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SODIUM BORATE GLASSES and PLATINUM OR GOLD u WETTING and REACTIONS

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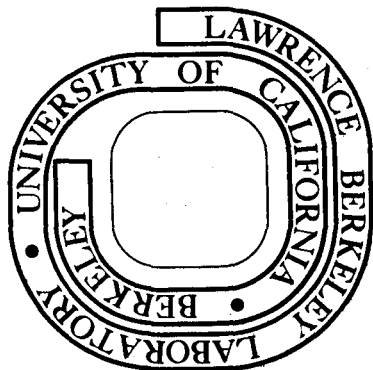
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ABSTRACT

Sessile drop experiments were conducted to analyze the wetting characteristics of molten B_2O_3 and sodium borate glass on platinum and gold. In the absence of carbonaceous gases, the contact angle was small and invarient over the ambient pressure range of 10^{-4} torr to one atmosphere at temperatures of 700 to 1000°C. Adsorption of carbon at the metal surface decreased the solid/vapor surface energy and increased the contact angle. The carbon was removed by oxidation. A thermo-dynamic analysis of this reaction for the platinum-carbon system yielded a bonding energy of 62 kcal/mol for the adsorbed carbon bond.

Absorption of water vapor by the glass resulted in a reaction at the solid/liquid interface, spreading of the glass on the substrate, and adherence. The possible reactions that can occur are examined.

I. INTRODUCTION

Wetting of platinum and gold by silicate glasses has been studied
in this laboratory.[1] Anomalous behavior was reported for platinum;
Volpe, Fulrath and Pask[2] observed a decrease in contact angle when
changing the ambient atmosphere from vacuum to oxygen. Their explanation
for this behavior was that oxygen diffused along the solid/liquid inter-
face which reduced the solid/liquid interfacial energy, $\gamma_{s\ell}$. However,
since those experiments, low energy electron diffraction (LEED) investi-
gations by Somorjai[3] revealed that carbon is readily adsorbed on platinum
or gold surfaces. The carbon could be oxidized and removed at elevated
temperatures by increasing the partial pressure of oxygen to a critical
value. The resulting increase of the solid/vapor interfacial energy,
γ_{sv}, could cause the observed decrease in contact angle. This study was
thus undertaken. Utilization of borate glasses allowed experimentation
at lower temperatures than those necessary with silicate glasses because
of viscosity differences.

II. EXPERIMENTAL PROCEDURE

(1) Glass

Three borate glasses were used: anhydrous boric acid[*] - 100% B_2O_3,
a solder glass[†] - 94% B_2O_3 and 6% Na_2O, and borax glass[*] - 69% B_2O_3 and
31% Na_2O. Compositions are listed in Table I. The values for the
solder glass were determined by spectroscopic methods; those for the
borax glass and boric acid were reported by U. S. Borax Company.

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*U.S. Borax Chemical Co.
†Dr. C. A. Levine, Dow Chemical Co., Walnut Creek, Calif.

All of the as-received glasses contained water vapor. Franz[4] reported the solubility of water in alkali borate glasses at 900°C: in B_2O_3, 0.6 wt% (2.2 mol%); in borate glass with 6.0 wt% or 5.5 mol% soda, 0.45 wt% (1.7 mol%); in borax, 31 wt% or 29 mol% soda, 0.28 wt% (1.0 mol%). These glasses were vacuum outgassed in platinum crucibles at 1000°C and 1×10^{-4} torr. Both outgassed and as-received glasses were stored in evacuated dessicators. Unless it was used immediately after outgassing, the 100% B_2O_3 glass always bubbled to a small degree when remelted in a vacuum environment. The soda containing glasses did not absorb water as readily during storage. Although the effect of hydroxyl ions on rheological properties is known,[5] there is no report of the water containing glasses taking part in a redox reaction with a substrate metal.

(2) Metals

Platinum and gold were of 99.99% purity.[*] The platinum foil (0.005 in. thick) and the gold foil (0.010 in. thick) were cut into 0.5 x 0.5 in. specimens. The specimens were ultrasonically degreased in tetrachloroethane, then in isopropyl alcohol. The platinum was annealed at 1450°C in air for 2 h and stored in plastic boxes. Immediately before use the specimen was heated at 1200°C for 10 min, air quenched to room temperature, and then introduced into the testing apparatus. The gold specimens were annealed in air at 1000°C for 10 h and stored in plastic boxes until used. Before performing a test, they

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[*]LBL Berleley

were preheated in air in the apparatus. The heat treatments were per-
formed to oxidize the sorbed carbon.

(3) Experimental Testing Apparatus

Controlled atmosphere experiments were conducted in a one in. dia-
meter fused silica tube furnace (Fig. 1). The tube was fitted with an
optically flat end for viewing and a quarter in. tubulation for gas
input. The other end was fitted with a half inch silica tubulation for
the attachment of the ion gauge and a spherical ground silica joint
(female). The male stainless steel spherical joint, equipped with a
thermocouple gauge, was soldered to a liquid nitrogen cold trap made of
copper. The cold trap was connected by five feet of three quarter inch
rubber vacuum hose to a valve manifold and diffusion pump. The input
gas tubulation was connected to a liquid nitrogen cold trap in line with
a leak valve and with a calcium sulfate dessicator. The dessicator main-
tained a $-100°F$ dew point (equivalent to 3 parts per million water) in
the flowing gas (typically air). A clam shell furnace enclosed the
center of the silica tube and heated a five inch length to a maximum
temperature of $1200°C$.

For experiments designed for carbon contamination of the metal
specimens the cold traps were not activated. The vacuum hose evolved
organic vapor, probably from the plasticizers in the hose. These vapors
coupled with some backstreaming from the diffusion pump were sufficient
to contaminate the platinum and gold surfaces with carbon. Most in-
teresting is the fact that the surface energy of the platinum, or gold,
substrate was always reduced by the same amount as indicated by the
wetting contact angles. This was repeatable and occurred regardless of

the time allowed (a few minutes to 18 h). The major source of carbon appeared to be gaseous hydrocarbons from the vacuum hose (plasticizers). These vapors decomposed to carbon and hydrogen gas on the substrate surface which apparently occurred quickly to a certain carbon concentration. Lambert et al.[6] have reported the growth of more than a monolayer of amorphous carbon on platinum by this hydrocarbon contamination method.

Contact angle measurements were made by observing the glass drop, illuminated from behind via a mirror, through a telescope equipped with a filar micrometer eyepiece. Angles were measured directly using a protactor connected to the eyepiece. In a few cases the accuracy of the method was checked by calculating the contact angle from values of the height and width of the drop assuming it to be part of a sphere. The estimated precision of the reported data is 2° except below values of 10° where the error was ± 3°.

(4) Gas Pressure Variation and Contamination Procedure

Heat treated platinum substrates with a 50 to 100 milligram piece of outgassed glass were placed on a ceramic (alumina 99%) support. This sessile drop assembly was then placed in the fused silica tube furnace. The male spherical joint was thermally linked to the cold trap. During operation of the trap, the metal glass joint was maintained at approximately 10°C or lower which reduced the vapor pressure of the silicon vacuum grease. When cold trapped, the grease at the spherical joint and that at the coupling to the ion gauge were the only sources of grease contamination directly accessible to the hot zone in the silica tube. The spherical joint was heated by infrared radiation from the hot zone; the ion gauge couple was not. The carbon-free experiments

indicated that these sites were not a significant source of contamination. The platinum would remain carbon free for as long as two hours when cold trapped. Without the cold traps, carbon contamination occurred rapidly. The ambient pressure was controlled by regulation of the leak valve. The partial pressure of oxygen was assumed to be approximately one-fifth of the total ambient pressure.

III. RESULTS AND DISCUSSION

(1) Wetting of Platinum

The data for all three borate glasses on platinum at 900°C were identical; it was thus concluded that the soda content of the glass does not significantly change $\gamma_{s\ell}$ or $\gamma_{\ell v}$ of the molten glass. The data for sessile drop contact angle vs ambient pressures from 1×10^{-4} torr to one atmosphere at temperatures of 700 to 1000°C for B_2O_3 on platinum under carbon contamination conditions are shown in Fig. 2. So many points were generated in the experiments that for clarity only average lines are shown in the figure.

For carbon free conditions the contact angle was invarient at $6° \pm 3°$ over the entire pressure range. This result indicates that in this test pressure range there is no oxygen or no additional oxygen adsorbed. The most active adsorption sites, kinks on a step, may already be filled at oxygen pressures less than 0.2×10^{-4} torr. Moreover, adsorption at other sites would require ambient pressures greater than one atmosphere.

As the pressure is increased, the carbon contaminated platinum shows a contact angle of 68° which drops precipitously to 6° at a critical pressure where the adsorbed carbon is oxidized. The oxidation

occurs at one value of pressure at a given temperature, which indicates that all the carbon is adsorbed at similar sites. On decreasing the pressure, a hysteresis effect was noted at 700 and 800°C. The temperature dependence of the critical pressure is shown in Fig. 3.

It can be assumed that the precipitous change in contact angle was due to a change in γ_{sv} and that $\gamma_{\ell v}$ and $\gamma_{s\ell}$ remain unchanged. Young's equation can be used to show the relationship of the interfacial energies for a system in which no bulk chemical reactions occur:

$$\gamma_{sv} - \gamma_{s\ell} = \gamma_{\ell v} \cos \theta$$

where θ is the contact angle. If at 900°C $\gamma_{\ell v}$ for the glass is 80 ergs/cm^2 [7] and the clean platinum has a γ_{sv} of 2000,[8] then at $\theta = 6°$ $\gamma_{s\ell} = 1920 \pm 1$ ergs/cm^2. For the carbon contaminated platinum where $\theta = 68°$ γ_{sv} can then be calculated to be 1970 $\pm$ ergs/cm^2. So the adsorbed carbon reduces the surface energy of the platinum about 50 ergs/cm^2. It is possible to calculate approximately the amount of carbon that is responsible for this reduction in γ_{sv}. The oxidation reaction and equilibrium constant are

$$C_{ads} + \frac{1}{2} O_2(g) = CO(g)$$
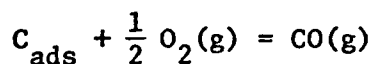
$$K_{eq} = \frac{P_{CO}}{\left(P_{O_2}\right)^{1/2} \cdot a_C}$$

where the partial pressures of O_2 and CO have been substituted for their activities as the gases are assumed ideal. We can estimate the activity of the adsorbed carbon by the following procedure.[9] The reaction occurred in slow flowing air at a measured pressure; at equilibrium the pressure of CO in the vicinity of the platinum was twice that of the oxygen. Further, if we assume the equilibrium constant for bulk carbon being oxidized to carbon monoxide to be applicable,[10] then at $1200°K$, $K_{eq} = 10^{9.479}$, $P_{O_2} = 10\mu = 1.316 \times 10^{-5}$ atm, $P_{CO} = 2.632 \times 10^{-5}$ atm, and $a_C = 2.4 \times 10^{-12}$ where $a_C = 1$ for a monolayer. Now, using Gibb's adsorption equation

$$d\gamma = - \Gamma RT\, d\ln P$$

where Γ is the adsorption density of the gas on the metal, the approximation for the amount of carbon responsible for the reduction of the platinum surface energy is 1.15×10^{13} atom/cm^2. On a platinum (111) surface there are a total of 1.5×10^{15} atom/cm^2.

Using the calculated carbon activity and the critical pressure-temperature dependence (Fig. 3) an approximation for the change in enthalpy of the reaction can be made:

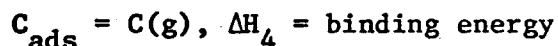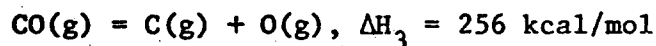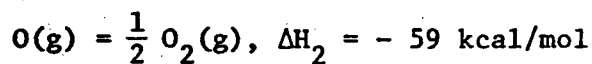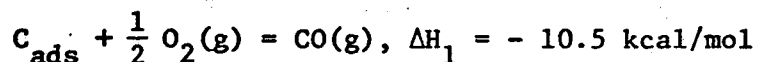$$\Delta H - T\Delta S = - RT\, \ln(K_{eq})$$

$$- \Delta H/RT + \Delta S/R = 1/2\, \ln P_{O_2} + \ln 2 - \ln (2.4 \times 10^{-12})$$

$$- 2 \Delta H/RT + 2\Delta S/R + 2(27.63) = \ln P_{O_2}$$

$$- 2 \Delta H/R = \text{slope of plot} = 10619$$

$$\Delta H = - 10.5 \text{ kcal/mol}$$

The binding energy of the carbon to the platinum can be calculated as follows:

$$C_{ads} + \frac{1}{2} O_2(g) = CO(g), \quad \Delta H_1 = - 10.5 \text{ kcal/mol}$$

$$O(g) = \frac{1}{2} O_2(g), \quad \Delta H_2 = - 59 \text{ kcal/mol}$$

$$CO(g) = C(g) + O(g), \quad \Delta H_3 = 256 \text{ kcal/mol}$$

$$C_{ads} = C(g), \quad \Delta H_4 = \text{binding energy}$$

$$\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3 = 186.5 \text{ kcal/mol}$$

The coordination of the carbon to platinum is assumed to be threefold corresponding to adsorption on a terrace. The experimental evidence indicates that the adsorption sites are identical in binding energy. Thus, the binding energy per platinum atom is 62 ± 1 kcal/mol.

A comment is in order concerning the apparent kinetic effect that takes place in the oxidation of the adsorbed carbon. From thermodynamic considerations the reaction would be expected to proceed stepwise. Experimentally, however, the carbon is apparently oxidized to completion

at a given temperature since an increase in temperature results in no
change of the sessile drop contact angle. This kinetic effect was also
noted by Somorjai.[11]

(2) Wetting of Gold

Similar behavior was observed with gold as a substrate. Contact
angle vs ambient pressures for B_2O_3 at 900°C are shown in Fig. 4.
Annealed or clean gold indicated a constant contact angle at all ambient
pressures. The pressure required to oxidize carbon at 900°C was higher
than that for platinum; hysteresis was also present.

The pressure-temperature dependence could not be accurately measured
since there was considerable scatter. It is postulated that at the test
temperatures a sufficient amount of carbon is absorbed into the bulk to
effect the equilibrium between the rates of adsorption and absorption.
The determination of equilibrium values was thus uncertain. The tempera-
ture pressure data for the oxidation of adsorbed carbon on gold is there-
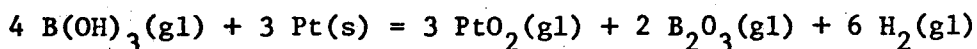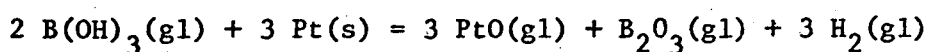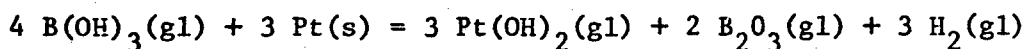fore yet to be determined.

(3) Spreading Due to Reactions

When sodium borate absorbed water from the atmosphere, it spread
rapidly on either substrate. When pure B_2O_3 absorbed water vapor,
spreading was hampered by the viscosity of the glass. The spreading
indicates an interfacial reaction involving the water. The free energy
of this reaction contributes to the lowering of the total interfacial
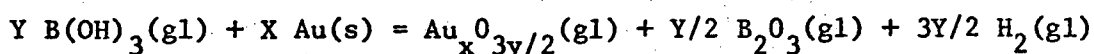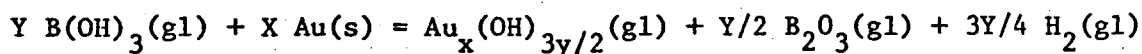solid/liquid energy by a sufficiently large amount to cause spreading.[12]

Development of adherence was associated with spreading. When sodium
borate glass was melted on platinum in the absence of water vapor, it
did not spread and was cleanly and easily removed. When spreading

occurred and the system was immediately cooled to room temperature, the adhesion test of bending the substrate to 90° showed an increased adherence but no attachment of glass particles to the substrate. However, if after spreading the specimen was held at temperature for a few minutes prior to cooling and bending, glass fragments always remained adhering to the substrate. Gold behaved similarly. Adherence of the glass to the gold did not appear to be as strong as that to platinum. The bonding between the glass and the substrate indicates the development of equilibrium compositions at the interface due to an interfacial reaction involving the substrate metal and the chemically absorbed water (hydroxyl ions) in the glass.
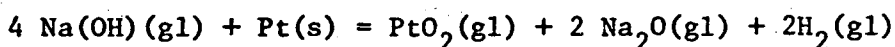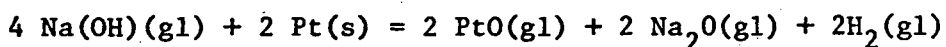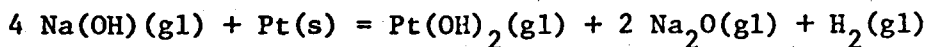
If possible reaction products are $Pt(OH)_2$, PtO or PtO_2, and $Au(OH)_4$ or AuO_x, reactions with B_2O_3 glass would be

$$4 \ B(OH)_3(gl) + 3 \ Pt(s) = 3 \ Pt(OH)_2(gl) + 2 \ B_2O_3(gl) + 3 \ H_2(gl)$$

$$2 \ B(OH)_3(gl) + 3 \ Pt(s) = 3 \ PtO(gl) + B_2O_3(gl) + 3 \ H_2(gl)$$

$$4 \ B(OH)_3(gl) + 3 \ Pt(s) = 3 \ PtO_2(gl) + 2 \ B_2O_3(gl) + 6 \ H_2(gl)$$

and

$$Y \ B(OH)_3(gl) + X \ Au(s) = Au_x(OH)_{3y/2}(gl) + Y/2 \ B_2O_3(gl) + 3Y/4 \ H_2(gl)$$

$$Y \ B(OH)_3(gl) + X \ Au(s) = Au_xO_{3y/2}(gl) + Y/2 \ B_2O_3(gl) + 3Y/2 \ H_2(gl)$$

With sodium borate glass the reactions would be

$$4 \ Na(OH)(gl) + Pt(s) = Pt(OH)_2(gl) + 2 \ Na_2O(gl) + H_2(gl)$$

$$4 \ Na(OH)(gl) + 2 \ Pt(s) = 2 \ PtO(gl) + 2 \ Na_2O(gl) + 2H_2(gl)$$

$$4 \ Na(OH)(gl) + Pt(s) = PtO_2(gl) + 2 \ Na_2O(gl) + 2H_2(gl)$$

and

$$Y \ Na(OH)(gl) + X \ Au(s) = Au_x(OH)_{y/2}(gl) + Y/2 \ Na_2O(gl) + Y/4 \ H_2(gl)$$

$$Y \ Na(OH)(gl) + X \ Au(s) = Au_xO_{y/2}(gl) + Y/2 \ Na_2O(gl) + Y/2 \ H_2(gl)$$
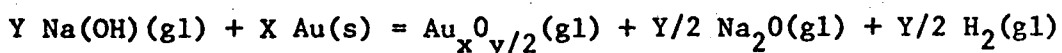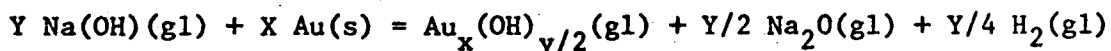
Thermodynamic data for the platinum and gold compounds are not available. Further experimental work is necessary to ascertain which reactions occur. Whichever the reaction product, the formation of and saturation of the interface with a compound of the substrate is consistent with the theory that the interface has to be saturated with a compound that is mutually soluble in both the metal and the glass.[1] It is assumed that this requirement for equilibrium compositions at the interface has been realized because of the low solubilities of the indicated platinum and gold compounds in the glasses and the resulting low flux rates into the glass.

IV. CONCLUSIONS

Borate glass sessile drop experiments on platinum and gold were conducted at a number of temperatures in a changing ambient atmosphere in order to observe any adsorption phenomena. Oxygen adsorption in the range of 10^{-4} torr to 1 atmosphere pressure was not observed on clean platinum or clean gold as indicated by a constant contact angle. Carbon adsorption occurred on both platinum and gold substrates decreasing the solid/vapor energy and causing a dramatic increase in the contact angle. Carbon was removed by oxidation at ambient pressures of about 5×10^{-3} torr to 10^{-1} torr in the temperature range of 700 to 1000°C. It should be noted that ordinary vacuum pressures of about 10^{-5} torr will not affect any adsorbed carbon; thus, it is extremely important to take proper precautions to prevent adsorption of carbon in surface-sensitive experiments.

For the platinum-borate glass system, thermodynamic approximations were made and the reduction in γ_{sv} by adsorbed carbon was calculated to

be 50 ergs/cm^2. The adsorption density was calculated to be 1×10^{13} atoms/cm^2. The enthalpy change for the carbon oxidation reaction was determined to be -11 kcal/mol. This value yielded a binding energy of 186 kcal/mol of adsorbed carbon. Assuming a coordination number of three, a bond energy of 62 kcal/mol is obtained. In predicting this bond energy, Weinberg and Merrill[13] averaged two estimates made from a theoretical model. Their result was 62.5 kcal/mol. The agreement is excellent. Similar experiments with gold yielded inconclusive data.

Conducting the sessile drop experiments in a humid atmosphere results in the glass absorbing water and changing its composition and wetting characteristics. The glass drop, whether B_2O_3 or sodium borate, spread on platinum or gold. The spreading is attributed to an interfacial reaction. The reactions proposed are the reduction of the hydroxyls in the glass structure by platinum or gold, and the formation of the metal hydroxides or oxides which saturate the interface. This condition of chemical bonding resulted in adherence.

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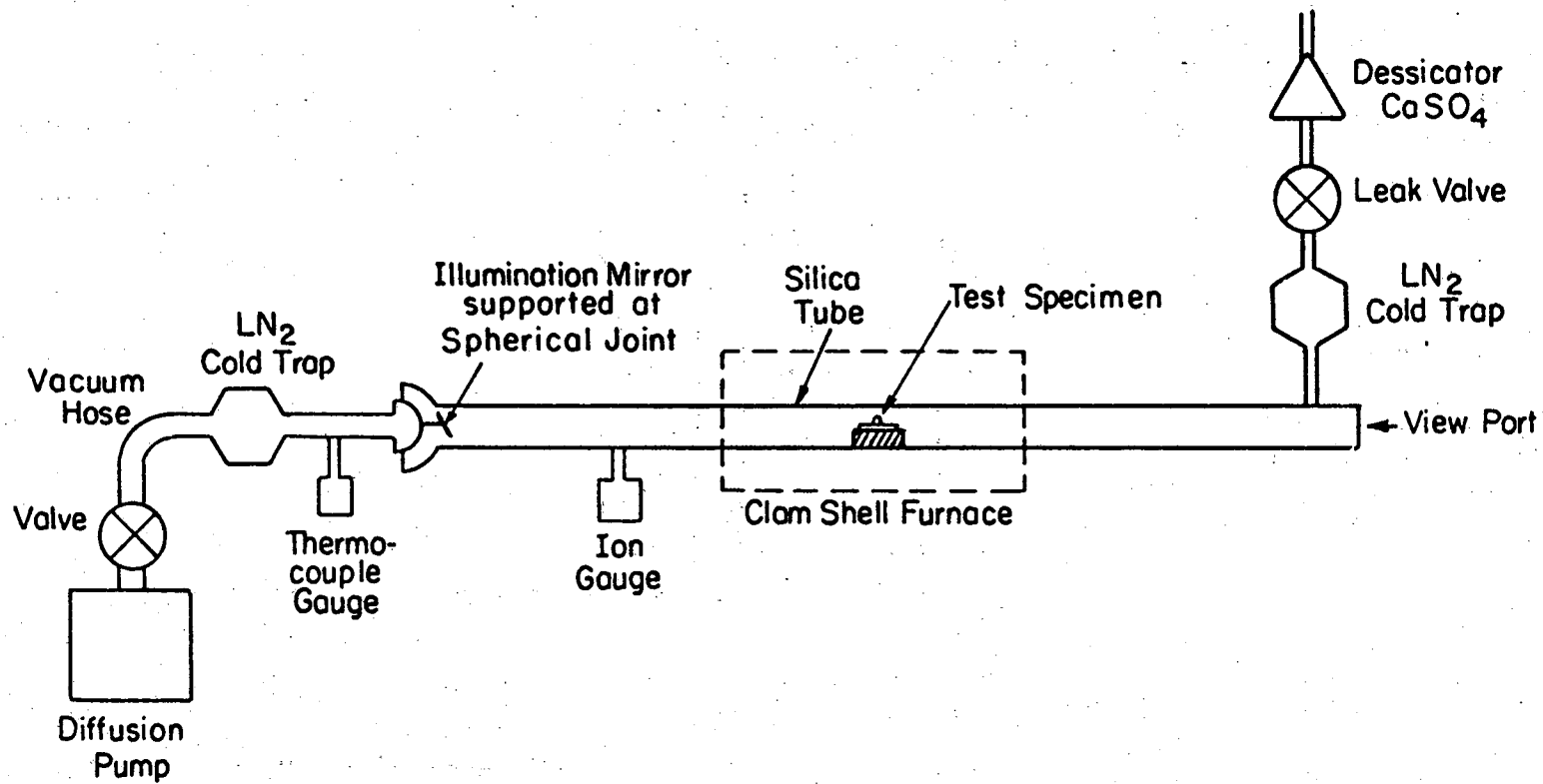Chemistry of Ethylene Adsorbed on Platinum," Sur. Sci. 41 [1] 312-
335 (1974).

Table I. Impurities in Glass

	B_2O_3* wt%	94-6 B_2O_3-Na_2O† wt%	69-31 B_2O_3-Na_2O* wt%
sodium oxide	0.015/0.1	6.0	31
silica	0.07/0.3	0.01	0.12/0.15
alumina	0.005/0.2	0.015	0.04/0.10
iron oxide	0.001/0.10	0.015	0.004/0.01
calcium	0.001/0.05	0.01	0.003/0.02
magnesia	0.007/0.02	0.003	0.05/0.15
sulfate	--	--	0.03/0.41

* Typical values/maximum values. (U.S. Borax Company)
† Semi-quantitative spectrographic analysis determined by American
  Spectrographic Laboratories, Inc., San Francisco, California.

FIGURE CAPTIONS

Fig. 1. Experimental testing apparatus.

Fig. 2. Contact angle vs ambient air pressure for B_2O_3 glass on platinum at 700°, 800°, 900° and 1000°C.

Fig. 3. Critical pressure vs. 1/T for data in Fig. 2.

Fig. 4. Contact angle vs ambient air pressure at 900°C for B_2O_3 glass on gold.

XBL 754-6190

Fig. 1

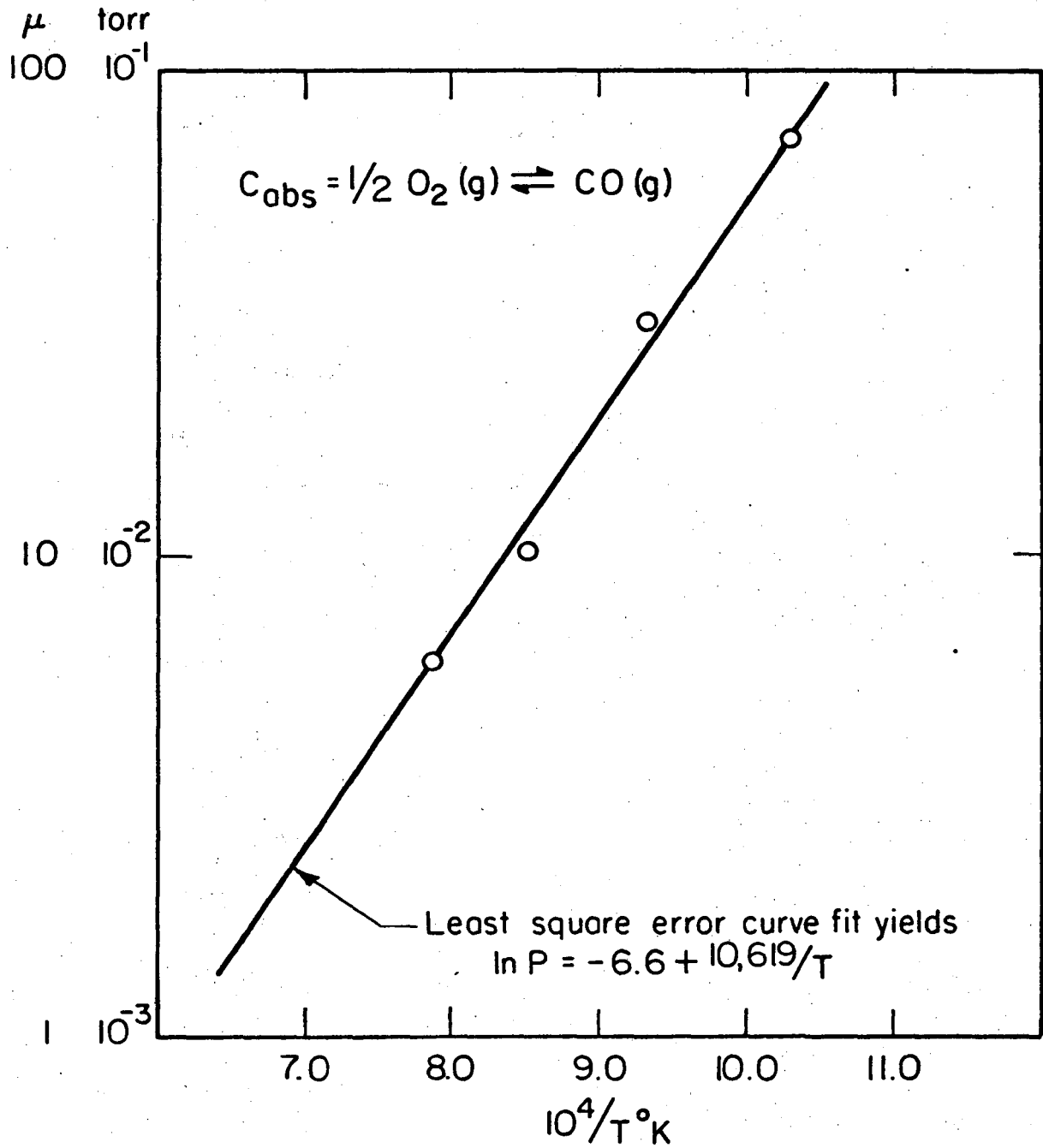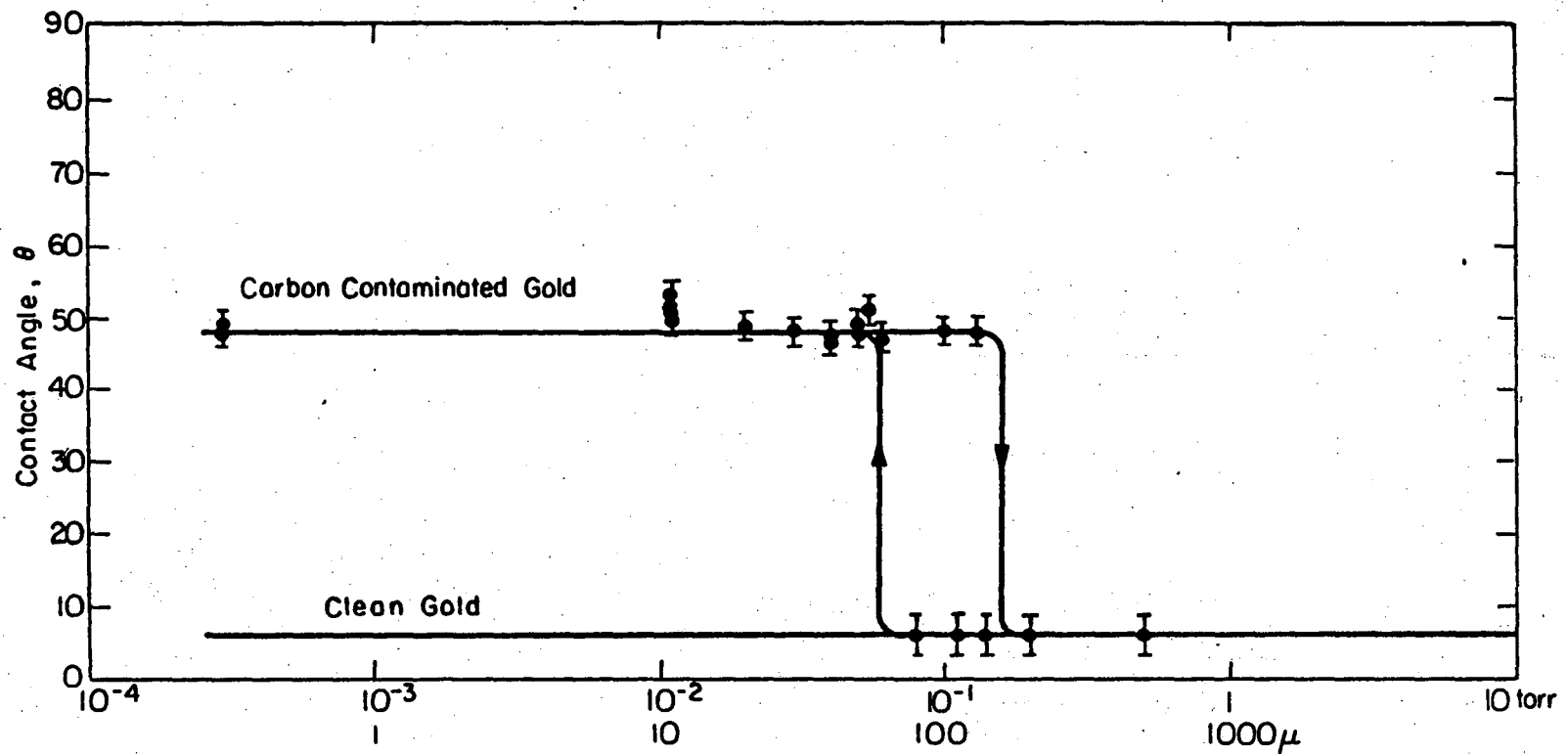XBL 754-6192

Fig. 2

$$C_{abs} = \tfrac{1}{2}\, O_2\,(g) \rightleftharpoons CO\,(g)$$

Least square error curve fit yields
$$\ln P = -6.6 + 10{,}619/T$$

μ torr axis: 100 / 10^{-1}, 10 / 10^{-2}, 1 / 10^{-3}

x-axis: $10^4/T\,°K$
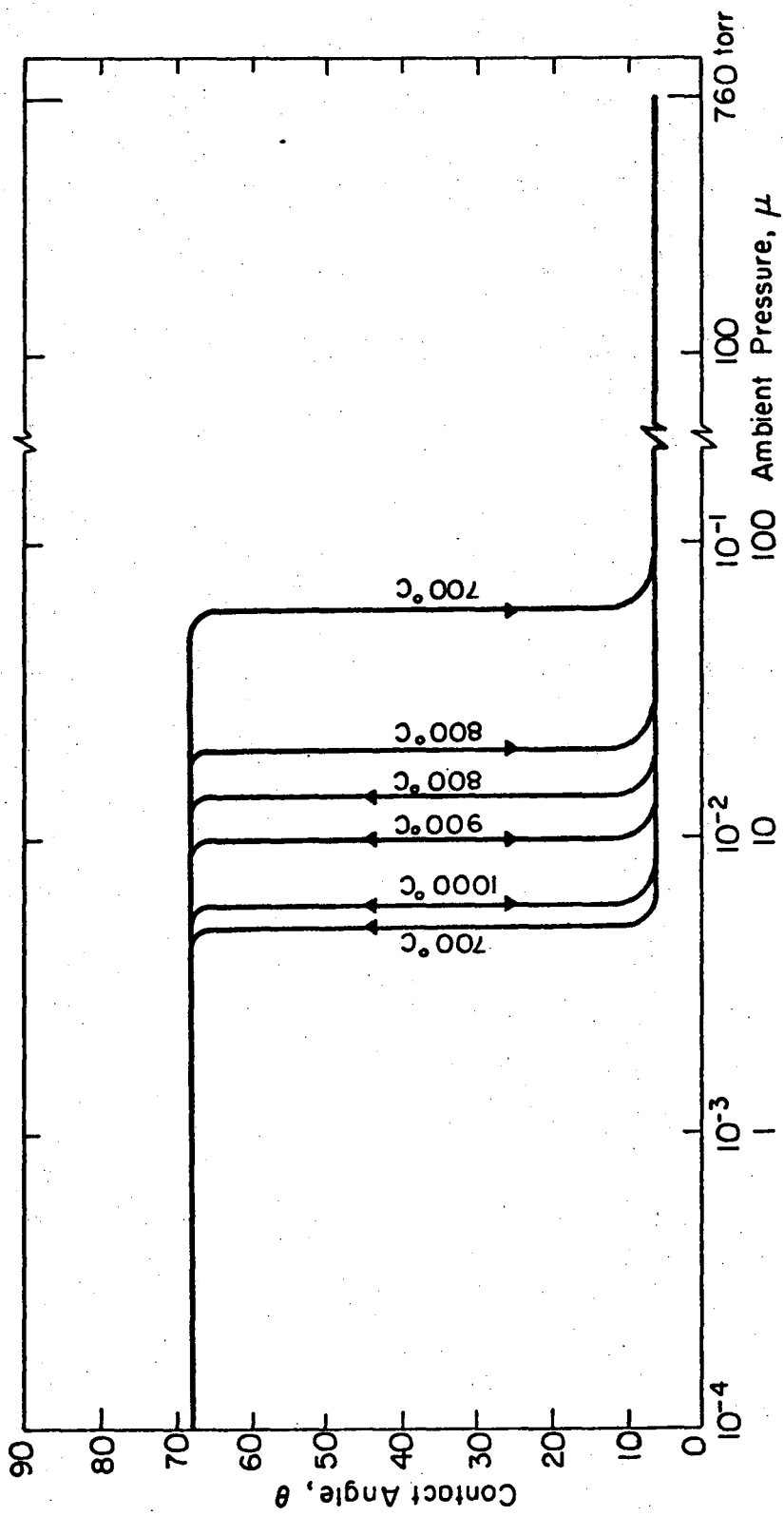
XBL 754-6194

Fig. 3

XBL 754-6193

Fig. 4