous reactions at realistic pressures. It is an easily instrumented method.

Since the electron current has a very rapid response to changes on the surface conditions, thermionic emission has been used to find the rate of methane decomposition on a hot platinum surface. This study will provide fundamental information about mechanisms and rates of carbon deposition. Little is known about the initial steps of deposition. Yet there is some evidence to indicate that formation of the first carbon monolayer radically alters the subsequent hydrocarbon decomposition rate.

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(Received 19/06/1987;
 in revised form 26/09/1990)

تقدير احتمالية تحلل غاز الميثان على سطح معدن البلاتين الساخن بطريقة الانبعاث الحراري للإلكترونات

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تحتوي المعادن على الكترونات حرة في مدارها الخارجي أقل ارتباطاً بالنواة من الالكترونات الداخلية، وهذه الالكترونات يسهل إنطلاقها عند إرتفاع درجة حرارة المعدن فوق ١٠٠٠ درجة مئوية، وتسمى هذه الظاهرة بالانبعاث الحراري للالكترونات. ويعتبر الانبعاث الحراري للالكترونات من السطوح المعدنية الساخنة عملية حساسة لتغير ظروف سطح المعدن، ويمكن الاستفادة من الانبعاث الحراري المستمر للالكترونات بمعرفة التغير في درجة إحتواء سطح المعدن على المواد المختلفة خاصة في المراحل الأولية لعملية الامتصاص. أن عملية امتصاص الغازات على سطوح المعادن عادة ما تسبب تغييراً في إنبعاث الالكترونات. ولذا، فإنه يمكن من دراسة هذا التغير إيجاد احتمالية تحلل هذه الغازات عند قربها من المنطقة الساخنة المحيطة بالمعدن.

ولقد تم إيجاد علاقة بين احتمالية تحلل المواد الهيدروكربونية والمعدل الإبتدائي لزيادة الانبعاث الحراري للالكترونات. وتم تطبيق هذه العلاقة معملياً في حالة تحلل غاز الميثان على سطح معدن البلاتين الساخن. أن سهولة

ودقة هذه الطريقة تزيد من أهميتها، وفي هذا البحث وصف لاستخدام ظاهرة الانبعاث الحراري للالكترونات لحساب احتمالية تحلل غاز الميثان على سطح معدن البلاتين.