

Thermionic emission from platinum in hydrocarbon flows at low pressure

Bret Halpern, Ibrahim Al-Mutaz, and Liselle Douyon^{a)}

Department of Chemical Engineering, Yale University, New Haven, Connecticut 06520

(Received 4 March 1981; accepted for publication 20 April 1981)

Thermionic emission from Pt filaments is increased by a factor of 1000 in a flow of hydrocarbons at ~ 1 Torr pressure and space-charge-free conditions. The effect can be used to trace the initial stages of hydrocarbon decomposition and carbon deposition, and it has possible application as an automobile exhaust sensor or a gas chromatograph detector.

PACS numbers: 79.40. + z, 82.65.Nz, 73.90. + f, 82.30.Lp

INTRODUCTION

Thermionic emission from metals has, since Langmuir's study of Cs adsorption,^{1,2} often been used as a high-vacuum, surface sensitive probe.³ With few exceptions, however, such as high-pressure thermionic converters,⁴ it is seldom used at pressures exceeding 1 Torr, either for fundamental studies or applications.⁵ In this work we exploit thermionic emission to monitor the deposition of carbon on a hot filament exposed, at $P < 1$ Torr, to flowing hydrocarbons. We also trace the reaction of deposited carbon with oxygen and show that thermionic emission can be useful in the study of high-temperature surface reactions at low pressure.

We find that emission, increased one thousandfold by carbon deposition, is sensitive only to the oxygen-hydrocarbon ratio, and insensitive to the presence of H_2O , CO_2 , CO , and NO in large excess. This combination of relative reactivities suggests thermionic emission from Pt as the possible basis of a combustion engine exhaust sensor for detecting unburned hydrocarbons and air-fuel ratio variations.

We are also able to infer some of the features of carbon layer formation in its initial, sub-monolayer stages, the subject of relatively few studies.⁶⁻⁸ This is done by means of a thermionic titration in which a measured flow of oxygen removes carbon atoms as they are deposited during pyrolysis. A decrease in emission current indicates the titration endpoint.

Finally, we utilize a low-pressure, space-charge-free diode as a gas chromatographic detector and contrast its performance with a related high-pressure thermionic diode device described in the literature.

APPARATUS AND PROCEDURE

The thermionic emission reactor and glass low-pressure fast flow system is shown in Fig. 1. The emitter is a heatable platinum filament (5-mil-diameter, 2-cm length) mounted on a brass and ceramic frame and positioned ~ 3 mm from a nickel wire collector. Voltage is supplied by a 9-V battery and emission current is measured by a Keithley 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 slightly different potential. The method avoids mechanical damage due to spotwelding, provides excellent thermal and electrical contact, and allows accurate placement.

It is convenient to use a thermocouple for measuring the filament temperature rather than voltage (resistance) taps. 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 filament temperature which is then impressed on the emission current. By monitoring the output of the Keithley electrometer, we found the peak to peak ripple in the current to be less than 5% of the dc level; this corresponds to a temperature variation of only several degrees in 1500 °C. The filament thermal response is sufficiently slow to assure 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.

Three gas inlets, regulated by needle valves, were con-

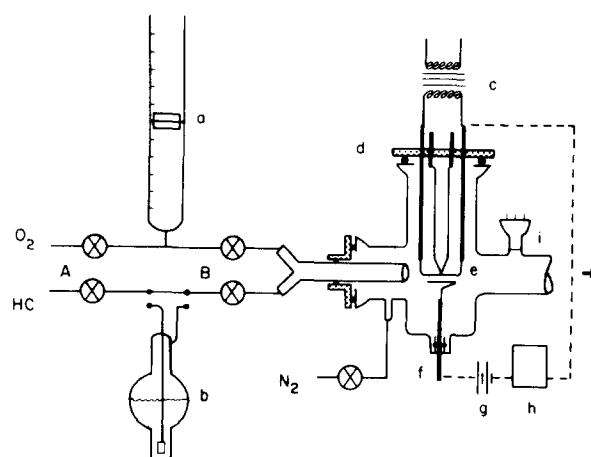


FIG. 1. (a) Mercury O ring piston flowmeter, (b) bubbler for liquid HC's, (c) stepdown transformer; Variac not shown, (d) flange for filament assembly, (e) Pt filament, (f) collector, (g) 9-V battery, (h) Keithley 610C electrometer, (i) thermocouple gauge.

^{a)}Summer Research Student 1978, Yale University, Department of Engineering and Applied Science.

ned to the reactor. One supplied an inert carrier gas, usually nitrogen. The two others 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 homemade mercury O-ring piston flow meters, one of which is shown in Fig. 1. (This is a 100-cc buret which bears a machine 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 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.

The vapors of liquid hydrocarbons such as pentane were admitted by saturating nitrogen gas at one atmosphere in a fritted glass bubbler placed between valves A and B.

Total reactor pressures were kept between $10\ \mu$ and 1 Torr to minimize space charge and assure free molecular flow conditions near the filament.

RESULTS

We performed two kinds of experiment. In the first kind we measured electron emission current j as a function of filament temperature in flows of nitrogen or hydrocarbon-nitrogen mixtures. The data give good Richardson plots of $\ln j$ vs $1/T$ as shown in Fig. 2. The lower curve is for a platinum filament cleaned by heating in oxygen and then nitrogen. The work function derived from its slope is 5.59 eV, in good agreement with literature values.⁹ The upper curve is for emission from a platinum filament in a flow of hydrocarbon. The large current increase and work function decrease are due to formation of a carbon layer which, according to available evidence,⁶⁻⁸ is of limited thickness, perhaps only a monolayer. The work function of this layer is 4.2 eV; it compares well with values for chemisorbed hydrocarbons or bulk graphite.⁹

At any temperature, the onset of hydrocarbon flow over a clean filament produces a ~ 3 order-of-magnitude jump in

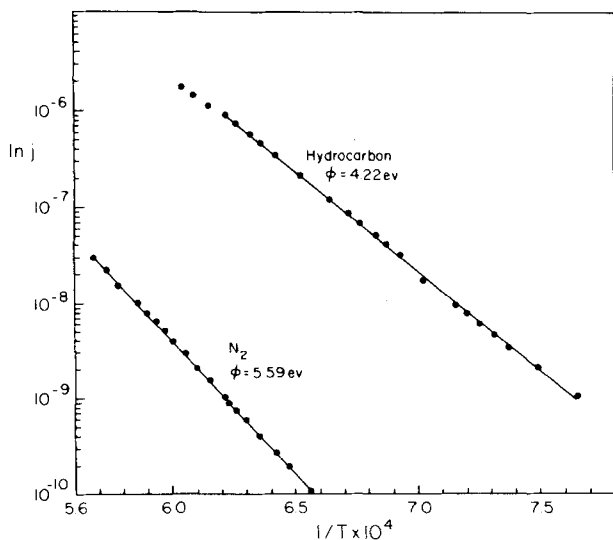


FIG. 2. Richardson plots: emission in N_2 (lower curve) and CH_4 (upper curve).

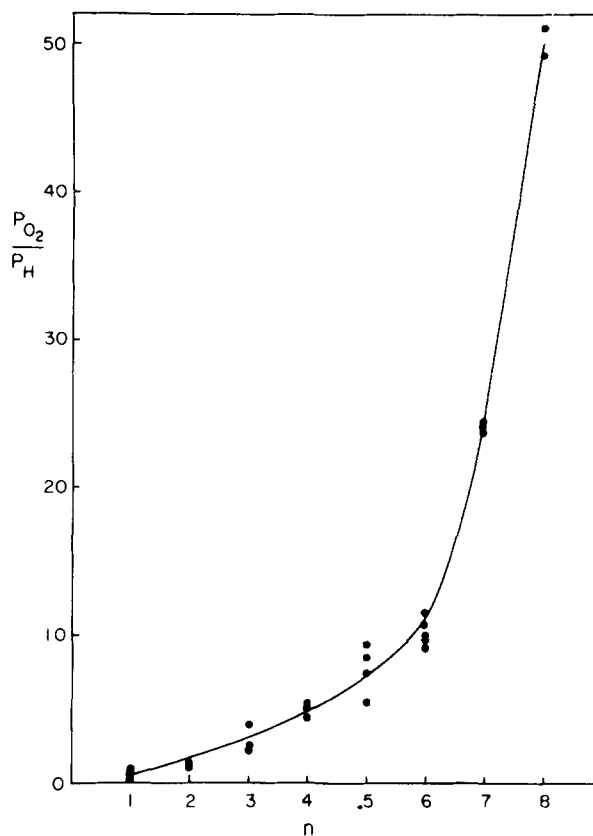


FIG. 3. Oxygen-hydrocarbon titration ratio as a function of the number of carbons per molecule.

current. This takes place abruptly because, at the hydrocarbon pressures we employ, the carbon layer forms rapidly.

In the second type of experiment, the flow of hydrocarbon was titrated with a flow of oxygen. Oxygen tends to remove the carbon layer, while hydrocarbon pyrolysis tends to replenish it. The oxygen flow rate is increased until a drop in emission current from the upper to the lower curve of Fig. 2 indicates the removal of the carbon layer. In practice this titration endpoint was taken to be a current close to, but not on, the lower curve.

We find that the value of the emission current on the upper curve does not depend significantly on the number of n of carbon atoms in the hydrocarbon pressure. By contrast, the ratio of the flow rate of oxygen to the flow rate of hydrocarbon at the titration end point is a strong function of n . This function is shown in Fig. 3.

DISCUSSION

The two salient results of thermionic emission in fast flowing, low-pressure hydrocarbons are (a) the work function decrease, or current increase, is independent of the number of carbon atoms in the hydrocarbon flowing over the hot Pt filament, and (b) the oxygen-hydrocarbon flow rate titration ratio depends strongly on the number n of carbon atoms in the hydrocarbon molecule.

The work function independence is easily understood. A hydrocarbon molecule striking a hot platinum surface will, if not reflected, be chemisorbed and pyrolyzed with release of hydrogen. At steady state, pyrolysis yields at least a monolayer of carbon independent of the source molecule. It

is known that carbon adsorbed on platinum reduces the work function by ~ 1 eV; we see an effect only slightly larger.

It appears that this work function change characterizes carbon deposition to the extent of one (or at most a few) monolayers. Sau and Hudson⁶ find that a graphite layer formed on Ni (110) at $T > 620^\circ\text{K}$ by ethylene absorption will no longer adsorb ethylene. Lang⁷ found from LEED studies that carbon deposition by ethylene on hot Pt ($T \sim 850^\circ\text{C}$) was limited no matter how long the exposure time. He concluded that a graphitic layer about three sheets thick was formed. Fabian and Robertson⁸ studied ethane decomposition on Pt in the range $1300^\circ\text{K} < T < 1800^\circ\text{K}$ and observed that, after several hours at 10^{-5} Torr, their filament became poisoned to all further ethane reactions. They attributed this to formation of a carbon layer which must be, by implication, of limited thickness. The carbon layer formation they saw in several hours at 10^{-5} Torr is consistent with our observed formation times of seconds at 10 – $100\ \mu$. All of the above studies were done in high vacuum where gas phase pyrolysis can not occur. Our work is similar in that it was done at under nearly free molecule flow conditions, thin filaments at sufficiently low pressure, where gas phase cracking and subsequent deposition can be ruled out.

As further evidence that the carbon layer is thin, we made the following observations. Prolonged exposure (15 min) to hydrocarbons at $100\ \mu$ and 1500°C does not result in blackening of the filament. Yet the initial jump to the high current regime is a matter of seconds. If graphitic multilayers were formed at that stage, it is reasonable to expect continued growth, even if no further change in work function occurred. The thickness after 15-min exposure would then be 10^6 – 10^7 layers, which would be easily noticeable. Such an effect was not seen. We have also noted that the time to clean off the carbon layer at low oxygen pressure does not depend on the time the filament was exposed to hydrocarbons. This implies that maximum thickness is rapidly attained. We therefore believe that the carbon layer is of limited thickness even under our relatively high-pressure conditions.

The second feature of interest is the shape of the oxygen-hydrocarbon titration curve in Fig. 3. It can be best discussed in terms of a simple mass balance. For a hot filament in a flow of oxygen and hydrocarbon at the titration endpoint, we assume that (1) hydrocarbon molecules, e.g., alkanes ($\text{C}_n\text{H}_{2n+2}$), strike the filament with flux f_h , chemisorb with sticking probability s_h , and liberate n atoms of carbon. (2) Oxygen molecules at flux f_o chemisorb dissociatively with sticking probability s_o . (3) Adsorbed oxygen atoms react with carbon to give CO; oxygen recombination is neglected. (4) The total coverage at the endpoint is very low, as the low thermionic current indicates.

The balance at steady state between oxygen and carbon fluxes can then be written:

$$nf_h s_h = 2f_o s_o.$$

Using Knudsen's relation to express the fluxes in terms of pressures P_h and P_o , and taking the mass of an n -carbon alkane to be $14n + 2$, gives

$$P_o/P_h = [2n/(7n + 1)]^{1/2} (s_h/s_o).$$

If the hydrocarbon sticking probability is independent of n , then this pressure ratio (equivalent to a ratio of flow rates in our configuration) would give a curve that is concave down ($\propto \sqrt{n}$) in contrast to Fig. 3. For O_2 impinging on hot clean Pt, s_o is known to be ~ 0.06 ,¹⁰ but values of s_h at high temperatures are not available. It is reasonable, however, that more complex molecules stick more rapidly, supply carbon atoms to the surface more efficiently, and thus require higher oxygen fluxes to maintain the low coverage at the titration endpoint. This is the simplest explanation of Fig. 3.

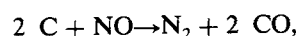
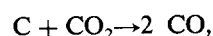
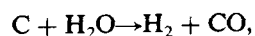
An alternative idea is suggested by the more pronounced increase at $n \sim 7$ and 8. These values of n correspond to molecules which, in a localized decomposition, would be most likely to form carbon rings, that is, generate a product most resembling a graphitic, less easily oxidizable layer.⁶ This layer could require a greater oxygen flux, in steady state, for its removal, as Fig. 3 shows.

In any case, the thermionic titration shows that emission is much more sensitive to fluxes of complex hydrocarbons, compared to simpler ones, than might be expected simply from their relative number of carbon atoms.

We justify assumption (3) in retrospect on the grounds that the P_o/P_h curve would not display a pronounced sensitivity to n if O atom recombination were more probable than oxygen-carbon reaction. This would especially apply at high n where a greater number of carbons are supplied to the surface per pyrolytic event.

The thousandfold change in emission current caused by changes in the hydrocarbon-oxygen ratio suggests that a thermionic diode, operated under space-charge-free, reduced pressure conditions, might serve as a simple oxygen-hydrocarbon sensor. It could be used to detect unburned hydrocarbons from an automobile exhaust or to indicate deviations from the optimum air-fuel ratio.

We do not consider here the actual mechanics of such a device, or the most advantageous pressure and flow conditions for its operation. But if such an application is to be possible at all, then the emission jump effect must be determined only by the ratio P_o/P_h and be insensitive to the presence of other exhaust constituents such as H_2O , CO_2 , CO, and nitrogen oxides (e.g., NO). It might be expected that a carbon layer replenished by a small flow of hydrocarbon would be effectively removed according to reactions such as



especially since, with the exception of the nitrogen oxides, all of the other exhaust species would occur in greater concentration than unburned hydrocarbons.¹¹ Accordingly we titrated each of the above reactants against a flow of a representative hydrocarbon (heptane or octane) on a Pt filament at $T \sim 1450^\circ\text{C}$. There was no oxygen present in any of these titrations.

The result was that none of these reactants, even in high excess, was able to deplete the carbon layer; electron emission remained at a high level. Thus, for example, when $3\ \mu$ of octane was titrated with ~ 2 Torr of H_2O , electron emission

was not cut off. Such a ratio of H_2O to hydrocarbon is of the order of that found in an actual exhaust. Likewise, $150\ \mu$ of NO in the presence of $4\ \mu$ of heptane failed to remove the carbon layer and reduce electron emission. This NO to hydrocarbon ratio is in excess of what might be found in an exhaust. (We did observe that a 10:1 ratio to NO to butane removed the carbon layer slowly; this must be, as previously discussed, because simpler alkanes do not supply carbon as efficiently as heavier alkanes.) We are therefore optimistic that a platinum filament thermionic diode would respond to the oxygen-hydrocarbon ratio alone, even in an excess of other exhaust products.

We have not yet investigated the effects of fuel additives, anti-knock compounds, or detergents which might conceivably act as surface poisons, and we have not looked at the behavior of a real fuel. We looked for similar electron emission behavior with iridium and rhodium filaments in flowing methane, but surprisingly, found little effect.

As a simple application we used a low-pressure, space-charge-free thermionic diode as a gas chromatograph detector. Hudson *et al.*⁵ have shown that a space-charge-limited diode operated at atmospheric pressure can be used for this purpose. It is instructive to compare the two devices.

In that of Hudson *et al.*, hydrocarbon peaks exiting a GC column flowed over a hot filament and produced large increases in electron emission. They explained this effect as a reduction in space charge due to electron capture by hydrocarbon molecules. Space-charge-limited operation is essential, and any molecule with an electron affinity greater than the helium carrier gas (e.g., oxygen) would produce a current increase or a peak as the hydrocarbon passed.

In our configuration, a low-pressure, space-charge-free diode was placed at the output of a GC column in a series with the usual thermal conductivity detector. The helium carrier gas plus the separated constituents (e.g., oxygen and propane) were bled through a needle valve into the diode until the desired operating pressure of ~ 1 Torr was reached. This pressure was maintained by a pump downstream of the diode. Figure 4 shows the traces from both the thermal conductivity detector and the thermionic diode detector for a small quantity of propane (125 ppm) in a large excess of oxygen. As expected, the thermal conductivity detector shows a large oxygen peak and an extremely small propane peak nearby. The thermionic diode trace differs from this in two respects. First, the oxygen and propane peaks have opposite polarity, one being above, and the other below, the carrier baseline. This arises because propane pyrolysis increases emission from a clean filament while oxygen reduces emission. Second, the propane peak is the larger, that is, the minor species has been enhanced by increased thermionic emission relative to the more abundant species, oxygen.

It may be asked why the carbon layer derived from the propane peak does not persist after the peak has passed, since carbon would not thermally desorb from Pt at these temperatures. Had it persisted only a net increase in current would be seen rather than a peak shaped output. The likely reason is that enough oxygen remains in the propane peak as a residue from the oxygen peak shoulder, since oxygen is in great excess. As the propane peak approaches, carbon depo-

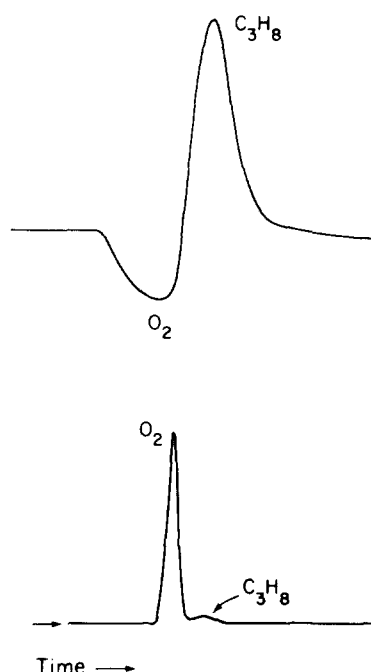


FIG. 4. Gas chromatograph detector response to oxygen-propane (125 ppm) upper trace—low-pressure thermionic diode, lower trace—thermal conductivity.

sition dominates removal by oxygen, and emission rises. As the propane peak recedes the carbon layer is reacted away and emission drops. Electron emission thus follows, in a nonlinear way, the propane concentration. The same effect can be produced by deliberately leaking oxygen into the diode in small amounts, rather than injecting it into the column. We were able to detect ppm of propane in oxygen in this manner; it would be interesting in light of Fig. 3 to investigate heavier hydrocarbons.

SUMMARY

We have investigated space-charge-free thermionic emission from incandescent Pt filaments in hydrocarbon flows at low pressure and moderate Knudsen number. Surface hydrocarbon deposition yields a carbon layer of limited thickness, a work function decrease, and a large current increase almost independent of the source hydrocarbon. Thermionic titration with oxygen shows that carbon deposition is more efficient for molecules with large number of carbon atoms than might be expected from a simple proportionality. H_2O , CO_2 , CO, and NO do not deplete carbon layers in the presence of hydrocarbons, so that current switching from high to low current regime is determined mainly by the oxygen-hydrocarbon ratio. We suggest this effect as a possible basis for an automobile exhaust sensor, or, under some conditions, a gas chromatography detector. We note finally that thermionic emission may be a useful method for monitoring some kinds of high-temperature heterogeneous reactions at elevated pressures or even high-temperature processes involving buildup of multilayer films.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge support for the work from NSF grant ENG 7808620 as well as the Yale Summer Research Program 1978.

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