

Effect of Adsorbed Water on the Critical Surface Tension of Wetting on Metal Surfaces

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ABSTRACT

Contact angles of a variety of pure polar and nonpolar, nonhydrophilic liquids, covering a wide range of surface tensions, were measured at 20°C on clean, smooth surfaces of 14 metals and one metal oxide. At low RH of only 0.6% and high RH of 95%, each of these high-energy, solid surfaces was converted to one of much lower critical surface tension of wetting γ_c by the physical adsorption of a thin film of water. The formation of only a fraction of a monolayer at 0.6% RH decreased γ_c to about 45 dynes/cm for each metal surface; additional water adsorption at 95% RH to form a more condensed film further lowered γ_c to a common value of 38 dynes/cm. Since γ_c values were nearly identical for each surface at each extreme of the RH, the surface energy of these hydrophilic solids must be independent of the constitution of the underlying solid substrate and dependent only on the surface concentration of the adsorbed water.

These results were the same as previously obtained for glass surfaces. We therefore propose the generalization that the surface energy of any clean, smooth, high-energy, hydrophilic surface, whether glass, metal, or metal oxide, after exposure to a humid atmosphere depends on the surface concentration of water adsorbed on the surface and that the chemical nature of the underlying hydrophilic substrate has little other effect on wetting and spreading properties.

PROBLEM STATUS

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

AUTHORIZATION

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EFFECT OF ADSORBED WATER ON THE CRITICAL SURFACE TENSION OF WETTING ON METAL SURFACES

INTRODUCTION

Recent investigations in our laboratory have demonstrated that γ_c , the critical surface tension of wetting, of soda-lime glass (1) and of borosilicate glass, fused quartz, and α -alumina (2) was essentially the same at each RH in going from low RH of only 0.6% to high RH of 95% at 20°C. We found that γ_c decreased as the RH increased, with $\gamma_c = 37$ to 40 dynes/cm for halogenated alkanes at 0.6% RH and $\gamma_c = 25$ to 30 dynes/cm for n-alkanes at 95% RH. Because the resulting values of γ_c at 0.6% and 95% RH were unchanged in going from soda-lime and borosilicate glasses to quartz and sapphire, we concluded that γ_c was defined principally by the adsorbed film of water rather than by the nature of the adsorbing solid beneath. We also concluded that only one condensed, physically adsorbed monolayer caused the decrease in γ_c in going from the dry high-energy solid surface to the moist surface at 95% RH. Therefore, we wondered if the same values of γ_c would be found at the same conditions of temperature and RH on other hydrophilic, high-energy, solid surfaces, such as metals and metal oxides. This report is concerned with the resulting investigation of the wetting properties of a variety of grease-free, pure, metal surfaces. However, no attempt was made to avoid any oxide which normally forms on each clean metal after being polished gently with aqueous polishing agents at room temperature in air.

EXPERIMENTAL MATERIALS AND METHODS

The metals investigated were chromium, copper, silver, gold, cadmium (each having a reported purity of 99.999%), aluminum, iron, nickel, germanium, zirconium, niobium, tantalum, molybdenum, and tungsten (each 99.9% pure or better). With the exceptions of the iron, chromium, and germanium specimens, which were rectangular pieces of various sizes and thicknesses, the other metals were all circular disks, 1 cm in diameter and 1 to 2 mm in thickness. The surface of every metal was prepared by abrasion under flowing water through 600A-grit silicon carbide paper, after which a mirror finish was imparted with a cloth polishing wheel and 0.3- μ alumina (Linde "Fine Abrasive" A-5175). Each specimen was then scrubbed on a clean polishing cloth under distilled water until all adhering alumina particles were removed. Next, it was rinsed copiously with distilled water and finally dried at room temperature in an air atmosphere from which organic contamination had been removed. The last few steps, starting with the alumina polishing, were repeated on each specimen between each set of contact-angle measurements.

The apparatus and method used for the contact-angle experiments have been described previously (1,2). The apparatus consisted essentially of a gas-purification train and a transparent observation chamber to hold the specimen. A metered stream of nitrogen gas, freed of organic contaminants, was fed into the chamber; by either leading the gas stream through water towers or bypassing them, any desired RH in the observation chamber from 0.6% to 95% could be achieved.

Slowly advancing contact angles (3) of a variety of pure polar and nonpolar, non-hydrophilic liquids were measured with a goniometer, whose illuminator and telescope could be moved laterally and independently from the viewing chamber containing the

metal specimen and sessile drop. The selection and purification of the organic liquids studied have been described previously (2). Each contact angle θ of the slowly advancing sessile drop of liquid was measured after a 2-hr equilibration period of the metal at the desired RH; the reported value in Tables 1 and 2 was the average obtained on at least three sessile drops of each liquid on three different surfaces. All measurements were made at $20^\circ \pm 1^\circ\text{C}$; the precision of the contact-angle determinations was ± 2 degrees.

EFFECT OF VARYING RELATIVE HUMIDITY ON CONTACT ANGLES

Table 1 gives the wetting liquids and the contact angle each liquid formed on each of 12 metals after the metal had been equilibrated for 2 hr at 0.6% RH. Table 2 lists the contact angles of the liquids after each metal had been equilibrated for 2 hours at 95% RH. Data obtained for silver and cadmium were not included, because several of the halogenated alkanes (especially methylene iodide) stained the silver on contact and created white deposits on cadmium around the periphery of the sessile drop. Obviously, some chemical reactions had taken place at room temperature which complicated interpretation of these contact-angle data. Discolorations by some halogenated n-alkanes were also observed on the pure iron surface; however, since neither the reproducibility nor the shapes of the sessile drops were affected, the contact angles on iron were considered worth reporting.

Contact angles of all liquids on every metal were considerably smaller at 0.6% RH (Table 1) than at 95% RH (Table 2). At 0.6% RH all hydrocarbons and all polar liquids whose surface tensions were below about 44 dynes/cm either spread spontaneously or exhibited contact angles lower than or equal to 6 degrees on all metal surfaces; the only exception was tantalum, on which contact angles were higher. Figure 1 shows the plot of γ_{LV} vs $\cos \theta$ on chromium at 0.6% RH and 95% RH. When straight lines were drawn through the points corresponding to the few compounds that did not spread on chromium at 0.6% RH (Fig. 1a), the intercept of that line with the horizontal line, $\cos \theta = 1$, was about 45 dynes/cm; hence, γ_c was 45 dynes/cm. The graph for chromium is representative of those obtained with the other metals. Thus, all aliphatic hydrocarbon liquids spread spontaneously ($\theta = 0$ degree) on all metals. Although the slopes varied somewhat, graphs for the aromatic compounds and the halogenated alkanes revealed that γ_c of every metal was close to 45 dynes/cm (Table 3).

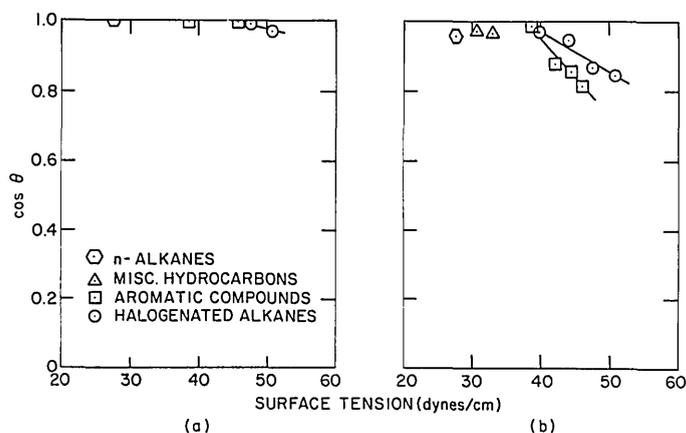


Fig. 1 - Comparison of the wettability of chromium: (a) 0.6% RH and (b) 95% RH

Table 1
Wettability of Metals after a 2-Hr Equilibration at 0.6% RH
(All Data Obtained at 20°C in Nitrogen)

Liquid Sessile Drop	Surface Tension (dynes/cm)	Contact Angle (degrees)												
		Cu	Au	Al	Ge	Zr	Nb	Ta	Cr	Mo	W	Fe	Ni	
n-Hexadecane	27.6	Spr.*	Spr.	Spr.	Spr.	5	6	5	<5	6	5	5	Spr.	Spr.
Methylene iodide	50.8	27	14	13	10	33	26	41	12	27	22	22	15	22
Tetrabromoethane	47.5	21	8	8	6	18	15	32	8	18	6	6	7	10
α -Iodonaphthalene	45.9	10	6	5	5	11	11	15	<5	12	6	6	6	10
α -Bromonaphthalene	44.6	12	<5	<5	<5	<5	5	8	<5	6	Spr.	Spr.	<5	7
1,2,3-Tribromopropane	44.0	10	5	7	—	7	6	20	<5	12	5	5	<5	5
o-Dibromobenzene	42.0	—	<5	—	—	—	<5	—	—	—	—	—	<5	—

*Spr. indicates that the drop spreaded spontaneously over the specimen surfaces.

Table 2
Wettability of Metals after a 2-Hr Equilibration at 95% RH
(All Data Obtained at 20°C in Nitrogen)

Liquid Sessile Drop	Surface Tension (dynes/cm)	Contact Angles (degrees)											
		Cu	Au	Al	Ge	Zr	Nb	Ta	Cr	Mo	W	Fe	Ni
Hydrocarbons													
α -Methylnaphthalene	38.7	7	<5	<5	22	13	12	15	8	12	10	6	10
Isopropyl biphenyl	34.8	7	Spr.*	Spr.	12	<5	<5	<5	<5	<5	<5	6	9
Dicyclohexyl	32.8	8	Spr.	16	15	18	17	14	15	12	16	9	12
Isopropyl bicyclohexyl	30.9	8	—	32	14	22	25	10	—	24	29	10	16
n-Hexadecane	27.6	Spr.	Spr.	Spr.	12	20	19	5	18	10	23	Spr.	12
Polar Liquids													
Methylene iodide	50.8	32	22	39	37	33	33	44	32	36	30	25	39
Tetrabromoethane	47.5	26	16	35	30	30	28	35	30	27	27	26	34
α -Iodonaphthalene	45.9	30	17	36	37	34	35	33	35	29	29	27	35
α -Bromonaphthalene	44.6	25	18	32	30	30	32	29	31	27	29	22	26
1,2,3-Tribromopropane	44.0	22	12	20	27	25	22	30	19	25	15	17	26
o-Dibromobenzene	42.0	23	11	25	27	28	26	28	29	26	26	16	22
1,2,3-Tribromobutane	39.9	14	—	14	18	15	13	18	14	10	9	12	15

*Spr. indicates that the drop spreaded spontaneously over the specimen surfaces.

Table 3
Comparison of Critical Surface Tension of Wetting for Twelve Metals
(All Data Obtained at 20°C in Nitrogen)

Metal	Atomic Radius*	Crystal Structure	0.6% RH		95% RH					
			Slope	γ_c (dynes/cm)	n-Alkanes		Aromatic Cpds.		Halogenated Alkanes	
					γ_c (dynes/cm)	Slope	γ_c (dynes/cm)	Slope	γ_c (dynes/cm)	Slope
Nickel	1.24	cubic f.c.	-0.012	45	26	-0.024	38	-0.017	36	
Iron	1.26	cubic b.c.	-0.007	46	>27	-0.014	37	-0.007	36	
Chromium	1.27	cubic b.c.	-0.007	45	—	-0.022	38	-0.012	36	
Copper	1.28	cubic f.c.	-0.014	44	>27	-0.016	38	-0.010	36	
Germanium	1.37	diamond	-0.005	46	27	-0.018	35	-0.014	36	
Molybdenum	1.39	cubic b.c.	-0.018	44	27	-0.016	37	-0.015	38	
Tungsten	1.39	cubic b.c.	-0.012	45	—	-0.018	37	-0.012	37	
Aluminum	1.43	cubic f.c.	-0.005	45	>27	-0.026	38	-0.017	37	
Gold	1.44	cubic f.c.	-0.006	45	>27	-0.010	40	-0.013	40	
Niobium	1.46	cubic b.c.	-0.018	44	—	-0.022	38	-0.013	38	
Tantalum	1.46	cubic b.c.	-0.026	42	27	-0.022	37	-0.022	37	
Zirconium	1.60	hexagonal	-0.028	45	—	-0.018	37	-0.013	37	

*R. T. Sanderson, "Chemical Periodicity," New York: Reinhold, pp. 26-28, 1960.

In Fig. 1b are plots of $\cos \theta$ vs γ_{LV} for each of the nonhydrophilic liquids on chromium observed at 95% RH and 20°C. Two distinct straight lines were obtained: one for the various aromatic compounds and another for the halogenated n-alkanes. The slopes of these straight lines were different, but the intercepts at the $\cos \theta = 1$ axis were very close to 38 dynes/cm for the former line and 36 dynes/cm for the latter (Table 3). Since the hydrocarbon liquids (Table 2) were not homologous compounds, their graphical points did not define a straight line, even though nonzero contact angles were obtained when γ_{LV} was above 27 dynes/cm.

We have discussed previously the significance of the differences in the values of γ_c of glass obtained with sessile drops of different homologous families of hydrocarbon compounds (2). The conclusion was that a given hydrophilic glass surface would exhibit the same value of γ_c using any homologous series of liquids unless the adhesive interaction between liquid and solid surfaces included, with the effect of London dispersion forces, a significant contribution from other types of interaction, such as arise from hydrogen bonding or the forces between permanent electrostatic dipoles. Since the unsaturated bonds in the aromatic hydrocarbon rings cause these compounds to be more hydrophilic than the analogous n-alkanes (4,5), γ_c for the aromatics in contact with any solid coated with an adsorbed water layer would be higher, as indeed was the case with every metal reported here.

Figure 1 is representative of the graphical results obtained with all the other metals. As at the low RH, no great differences were observed among the individual metals at 95% RH. Although the straight lines for the aromatics, as well as those for the halogenated alkanes, had slightly different slopes, γ_c for all metals except gold did not vary more than ± 1 dyne/cm and remained between 37 and 38 dynes/cm (Table 3); γ_c for gold was higher by 2 dynes/cm (Fig. 2).

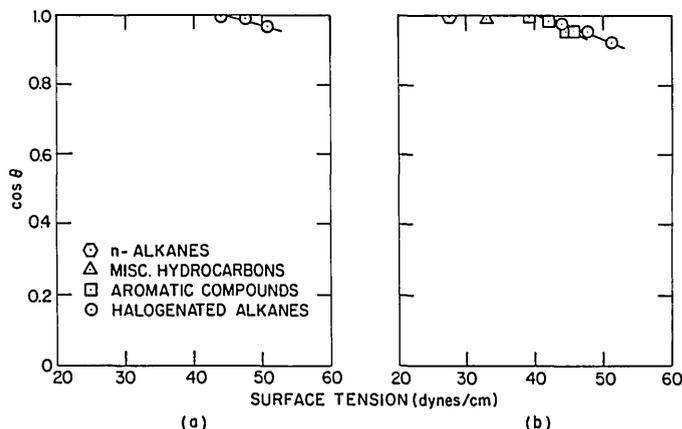


Fig. 2 - Comparison of the wettability of gold: (a) 0.6% RH and (b) 95% RH

Figure 3 is a composite graph of $\cos \theta$ vs γ_{LV} made by plotting the average values of $\cos \theta$ obtained with a given liquid on all of the metals (except silver and cadmium); the vertical lines indicate the spread in $\cos \theta$ among that group of metals.

EFFECT OF METAL OXIDE COATING

It is well known that the majority of the pure metals are not stable indefinitely in air at room temperature; they more or less readily form oxides, and many metals also tend

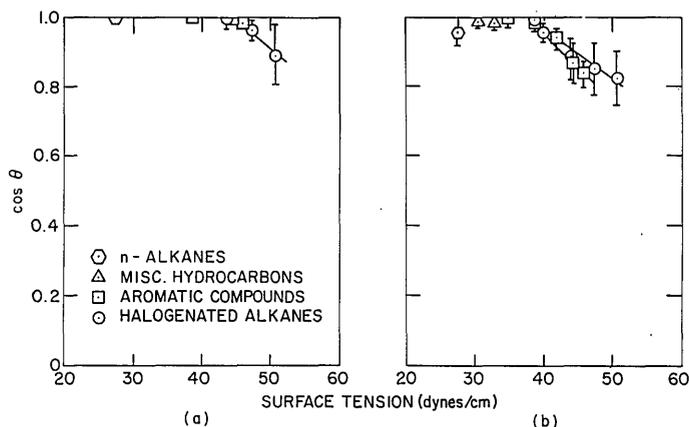


Fig. 3 - Wettability averaged for twelve metals: (a) 0.6% RH and (b) 95% RH

to form nitrides. The rate of oxidation in many instances is very low at ordinary or low temperatures. Although most investigations on the atmospheric oxidation of metals had been made at temperatures above 25°C, the metals most commonly used in industrial applications have been studied extensively at ordinary and low temperatures; these include iron (6-11), copper (6,9,12-16), aluminum (9,12,17-20), chromium (12), and nickel (21-24). Less abundant metals that also have been given much attention include cadmium (25), zirconium (26,27), tungsten (12,27-29), molybdenum (26,27), and tantalum (26).

Oxide films from 10 to 50Å thick are formed on such metals as copper and iron within the first few minutes of atmospheric exposure (6-9,16,18). Oxide buildup is much slower at 25°C on other metals, such as silver, cadmium, zirconium, and tantalum (13, 25,26). The presence of water vapor has been found to accelerate to various degrees the formation of oxide coatings on aluminum (18), iron (9), and nickel (21); it is reported not to affect, and even sometimes to delay, the oxidation of copper (7,15), cadmium (25), and tantalum (26). Most of the above-cited investigations were made after the metals had first been carefully degassed in a vacuum chamber or given other special treatments to assure that the metal surfaces were initially pure. In the present investigation, no elaborate precautions were taken to prevent metal oxidation in the air at room temperature. However, much care was taken to assure that a drop of grease-free distilled water would spread spontaneously on each polished specimen surface. In this way we could be certain that as each metal specimen was placed in the observation chamber, it was free of even as little as one hundredth of a monolayer of adsorbed organic contamination.

Since it was impossible to prevent metal oxidation completely in these experiments, we also performed identical contact-angle experiments on a known, well-defined iron oxide surface. A single crystal of pure spinel Fe_3O_4 , kindly made available by the Smithsonian Institution, was cut by us into a disk 1 cm in diameter and 5 mm in thickness. Prior to studying the specimen, it was polished and cleaned in the same manner as the pure metals. The resulting graphs of $\cos \theta$ vs γ_{LV} (Fig. 4) were very much like those of the pure metals; γ_c was 45 dynes/cm at 0.6% RH and 38 dynes/cm at 95% RH. Therefore, we can conclude that the thin, epitaxial oxide layer formed on a pure iron surface during the experiments would not exhibit different results if the oxide were allowed to become thicker and assume a different crystal structure.

WETTABILITY OF GOLD

During the last few years, White (30) and Erb (31) claimed that only the presence of an oxide layer on the gold permitted water to spread spontaneously over it. They

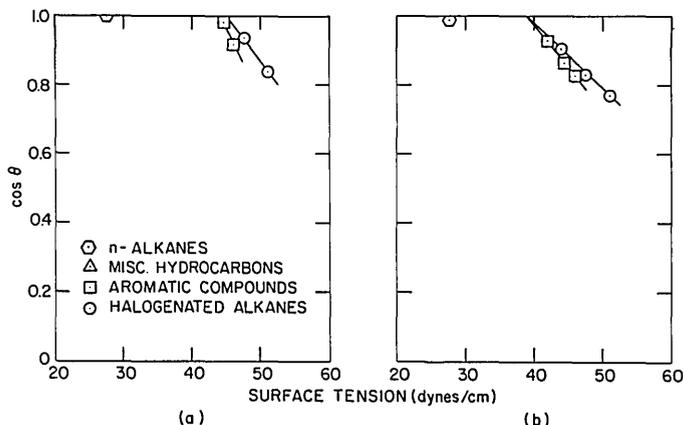


Fig. 4 - Comparison of the wettability of spinel-single-crystal Fe_3O_4 : (a) 0.6% RH and (b) 95% RH

presented data to show that a pure, unoxidized gold surface at ordinary temperature is hydrophobic with a water contact angle of roughly 60 degrees. Bewig and Zisman (32) subsequently reported experiments to prove that pure gold, if kept free from organic contamination in the surrounding atmosphere, always exhibited a water contact angle of 0. White and Drobek (33) then claimed it was the presence of residual alumina abrasive used in the final metal-polishing procedure which was responsible for the spontaneous spreading of water on gold reported by others.

Many years ago Ende (34) reported that when emery was used as a polishing agent on brass or nickel, particles left imbedded in the surface gave rise to false contact potential differences as great as 0.5 v. Zisman and Yamins (35) confirmed these results and found the same was true of rouge polishing materials; however, they reported that polishing the metal surface gently on a grease-free cloth immersed in water was sufficient to remove all of the spurious potential caused by the imbedded particles. Because of the great sensitivity of contact potentials to such extraneous materials left in the surface, their results revealed a simple technique for removing these imbedded particles. Ever since then, our work with polished metal surfaces has always involved such a wet-scrubbing step before finally drying the specimen and measuring any surface properties. In the present investigation, as in the preceding one by Bewig and Zisman (32), the gold specimen was thoroughly wet-scrubbed before drying it. But to add further conviction to our results on the wettability of gold, an electron-diffraction examination with a Hitachi Model HU-11A was made of the resulting gold surface by our associate, Dr. Robert L. Jones, who used the glancing-angle electron-diffraction technique, the same technique as used by White and Drobek (33). Reflection electron-diffraction patterns (50 kv) obtained from the gold surface after such a polishing procedure showed no evidence of alumina particles when compared to transmission electron-diffraction patterns obtained from a standard gold surface.

In the above reports of White (30), White and Drobek (33), and Erb (31), only water contact angles were observed during their experiments with gold and several other metals. Since these water contact angles were significantly large, it would have been informative to have investigated also the contact angles exhibited by other pure liquids. After all, if gold has a low-energy surface with a water contact angle of 60 degrees, θ should not be 0 for some pure nonaqueous liquids. The value of such an approach is that the resulting contact angles and the derived values of γ_c would establish whether or not their metal surfaces were really clean or were contaminated with an organic adsorbed film. In the present investigation, θ was measured for a variety of pure, nonhydrophilic, and

nonaqueous liquids on gold; therefore, values of γ_c were obtained from the plots of $\cos \theta$ vs γ_{LV} . The results in Tables 1, 2, and 3, as well as Fig. 2, demonstrate that our gold surfaces were free from organic contamination, were always hydrophilic, and exhibited the same values of γ_c as those observed for glass, quartz, sapphire, and a variety of metals and metal oxide when covered with a monolayer (or less) of adsorbed water. Hence, we are led again to conclude that a pure, clean gold surface at 25°C is always spontaneously wet by water, and the water contact angle is 0.

CONCLUSIONS

This investigation has demonstrated that the adsorption of water converts the clean, mirror-polished surface of each of 12 metals and one metal oxide of known composition to a surface of much lower γ_c (and therefore also lower surface energy γ_{S^0}); furthermore, γ_c was nearly identical for each surface regardless of the type of metal. Since γ_c of a Fe_3O_4 spinel crystalline surface was also converted to the same low value by exposure to high RH, it is concluded that the type of the oxide formed on the metals at room temperature does not play as important a role in determining γ_c as does the presence of the adsorbed water film.

Recent investigations on the effect of adsorbed water on the surfaces of soda-lime glass (1) and of borosilicate glass, fused quartz, and α -alumina (2) had shown a lowering of γ_c for each of these surfaces to the same values of 45 dynes/cm at 0.6% RH and 36 to 37 dynes/cm at 95% RH. We therefore propose the generalization that the surface energy of any clean, smooth, high-energy, hydrophilic surface, whether glass, metal, or metal oxide, after exposure to a humid atmosphere depends mainly on the surface concentration of water adsorbed on the surface and that the chemical nature of the underlying hydrophilic substrate has little other effect on wetting and spreading properties.

Although at the low RH of 0.6%, less than a close-packed monolayer of water was physically adsorbed on the metal or glass surface, this low surface concentration was still sufficient to lower γ_c drastically below that of a perfectly dry surface.

When the adsorbed water molecules form a condensed monolayer, such as at 95% RH, the additional decrease of γ_c is much smaller.

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REFERENCES

1. Shafrin, E.G., and Zisman, W.A., J. Am. Ceram. Soc. 50:478 (1967)
2. Bennett, M.K., and Zisman, W.A., "Effect of Adsorbed Water on Wetting Properties of Borosilicate Glass, Quartz, and Sapphire," to be published, *NRL 6705, May 1968*
3. Zisman, W.A., in "Contact Angle, Wettability, and Adhesion," Advances in Chemistry Series 43, Washington: American Chemical Society, p. 1, 1964
4. Pomerantz, P., Clinton, W.C., and Zisman, W.A., J. Colloid and Interface Sci. 24:16 (1967)
5. Shafrin, E.G., and Zisman, W.A., J. Phys. Chem. 71:1309 (1967)

6. Evans, U.R., and Miley, H.A., *Nature* 139:283 (1937)
7. Gulbransen, E.A., *Trans. Electrochem. Soc.* 81:327 (1942)
8. Winterbottom, A.B., *J. Iron Steel Inst.* 165:9 (1950)
9. Vernon, W.H.J., *Trans. Faraday Soc.* 23:150 (1927)
10. Sewell, P.B., Stockbridge, C.D., and Cohen, M., *J. Electrochem. Soc.* 108:933 (1961)
11. Kruger, J., and Yolken, H.T., *Corrosion* 20:29t (1964)
12. Cabrera, N., *Phil. Mag.* 40:175 (1949)
13. Campbell, W.E., and Thomas, U.B., *Trans. Electrochem. Soc.* 76:303 (1939)
14. White, A.H., and Germer, L.H., *Trans. Electrochem. Soc.* 81:305 (1942)
15. Campbell, W.E., and Thomas, U.B., *Trans. Electrochem. Soc.* 91:623 (1947)
16. Rhodin, T.N., Jr., *J. Am. Chem. Soc.* 72:5102 (1950)
17. Hass, G., *Z. Anorg. Chem.* 254:96 (1947)
18. Tolley, G., *Metal. Ind. (London)* 77:255 (1950)
19. Keller, F., and Edwards, J.D., *Metal Progr.* 54:35 (1948)
20. Hunter, M.S., and Fowle, P., *J. Electrochem. Soc.* 103:482 (1956)
21. Vernon, W.H.J., *J. Inst. Metal* 48:121 (1932)
22. Germer, L.H., and Hartman, C.D., *J. Appl. Phys.* 31:2085 (1960)
23. Germer, L.H., MacRae, A.U., and Hartman, C.D., *J. Appl. Phys.* 32:2432 (1961)
24. Germer, L.H., and MacRae, A.U., *J. Appl. Phys.* 33:2923 (1962)
25. Gilbert, P.T., and Hadden, S.E., *J. Electrodepositors' Tech. Soc.* 25:41 (1950)
26. "The Corrosion Resistance of Some 'Minor' Metals," *Metal Ind. (London)* 80:111 (1952)
27. Kubaschewski, O., and Hopkins, B.E., "Oxidation of Metals and Alloys," New York: Academic, pp. 161-182, 1953
28. Propst, M., and Piper, T.C., *J. Vacuum Sci. Tech.* 4:53 (1967)
29. McCarroll, B., *Surface Sci.* 7:499 (1967)
30. White, M.L., *J. Phys. Chem.* 68:3083 (1964)
31. Erb, R.A., *J. Phys. Chem.* 69:1306 (1965)
32. Bewig, K.W., and Zisman, W.A., *J. Phys. Chem.* 69:4238 (1965)
33. White, M.L., and Drobek, J., *J. Phys. Chem.* 70:3432 (1966)
34. Ende, W., *Phys. Z.* 30:477 (1929)
35. Zisman, W.A., and Yamins, H.G., *Physics* 4:7 (1933)

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13. ABSTRACT Contact angles of a variety of pure polar and nonpolar, nonhydrophilic liquids, covering a wide range of surface tensions, were measured at 20°C on clean, smooth surfaces of 14 metals and one metal oxide. At low RH of only 0.6% and high RH of 95%, each of these high-energy, solid surfaces was converted to one of much lower critical surface tension of wetting γ_c by the physical adsorption of a thin film of water. The formation of only a fraction of a monolayer at 0.6% RH decreased γ_c to about 45 dynes/cm for each metal surface; additional water adsorption at 95% RH to form a more condensed film further lowered γ_c to a common value of 38 dynes/cm. Since γ_c values were nearly identical for each surface at each extreme of the RH, the surface energy of these hydrophilic solids must be independent of the constitution of the underlying solid substrate and dependent only on the surface concentration of the adsorbed water. These results were the same as previously obtained for glass surfaces. We therefore propose the generalization that the surface energy of any clean, smooth, high-energy, hydrophilic surface, whether glass, metal or metal oxide, after exposure to a humid atmosphere depends on the surface concentration of water adsorbed on the surface and that the chemical nature of the underlying hydrophilic substrate has little other effect on wetting and spreading properties.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Surface properties Adsorption on metals Spreading Contact-angle measurement Wettability Critical surface tension Hydrocarbons Polar liquids						