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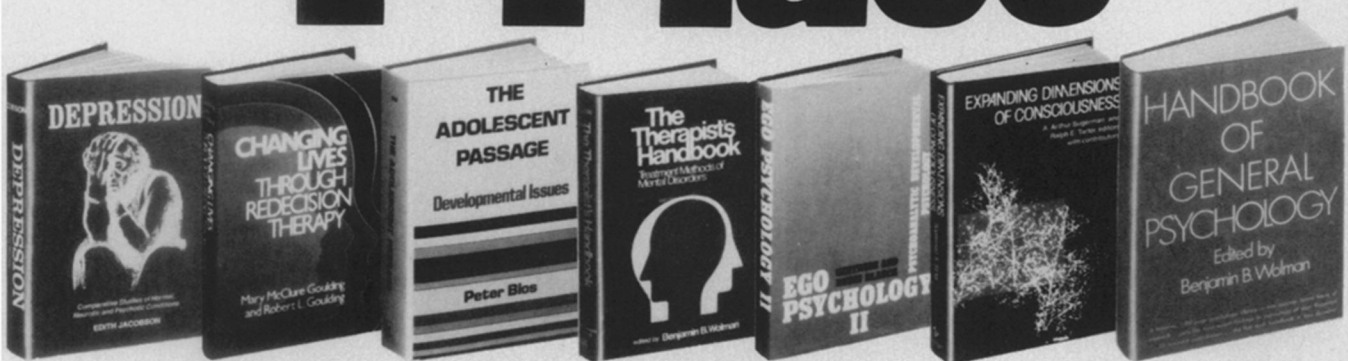
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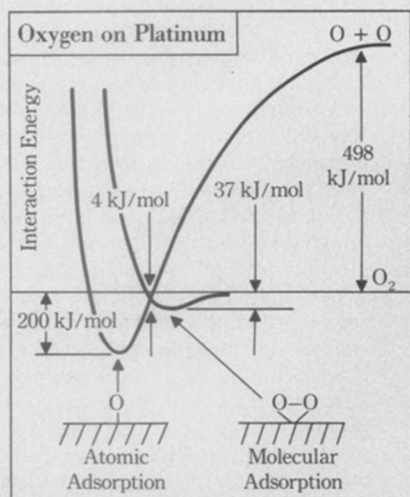
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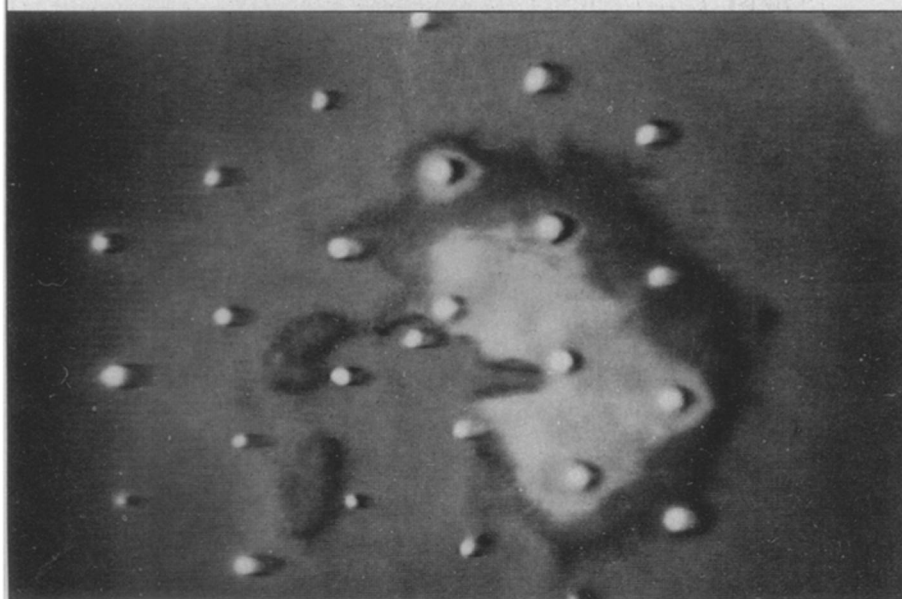
# The Atomic Arrangement

*In a recent experiment, scientists at the General Motors Research Laboratories studied changes in chemical bonding during the dissociation of oxygen molecules on platinum. Preliminary surface work has explored an interesting new phenomenon: the mechanism of oxygen dissociation over a wide range of temperatures.*



*A simplified schematic illustrating the reaction potential energy surface for oxygen-adsorption on a close-packed platinum surface.*

*An electron diffraction pattern which shows diffraction patterns from an oxygen-covered hexagonally close-packed platinum surface at 0° C.*



**U**NDER what conditions will oxygen molecules dissociate into single atoms on a platinum surface? What is the mechanism for oxygen dissociation? Those are the kinds of questions that Dr. John Gland and his colleagues at the General Motors Research Laboratories are investigating to get a better understanding of the chemistry behind catalysis.

Their work has valuable practical implications for the automotive field, where catalysis is used to remove harmful emissions from automobile exhaust. Most cars built in the U.S. use catalytic converters filled with beads containing platinum to chemically transform carbon monoxide and unburned hydrocarbons into harmless CO<sub>2</sub> and water.

While it has long been known that catalysts are an effective way to

convert these gases, little is known about precisely why and in what order the basic atomic reactions occur.

In seeking answers to these questions, surface chemists study the elemental composition and geometric arrangement of atoms in the first few atomic layers of the surface and the means by which atoms and molecules from the gas phase bond to the surface.

In his most recent work, Dr. Gland has been studying the adsorption and desorption of oxygen on platinum single-crystal surfaces. This is important because oxygen is the agent that must be adsorbed on the surface to react with carbon monoxide and hydrocarbons to convert them to CO<sub>2</sub>.

The experiments were conducted in a stainless steel ultrahigh vacuum system equipped with an electron energy analyzer and a mass spectrometer. The electron energy analyzer allows one to measure the concentration and character of the oxygen adsorbed on the platinum surface. The mass spectrometer is used to measure the desorption of O<sub>2</sub> as the platinum surface is heated. Mathematical analysis of the desorption process allows one to characterize the chemical bond between the oxygen and the platinum surface.

In these experiments, the platinum surface is covered with oxygen at the extremely low temperature of -179°C (almost the temperature of liquid nitrogen) by exposing it to gaseous O<sub>2</sub> molecules. The oxygen remaining in the gas phase is pumped away, and then the desorp-

tion of oxygen from the surface is observed as the platinum crystal is gradually heated to 1000°C.

The oxygen was found to desorb from the surface in two distinctly different temperature regimes—part at -125°C and the rest at about 425°C. By using the oxygen-18 isotope, it was established that the low temperature desorption represents oxygen that was adsorbed on the surface in a molecular form while the higher temperature desorption corresponds to oxygen adsorbed in the atomic form. From an analysis of the desorption process, it was possible to establish the complete energetics. Oxygen molecules from the gas phase strike the surface and are weakly bound (37 kJ/mol). The adsorbed oxygen molecule can either desorb into the gas phase (37 kJ/mol) or dissociate into atoms (33 kJ/mol). The atoms are bonded very strongly (200 kJ/mol) to the surface.

**F**ROM the desorption analysis, it was also possible to deduce the mechanism for the dissociation process. The interesting conclusion that results is that the formation of O atoms on platinum is a two-step process—oxygen is adsorbed in a molecular state and then dissociates to form atoms.

The GM scientists were most interested in learning how this adsorbed molecular species is bonded to the platinum surface. Fortunately, another technique was available to determine the bonding. The tech-

nique is called electron energy-loss spectroscopy and is quite new—there are only six or seven such instruments in the world. The measurements not only confirmed the existence of the adsorbed molecular oxygen but showed that it was bound by the transfer of two electrons from the platinum surface into the antibonding  $\pi_g$  orbitals of oxygen. "This was most exciting" said Dr. Gland, "because this is the first time that this type of oxygen bond has been observed on a metal surface.

"We're getting closer and closer to a more specific understanding of catalysis," says Dr. Gland. "The more we learn about simple chemical systems, the better we'll be able to control more complicated systems. That has excellent implications for protecting the environment."

### THE MAN BEHIND THE WORK

Dr. John Gland, 32 years old, is a Senior Research Scientist in surface chemistry at the General Motors Research Laboratories. He heads a group of 7 investigators, 4 with Ph.D.s, all involved in work relating to the basic surface chemistry of catalysis.

A graduate of Wittenberg University in Ohio, Dr. Gland received his Ph.D. in physical chemis-

try at the University of California, Berkeley, in 1973 and joined the General Motors staff that year.

Dr. Gland comments: "I came to GM Labs because I wanted to get in on the ground floor of an exciting new field. The atmosphere here is very open, with lots of cross-pollination among departments. With several hundred people with Ph.D.s here, we've got a lot of human resources to draw on in all the basic sciences.

"Typically, management defines a broad problem, then we're free to tackle the solution in any way we choose. They give us the freedom, equipment and support to get the job done correctly."

In addition to his research, Dr. Gland enjoys backpacking in Wyoming and in the Sierra Nevada Mountains in California.



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