

EXO-ELECTRON EMISSION DURING HETEROGENEOUS CATALYSIS

by

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PREFACE

Heterogeneous catalysis is a well known phenomenon. In almost all gaseous reactions there are substances which increase or decrease the rate of reaction but do not themselves undergo any permanent change. Substances of this type are called catalysts and their industrial importance has generated a great number and variety of research programs. However, to date there is no general theory which explains the complete process of catalysis and why some catalysts accelerate a particular reaction and others do not.

In this study the oxidation of several gases (H_2 , NH_3 , CO) was catalyzed on a platinum filament at very low pressures, (10^{-6} torr). During the reaction exo-electrons were emitted by the catalyst and this emission was related to the rate of reaction, which was monitored by a mass spectrometer.

Exo-electron emission is a general term for any form of electron emission other than the usual thermal, photoelectric or field emission effects. Exo-electron emission occurs whenever a solid surface is disturbed by alloying, sintering, grinding, melting, annealing, a phase change or oxidation. A survey of this phenomenon was done by L. Gruenberg in 1958. In a catalytic process one or more of the reactants are adsorbed by the catalyst. The idea of relating exo-electron emission to catalysis follows from the work of T. Delchar who observed that adsorption of oxygen by nickel induced exo-electron emission. If

adsorption occurs before catalysis, one might expect electron emission to occur during catalysis.

Another reason for expecting that there is a connection between exo-electron emission and catalysis comes from the work of V. J. Lee and W. Hsu in 1967. They showed that the frequency of an AC electric field could affect the rate of catalysis of benzene to cyclohexane over brass. Lee found similar results in oxidation of carbon monoxide over nickel oxide. The rate of conversion was a maximum for frequencies between 100 and 200 Hz at 22,000 volts. Also in 1967 Sato and Seo observed a linear relationship between exo-electron emission and the rate of oxidation of ethylene over AgO. This phenomenon is thought to occur in many catalytic relations and it was the hope of developing a monitoring technique that led to this study.

Beyond merely monitoring catalysis one would hope to actually control the rate of reaction, perhaps by means of an external electric field. The phenomena involved are not yet clear but electric field effects on semiconductor adsorption are well known. In 1963 F. Volkenstein presented a theory explaining how one might expect adsorption and catalysis to be effected by electric fields because of bending of Fermi level at the surface. This theory was valid only for semiconductor catalysts. Hoenig and Lane experimentally verified that electric fields can effect adsorption of oxygen on zinc oxide.

At the moment no theoretical connection between metallic catalysis, exo-electron emission and electric fields has been offered. We shall suggest that catalysis induces surface mass migration of the

catalyst itself and this results in exo-electron emission. If this surface migration is affected by external electric fields this would explain our results. At the moment this latter idea is pure speculation.

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ABSTRACT

Exo-electron emission was observed during catalytic oxidation of CO, H₂, and NH₃ on hot platinum. The emission current was used to monitor the rate of reaction. It was shown that suppressing or enhancing the exo-electron current decreased or increased the rate of reaction.

CHAPTER 1

INTRODUCTION

Human knowledge and use of catalysis dates to the beginning of history. One of the earliest observed reactions was a biocatalytic process, alcoholic fermentation [1]. This is believed to have occurred at the beginning of the Neolithic period which is considerably earlier than the discovery of the metallurgies of bronze and iron.

In the 19th century rigorous studies by scientists like Kirchhof, Thénard, Davy, Dobereiner and Dulong demonstrated that some substances were capable of starting or speeding up reactions in a gaseous or liquid media, simply by their presence and without themselves undergoing any changes [1]. In 1836, Berzelius grouped together the first scientific data on such substances and gave them the name catalysts. He concluded as follows: "It has been proven that a number of simple and composite soluble and insoluble substances possess the property of exercising upon other substances an effect quite different from chemical affinity. By means of this effect they produce decomposition of the elements of these substances and different recombinations of the same elements, from which they remain separate [in Prettre, 1, p. 2]."

Throughout the 19th century discovery of new catalysts depended on pure chance and progress in this area was limited due to lack of knowledge of the laws of chemical reactions and especially to the role of catalyst poisons.

Chemical kinetics was founded between early 1880 and 1900 by investigators such as van't Hoff and Arrhenius. The precise study of catalytic reactions and analysis of their mechanisms did not really get under way until the decade between 1920 and 1930.

In 1927 Taylor suggested that catalysis took place at certain locations on the surface which he called "active sites." He was not able to explain the exact process occurring at these sites [in 2]. Later works showed that there was no general relationship between these sites and visible surface features, and the true existence and nature of "active sites" is still a matter of conjecture. Since 1927 new catalytic syntheses and transformations have been discovered at an increasing rate. The synthesis of methanol, the synthesis of liquid fuels, petroleum chemistry, synthetic rubber, plastics and resins are a few examples of such catalytic syntheses.

As a result of years of research and investigation, vast amounts of data and a number of theories on catalysis have been presented, but no theory has been generally accepted. Nevertheless, these concepts and results form the basis of the science of catalysis today. It is important to investigate the possibilities of monitoring and controlling a catalytic reaction and to study any parameters that may influence the rate of reaction. It will be shown that exo-electron emission at the surface of the catalyst can be used to monitor the rate of reaction. This phenomenon was also used to study the diverse effects of increasing or decreasing the exo-electron emission level, on the steady state rate of a catalytic reaction.

CHAPTER 2

DEFINITIONS

Assuming there is no catalytic intervention, chemical reactions can be divided into two groups. The first are reactions that do *not* involve a chain mechanism. When they occur in the presence of a catalyst they display certain properties that are grouped under the title of *true catalysis*. These reactions can only be accelerated, i.e., catalyzed, as defined above by Berzelius. The second group consists of chain reactions whose rates are very sensitive to the presence of certain catalytic substances. Such reactions, unlike the non-chain reactions make up the *generalized concept of catalysis* [1]. Both chain reactions and reactions under the heading of true catalysis normally involve several chemical steps before the final stage of the reaction system. In chain reactions, under certain experimental conditions, the initial step produces very unstable, but very reactive, atoms or free radicals. These species react with the molecules of the system to produce the final product and to generate more atoms or radicals that behave the same way.

Stages involved in true catalysis, however, occur successively and the slowest one determines the rate of the overall reaction. In true catalysis several reactions occur in series before the final product is formed, but in chain reactions several reactions, all

producing the final product, occur simultaneously in parallel. To accelerate the overall reaction in true catalysis, the slowest process can be replaced by a sequence of more rapid steps that are not possible without the presence of the catalyst itself. A catalyst must meet this condition, otherwise it is inert for the reaction.

True catalysis can be further divided into two different categories: homogeneous catalysis and heterogeneous catalysis, depending on whether or not the catalyst and all the reactants belong to a single phase. The most common examples of heterogeneous catalysis are those in which the reactants are either gaseous or liquid in the presence of a solid catalyst.

It is interesting to note that reaction at the surface of a solid catalyst is usually much more rapid than at any other point throughout the rest of the fluid system, even though the molecular collision rate per unit area at the surface of the catalyst is much smaller than the rate in the other parts of the system. This is due to the fact that the catalytic reaction rate at the surface of the catalyst does not usually depend upon the collision rate. In the gas phase, the reaction rate for the rest of the system is a function of collision rate. For a second order reaction (a reaction in which the rate is proportional to the second power of the concentration of a reactant) the rate varies directly with the collision rate [3].

For a biomolecular reaction, the surface collision rate is approximately 10^{12} times slower than that in the gas. For an accelerating effect to take place, a process of chemical nature must take place

at the surface involving the catalyst and the catalyzed material. Such processes, which result in new chemical bonds between the separate reactants and the surface of the catalyst, are called *chemical adsorption* or *chemisorption*. It is usually stated that in order for a catalytic reaction to take place one or both of the reactants must be adsorbed. It is on this basis that we say adsorption must precede catalysis. Since the adsorption step is the rate limiting one in most heterogeneous catalytic reactions the study of adsorption is intimately related to any investigation of catalysis. The number of chemisorbed atoms or molecules is usually only a small fraction of the number of physically adsorbed molecules but their removal from the solid involves strenuous reduction and outgassing techniques. Experiments have shown heats of chemisorption to be comparable to heats usually involved in chemical reactions.

CHAPTER 3

KINETICS OF CATALYSIS

In a heterogeneous catalytic reaction involving gases, the reaction rate may be a complex function of the reactant pressures and temperatures as well as the catalyst properties. Several mechanisms involving these parameters are discussed below.

Diffusion Theory of Nernst

In 1904 W. Nernst argued that equilibrium is reached very quickly at the interface between the metal catalyst and the gaseous reactants. He also postulated that the rate of any chemical change occurring at the surface depends primarily on the rate of diffusion of a reactant (or reactants) to the phase boundary [in 4].

In 1906 M. Bodenstein and C. G. Fink [in 4] explained that catalytic oxidation of sulfur dioxide to sulfur trioxide, (the oxide of sulfur used to make sulfuric acid, an important industrial chemical) through Nernst's diffusion theory. In fact, they obtained data which showed that the rate of production of sulfur trioxide was indeed a function of diffusion rate, the initial concentration of sulfur dioxide and the amount of sulfur trioxide formed. They further explained that the rate of reaction was determined by the diffusion of the sulfur dioxide to the catalytic surface through a gaseous layer of sulfur trioxide.

Langmuir-Hinshelwood Mechanism

Langmuir suggested that in order for two molecules A and B to react they must be adsorbed on adjacent sites [in 4], also referred to as "active centers." This is known as an adjacent interaction or adjacent adsorption mechanism. Assuming that the velocity of reaction is dependent on interactions occurring in the adsorbed layer, and not by rates of adsorption and of desorption, then the rate should be proportional to $\theta_A \theta_B$ where θ_A and θ_B are the fractions of equivalent sites covered by substances A and B respectively. In this case, the rate R is given by

$$R = K \theta_A \theta_B \quad (1)$$

where K is a constant. Now if θ_A and θ_B are functions of the pressure of "A" and "B" it follows that,

$$R = K k_1 k_2 p_A p_B \quad (2)$$

where k_1 and k_2 are constants and p_A and p_B represent the partial pressures of gases A and B respectively.

Equation (2) is generally valid for $\theta_A \ll 1$ and $\theta_B \ll 1$, i.e., both reactants are weakly adsorbed. From Equation (2) it is apparent that for the case of strong adsorption of both reactants, the rate of reaction depends directly on how much each or both reactants are adsorbed. Equation (2) also suggests that when neither reactant is strongly adsorbed the rate depends on the partial pressures (concentrations) of the reactants.

Another case exists when gas A is weakly adsorbed ($\theta_A \ll 1$) and gas B is strongly adsorbed ($\theta_B \sim 1$). For this case R is given by

$$R = (K k_1/k_2) (p_A/p_B) . \quad (3)$$

This indicates that as p_B increases, more sites are covered by B molecules. This leaves fewer sites available for A molecules and the net effect is a decrease in reaction rate R. In a later work, [in 4], Hinshelwood supported Langmuir's theory for reactions on metals. He concluded that Langmuir's equations, based on adsorption theory, gave an adequate description of the kinetics of surface catalysis. He also suggested that the catalyst surfaces contained centers of activity (active sites) but that the surfaces were not as uniform as Langmuir had assumed. In fact, it appears that the adsorption sites for two different gases are not the same. The blocking effect suggested by Langmuir (Equation 3) does not usually occur. Here again we must note that true nature and existence of such sites is still under study.

Absolute Rate of Heterogeneous Catalysis on Metals

In 1931 B. Topley proposed that the rate of reaction involving a single gas adsorbed on a metal surface, would be given by:

$$R = F n \exp(-E'/RT) . \quad (4)$$

Where R is the gas constant in molecules $\text{cm}^{-2} \text{sec}^{-1}$, n is the number of molecules adsorbed per cm^2 and F is the frequency factor, taken equal to 10^{12}sec^{-1} . Equation (4) is an application of the Arrhenius equation.

The term $F \exp(-E'/RT)$ is just the Arrhenius rate constant for a surface reaction with activation energy E' , [3]. E' is the difference in energy between a transition state on the surface, E^* , and energy E of an adsorbed molecule of the reactant on the surface. A transition state refers to the state of molecule in which a bond is in the process of being broken or formed. This molecule is often referred to as the activated complex. For molecule A to be converted to B it is necessary for it to be activated to energy E^* (activated complex). This is true for the reverse reaction as well. Only collisions with energies equal to or greater than the activation energy result in a reaction. For this reason fast reactions generally have very small activation energies. In this case almost every molecule that arrives at the surface reacts and the reaction rate is limited only by diffusion. Topley's equation can be applied to surfaces of known area and uniform activity [in 4].

For zero order reactions (reactions in which the rate is independent of the gas pressure, $\theta \sim 1$) Topley let $n = 10^{15} \text{ cm}^{-2}$ which is the number of molecules in a close-packed monolayer. He then found E' experimentally for several reactions and observed a result very close to those calculated by the use of Equation (4) with $F = 10^{12} \text{ sec}^{-1}$.

He found similar results with first order reactions (reactions in which the rate is proportional to partial pressure of a reactant) in which he found n as a function of pressure and temperature before applying it to Equation 4.

Many other theories have been suggested to explain mechanisms involved in specific catalytic reactions. Presently, however, there

are no explanations available that could be applied in a complete fashion to *all* catalytic reactions. Design of catalysts is still a black art today simply because catalysis itself is not well understood.

CHAPTER 4

METAL CATALYSTS

Proposed Theories of Catalysis by Metals

Catalysis by metals has been described by many investigators in terms of the electron theory of metals. There are also proposed explanations relating the behavior of semiconductor catalysts to metal catalysts. Volkenstein wrote: "In most cases a metal is enclosed in a semiconducting coat and the processes which apparently take place on the surface of the metal actually take place on the surface of this semiconducting coat, whereas the underlying metal frequently takes practically no part in the process [in Volkenstein, 5, p. 156]."

Formation of such a layer on the catalyst surface may explain the effect of electric fields on the reaction if it is treated as a semiconducting layer on the metal surface. Volkenstein [5] argues that applying an electric field of the proper polarity to a semiconductor layer of thickness L , could have the following effects: the concentration of electrons on one of the surfaces ($x = 0$) would be increased and the hole concentration lowered, i.e., the Fermi level would be displaced upwards. Similarly at $x = L$, the electron concentration would be lowered and the hole concentration raised, i.e., the Fermi level would be displaced downwards. This effect would increase the adsorption capacity for electron acceptors at one surface ($x = 0$) and decrease it at the

other ($x = L$). This effect was demonstrated by Hoenig and Lane [6]. Since adsorption precedes catalysis it is expected that the catalytic activity of the specimen must also change, which in turn would change the rate of reaction. This theoretically expected effect has not been examined experimentally.

Roginski presented a new quantum mechanical approach to gas-metal catalysis and about the same time E. K. Rideal and O. H. Wansbrough-Jones discovered that the activation energy E for oxidation of platinum, tungsten and carbon, was related to the work function ϕ as $\phi - E = \text{constant}$ [in 4, p. 126].

Rideal [in 4, p. 127] suggested that during adsorption, the reactant molecules enter the intrinsic field of the metal surface and are deformed. This deformation would increase the potential energy of the system and thereby promote the reaction. He further proposed that this source of potential energy lowered the required activation energy permitting the transfer of an electron from the adsorbent atom to the adsorbate atom. Rideal, however, failed to clarify how deformation of adsorbate molecules due to adsorption causes them to gain potential energy.

Another well known theory for metal catalysts is the d-band theory of Dowden [7]. He noted that most common metal catalysts are all transition elements. These elements have incomplete valence bands possessing electron vacancies. This property enables these metals to take electrons furnished by adsorption of an ionized molecule. They can also provide electrons for molecules with strong electronic affinity.

Any process affecting the number of "electron vacancies" in these metals changes their adsorption properties. Producing dislocations in the metal or any other disturbance in the crystal lattice, changes the position of energy bands. Introducing impurities into the crystal lattice by substitution or insertion also changes the chemisorptive properties [4].

Catalysis over metals involves the adsorption of the reactants involved. From this point of view it is interesting to observe some of the effects of adsorption on metal surfaces. In 1954 Shurman [in 1] found that metallic films exposed to various gases exhibited changes in their electrical resistance and photoelectric sensitivity. When an easily ionized material is adsorbed, at least one electron is taken up by the adsorbent phase. This increases the electron density in the adsorbent; the electrical resistance is reduced; and the photoelectric sensitivity is increased. The situation is reversed when the material being adsorbed has a much higher electronic affinity. This results in removal of electrons from the solid. The variations in this case are exactly opposite to those observed in the previous case. The resulting ions in both cases are held to the surface by the reduced image forces.

Shurman also examined the case when a covalent bond is formed. This case occurs when the difference in electronic affinity is not high enough for complete removal of an electron from one of the two phases. Instead a covalent bond is formed which immobilizes the electrons on the adsorbent phase on the surface. In this case the photoelectric sensitivity and the electrical resistance of the adsorbent are increased.

Surface Mobility of Metal Atoms

Experiments have shown that certain gas reactions and gas adsorptions on metal surfaces induce mobility of the metal atoms. The tendency for such mobility seems to be much higher when thin metal films are used.

In 1908 Turner [in 4] performed an interesting experiment in which he heated a thin film of silver and exposed it to various gases. The silver film was first heated in vacuum to 500°C. There was no observable change. The same procedure was repeated in the presence of oxygen at 15 torr pressure and the film turned into a white powdery material with much smaller bulk even though neither the weight of the film nor the volume of the oxygen had changed. Turner suggested that the finely divided silver was at equilibrium with its oxide in a "peculiar amorphous fashion."

Thin films exhibit mobility in vacuum at temperatures far below the melting point of the metal [4]. In 1917 Andrade showed that surface mobility occurs above a critical temperature which depends on the thickness of the metal film. He also concluded that the gas like layer might be one or more atoms thick. Copper has been shown to form different patterns on its various crystal surfaces when exposed to different ambient gases.

Diffraction pattern observations by Swanson and Bell [8] showed that oxygen contamination of platinum was nearly impossible to remove. They also concluded that adsorption of oxygen on platinum caused rearrangement of the top layer of platinum atoms (the rearrangement of

atoms was actually observed by field ion microscopic techniques). The same phenomenon did not occur in adsorption of carbon monoxide, cesium, hydrogen and nitrogen. It is suggested that such a rearrangement may be the source of exo-electron emission during catalysis. Swanson and Bell did not mention whether such a rearrangement occurred continuously during oxygen adsorption or whether it took place at the beginning of exposure and remained in a steady state condition the rest of the time.

Platinum Catalysts

Platinum in a nearly pure form, or alloyed with a small quantity of another metal, is a good catalyst in oxidations, hydrogenations and dehydrogenations. Platinum may also be used as a supported catalyst. This means that a small quantity of platinum along with a carrier substance is deposited on a substance like alumina which is the support. The alumina is then heated to activate the deposited catalyst. This support technique is usually used because of the very high cost of the metal, but there may be catalyst-support interactions which result in improved properties. Silica gel is often used as a platinum support for industrial oxidation of pure sulfur dioxide because it produces an effective surface area ten to twenty times greater than alumina [4]. Pure platinum in the shape of a very fine gauze is the sole catalyst used today for high temperature oxidation of ammonia to nitric oxide. This was one of the reactions investigated in this study.

Platinum catalysts have to be activated by various methods depending on the reaction they are going to be used in. High temperature heating in ultra high vacuum is often used to evaporate certain impurities off the surface. Other impurities diffuse deep into the bulk of the catalyst where they do not interfere with the processes occurring at the surface during catalysis. Carbon impurities are removed by prolonged high temperature exposure to oxygen at low pressures.

Microscopic examination of the surface after a prolonged high temperature treatment reveals that pits and grooves have replaced the originally smooth surface. This type of surface has a much higher catalytic activity than the original smooth surface, [4].

Surface reduction by hydrogen is also used to clean the surface. Positive ion bombardment is another method that is sometimes used to activate the surface. This process produces defects on the surface and sputters off the impurities. 200 - 600 ev ions are used in a background gas of argon at .025 torr.

It is very important to "activate" or "clean" the catalyst surface of all impurities. Some impurities act as "poisons" that partially or completely block the catalytic process. Lead and especially sulfur, are well known catalytic poisons. Less than a monolayer of sulfur may completely neutralize platinum of its catalytic properties. This is the phenomenon which led to the belief that catalysis is a localized process (active sites) and does not occur uniformly over the whole surface.

More research is needed to investigate the mechanisms by which these poisons neutralize a catalyst. Clarification of such mechanisms may yield a better understanding of catalysis itself.

CHAPTER 5

DESIGN OF EXPERIMENTAL SYSTEM

Vacuum System

The vacuum system consisted of a Varian type stainless steel chamber with copper gaskets, a Welch Duo-Seal rotary mechanical pump, a 300 watt Consolidated Vacuum Company oil diffusion pump, a 50 liter/second Varian Vac-Ion pump, a Consolidated Vacuum Company Pirani vacuum gauge for pressure above 5 microns, and a Vacuum Industries discharge vacuum gauge for monitoring low pressure ranges (Figure 1).

The system was first pumped down by the mechanical pump to a pressure of .05 torr at which point the oil diffusion pump was turned on. After the components inside the vacuum system had outgased, the diffusion pump brought the pressure down to the Vac-Ion pump range, about 10^{-4} torr. At this stage the Vac-Ion controller was turned on and the system was isolated from the diffusion pump by means of a high vacuum valve. After 12 hours, pressures at or below 10^{-7} torr were achieved with no bake out of the system.

The vacuum chamber contained the ionizer assembly of the Quad 250, the filament assembly, and the electron collector screen. The Vac-Ion pump and the reaction chamber were connected in such a way that the opening of the pump was not in a direct line with the electron collector. Tests were made to see if ion pump operation affected the electron measuring system. Results were negative.

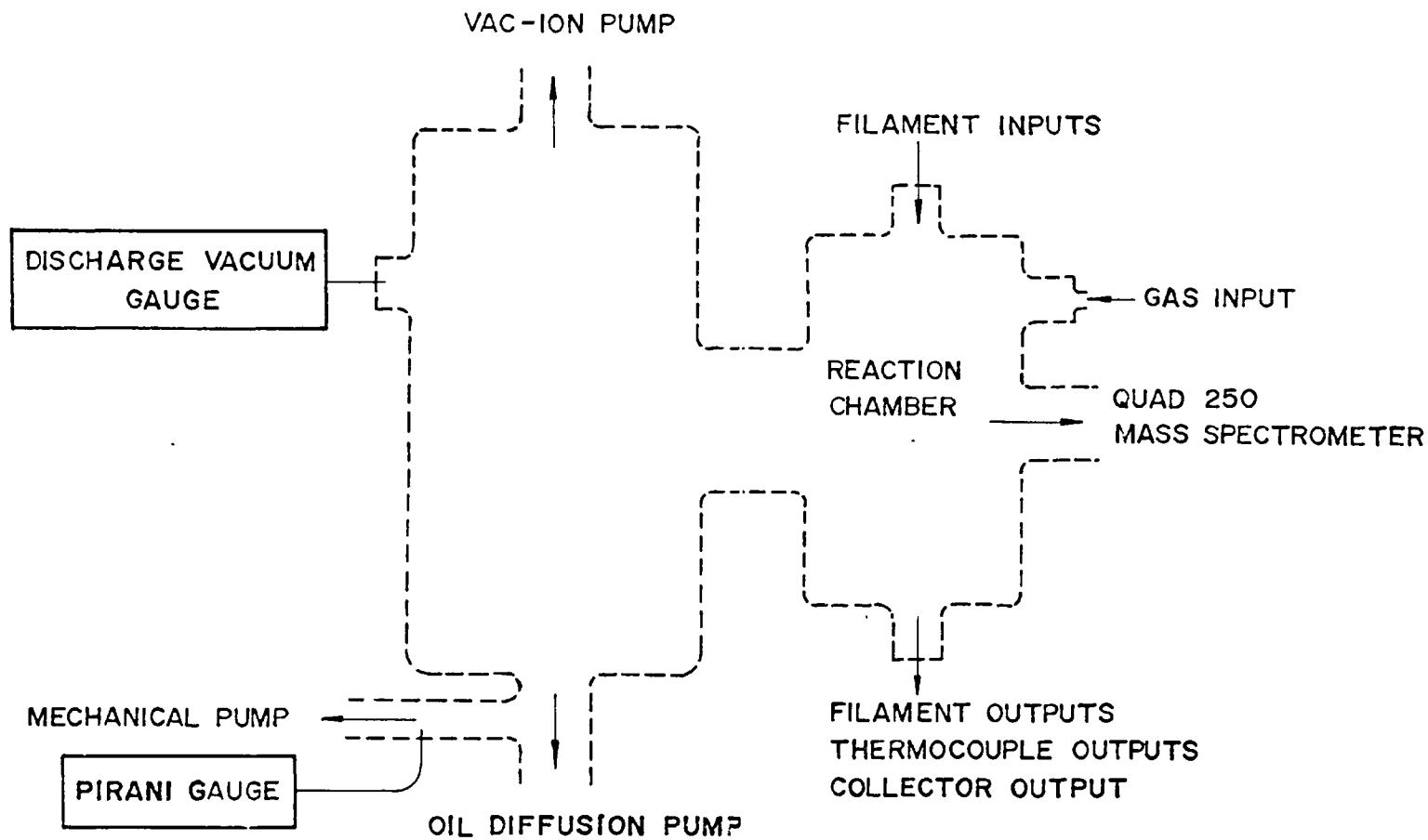


Figure 1. Vacuum System

Mass Spectrometer

An Electronics Associates, Incorporated Quadrupole 250 residual gas analyzer was used to monitor the concentrations of gases and ions present in the system. The relative concentrations were displayed on a HP-130C oscilloscope as amplitude versus m/e ratios (peaks). The mass spectrometer could be adjusted to continuously scan any number of such peaks in the range of mass numbers 1 to 50. The output of the mass spectrometer was recorded on film or a chart recorder. Figure 2 shows a typical scan of mass numbers from 1 to 34.

The Reaction Chamber

The reaction chamber is shown schematically in Figure 3. All electrical connections into the chamber were made through Varian high vacuum connectors.

The catalyst filaments were supported by brass terminals and were isolated from ground by a boron nitride support. Three filaments were installed at a time to avoid frequent pump down of the system in case of burn out. A chromel-alumel thermocouple welded onto one of the filaments was used to record the filament temperature. A Hewlett-Packard 425A DC micro volt-ammeter was used to measure the thermocouple potential. The output of HP-425A was plotted by a servo-recorder as a measure of the time variations of temperature.

Exo-electrons from the filaments were detected by a semi-circular stainless steel screen collector biased at +30 volts. The currents from the collector were measured by a Keithley 417 high speed picoammeter whose output was again plotted by a recorder.

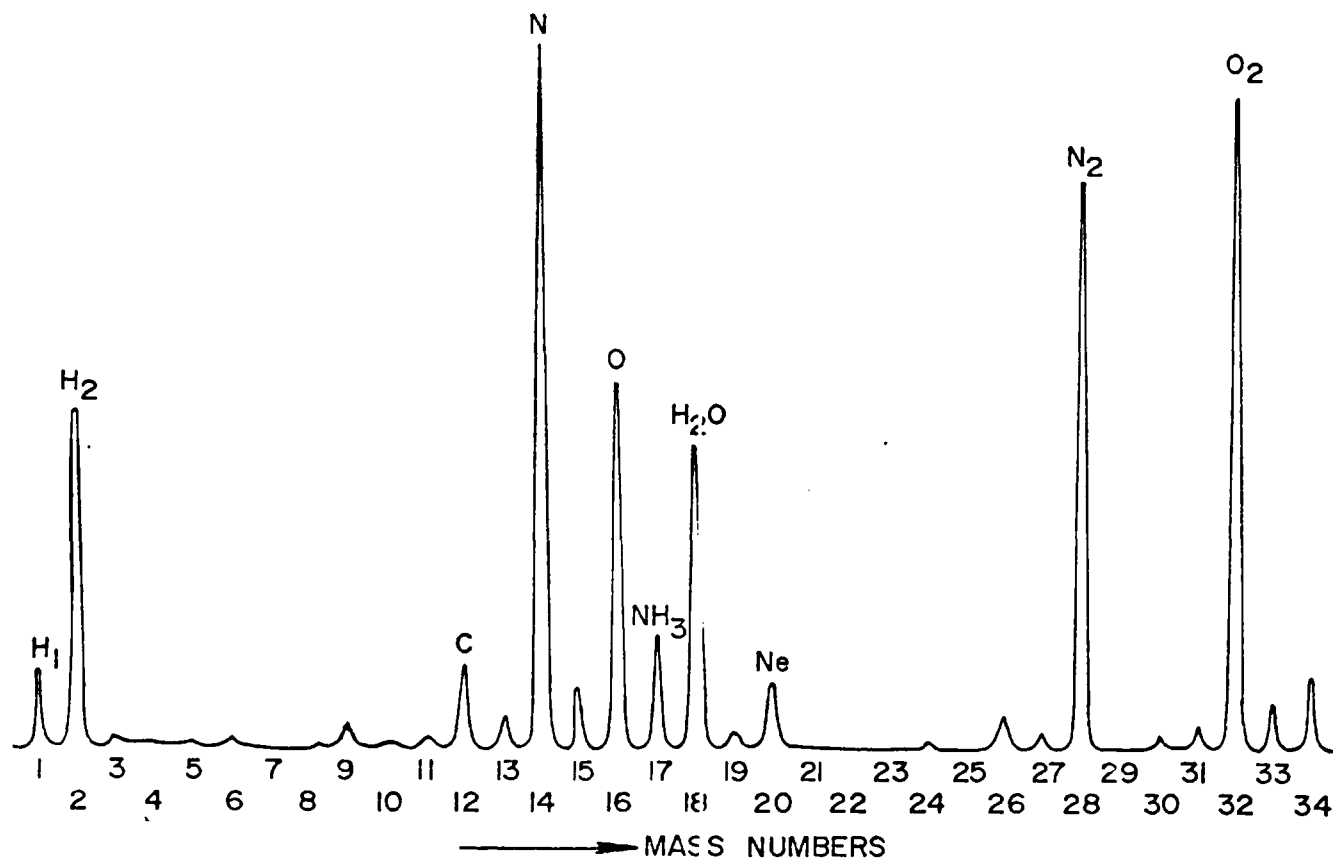


Figure 2. Mass Spectrometer Scan Output

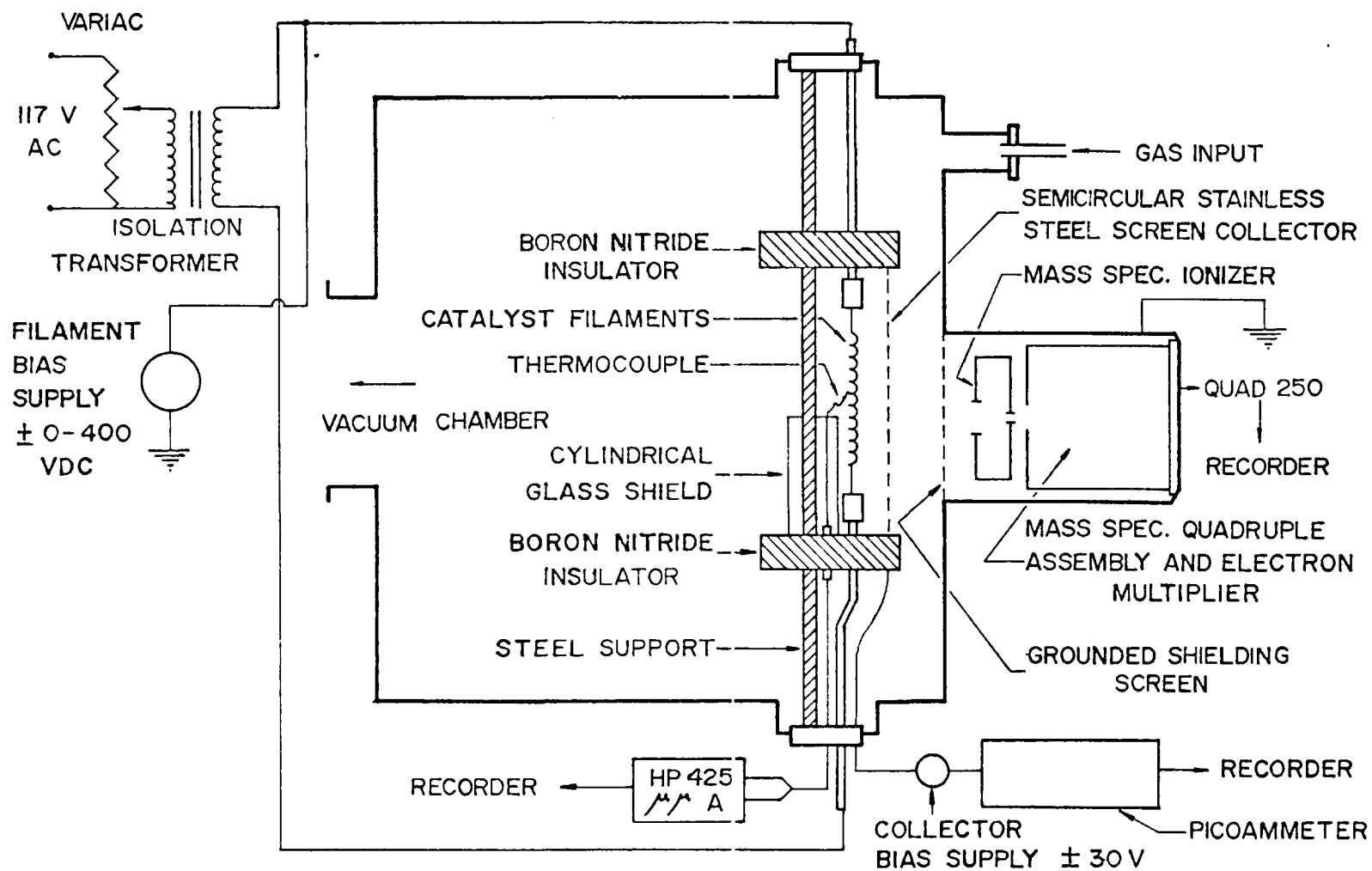


Figure 3. The Reaction Chamber

The Quad 250 ionizer assembly was situated such that the ionizer opening, the accelerator, focussing plates, quadrupoles and the electron multiplier were directly in line with the catalyst filaments. This reduced the response time between the start of a catalytic reaction and the time when the reaction products were observed.

The catalysts were in the form of wires .25 mm in diameter. A catalyst assembly consisted of three such wires, each approximately 10 cm long, which were twisted together. The catalyst materials were high purity grade platinum (99.995%), silver and palladium. The gases used were commercial grade CO, NH₃, H₂, and O₂, taken from standard cylinders.

Power Supplies and Recording Instruments

The catalyst filaments were heated by AC current which was supplied by a combination of an isolation transformer and a variac. This allowed the filaments to be biased above or below AC ground. The filament bias potentials were provided by a Fluke 407D power supply. Bias voltage could range from "0" (ground) to 600 V DC. Time variation of catalyst temperature, exo-electron current, and relative peaks of reaction products (Quad output) were recorded by three Heathkit EUW-20A servo-recorders.

CHAPTER 6

EXPERIMENTS AND RESULTS

Chemisorption Effects

The first experimental studies involved oxidation of CO , NH_3 and H_2 with gaseous O_2 . The reactant partial pressures were held at about 1.10^{-6} torr during experiments. The total pressure was also observed to note any loss of pressure due to overheating of the Vac-Ion pump.

To investigate the background effects the filament (catalyst) was grounded and the collector was biased at +30 volts with the pressure at 10^{-8} torr. Each of the gases under study was admitted through a leak valve until the system pressure increased to 10^{-6} torr. For each gas, the platinum filament was gradually heated from 20°C to 800°C . The mass spectrometer and the picoammeter were used to look for catalytic products and exo-electrons respectively. (It should be noted that the mass spectrometer and the picoammeter could not be used simultaneously since some ion emission from the spectrometer ionizer was picked up by the exo-electron collector.) Therefore when making exo-electron measurements, the ionizer was always turned off.

In these studies no reaction products were observed. However, there was some exo-electron emission due to changes in the work function of the filament induced by chemisorption and surface rearrangement [9].

The effects are shown in Figure 4. Oxygen increases the work function while hydrogen decreases it. Emissions with NH_3 and CO were lower than the vacuum level.

Catalytic Reactions

The first catalytic reaction studies was that of oxidation of hydrogen by oxygen over platinum. This reaction took place even at room temperature but the rate was very slow. The rate of catalysis rose sharply as the filament was heated to the operating temperature of 775°C . Figure 5 shows how exo-electron emission followed the rate of catalysis. Here the rate K is given in arbitrary units* and emission I_e is given in amperes. K and I_e are plotted as a function of time. The data on K was obtained by recording the water peak using the mass spectrometer. Water is the product of the oxidation of hydrogen and the rate of reaction is directly proportional to its concentration.

Notice that the exo-electron current follows the rate of reaction and is somewhat erratic until K reaches a steady state value, at which time I_e drops to a slightly lower level. Similar data was obtained as the experiment was repeated. It was noted that at higher filament temperatures it took less time for K and I_e to reach steady state. Similarly at lower temperatures the time to reach a constant

*The value of (K) cannot be given in absolute units because the electron multiplier in the quadrupole was subject to changes in efficiency as a function of the ambient gas in the vacuum system. The efficiency is known to rise in the presence of CO and drop when O_2 is introduced. These long term drift effects do not invalidate our conclusions.

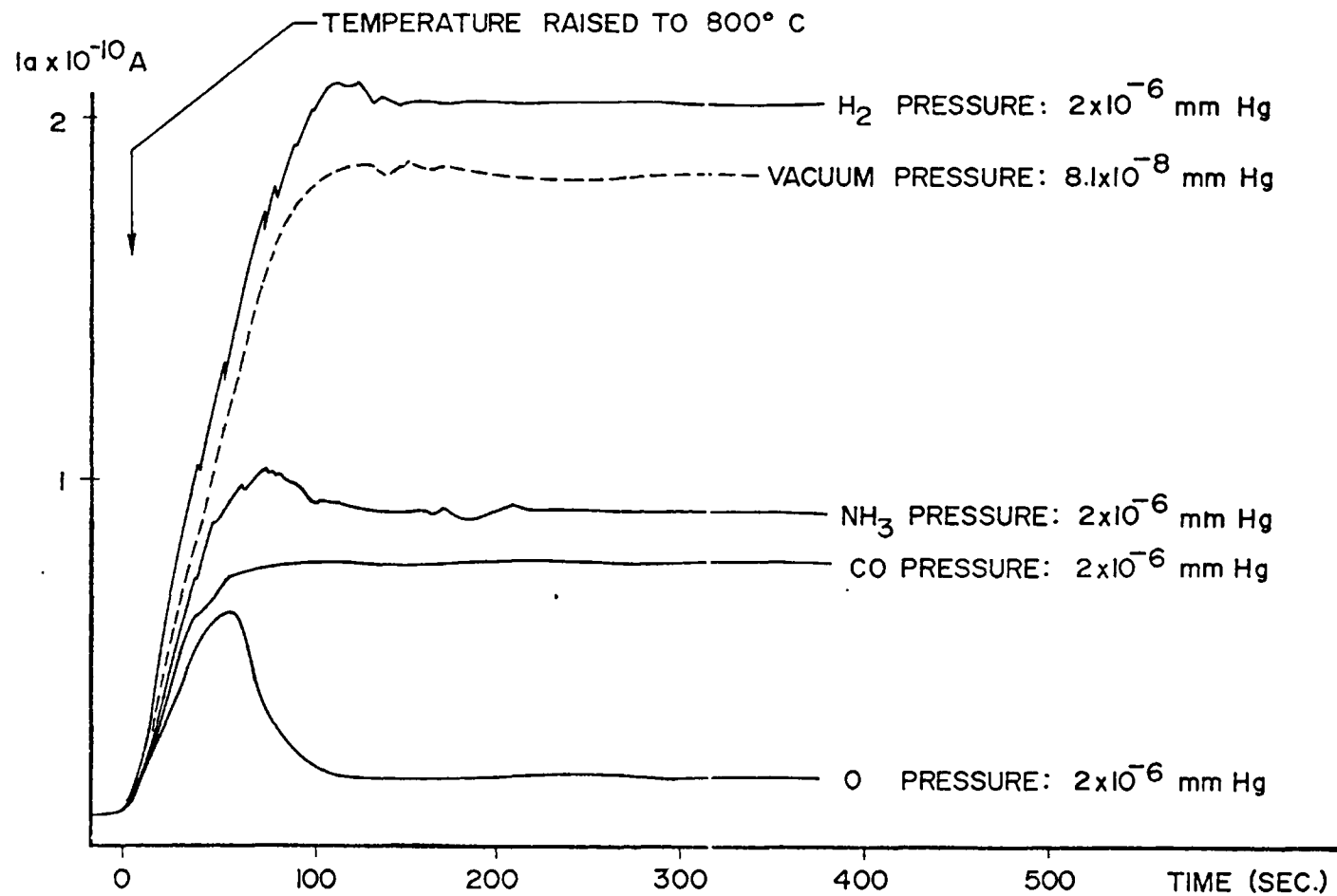


Figure 4. Effect of Various Gases on Exo-Electron Emission from Platinum

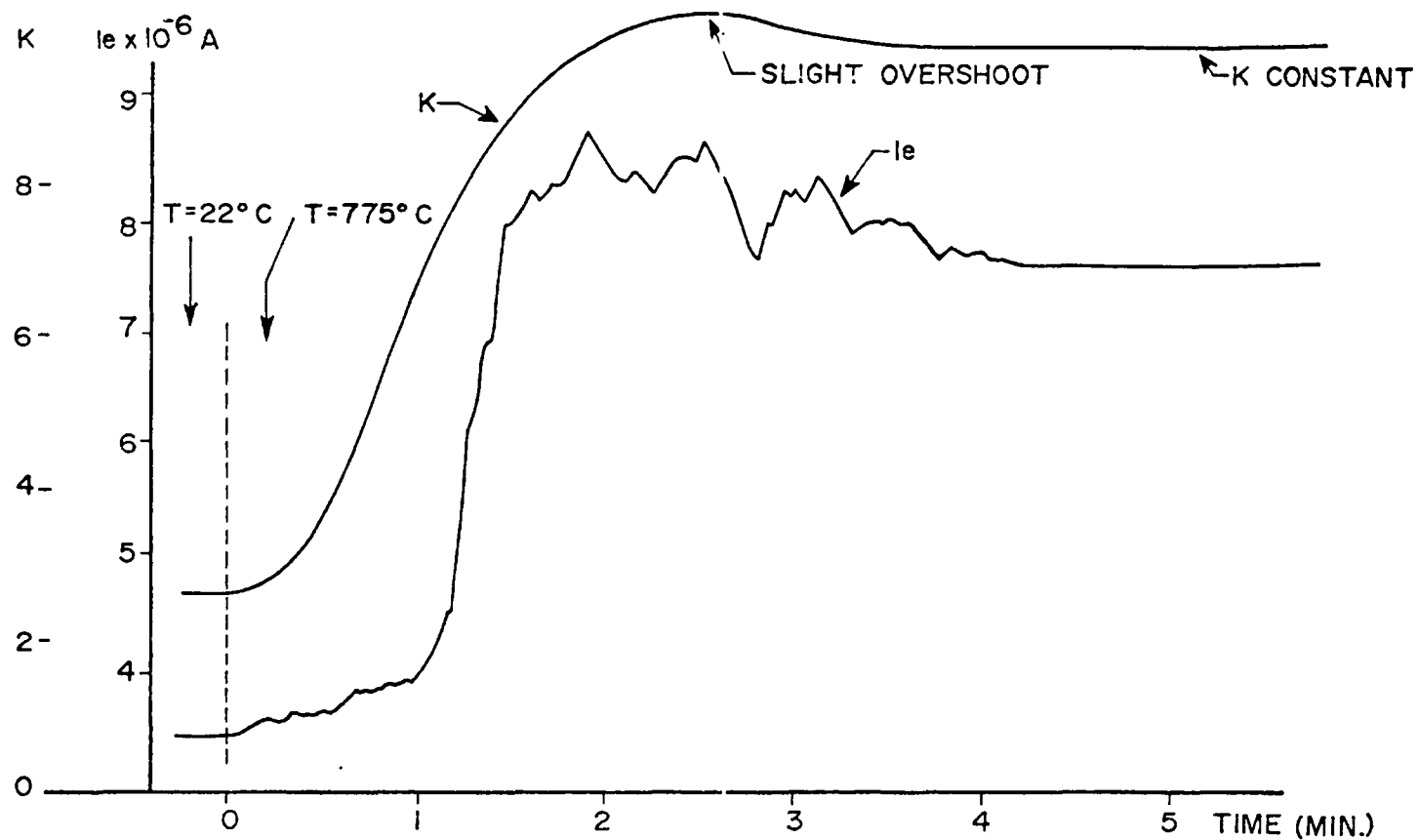


Figure 5. Rate of Reaction and Exo-Electron Emission Versus Time-Oxidation of H_2

level increased. At 800°C it took 7 minutes for K to drop and I_e fell to the lower level. At 700°C a longer time (15 minutes) was required.

It seemed that once the steady state condition was achieved, the system was quite stable. A variation of catalyst temperature by $\pm 50^\circ\text{C}$ did not appreciably effect K or I_e.

Figure 6 shows similar results for oxidation of CO. Notice the surge in both K and I_e as the filament is turned off. This is not an electrical transient effect. The heating current was observed on an oscilloscope to check for any transient effects or surges at the time when the filament was turned off. All tests were negative and at a later point we shall suggest that this "cooling" surge is due to surface mass migration as the catalyst cools off. At this point we will only comment on the almost linear relationship between the rate of reaction (K) and the exo-electron current I_e.

The qualitative behavior in oxidation of CO was very similar to that of oxidation of H₂. In Figure 7 results of the catalytic oxidation of NH₃ are shown. Here again exo-electron emission follows the reaction. The "cooling" surge was observed again. This phenomenon seemed to occur whenever the catalyst was cooled down to room temperature from its operating temperature, and we must note that the decay time is much too long for it to be a switching transient. It will be noted later that the form of the curve decay following the surge was effected by changes in the filament bias. It will be suggested that surface mass migration is responsible for the "cooling" surge in exo-electron emission, [9].

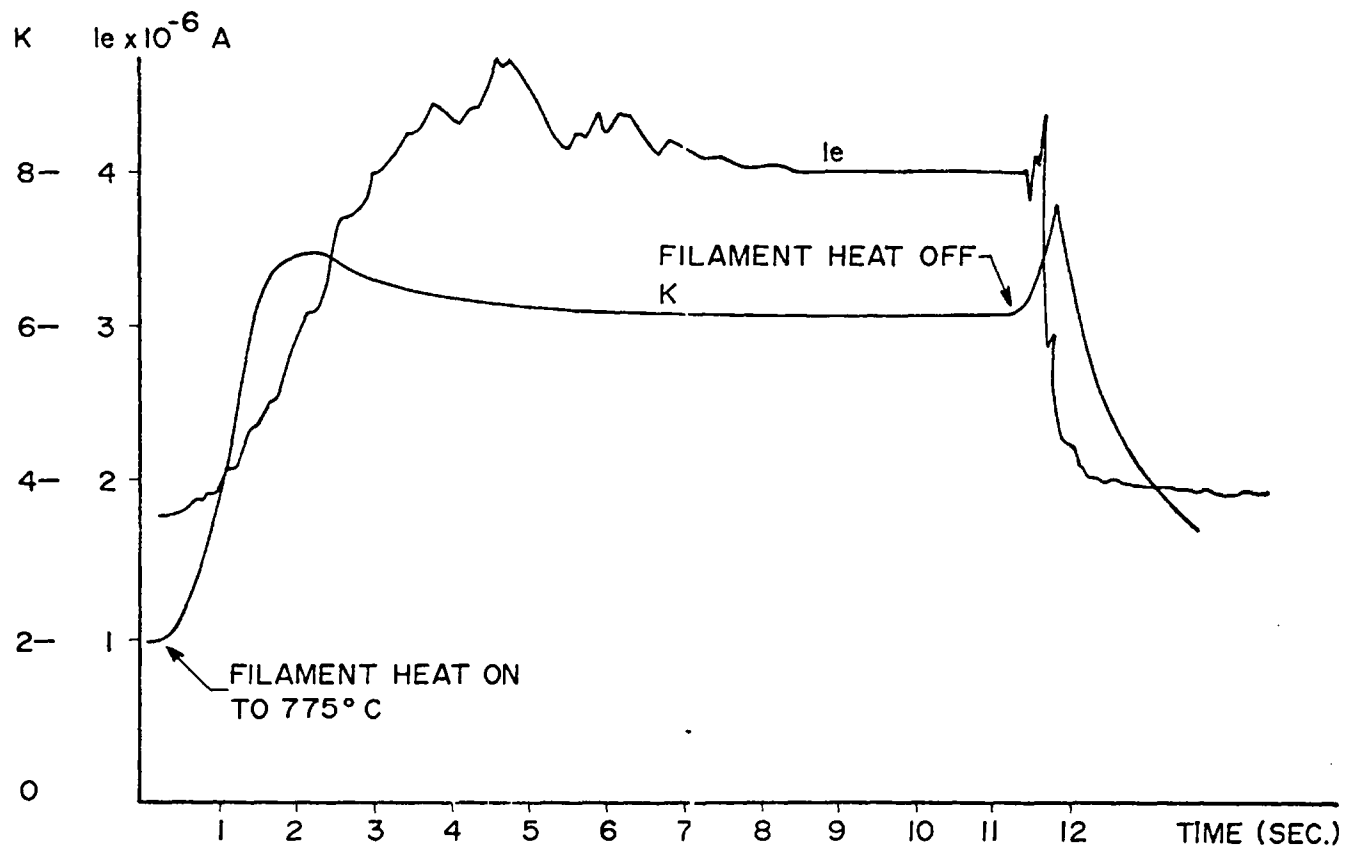


Figure 6. Rate of Reaction and Exo-Electron Emission Versus Time-Oxidation of CO

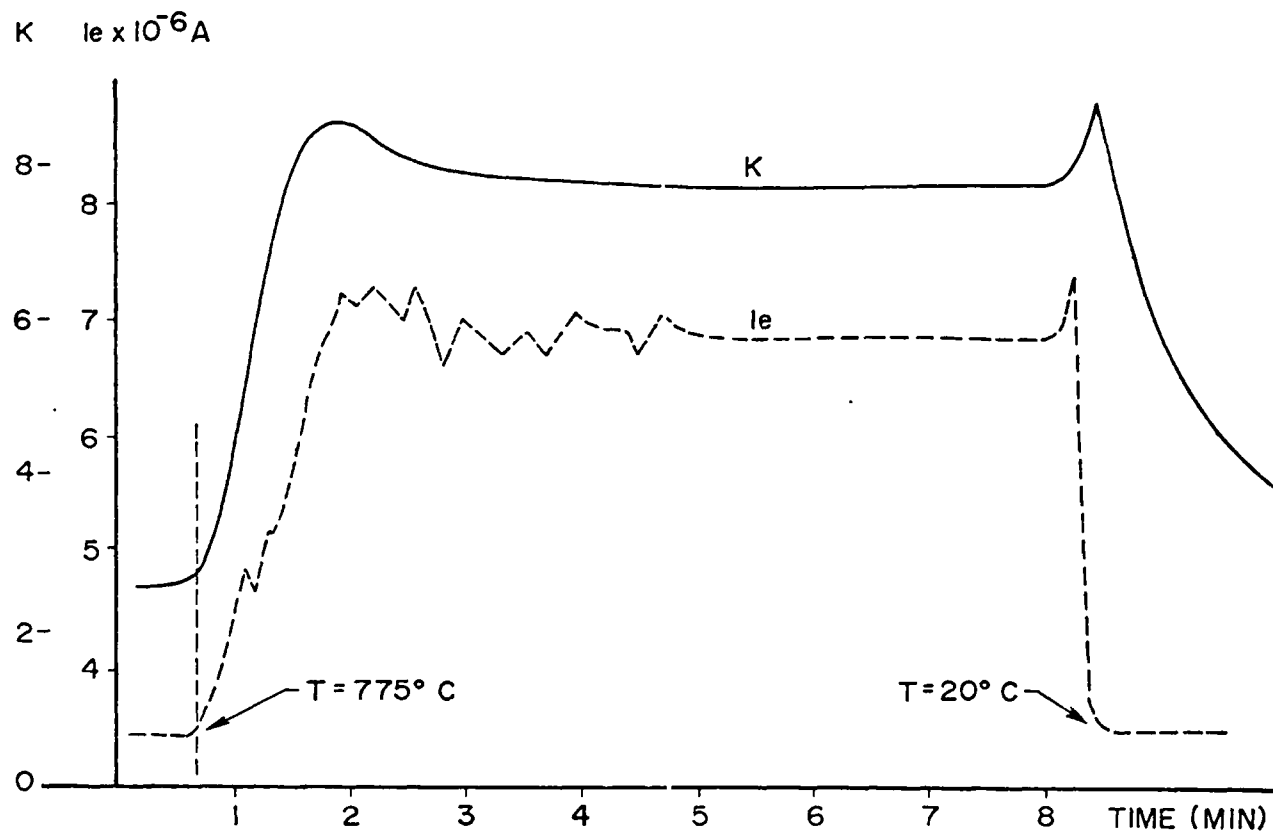


Figure 7. Rate of Reaction and Exo-Electron Emission in Time-Oxidation of NH_3

Temperature Effects

Figure 8 shows the effect of changing the operating temperature, for different reactions under identical conditions, on the reaction rate K and the electron current I_e . The reaction under study was oxidation of ammonia. This data demonstrates the possibility of following a reaction by exo-electron current. (Thermal effects occur at temperatures above 800°C .) It must be noted that rate of heating effected the overall activity of the filament and the rate of cooling changed the form of the final decay. To avoid this difficulty the filaments were turned on and off with a snap switch to decrease the heat up time. Slow warm up of the filaments decreased the activity of the catalysts. This phenomenon was also reported by Bernstein, Kearby, Raman, Vardi, and Wigg, in oxidation of NO_x over monel [10].

Activation Energy Comparison

For relatively small temperature ranges, dependence of rate constant on temperature is given by an empirical equation proposed by Arrhenius, [in 3],

$$k = A \exp(-E_a/RT)$$

where A is the frequency factor also known as the pre-exponential factor and E_a is the activation energy. The above equation can be written as

$$\text{Log } k = -E_a/(2.303 RT) + \text{Log } A \quad (5)$$

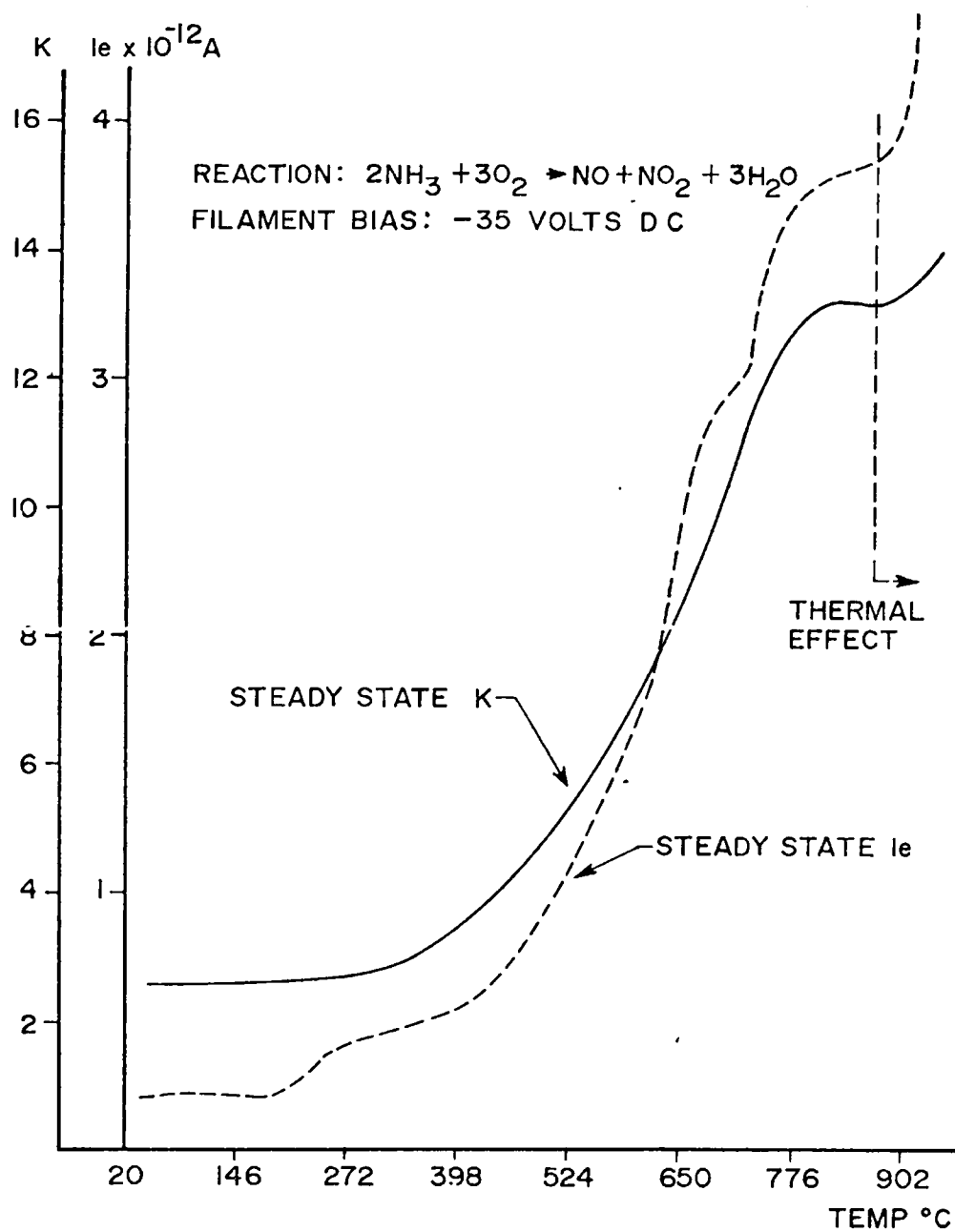


Figure 8. Rate of Reaction and Emission Current Versus Temperature for Successive Reactions at Different Temperatures

Since K values recorded experimentally are all relative, let

$$k = f K \quad (6)$$

where f is a constant. Then,

$$\text{Log } K = - E_a / (2.303 RT) + \text{Log } A - \text{Log } f \quad (7)$$

or

$$\text{Log } K = - [E_{aK} / (2.303 R)] [1/T_K] + \text{Constant} \quad (8)$$

Similarly,

$$\text{Log } I_e = [- E_{aIe} / (2.303 R)] [1/T_{Ie}] + \text{Constant} \quad (9)$$

It must be noted that f is also a function of concentrations of reactants of the reaction in question. Dependence of f on concentration varies with the order of the reaction.

Equations (8) and (9) were used to produce the Arrhenius plots shown in Figure 9 for both K and I_e. The data was obtained from the plots in Figure 8 for temperatures between 583°C and 986°C. Slope of each line represents the activation energy of the corresponding process. Activation energies of the two processes involving K and I_e respectively were calculated to be 7.3 and 8.1 kcal mole⁻¹ respectively, clearly very close in magnitude. This is of importance if one process is related to the other.

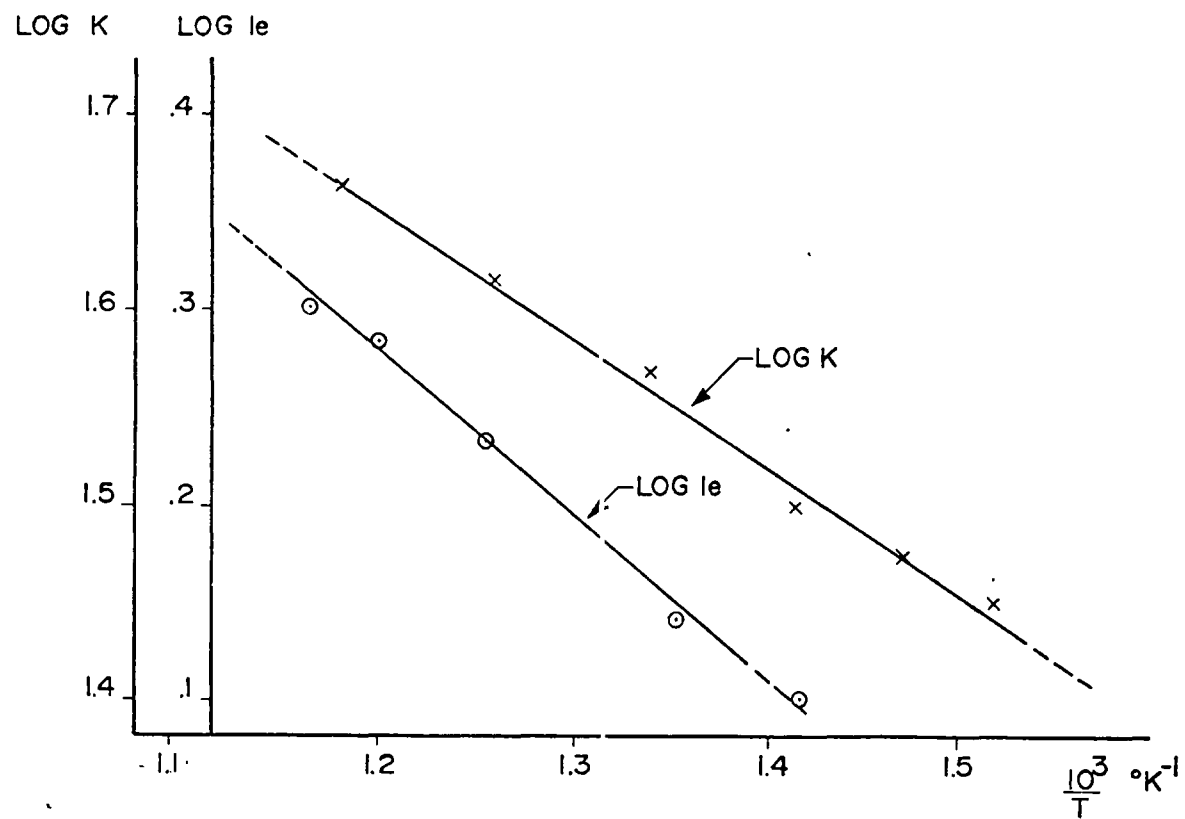


Figure 9. Comparison of Activation Energies for Rate of Reaction and Exo-Electron Emission

Turning to other experimental results we should note that throughout this text whenever a particular effect is reported with the oxidation of CO , H_2 , or NH_3 , the same effect is seen in experiments with the other two gases. If the results are qualitatively similar, the matter is not discussed any further. However, any significant differences are reported in the text.

Electric Field Effects

In the early experiments on electric field effects, the catalyst was biased to enhance or reduce electron emission to see what effect, if any, there was on catalysis. The catalyst was heated to its operating temperature (770°C) and then biased to ± 28 volts. The data indicated that changing the bias voltage in the middle of a reaction changed the value of I_e but the value of K was unaffected. A different effect was observed when the filament was biased *before* the catalyst was heated. This is shown in Figure 10 for oxidation of CO . A -28 volt bias increased both I_e and K over the no bias values while a $+28$ volt bias decreased both I_e and K below the no bias values. It should be noted that the positive bias potential was not nearly as effective in lowering K as the negative bias was in increasing it. The no bias K value is much closer to the $K = +28$ level than the $K = -28$ level, and it was not shown to avoid confusing the figure. Figure 11 shows more detailed data on the effect of filament bias voltage on K . Bias voltage was changed each time the filament was cooled to room temperature (approximately 20°C). Then the catalyst was heated to 770°C and held there until K reached a steady state level. At this time the

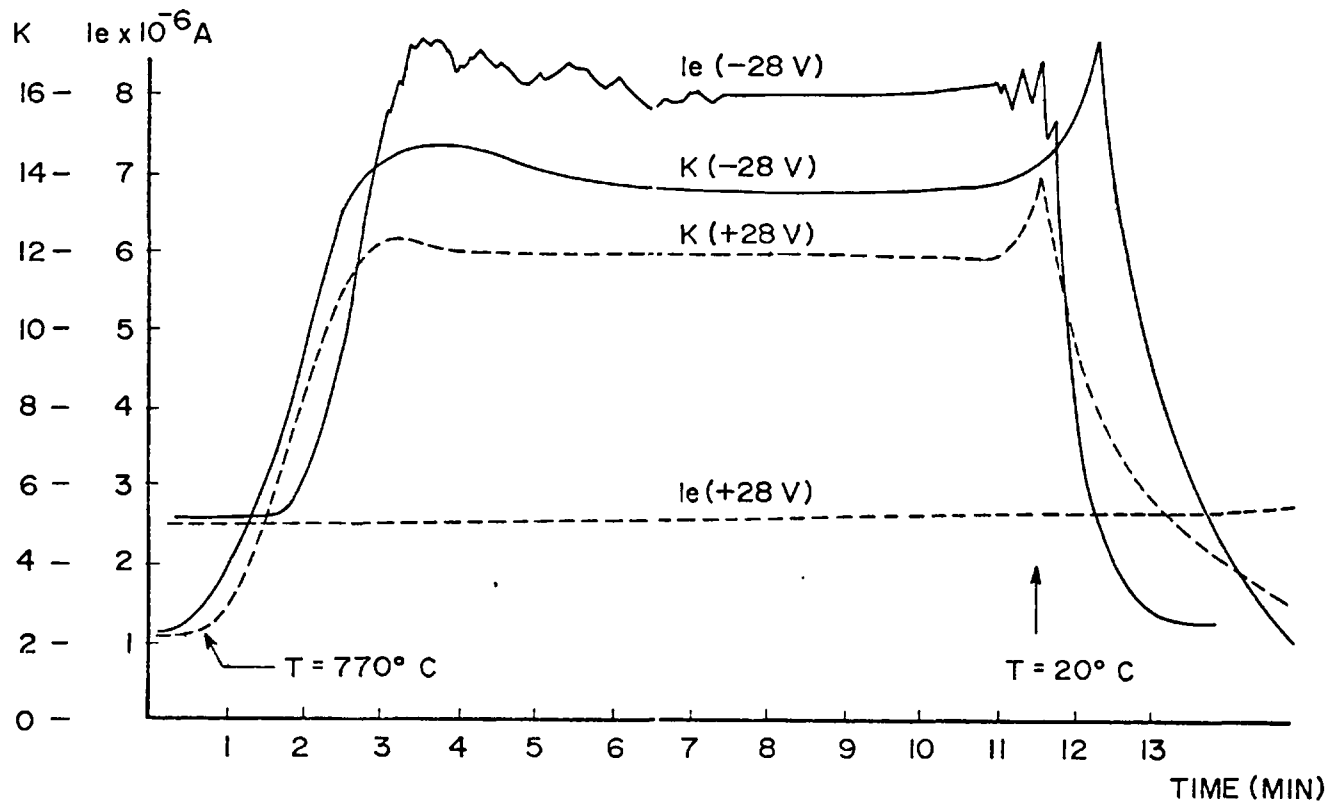


Figure 10. Effect of an External Electric Field on Catalysis of CO Oxidation

filament was cooled back to 20°C. The data showed that for higher negative potentials K increased rapidly when the filament was turned on and died out quickly when it was turned off. The pulse occurring at cooling was much steeper and stronger. At low voltages however, (-30V) the rise occurs much more slowly and the decay is significantly longer.

Other experiments showed that small positive filament bias voltages (+28V) reduced K slightly whereas higher positive voltages (+80V) did not have noticeable effect. It must be noted that the exo-electron emission current at (+80V) was nearly down to zero.

There was evidence that when a filament was positively biased during a reaction it was conditioned such that the effect was carried on to the next reaction also. In other words, a filament which was used previously in a catalytic reaction with a positive bias was less active than a filament which was previously either grounded or negatively biased. We suggest that positive bias can condition the filament against catalysis. This effect is shown in Figure 12. Here K was plotted against time for three consecutive runs. It must be noted that the plot shows only the time during reactions and the filament heating time after the second reaction is not shown. The reaction under study was oxidation of CO. The filament was first biased at +30 volts to retard exo-electron emission. It was then cooled to 20°C and -30 volts was applied. The increase in K was significantly lower than that usually observed at -30 volts. It is suggested that the positive bias had somehow "formed" the catalyst into an ineffective state. The catalyst was then annealed by heating at 950°C in vacuum without any

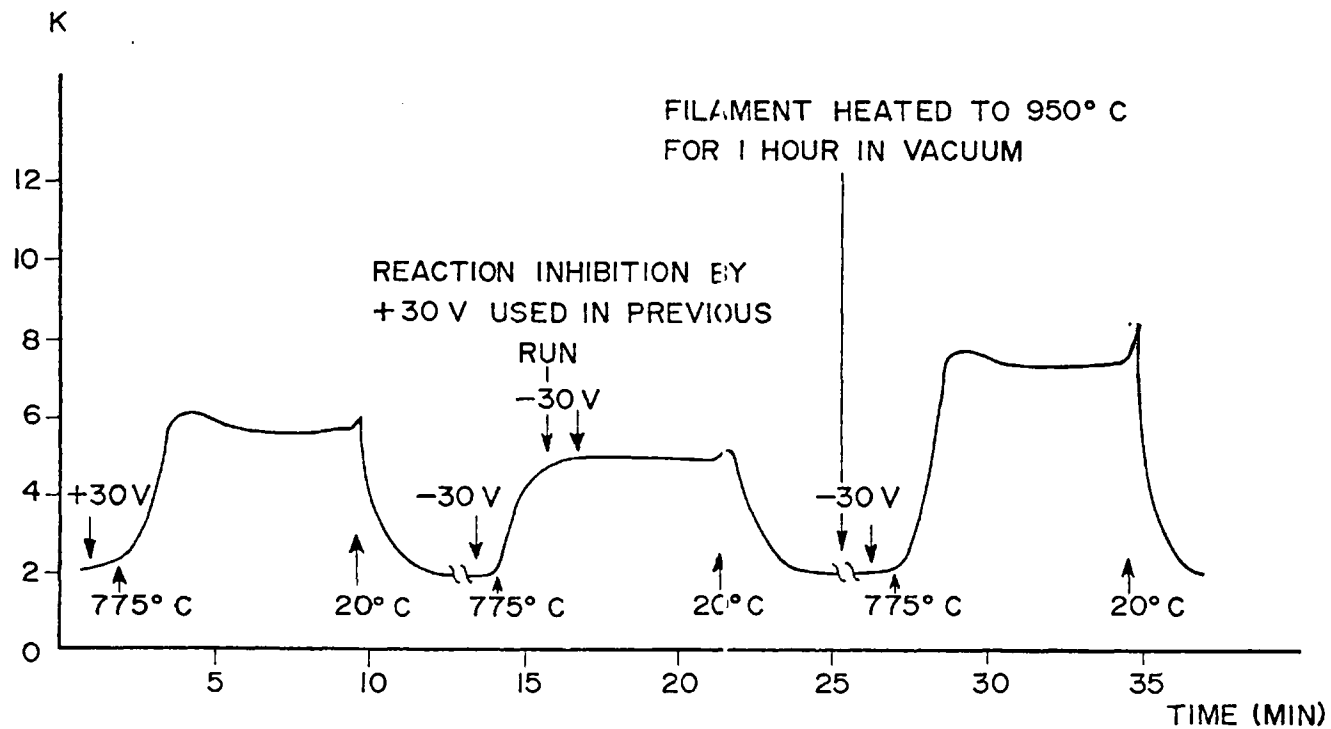


Figure 12. Effect of Previous Exposure to Positive Voltage on Catalysis of CO Oxidation

applied potential for one hour and cooled down to room temperature. The same experiment was repeated with -30V bias, (K) increased to its normal level at this potential.

One study was done to determine if the emitted exo-electron current had a complex energy spectrum. This spectrum might be related to the presence of "activated complexes" as reaction intermediates, [9]. To do this, the filament was turned on with no bias and the reaction was allowed to stabilize. Then the filament voltage was increased very slowly in steps to +33V. The exo-electron current monotonically decreased as the filament voltage increased. No structure other than capacitive switching effects was observed in the I_e versus voltage curve. One would expect that the intermediate active states involved in a catalytic reaction would emit electrons at characteristic energies. If these states existed in this reaction they should have appeared as discontinuities in the plot of bias versus I_e . The results were negative.

Effects of Removing One of the Reactants

The next group of experiments involved shutting off one of the gases, either the oxidizing gas (O_2), or the reducing gas (CO , NH_3 , H_2), after the reaction reached steady state. The electron emission levels were recorded and compared with the three gases. The resulting data is shown in Figure 13. It is clear that presence of oxygen alone lowered the emission substantially. Electron current level with both reactants present is higher than that with only oxygen present. This may be due

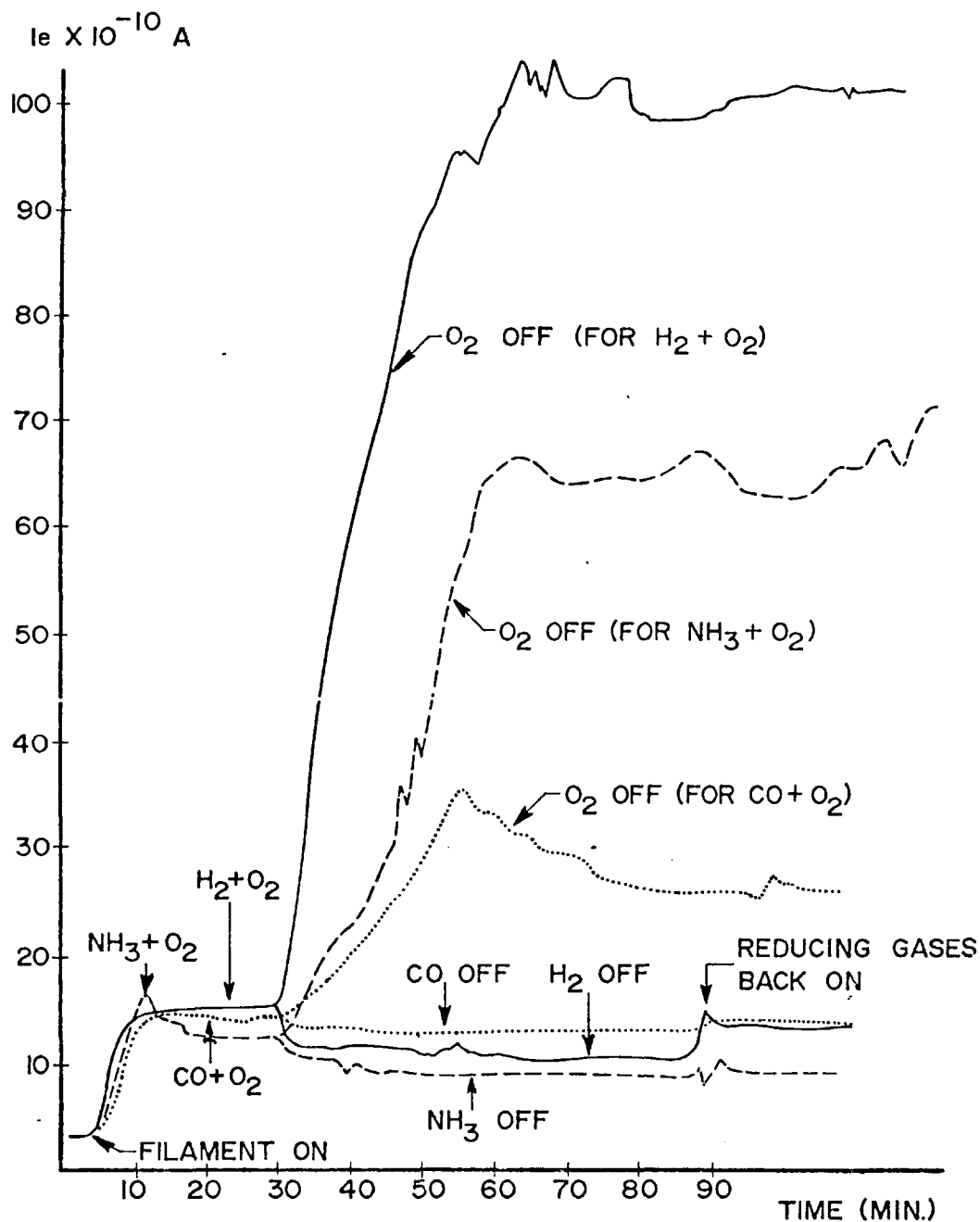


Figure 13. Effect of Removing One of the Reactants on Exo-Electron Emission

to formation of an adsorbed oxide layer at the surface which changes the work function of the metal surface.

Further study was made to see if highly oxidized catalyst was more active than a reduced catalyst. To do this, a platinum filament was heated in ammonia at 900°C for 5 hours at a pressure of 2×10^{-6} mm Hg. This was done to reduce (clean) the surface of all oxides. The filament was then cooled down to room temperature. After 30 minutes of cooling, the filament was heated up again to 700°C in ammonia at a pressure of 2×10^{-6} mm Hg., and the waterpeak (one of the products of oxidation of ammonia) was recorded. It must be noted that the only oxygen present in the system was part of the background gas, approximately 1×10^{-7} torr, while ammonia was constantly being fed in.

The same experiment was repeated except that the initial heat treatment at 900°C was done in oxygen at 2×10^{-6} mm Hg., instead of ammonia. It was observed that the filament was approximately 5 to 10 percent more active after being treated in oxygen.

Oxidation of Alcohol Over Silver

Another reaction examined in this study was oxidation of alcohol over silver. The reaction started at about 200°C. The optimum temperature was about 560°C. The length of time to reach steady state depended on the filament temperature as was the case with platinum. The catalytic activity seemed to vary greatly with:

1. *The length of time before the previous reaction.*
2. *Ratio of mixture.*
3. *Pressure.*

There was also evidence that longer "rest periods" between reactions increased activity. This was also true when the filament was heated in oxygen and cooled again before the reaction.

Two consecutive reactions seldom showed identical activities although corresponding test runs of two different sets of experiments showed similarities in behavior. Due to this property it was very difficult to keep all parameters constant in order to study the effect of electric fields on the filament's activity.

Comparison of Activity in Platinum and Palladium

Final phase of this study involved comparison of the catalytic activities of platinum and palladium. It was pointed out earlier that some of the theories relating catalysis to crystal geometry had failed since similar geometries did not exhibit similar catalytic activities. Eight runs were made for each filament at various temperatures. Oxidation of hydrogen was monitored and the steady state H_2O level was recorded for each run. The data is given in Figure 14. As expected, the platinum filament had higher activity. This was the case for all gases tested.

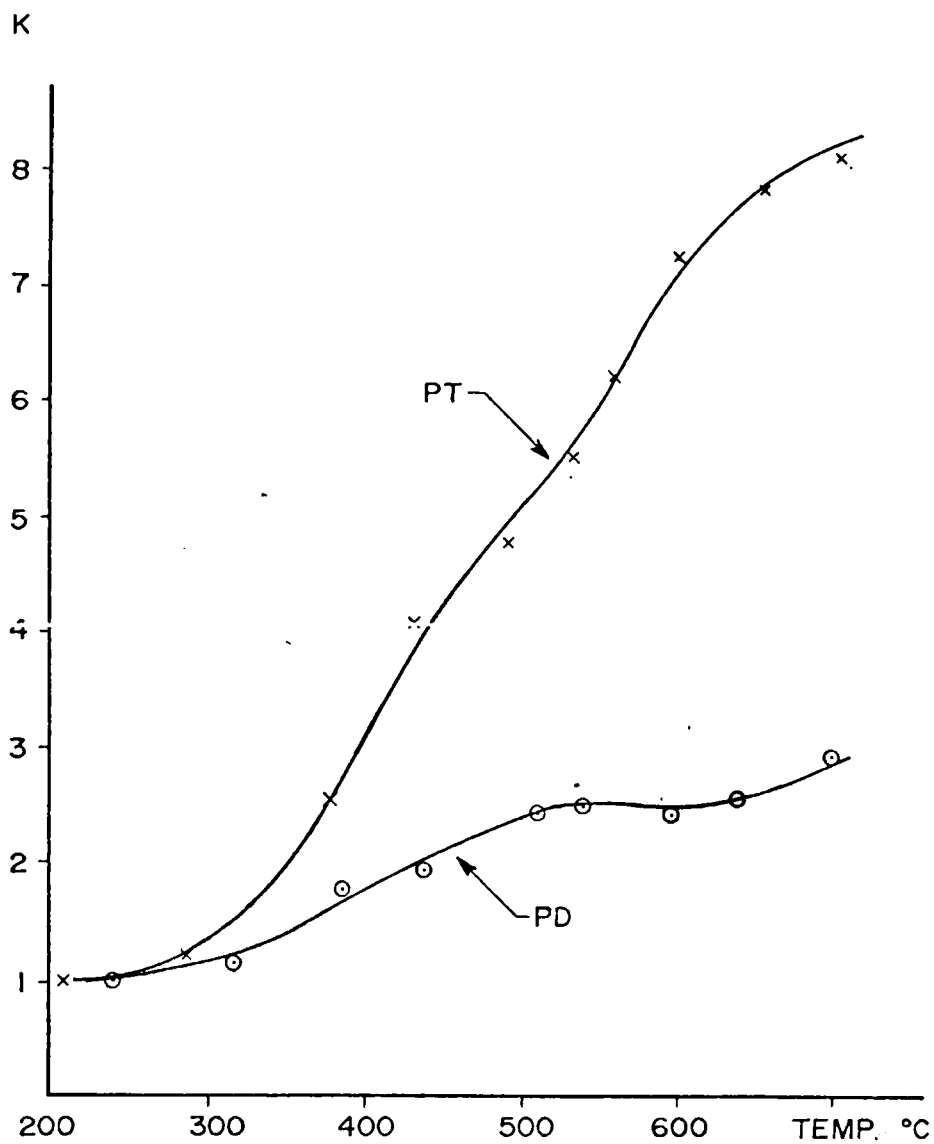


Figure 14. Comparison of Catalytic Activities of Platinum and Palladium

CHAPTER 7

DISCUSSION AND CONCLUSIONS

Exo-electron emission can clearly be used to monitor the rate of certain reactions. A linear relationship between exo-electron emission and oxidation rate of ethylene over silver oxide was reported by Sato and Seo [11]. Although emission level in our study was not significant for slow reaction which took place at or near room temperature, it was definitely a measurable quantity varying very nearly in the same fashion as the rate of reaction at temperatures above 500°C. The change in electron emission and rate of catalysis with electric fields indicates that some reactions can be partially controlled by external electric field potentials.

The mechanism for these phenomena is not entirely clear at this time, but it is suggested that the large values of K and I_e observed during the induction period are due to mass migration on the catalyst surface, [9]. Surface migration during catalysis is well known, [12]. Catalyst surfaces are often grooved and twisted after long use.

Delchar [13] has observed exo-electron emission from nickel during adsorption of oxygen, but the electron current level dropped as the surface became saturated. Similar phenomenon was observed in this study and it is suggested that the steady state electron current is

due to the adsorption step in the reaction. It is further suggested that the steady state level indicates a continuous adsorption which would be necessary for a continuous catalytic activity.

The surge seen during cooling may be due to relaxation of the "activated" surface, which exists during catalysis, back to its normal state. Effects of this nature have been reported in thermal faceting of silver, [14]. Thermal facets at 865°C disappeared as the temperature was raised and reappeared as temperature went down again. Copious exo-electron emission would result from such extensive surface migration [9].

It was shown earlier that electric fields are effective (if at all) only when applied before the catalyst is heated for reaction. Electric fields, if applied during surface rearrangement, have been shown to change the final state of a surface in thin films, [15]. In that study, the electric field was applied during deposition and was shown to effect the orientation of the deposited film. The electric field was not effective when applied to the completed film. Kennedy, Hayes, and Alsford [16] demonstrated that for a given metal film thickness higher resistivity films are obtained for evaporation onto an electrically isolated substrate, whereas lower resistivity films result from the application of an electric field (10 volts/cm) in the plane of the substrate or by removal of residual electrostatic positive charges from the incident vapor stream. In their experiment the major structural effects took place at the *early stages* of growth. Other studies by Sinclair and Calbick [17] on orientation effects of applied DC

electric fields on sodium chloride films deposited on silica glass, and one by Little [18] on inhibition of condensation by intense electromagnetic fields, indicate that electric fields have a definite effect on formation of thin films when applied during their growth. A catalyst surface at the beginning of a catalytic reaction may be compared to a thin film during growth due to rearrangements caused by surface migration. It is suggested that the final surface state, after the mass migration has ceased, is different for cases where electric fields are applied during the formation. It must be noted that the parallelism used here is not exact. The materials used in References 15, 16, 17 and 18 were not the same as our catalysts and the fields were in the same direction as the planes of films rather than perpendicular to them. These experiments are brought up as examples of phenomena which take place during the induction period when an external field is applied. Similar processes may be occurring on the catalyst surface which would explain the observations of the effect of electric fields.

In other studies an increase in reaction rate, for oxidation of isopropyl alcohol over silver at 476°C, was reported [19] due to application of a negative bias. However, the text does not show whether the field was applied during or before the catalyst was heated.

Lee and Hsu [20] demonstrated that catalytic activity may be effected by AC bias voltages of various frequencies. Lee [21] also showed that catalysis could be effected by applying fields that could be varied both in amplitude and frequency.

Stadnik and Fensik [19] have suggested that the applied field may have induced excess electron emission from the catalyst. This agreed with the results in this study.

The experiment on palladium showed that although palladium has a very similar crystalline structure to platinum, it does not exhibit similar catalytic activity. It is further suggested that the initial clean metal surface is "covered" by a semiconducting gas-metal compound, formation of which brings about the surface migration discussed earlier. This happens at the start of the reaction and accounts for the initial instability of exo-electron emission current. After a stable "surface state" is reached the emission level and the reaction rate both reach a steady state level. Electrons are emitted as reducing gas "molecules" are oxidized upon collision with the gas-metal interface. Negative electric potential increases catalytic activity possibly by increasing the adsorption capacity of the semiconducting layer due to bending of the Fermi level at the surfaces, (Volkenstein). Increased adsorption brings about an increase in contact between the reducing gas and the surface layer.

It is also suggested that absence of oxygen reduces this semiconducting layer and exposes the clean metal surface which accounts for the sudden increase in exo-electron emission, even though the reaction rate goes to zero. This was shown in the last set of data. Same data showed that formation of the proposed gas-metal layer requires the presence of both oxygen and the reducing gas. The final surge is due to disappearance of the surface layer as the temperature drops.

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