

# The Wetting of Gold and Platinum by Water

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## ABSTRACT

When a sessile drop of pure water is placed on a clean surface of pure polished gold or platinum, it will spread spontaneously over the metal and exhibit a zero contact angle. However, in order to rid surfaces of these metals of adsorbed hydrophobic contaminants, it is necessary to heat them to white-hot temperatures in flowing streams of high-purity hydrogen, nitrogen, argon, krypton, or air. Such a treatment gives surfaces which are completely wetted by pure water and exhibit zero contact angles in gases freed from trace contaminants by an adsorbent cold trap. However, prolonged exposure of the metals to these gases renders them nonwetting because of the gradual adsorption of trace hydrophobic contaminants present in the gas streams.

## PROBLEM STATUS

This is an interim report; work is continuing on the problem.

## AUTHORIZATION

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## THE WETTING OF GOLD AND PLATINUM BY WATER

## INTRODUCTION

There has been a fifty-year history of difficulties in determining the surface properties of inorganic solids in the absence of organic contaminating films. The contaminant problem has been especially important in fundamental studies of the wetting, adhesive, and frictional properties of such solids because of the well-demonstrated fact that an adsorbed monolayer of an organic compound can cause major changes. Much of the early research in these properties was vitiated by inadequate attention to this problem. N.K. Adam (1) briefly summarized in 1941 the state of knowledge of the spreading of ordinary liquids on inorganic solids with the statement, "Most organic liquids and water form zero contact angles with clean glass and silica, also with clean metallic surfaces." Authoritative reviews by Sutherland and Wark (2) and Gaudin (3) covering the field of ore flotation reveal that thoroughly clean surfaces of nearly all minerals, including oxides and sulfides, have zero or small contact angles. The later extensive investigation of the wetting of high-energy surfaces by Fox, Hare, and Zisman (4) led to the conclusion that all pure liquids spread spontaneously on high-energy surfaces unless they belong to the special class of organic liquids which are either "autophobic" or are hydrolyzed on contact with the solid surface. From their work as an important special case, it can be concluded that pure water will spread on any high-energy surface which is free from adsorbed organic films.

Prolonged exposure of a clean (i.e., organic-free) hydrophilic solid surface to any atmosphere other than a most carefully purified gas will result in the surface exhibiting water contact angles of from a few degrees up to  $90^\circ$ , depending on the nature of the organic contaminant present and its surface concentration. As recently demonstrated (5), even nonpolar organic vapors such as those of pure hexane or benzene can adsorb on clean metal surfaces, including gold and platinum; and the last monolayer of the resulting film will not evaporate from the surface unless the temperature of the metal is raised by  $100^\circ\text{C}$ . The apparent irreversibility encountered arises from polarization of the adsorbed vapor by the electrostatic field emanating from the metal surface. Such monolayers are usually adsorbed with the molecules lying as flat as possible in the surface; the condensed monolayer causes the water contact angle to be from  $55^\circ$  to  $75^\circ$ , depending on the metal surface.

However, in the past twelve years a few investigators have reported results to the contrary. Special emphasis was given in their experiments to such readily cleaned metals as gold and platinum. F.E. Bartell and J.T. Smith (6) obtained advancing water contact angles on gold in water vapor or air of  $7^\circ \pm 1^\circ$ . More recently White's (7) experiments on the contact angle of condensed water vapor on gold in a Pyrex and metal system led him to conclude that an unoxidized surface of pure gold is hydrophobic, and only when there is a surface oxide present is there a zero water contact angle. Erb (8) also measured the contact angle of water on pure gold under continuous condensing conditions in pure steam and observed contact angles of  $55^\circ$  to  $85^\circ$ . He concluded that physically adsorbed organic contamination could be removed in his apparatus within a few hours and chemisorbed contamination within a few days. After several thousand hours of continuous operation in his apparatus, the metals should have been clean; yet gold continued to exhibit an advancing contact angle of from  $50^\circ$  to  $90^\circ$ . He concluded that gold also needed surface oxidation to exhibit a zero contact angle with water.

Because of these recently published observations and opinions, we have re-examined the wetting of pure gold and platinum surfaces in a much simpler system by first reducing the metals in extremely pure flowing hydrogen gas streams at high temperatures and then measuring the water contact angle of the cooled surface at different times after each heat treatment. We have also conducted similar experiments in atmospheres of other pure gases. The results are summarized here.

## EXPERIMENTAL TECHNIQUES

The same procedures used in our previous study (5) of the changes caused in the contact potentials of metals by adsorbed nonpolar compounds were also followed here in the first stage of preparing the gold and platinum specimens. Three gold specimens were employed from the following sources: (a) Englehard Industries, 99.99% purity; (b) Handy and Hartman, 99.9999% purity; and (c) National Bureau of Standards electrolytic gold, kindly supplied by Dr. E. Wichers, and later molded into an ingot using special molybdenum crucibles in an inert argon atmosphere by E.J. Chapin of the Metallurgy Division of NRL. The platinum used was supplied by Englehard Industries and was 99.99% pure. Each metal specimen was abraded, polished, and dried as in the previous work (5). Metal specimens were 3/8 in. in diameter and 1/16 in. thick; each had been fabricated with an integral pin of the same material 1/10 in. in diameter and 1/4 in. long on its back surface in order to facilitate the mechanical handling of the specimen and to be sure that the free surface would not be touched during manipulations.

Each metal specimen to be studied was next introduced into the glass system shown in Fig. 1. In this system the only nonglass materials present between the gas-adsorbent system and the specimen chamber were two small, clean Teflon connecting collars in the gas stream. The simple, compact specimen chamber (volume only 50 ml) was devised, because it was necessary that each piece of glassware in it be capable of being disassembled and cleaned by acid washing and baking just before each experiment, in order to avoid the evolution of organic contaminants by the interior wall to contaminate the gas stream. The cold trap and adsorbent system cooled by liquid nitrogen is of the same design used successfully by the National Bureau of Standards (9) in the purification of helium gas; it contained Fisher activated coconut charcoal adsorbent, 6 to 14 mesh, which was outgassed frequently at 320°C and  $10^{-4}$  mm Hg. Without this cold trap to remove the last traces of organic contaminants in the gas stream, appreciable contact angles were encountered on the metal specimens even when the purest obtainable commercial hydrogen gas was used. Hydrogen cylinder gas used was Linde Company research grade having the following analysis of impurities: oxygen < 1 ppm, nitrogen < 5 ppm, carbon monoxide < 1 ppm, carbon dioxide < 1 ppm, argon < 1 ppm, hydrocarbons < 1 ppm, methane < 1 ppm, and moisture < 1 ppm.

After each metal specimen was polished and cleaned as previously described, it was placed in the specimen chamber on the quartz tube holder. A gas flow rate of 150 ml/min at 15°C was allowed to purge the specimen chamber for 30 min. Then the metal specimen was heated with a high-frequency induction heater for 3 min while remaining in the flowing gas stream. The specimen was next allowed to cool to the temperature of the flowing gas stream, which usually required 10 min. After that the ground-glass cap of the specimen chamber was removed, a small sessile drop of clean pure water was touched to the polished metal surface by means of a previously flame-cleaned platinum wire, and the chamber was closed again by replacing the cap. This operation required about 1 sec. The test water was obtained by passing the effluent of a Stokes wall still through an Amersil Bi-Distillation unit of fused quartz. If the water drop did not spread completely over all of the plane surface of the metal disk, its contact angle was measured by means of a telescope fitted with a goniometer eyepiece (10). No attempt was made to distinguish between an advancing and a receding contact angle.

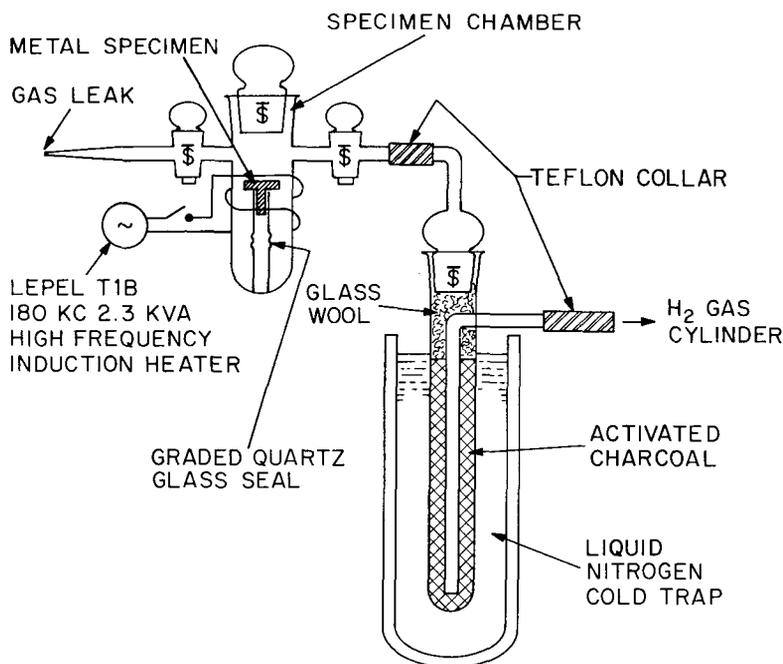


Fig. 1 - Gas purification apparatus and metal specimen heat cell

## EXPERIMENTAL RESULTS

### Results of Heating and Cooling Metal Specimens in a Hydrogen Stream

The output power of the induction heater was adjusted to heat the metal specimen to an initial observable dull red color. Results on the wettability were erratic with both gold and platinum. Occasionally, each metal was completely wet by the water drop and showed zero contact angles. In repeat experiments the water drop sometimes did not completely wet either metal, and contact angles between  $4^\circ$  and  $8^\circ$  were observed. Increasing the time of heating to a dull red from 3 min to as long as 30 min did not improve reliability. Increasing the hydrogen flow rate from 150 to 500 ml/min also produced no observable change in the results of repeated experiments. Reducing the hydrogen flow rate to zero by closing the stopcocks on either side of the specimen chamber increased the contact angles to about  $6^\circ$  to  $13^\circ$ , and no zero contact angles were observed.

The metals were next heated until white hot, and great care had to be exercised with the gold in order to prevent it from melting. In fact, the output coupling of the induction heater was increased until the surface of the gold was observed to begin melting; then the output coupling was reduced just below the setting where melting of the gold would not occur under continuous prolonged heating. After the 3-min heat treatment followed by quick cooling in a 150 ml/min hydrogen stream, the platinum and the three gold specimens always exhibited zero water contact angles. When the hydrogen flow rate was cut off, water contact angles of about  $6^\circ$  to  $13^\circ$  were again observed; however, in three of these experimental runs zero contact angles were still obtained. Longer metal heating times did not change the results.

From 10 to 15 repeated experiments were made on each one of the platinum and gold specimens. If a completely wetting water film was allowed to evaporate in the 150 ml/min

dry hydrogen stream, after 6 min the film began to recede as a flat lens from the edges of the metal surfaces. These water lenses showed unmeasurably small contact angles ( $<1^\circ$ ), and optical interference colors could be observed beyond the edges of the evaporating flat water lens by reflecting light from a white paper card placed behind the specimen chamber. The light source was either a focused microscope lamp with a blue filter over its object lens or a Gates sodium-vapor lamp.

In other experiments after the white-hot heat treatment of the metal specimen, it was allowed to remain in the flowing hydrogen stream for extended times beyond the 10 min required for cooling off. After 30 min in the hydrogen stream, small water contact angles began to be observed, and after 60 min contact angles of  $5^\circ$  to  $11^\circ$  were observed on gold and on platinum specimens. Experiments lasting longer were not conducted, in order to conserve the supply of research-grade hydrogen.

#### Results of Heating Specimens in Room Air and in Navy-Grade Water-Pumped Breathing Air

For comparison with the preceding results observed in a pure hydrogen atmosphere, the ground-glass cap on the specimen chamber was removed, and the metal specimen was heated to a white heat while being exposed to the laboratory air. In no case was complete wetting by water obtained after this treatment; contact angles varying from  $6^\circ$  to  $21^\circ$  were measured on successive days of the experiment. There were no significant differences in experiments with gold and platinum.

In another experiment, a cylinder of Navy-stores, water-pumped breathing air was substituted for the Linde research-grade hydrogen gas cylinder. This air was also run through the cold gas-adsorption trap and the closed specimen chamber at a flow rate of 150 ml/min; an acetone/dry-ice mixture was used as a refrigerant instead of the liquid nitrogen. After heating the metal specimen to a white heat and then cooling it, the results of placing drops of water on both the gold and platinum metals were practically identical with those observed in the hydrogen gas reduction treatment. These experiments were run for as long as 120 min after heating the specimens, and zero contact angles were still obtained. Since sufficient quantities of breathing air were available, elapsed time runs of 24 hours were also made; after such long exposures to the air, the gold and platinum specimens gradually exhibited increasing water contact angles which attained values of from  $24^\circ$  to  $30^\circ$  because of the accumulated adsorption on the clean metal of hydrophobic contamination from the air stream. Thus, even after passage through the gas-adsorption trap, cooled by acetone and dry ice, the air still contained a trace of organic contamination.

#### Results of Heating Specimens in High-Purity Inert Gases

Further experiments were performed using cylinders of the following Linde Company research-grade gases: krypton, neon, argon, and nitrogen. The procedures were identical with those employed using hydrogen, except that a mixture of acetone and dry ice was used as a refrigerant in order to prevent these gases from liquifying in the cold trap. The output coupling of the induction heater also had to be decreased, since the inert gases have lower thermal conductivities than hydrogen; consequently, the efficiency of the induction heater was increased. Complete wetting and zero contact angles could always be obtained with white-hot heating of the gold and platinum metals. At dull red heating, just as with the hydrogen stream, finite contact angles were observed with each of these gases. The exposure times for which spontaneous wetting could be maintained after the heat treatment of the metals varied from 30 to 120 min. The concentrations of impurities in these inert gases (as specified by the supplier) were close to those present in the cylinder of research-grade hydrogen.

## DISCUSSION

According to Kubaschewski and Hopkins (11), although platinum is considered to be a noble metal and in bulk is not easily converted into oxides, a strongly adsorbed layer of oxygen is formed during exposure to air. Even at temperatures above 1200°C, repeated hydrogen reduction and vacuum outgassing are required in order to remove this adsorbed oxygen film. On the other hand, recent papers by Mair et al. (12,13,14) describe low-energy electron diffraction, electron microscopy, and x-ray emission experiments which indicate that heating gold in oxygen does not produce stable oxides on the surface at room temperature, and heating it to about 900°C in oxygen can remove contamination more readily than heating in other gases.

Thus, the high-temperature reduction of our very pure gold specimens in cleaned-up research-grade hydrogen was an assurance that an oxide was not present on the surface. Certainly no gross anodic oxide as mentioned by White (7) and referred to by Erb (8) could have been present on these gold surfaces. Even in the case of the platinum specimen, the high-temperature hydrogen reduction treatment used made very improbable the presence of any significant oxide or adsorbed oxygen.

The inconsistent wetting results obtained with lower, dull red temperatures was somewhat surprising. However, Wheeler (15) and Kaminsky (16) state that the temperature required to guarantee an adequate thermal cleaning of a metal surface can be estimated roughly as 20 times the binding energy in kcal/mole of the layer of impurity atoms on the surface. Thus, according to Kaminsky (16), a temperature of 1770°C would be required to desorb ethene from tungsten.

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