

ester molecule into an acetyl and a methoxy radical. The observed products are formed in secondary reactions of these radicals.

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Reproducible Contact Angles on Reproducible Metal Surfaces. I. Contact Angles of Water against Silver and Gold¹

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Data in the literature show that contact angles formed with water drops on paraffin and on other soft hydrophobic solids have been readily reproducible on different samples of the same solid, while contact angles formed with water on relatively hard solids have not been readily reproducible when different samples of the same solid were used. Apparently the surfaces of different samples of a given hard solid did not have identical properties even though the investigator may have used reasonable care in the preparation of these surfaces.

The surface tensions (and the corresponding free surface energies) of soft solids are low and adsorption effects must be low likewise. In contrast, the surface tensions of hard solids are relatively high, adsorption readily occurs and the clean surface of a pure solid may quickly become highly contaminated and thus altered in properties. It seems probable, then, that the failure of previous investigators to obtain reproducible contact angles upon surfaces of given hard solids has been due not so much to defects in methods of measurements as to the fact that the original surfaces of the solid material had become contaminated to different degrees.

Numerous investigators have observed that for a given system the angle of contact was not definite, but that it varied between limits. In some cases the difference between these limits was small, in other cases it was as great as 60° to 90°. The contact angle formed when a liquid was caused to advance over a solid was usually greater than the angle formed when the liquid was caused to recede. This difference in angles has been re-

ferred to as "hysteresis" of contact angles.^{1a-6} Although various explanations have been offered to account for the existence of two different and fairly definite angles for a single three-phase system, no generally accepted explanation has been offered.

The principal objective of the present research was to determine the factors which have been responsible for the difficulties which have been experienced by those who have attempted to obtain reproducible and significant measurements of contact angles. This necessitated the preparation of solid surfaces with reproducible properties, and the development of a procedure for the formation and measurement of contact angles of a system which could be maintained under exact control.

Method of Preparing Solid Surfaces with Reproducible Properties.—In the preparation of the solid surfaces it was deemed desirable to know not only the final treatment history of the solid but also the complete history of the substance as a solid. To accomplish this the solid was formed in vacuum from the vapor phase. The relatively inert metals silver and gold seemed most suitable for study. Films of these metals were formed on Pyrex glass tips by vaporizing the metals in a vacuum of 10⁻⁵ mm. Vaporization of the metal was accomplished by suspending small bent pieces of the pure metal over a tungsten wire coil connected with a 220 volt circuit. The Pyrex tips had previously been polished optically plane. A small capillary hole extended through the tip downward from the center of its surface. After the surface of the tip became coated, it was allowed to cool in the vacuum and was quickly transferred to the contact angle cell just prior to use. Excellent mirror surfaces were obtained with both silver and gold.

Method for Observing and Measuring Contact Angles.—The method adopted for producing and measuring contact

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(1a) Ablett, *Phil. Mag.*, **46**, 244 (1923).
 (2) Adam and Jessop, *J. Chem. Soc.*, **127**, 1863 (1925).
 (3) Bosanquet and Hartley, *Phil. Mag.*, **42**, 456 (1921).
 (4) Pöckels, *Physik. Z.*, **15**, 39 (1914).
 (5) Rayleigh, *Phil. Mag.*, **30**, 397 (1890).
 (6) Sulman, *Trans. Inst. Min. Met.* (1920).

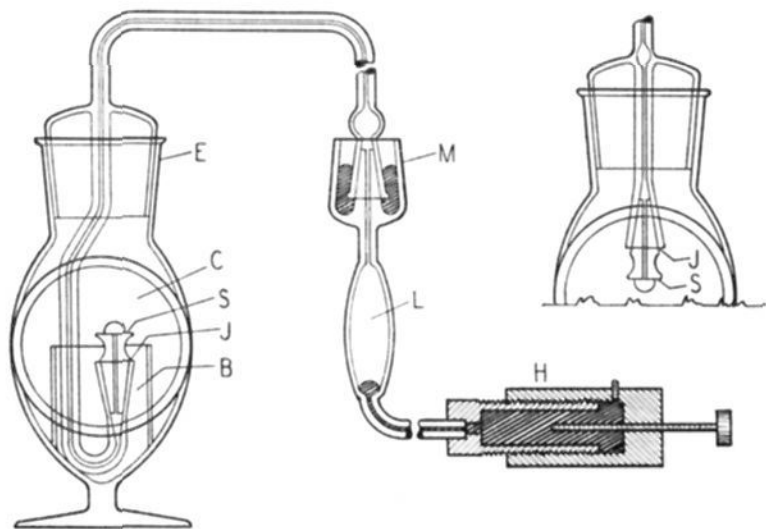


Fig. 1.—Contact angle apparatus.

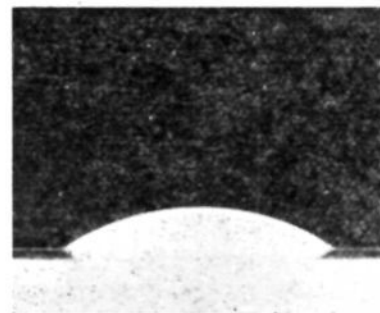
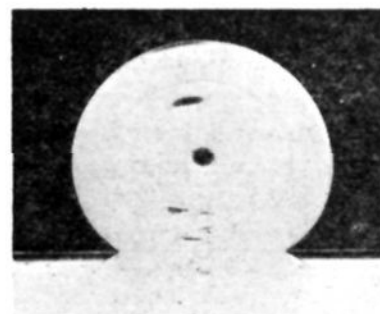
angles was a sessile drop or bubble method similar to one previously used in this Laboratory,^{7,8} Fig. 1. One important improvement was a device which made possible exact control of movements of the drop. This device consisted of a stainless steel cell, H, filled with mercury into which a small screw plunger extended. The glass tube and reservoir, L, made connection between the Pyrex tip and the mercury cell. The reservoir was filled with the liquid which was to be used in the formation of a drop. Movement of the plunger caused movement of liquid and the drop formed on the tip could be caused to advance or to recede, or it could be maintained at a fixed position on the metal surface on the tip. The tube carrying the metal coated tip made connection by means of the ground glass joint, E, to the glass cell, C, which had plane parallel plate glass windows through which the drop could be observed. The apparatus was kept in an air-bath with temperature maintained at $25 \pm 0.05^\circ$.

Measurement of Contact Angles.—When the contact angle to be measured was that formed by a liquid drop in air, the reservoir, L, was first filled with liquid; the air in the cell, C, was saturated with the liquid vapor by introducing a small amount of the same liquid into compartment B, and the liquid drop was then formed by manipulating the screw plunger adjustment. When the contact angle to be measured was that formed by a bubble of air within the liquid, the metal coated tip was placed in an inverted position, immersed in the liquid under study, and air was forced out as a bubble on the underside of the tip.

Photographs were made of the drops or bubbles (see Figs. 2 and 3). The lamp used as a light source was tilted slightly to give a clear image of the drop or bubble at its contact with the solid. In the early work photographs were taken on lantern slides but later directly upon bromide paper. No appreciable error was introduced by using the paper directly. The diameters of the liquid drops and the air bubbles were between 1 mm. and 3 mm. They were magnified from fifteen to twenty-five diameters in the photographs. The contact angles were measured from the photographic profiles with a tangentmeter. The reproducibility of the contact angles varied somewhat with the different systems, ranging from ± 0.5 to $\pm 1^\circ$.

Materials Used.—The silver for this investigation was a "pure" grade and was in the form of foil. The gold was

No. 24 B. & S. gage wire of "24 karat" grade. The water was of "conductivity" grade.

Fig. 2.—A water drop on gold in air forming a contact angle of 34.5° (measured through water).Fig. 3.—An air bubble on gold in water forming a contact angle of 34° (measured through water).

Experimental

Contact angle measurements were made for a drop of water on a solid in air and for a bubble of air on a solid in water. The data obtained for the solid-air/water drop systems are presented in Table I, those for the solid-water/air bubble systems appear in the text. Each value reported is the average of at least twenty measurements. In order that the data of the two systems can be directly compared, the *values of the contact angles will always be expressed as measured through the water phase.*

In the early stages of the work it was found that the magnitude of the advancing contact angle formed when a water drop was placed on a silver or gold surface depended upon the length of time the solid had been in contact with air. The initial change of the metal surface in air was so rapid that values for advancing angles of water drops on silver or gold which had been in air *less* than five minutes could not be exactly duplicated. After the metals had stood in air for a five-minute period or longer, advancing contact angles formed by water drops could be duplicated to within 1° .

It required a few seconds to remove the metal surface from the vaporization chamber and to form a water drop upon it. During this brief time the surface became altered. Thus initial values obtained for advancing angles of water drops on the metals which had been in air for a few seconds were probably somewhat higher than the true values for water on freshly prepared, unaltered metal surfaces.

All the receding angle values in Table I were obtained by withdrawing the drops of water immediately after they had been advanced. This procedure gave maximum values. The size of the angle remained practically constant during the withdrawal of the drop provided that but little time elapsed during the process. If the drops were

(7) Bartell and Bristol, *J. Phys. Chem.*, **44**, 86 (1940).

(8) Bartell and Hatch, *ibid.*, **39**, 11 (1935).

allowed to stand even a little time (in some cases but one or two minutes) before they were receded, the angles obtained were found to be somewhere between the maximum values given in the table and the zero value.

The values presented in Table I are for metals which were allowed to stand in contact with air saturated with water vapor. If the metals were allowed to stand in dry air it was found that the advancing angles were the same as those given in the table but that the receding angles were always zero.

TABLE I
CHANGE IN SOLID-AIR-WATER CONTACT ANGLES WITH
TIME OF STANDING OF SOLID IN AIR BEFORE FORMATION
OF WATER DROP

Time solid was in air	Silver-Air-Water		Gold-Air-Water	
	Advancing angle	Receding angle	Advancing angle	Receding angle
Few seconds	40 to 46°	0°	37 to 43°	0°
5 minutes	67°	0°	53°	0°
1 hour	76°	9.5°	65°	8°
2 hours	81.5°	14°	75°	13.5°
3 hours	84°	17°
4 hours	79°	22°
6 hours	88°	24.5°
7 hours	88°	28.5°
8 hours	92°	32°
9 hours	92.5°	33°
10 hours	94°	35°
12 hours	95°	37°	92.5°	35°
18 hours	95°	37°	92.5°	35°

The data obtained with air bubbles were similar to those obtained with water drops. When the air bubble was caused to recede (*i. e.*, the water caused to advance) the water advancing angle formed was found to depend upon the length of time the air bubble had been allowed to stand on the metal surface before it was withdrawn. The minimum water advancing angle, obtained when the air bubble was caused to recede immediately after it had made contact with the metal surface, was reproducible. It was 39° for silver and 34° for gold. These values are somewhat less than the minimum values obtained by the water drop method and probably represent the true water advancing angle for metal surfaces unaltered by air, since by the air bubble method the measurement can be made after a shorter exposure of the metal to air, and since the values are reproducible. The maximum water advancing angles were obtained when the air bubbles were left on the metal surfaces for sufficient time to allow maximum alteration by air. The time required for the silver surfaces was one hour and that for the gold surfaces was one and one-half hours. The maximum water advancing angle for silver was 95°, that for gold was 92°. These values are the same as those obtained with the water drop. Intermediate values could be obtained when air bubbles were left for intermediate periods of time on the metals and these values could be reproduced.

The receding water angle formed by an air bubble advancing over a silver surface was 39°, that for gold was 34°. When the air bubble was formed on a silver surface which had been immersed in water for a few minutes the contact angle of 39° was immediately obtained, but when

the air bubble was formed on a silver surface which had been immersed in water for a few hours it appeared to require a minute or more for the bubble to remove the water and make actual contact with the silver. In the latter case the initial contact angle was a few degrees (never more than 4°) smaller than 39°, but on standing a minute or more the air bubble always moved outward of its own accord to give a contact angle of 39°.

Discussion of Results

The data bring out clearly the fact that there are definite, reproducible and limiting contact angle values for both advancing and receding angles for each of the systems silver-air-water and gold-air-water. Since the behaviors of the contact angles on silver and on gold are so nearly the same for corresponding systems the following discussion will relate specifically to data obtained with the silver systems.

The most significant angle for the silver system appears to be a $38 \pm 1^\circ$ angle. This angle was formed (a) when a drop of water was caused to advance over a new and uncontaminated silver surface, (b) when a water drop was caused to recede quickly after having been quickly advanced over a surface upon which there was a maximum of adsorbed air, (c) when an air bubble was caused to advance (*i. e.*, water to recede) over the surface which had been submerged in water, and (d) when an air bubble was caused to recede immediately after being advanced over the surface immersed in water. In the four cases just cited, advancing angles were of the same values as the receding angles, also angles formed by water drops in air were of the same value as angles formed by air bubbles in water. Since in each of these four cases the surface had been exposed to air only briefly or had subsequently been covered by water (which apparently causes desorption of air), this $38 (\pm 1^\circ)$ angle appears to be an equilibrium angle for water on fresh and uncontaminated silver.

The maximum advancing angle of 95° was readily reproducible, was obtained both with the water drop in air and with the air bubble in water, and was the angle always obtained when the silver surface had been exposed to air for a relatively long time so that maximum air had apparently become adsorbed upon it. The advancing angles with values between 38 and 95° appear to be the result of effects due to different degrees of completeness of adsorption of air on the surface. When there is maximum of adsorbed air this adsorbed air may be present as a complete and condensed layer, but this layer probably does not en-

tirely mask the properties of the underlying metal as is shown by the fact that the angles obtained on gold and silver are somewhat different.

It has been observed by other investigators^{4,9,10} also that the contact angles of water on solids are increased by the adsorption of air upon the solids; and Ströhacker¹¹ has presented evidence that air is adsorbed on gold and may form a unimolecular layer. From the experiments with the air bubble and the water drop herein reported, it appears that silver and gold adsorb air more readily from an air bubble within water than from an atmosphere of air saturated with water vapor. The increased rate of adsorption of air from the bubble may have been due to the bubble's being under a slightly higher than atmospheric pressure, but the fact that the same advancing angle could be obtained either with bubble or drop is proof that there could not have been pressure sufficient to alter appreciably the contact angle of the bubble.

Since the magnitude of the advancing water angle was greater for the silver surface altered by air action than for the fresh and clean silver, the possibility that the silver surface had become altered by oxidation with the air was practically eliminated. A silver oxide surface is undoubtedly more hydrophilic than a metallic silver surface and water would therefore form a smaller angle of contact on silver oxide than on metallic silver. The larger angle of contact indicated that the altered surface was more hydrophobic in nature than was the original silver surface. This can be explained only by assuming that a layer of air had become adsorbed upon the silver surface and that this layer of air had produced a surface which was highly hydrophobic.

The 0° receding angle was always obtained when a water drop was formed on the silver surface, was allowed to stand for a few minutes, and was then caused to recede. In those cases in which the solid had not previously been allowed to stand in air the 0° angle was obtained even if the drop was formed quickly and then was caused immediately to recede. If, however, the solid had stood in air saturated with water vapor for a period of time before the water drop was caused to advance, it then became necessary to allow the drop to remain for a minute or two before receding it in order to obtain the 0° receding angle. In

case the drop was allowed to stand for a shorter interval of time the receding angle had a value between 38 and 0° , the exact value depending both upon the length of time the plate had been exposed to air prior to formation of the drop and upon the length of time the drop had stood before it was receded.

There appears to be no definite evidence which will serve satisfactorily to explain the 0° angle. One possible explanation is that its formation may have been caused by retention, due to capillary action, of water in sub-microscopic surface pores or cracks so that when water was removed from the drop, the drop did not actually recede but was held at the periphery until all liquid had been removed, thus giving a 0° angle which was not a true receding angle. Such a condition was not reproduced in the air bubble method.

Summary

1. Solid surfaces with reproducible properties were obtained by vaporizing the solid in a vacuum, condensing the vapors as a film or coating upon a supporting medium, and subsequently protecting the surface from alteration by adsorption, or by regulating the extent of alteration.

2. The maximum advancing water contact angle measured for silver was $95 \pm 0.5^\circ$. That for gold was $92.5 \pm 0.5^\circ$. The maximum receding contact angle was $38 \pm 1^\circ$ for silver, and $34 \pm 1^\circ$ for gold. Corresponding angles were the same whether measured with water drop or air bubble.

3. Adsorption of air on the metal surfaces caused the surfaces to become more hydrophobic, thus causing the relatively large maximum advancing contact angles. Water, in contact with the metal surface upon which air had been adsorbed, tended to desorb the air. "Hysteresis" effects for these systems appeared to be closely related to alteration of the metal surfaces by processes of adsorption and desorption of air. Where the metal surface was in the same condition for advancing and receding angles, these angles had the same value.

4. When a water drop was allowed to stand for a few minutes on a silver or gold surface and was then caused to recede, the periphery of the drop became immobilized and as the bulk of the liquid disappeared the receding angle approached, or actually became, zero.

(9) Bartell, Culbertson and Miller, *J. Phys. Chem.*, **40**, 881 (1936).

(10) Bartell and Miller, *ibid.*, **40**, 889 (1936).

(11) Ströhacker, *Z. Physik*, **64**, 248 (1930).