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Citation: [The Journal of Chemical Physics](#) **16**, 237 (1948); doi: 10.1063/1.1746849

View online: <http://dx.doi.org/10.1063/1.1746849>

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Poisoning of Platinum Catalysts at High Temperatures

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(Received December 17, 1947)

Poisoning films of exceptional thermal stability are formed on a platinum catalyst when heated in a silicone vapor (hexamethyldisiloxane) at pressures of the order 10^{-3} mm. These films prevent the combination of hydrogen and oxygen at low pressures and are not removed until heated to about 1440 K in the presence of hydrogen (or to higher temperatures in oxygen). It is suggested that the film may consist of a silicon oxide oriented with the silicon atoms attached directly to the platinum and presenting an outer layer of oxygen atoms, effectively shielding the catalyst.

INTRODUCTION

THE poisoning of platinum catalysts by various gases at ordinary temperatures has been observed by chemists for over a century. The reaction between hydrogen and oxygen at low pressures provides a convenient means for studying this poisoning. At a known temperature the reaction velocity serves as a measure of extent of the active surface. Although large differences exist in the behavior of the known gases which cloak the platinum and which are responsible for the poisoning, it has been apparent that all of these gases are easily removed with restoration of the catalytic activity merely by heating the surface to incipient color. In this connection, Langmuir found¹ that the H_2+O_2 reaction is not sensitive to the previous treatment of the platinum when heated to the range 700 to 1900 K: the platinum in this temperature range showed no poisoning effect. This, in contrast to the known behavior of tungsten, certainly illustrates the ease with which adatoms on platinum are generally removed. Use of these characteristics is made, for example, in the microanalysis of gases,² where the usual procedure is simply to heat the platinum filament to a dull red to complete the combustion of oxygen and hydrogen (or of other mixtures).

In connection with a study of gas reactions occurring at low pressures in the region around the minute heated areas of carbon brush contacts, we found that a platinum filament used for the ignition of hydrogen and oxygen was

mysteriously poisoned so that no combination of these gases would occur at the dull red heat. Upon raising the filament temperature, the inactivity was found to persist up to 1340K. Even at this temperature no reaction was detectable in the apparatus, which was sensitive to pressure changes of the order 0.1 micron. Finally the activity was restored by flashing at white heat; within 10 seconds, 50 percent of the gas mixture was cleaned up by condensation of the water in a cold trap. The unusual stability of the poison film, initially of unknown origin, led us to the following brief study of its nature and properties.

APPARATUS

The apparatus consisted of a Pyrex-Nonex vacuum system (10-mm average bore) containing McLeod and Pirani gauges, cold traps, mercury cut-offs, gas storage bulbs and, in a side arm, the tube containing the filament (a 10-mil diameter wire in the form of an inverted loop, spot-welded at the ends to the leads). This system had been used in other work and was not changed for the study of the poisoning (although other arrangements would clearly have been more convenient) because the source was indicated to lie in the system, and it was intended not to disturb this.

Gas or vapor pressures were read in terms of the unbalance current indicated by microammeters which were connected in a calibrated bridge containing the Pirani indicator and compensator. The filament brightness temperatures were measured with a disappearing-filament pyrometer and were corrected to absolute tem-

¹ I. Langmuir, *Trans. Faraday Soc.* **17**, 621 (1921).

² F. J. Norton and A. L. Marshall, *Am. Inst. Mining Met. Eng. Tech. Pub. No. 1643* (1944).

peratures from data in the *International Critical Tables* (5, 245; 1929).

INITIAL EXPERIMENTS

Source of the Poison

At first, with this apparatus, many attempts were made to duplicate the original accidental poisoning by exposing the platinum at various temperatures to the gases which had been under study at the time. All of these failed. It was then recalled that the apparatus had been exposed to a silicone vapor (hexamethyldisiloxane*) a few days previously, and it was found that the glass walls were still evolving this vapor at a rate sufficient to build up a pressure of 1 to 2 microns when the pump had been closed off for an hour. The vapor was suspected as having contributed to the effect and, accordingly, a fresh quantity was admitted (25-micron pressure). Upon heating the platinum in this vapor for about 30 seconds, the poisoning occurred: mixtures of hydrogen and oxygen, tested subsequently, would not combine perceptibly although the platinum was held at the high temperature (1340 K) for several minutes, Fig. 1 (curve A). The test consisted in observing the gas pressure while the filament was heated and while one of the traps was chilled with liquid nitrogen to condense the reaction product.

Next it was found, consistent with the initial observations, that the film responsible for this

poisoning was quickly destroyed and rapid clean up of the gases occurred immediately (Fig. 1, curve B) when the filament temperature was increased to 1440 K in the hydrogen-oxygen mixture.

It was further found that the poisoning could be reproduced easily, a silicone pressure as low as 10^{-3} mm being adequate. The introduction of fresh silicone for each experiment was not necessary because the silicone continued to evolve slowly from the glass after a single exposure of the system to it, and this residual vapor was sufficient to provide an effective pressure for many trials although the apparatus was repeatedly evacuated below 0.01 micron. Thus when a low pressure of the silicone was required for an experiment, the system was exhausted and closed off from the pumps, and the trap chilled with liquid nitrogen; then after warming the trap to the range -110 to -80°C , the residual silicone pressure would gradually build up to one or two microns, and these low pressures were used for poisoning.

METHOD OF TESTING

In order to estimate the relative extent of the poisoning resulting from the different experimental treatments which were tried, the filament was tested immediately after each treatment by heating to 1340 K in a mixture of hydrogen and oxygen** at a total pressure of 20 to 40 microns; then, from the observed clean-up rates, the half-time (τ) for hydrogen clean up was determined. This will be illustrated in the following paragraphs.

Effect of Temperature upon the Poisoning

The effect of the filament temperature (as maintained during exposure to the silicone) upon the poisoning subsequently evaluated is shown in Fig. 2. The slopes indicate the rates of gas clean up at the filament test temperature 1340 K, following exposure to the silicone at the different poisoning temperatures indicated for the pretreatments for each of the curves. Curve A gives the reference slope for the clean platinum.

From the known initial partial pressures of the component gases in these experiments, separate

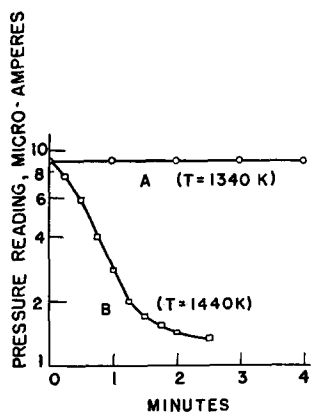


FIG. 1. Clean up of $\text{H}_2 + \text{O}_2$ mixture by platinum at 1340 and at 1440 K after poisoning at 1340 K. For H_2 , 1 microampere = 1.8-micron Hg; O_2 , 1 microampere = 4.0 microns-Hg.

* $[(\text{CH}_3)_2\text{Si}]_2\text{O}$, vapor pressure 40 mm (mercury) at room temperature.

** The concentration of oxygen was a few microns in excess of that necessary for complete combustion.

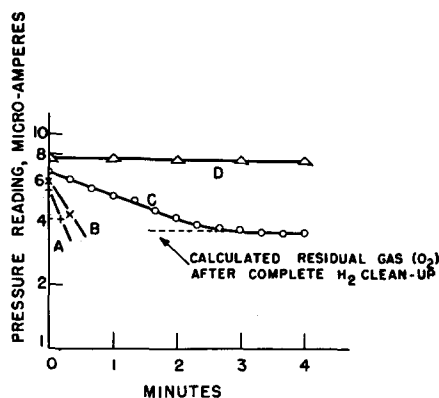


FIG. 2. Clean up of H_2+O_2 mixture by platinum at 1340 K. Pre-treatment: A—fire 1800 K, vacuum. B—heat 523 K, residual vapor. C—heat 723 K, residual vapor. D—fire 1340 K, residual vapor.

clean-up curves for each of the cases in Fig. 2 were plotted, as shown, for example, in Fig. 3. From the slopes of the hydrogen curves thus obtained, the half-times were determined. These are given in Table I. From these data it is seen that the poisoning effect begins at a platinum temperature between 523 and 723 K and is nearly complete at 1340 K ($\tau=28$ minutes).

Stability of the Poisoning Film

It was mentioned earlier that the filament was cleaned by high firing to 1440 K or above in the gas mixture or in vacuum. Rapid clean up of the hydrogen-oxygen mixture followed reproducibly at the test temperature 1340 K. Further study showed that this reactivation process did not occur readily when the high firing was carried out in oxygen alone. For example, when the poisoned filament had been fired to 1610 K in oxygen and was tested subsequently in the gas mixture (test-temperature 1340), the half-time τ was found to be 50 minutes, indicating that only slight reactivation had occurred. In contrast, when the poisoned filament had been fired in the hydrogen-oxygen mixture, to the considerably lower temperature 1440, τ was found in the subsequent standard test to be 0.1 minute representing a clean filament. Thus the chemical stability of the poisoning film was much lower with hydrogen present than in oxygen.

This stability of the film was affected not only by the chemical environment when fired, after the poisoning, but also by the history of the

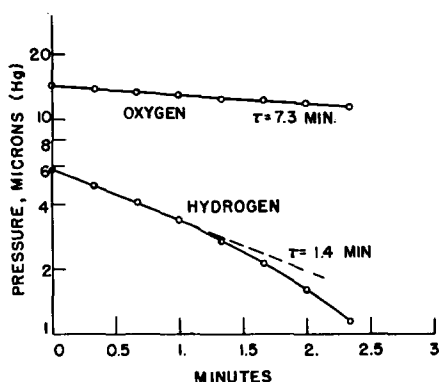


FIG. 3. Clean up of H_2 and O_2 by platinum at 1340 K after poisoning at 723 K (Fig. 2, C).

platinum prior to the silicone exposure. For instance, the perceptible pressure fall noted on Fig. 2 after the 1340 treatment (curve D), for which $\tau=28$ minutes in Table I, was inconsistent with earlier observations where the clean-up rate had been zero ($\tau=\infty$). It was finally shown that the film stability was lowered if the platinum had been exposed to a small amount of oxygen (about 0.5 micron) while being heated just before or during the exposure to the silicone. It was next found that the most stable film could be readily formed by cleaning the platinum in hydrogen and then poisoning it by exposure to a mixture of hydrogen and silicone vapor at 1340 K. This procedure effectively excluded oxygen. Thereafter the filament was completely inactive when tested in a hydrogen-oxygen mixture ($\tau=\infty$). In contrast, the effect of an oxygen pretreatment (before poisoning) was to lower the stability of the film subsequently formed so that when finally tested τ was found to be only a few minutes.

NATURE OF THE POISONING FILM

The composition of the film formed on the platinum by the silicone exposure is not known. The quantity of vapor required to form a monolayer on the filament in our apparatus (volume = 530 cm^3) would require a pressure difference of much less than 1 micron. As might be expected, no pressure changes have been observed during the film formation. The solid reaction products have not been isolated. The micro-manipulation of gases in the system containing the silicone vapor has presented unexpected

TABLE I. Half-time for the hydrogen clean up in relation to platinum poisoning temperature.

Curve	Poisoning exposure minutes	Filament pre-treatment Atmosphere	Temperature °K	Filament test in H ₂ +O ₂ mixture: half-time for H ₂ τ (minutes)
A	0.	(Fired in vacuum) 15 seconds	1800	0.11
B	2.	Silicone vapor	523	0.10
C	2.	Silicone vapor	723	1.
D	0.5	Silicone vapor	1340	28.

complications, owing to preferential sorption effects between the silicone and water vapor, which compete for the glass surface. For example, following the condensation of the reaction product (water) in the cold trap during a clean up of the gas mixture, the condensate was sealed between the mercury cut-offs and the trap was warmed. Previously the silicone pressure had been low (1.3μ), and it was anticipated that the vapor from the trap would be mainly water. The total pressure of the evolved vapor (17μ) was reasonably close to that of the water which was calculated as having condensed, but upon closer study this vapor was found to contain *only a small percentage water* (1.6μ) and was mainly silicone. This curious effect was noted repeatedly and was one of the factors which interfered with the analytical handling of the gas samples. It was proven to be the result of the competitive and preferential sorption already mentioned.

From the clean-up effects alone, however, some conclusions can be drawn regarding the nature of the films which poisoned the platinum. There are seemingly two types: (1) that which combined with the clean platinum and (2) that which combined with the oxygen-coated platinum.

It is suggested that the first of these, which is the more stable and which possesses the more reproducible characteristics, is an oxide of silicon, oriented so that the silicon atoms are attached directly to platinum atoms, the outer surface of the film being composed of oxygen atoms. (This is analogous to the carbon monoxide film which poisons platinum at low temperatures and which is known to be oriented with the carbon atoms attached directly to the platinum.)¹

The observed properties of the film, as described, support this view in the essential details. A silicon monoxide film chemically bonded to the metal would show the low vapor pressure which is the outstanding characteristic of the present film and also would evaporate in some reproducible temperature range near white heat, as this film apparently does during the reactivation of the filament. Further, the evaporation would occur at a higher temperature in oxygen than in hydrogen-oxygen mixtures: with hydrogen present and at the lower temperature, the oxide would be reduced with the formation of a volatile product.

The formation of a silicon monoxide film would be expected to begin with the cleavage of the Si—O bond in the silicone molecule and adsorption of the organosilicon fragments on the clean platinum. The subsequent oxidation or loss of the methyl groups would then yield the stable silicon oxide on the metal and traces of CO₂ and water in the ambient. If this is correct, we should expect other alkyl silicones to produce similar poisoning.

A monolayer of silicon monoxide derived from the silicone vapor thus appears to account for the unusually stable poisoning film described. It is not known, however, whether the filming process would stop upon completion of the monolayer since at the rather high temperatures of these experiments, continued decomposition of the vapor may occur. Bearing upon this, it has been observed that the silicone vapor in the absence of oxygen is not cleaned up at a perceptible rate by the hot filament through the temperature range up to 1500 K; and this would indicate that the rate of film formation, after the initial monolayer, is, at most, relatively low. It is probable that the silicone molecule is much more stable toward the (suggested) monoxide surface than toward the clean platinum, in which case the rate may fall to zero upon completion of the initial layer.

In a later paper, it will be shown that carbon (or graphite) is coated similarly when heated in silicone vapor so that it also shows remarkable properties, among which is that of not combining with oxygen at temperatures up to at least 1200 K.