

NRL Report 6200

UNCLASSIFIED

DLI-3 has retained copies

for Technical Library collection

Changes in Contact Potentials of Metals Caused by Adsorbed Monolayers

K. W. BEWIG, C. O. TIMMONS, AND W. A. ZISMAN

Chemistry Division

February 12, 1965



U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

Copies available from
Clearinghouse for Federal Scientific and
Technical Information (CFSTI)
Sills Building, 5285 Port Royal Road
Springfield, Virginia 22151
\$.75

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
PROBLEMS OF TECHNIQUE AND CONTROL	2
PREPARATION OF WELL-DEFINED ADSORBED MONOLAYERS	5
INTERPRETATION OF HELMHOLTZ EQUATION	6
SOME FUNDAMENTAL EXPERIMENTS ON ADSORBED POLAR MOLECULES	7
SOME FUNDAMENTAL EXPERIMENTS ON ADSORBED NONPOLAR MOLECULES	12
GENERAL REMARKS	21
REFERENCES	23

ABSTRACT

A classic problem in the physics and chemistry of surfaces has been the successful utilization of changes in the contact potential difference between two metals as a means of studying surface properties and adsorption. Recent advances in experimental techniques, especially the use of a fluorocarbon coating on the reference electrode, have made possible a number of advances in the study of the surface potential changes resulting from the adsorption of monolayers of nonpolar liquids and of the higher molecular weight polar compounds. Studies have been made of adsorbed nonpolar liquid compounds including the various hydrocarbons and carbon tetrachloride. Polar-nonpolar compounds, such as the homologous families of the fatty acids and amines as well as certain aromatic phosphate esters, have also been investigated with the new techniques. Reproducible and interesting results have been obtained, even though the measurements were made in the presence of atmospheric oxygen, nitrogen, and water vapors as well as any surface oxide development on the metal at ordinary temperatures; however, it was necessary to control the relative humidity and air temperature carefully, to use an atmosphere entirely free of organic vapors or polar inorganic compounds, to take great care in cleaning the metal surfaces, and to employ compounds of extremely high purity.

PROBLEM STATUS

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

AUTHORIZATION

NRL Problem C02-10
Project RR 001-01-43-4751

Manuscript submitted October 2, 1964.

CHANGES IN CONTACT POTENTIALS OF METALS CAUSED BY ADSORBED MONOLAYERS*

INTRODUCTION

Ever since Alexander Volta (1) discovered in 1797 that two unlike metals placed in contact directly, or indirectly by means of a third metal, became charged with opposite kinds of electricity, the contact potential differences between metals has been almost continuously the subject of research and controversy. A list of the investigators would read like a "Who's Who" among physicists in the nineteenth and twentieth centuries. Since the first review by Oliver Lodge (2), it has been established that the contact potential differences between metals at the same temperature are real, intrinsic properties of the metals even though they are much altered by any films left on them, including oxides, water, or organic materials. In measuring the intrinsic contact potential difference between two metals, it is necessary to resort to extreme conditions of evacuation and preparation of clean, oxide-free, metal surfaces to obtain reliable, reproducible values. A large body of theoretical research has developed the relation of these intrinsic contact potential differences to the electronic nature of metallic conductors and to the surface equilibrium of the electrons and ions in each metal lattice; this work has been fully reviewed by Herring and Nichols (3). The use of contact potentials and the related work functions of metals in the study of adsorption, and especially chemisorption, has been reviewed by Suhrmann (4) and by Culver and Tompkins (5). A variety of methods exists for measuring the contact potential differences between metals either in vacuum or in a gaseous environment; these were reviewed in 1951 by Patai and Pomerantz (6).

Because the contact potential difference between metals is greatly altered by the presence of an oxide or an adsorbed film of a polar organic (or inorganic) compound, numerous investigations have resulted on the effects of surface oxidation, adsorption, and surface states. In investigations of surface adsorption processes it is necessary to have one electrode serve as a "reference" electrode and the other as an "active" electrode. However, any gas or vapor which is able to adsorb on the active electrode usually adsorbs to some extent on the reference electrode. This difficulty can be decreased by employing as the reference electrode a well-aged gold, platinum, or other metal surface. Unfortunately, this is usually an unreliable method in variable atmospheres.

In research on the behavior of insoluble polar monolayers adsorbed on the surface of bulk water, the contact potential difference between a reference metal electrode maintained in the air above the water and an electrode immersed in the water is used to study the change, with film pressure, in the packing and orientation of the adsorbed monolayer. These "contact potential" measurements have been made for about 40 years by either the ionization method (7,8) or by the vibrating condenser method (9,10). Especially troublesome in such measurements is the problem of maintaining a constant surface state in the reference electrode because of its proximity to the surface of such a volatile, adsorptive, and polar liquid as water.

Many investigators attempting to use the contact potential difference between metals as a tool for studying the adsorption of vapors of polar compounds in gases (11-18) have

*Presented at Conference on "Surface Effects in Detection," sponsored by Illinois Institute of Research, Illinois Institute of Technology, Brookings Institute, Washington, D.C., June 29-July 1, 1964.

been concerned about the adsorption occurring on the reference electrode. In an early study, Frost and Hurka (13,14) used a coating of paraffin wax on a metal as a reference electrode. Phillips (19), employing the vibrating condenser method with a recording system and using gold-plated steel coated with a Langmuir-Blodgett multilayer of calcium palmitate as the reference electrode, investigated the possibility of detecting trace contaminants in the atmosphere by the adsorption of a film on a bare stainless steel electrode. It is of particular interest here that Phillips succeeded in detecting concentrations of 1 part in 10^7 by weight of ethyl alcohol, ethyl chloroacetate, ether, acetone, nitrobenzene, and amyl acetate; concentrations between 1 part in 10^6 and 1 in 10^7 of hydrogen chloride or ammonia were also detected.

Bewig and Zisman (20) have shown the many advantages of using a coating of a per-fluorocarbon resin, such as FEP Teflon, on the reference electrode. Because of the remarkably low surface energy of the resulting surface, the adsorption of a gas or vapor is very small unless cryogenic temperatures are used to cause condensation. Investigations with this technique include studies by Bewig and Zisman (20,21) of the adsorption from solution of the fatty amines, alcohols, and acids; by Timmons and Zisman (22) of octanol and several aryl phosphate esters and chlorinated aromatic hydrocarbons; by Bewig and Zisman (23) of the polarization during adsorption of various nonpolar compounds; and by Timmons and Zisman (24) of the family of fatty acids adsorbed on various metals. We propose to review here the results of these investigations and to discuss some of the future possibilities of using the contact potential differences between metals to detect and measure the presence of trace contaminants in the atmosphere.

PROBLEMS OF TECHNIQUE AND CONTROL

Although it is true that the contact potential measurements require careful control of the atmospheric and the surface conditions to obtain reproducible and meaningful data, many past investigators have not recognized that the extraordinary sensitivity of the method requires that extraordinary care be exercised in choosing and preparing the electrodes, in controlling all chemicals used in adsorption studies, and in coping with trace chemicals present in the surrounding atmosphere.

Much care is needed in preparing the electrodes. It is essential to remove any polishing agents, such as emery, chromium oxide, rouge, or aluminum oxide, which may have become imbedded in the metal surface in order to avoid spurious electrostatic potentials created by the presence of such dielectric particles (11,25). Vigorous scrubbing of the polished surface with clean, grease-free tissues wet with distilled water will suffice unless the metal is soft. For the reference electrode we have found it generally advisable to use an inert metal like pure bulk gold or platinum. Freedom from base-metal impurities is desirable because such materials tend to diffuse gradually to the surface thus causing a change in the contact potential. In investigations using the vibrating condenser method (20,21,23), the reference electrode was constructed as shown in Fig. 1, the coating having been deposited on the electrode using the fluidized bed technique (26). An essential precaution is to eliminate any electrostatic charging of the surface of the FEP Teflon-coated electrode. Any slight movement of a liquid or a solid upon the surface of the coating during preparation or handling will create frictional charges giving rise to large and spurious potentials. If they do develop, the surface charges generally can be removed quickly by radiating the atmosphere in the vicinity of the reference electrode with a weak source of α -particles, such as the commercial "Static-Master." Once this has been done, great care must be exercised in avoiding further handling of the reference electrode.

Once the active electrode has been polished and cleaned, it is extremely effective in adsorbing trace contaminants by contact or by adsorption from the atmosphere. In general, it is undesirable to use organic solvents of any kind, polar or nonpolar, to clean the active

electrode in the last stage of surface preparation, since an adsorbed monolayer of even a pure volatile solvent may be left (23) which is usually difficult to remove completely without heating the electrode to a temperature of 100°C or more. Neglect of this precaution can result in spurious effects of several hundred millivolts.

An active metal surface is not suitable for adsorption investigations unless it remains free from organic contamination up to the instant the substance to be studied has been adsorbed. The complete and spontaneous spreading of clean distilled water is one of the most sensitive and useful tests for freedom from organic contamination of the metal surface. A small piece of polished platinum foil when flamed and then exposed to the atmosphere in the vicinity of the active electrode is tested with a drop of clean distilled water occasionally to be sure that atmosphere has not been a source of hydrophobic contamination. The most reproducible results with active metal electrodes were obtained by abrading, then wet polishing on grease-free cloths, scrubbing the surface with flowing, grease-free distilled water, and finally drying each in a clean dessicator or chamber.

One of the most troublesome problems is to eliminate traces of organic impurities in the gases used. Much previous work on metal contact potentials has been compromised by inadequate attention to this problem. The most common difficulty arises from the presence of traces of organic compounds in the air or in compressed gases, which adsorb on the active electrode to form hydrophobic films altering the contact potential by from 50 to 500 millivolts. Because of this difficulty it is advisable to avoid any plastic materials including tubing (except Teflon) in the vicinity of the active electrode or the gas stream (20).

The two electrodes form a two-plate condenser, which has been made as small in area as possible because of the difficulty of obtaining sufficiently homogeneous and pure metals and of maintaining the polished surfaces sufficiently clean. Freedom from metallic impurities may have to be extreme in some investigations because in many metals a trace of an impurity may diffuse to the surface and disproportionately affect the surface composition and surface potential. For this reason our reference electrodes have been made of gold or platinum of 99.999 wt-percent purity. The separation d between electrodes (Fig. 2) should be sufficiently small as compared to the diameter to avoid any difficulties arising from electrostatic edge or fringing effects. Some past investigators have complained of the effect of varying d on the contact potential difference; this difficulty will arise from neglecting the effect of the fringing field; it is exemplified in Fig. 2 which shows the results of varying d using two aged electrodes having the dimensions indicated (27).

Water adsorption can alter the contact potential difference by as much as 500 millivolts because of the large dipole moment ($\mu = 1.8 \times 10^{-18}$ esu.) and the strong hydrogen-bonding ability of the water molecule. One of the reasons why bare metal electrodes are unreliable for reference electrodes is the large effect on the contact potential caused by differences in water adsorption as the relative humidity and temperature vary. Because of the hydrophobic property of the FEP Teflon coating on the reference electrode, the surface is made much less sensitive to water adsorption; because of the chemical stability of the coating, drift caused by oxidation or hydrolysis of the plastic is avoided. The former effect shown in the upper curve of Fig. 3 by the contact potential difference (ΔV) between aluminum and iron as a function of the relative humidity of an atmosphere of nitrogen at 25°C. The lower curve (Fig. 3) is ΔV for the same two metals coated with FEP Teflon (20). Figure 4 plots measurements of ΔV for bare, clean platinum (and gold)

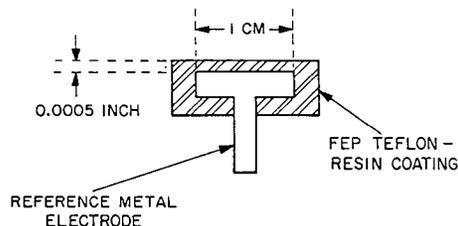


Fig. 1 - Cross section of reference electrode

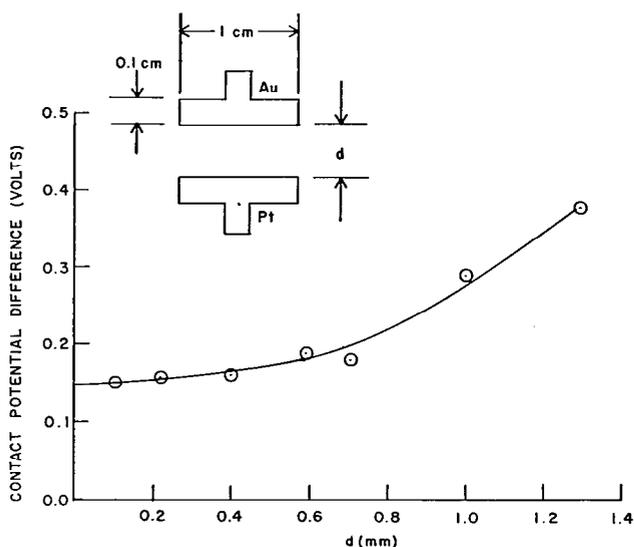


Fig. 2 - Typical measured contact potential difference of two aged metals as d is varied

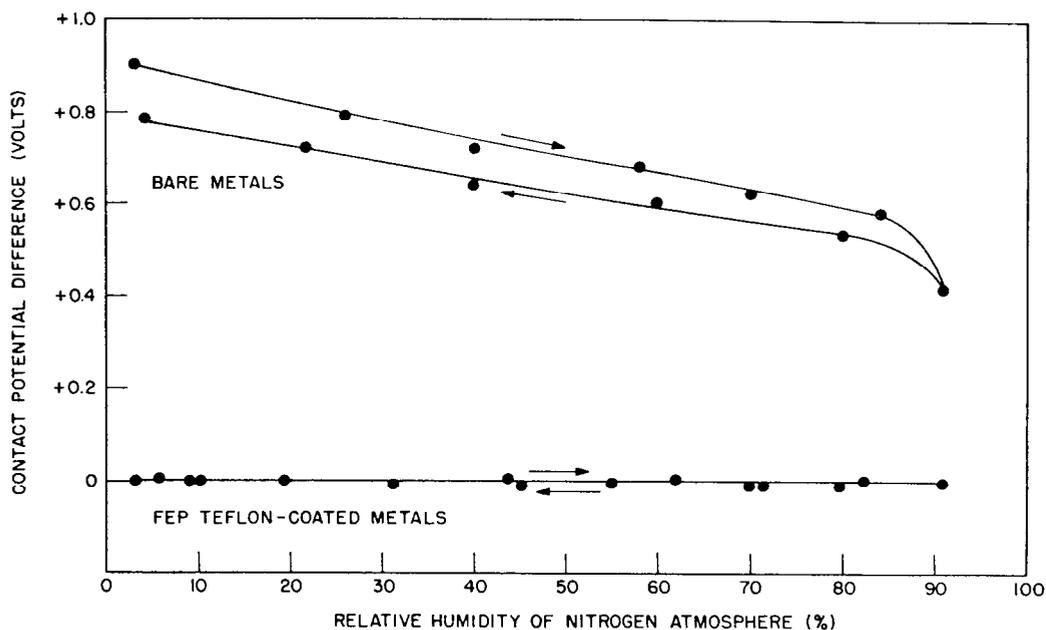


Fig. 3 - Contact potential difference of aluminum relative to soft steel compared to the same metals coated with FEP Teflon; temperature variation 21° to 24°C , total elapsed time 32 hours

against gold coated with FEP Teflon resin. As seen there is only a minor effect on ΔV of varying the relative humidity when it is in excess of 1% but less than 75%. Since some (or all) of the attached water is usually reversibly adsorbed and can cause major changes in ΔV , it is obvious in contact potential studies of adsorption on metals that either the water in the atmosphere must be completely removed, which is very difficult, or else the amount adsorbed on the electrodes must be maintained as low and constant as possible during a given experiment. Usually we have resorted to the latter approach and hence have carefully controlled the temperature and relative humidity.

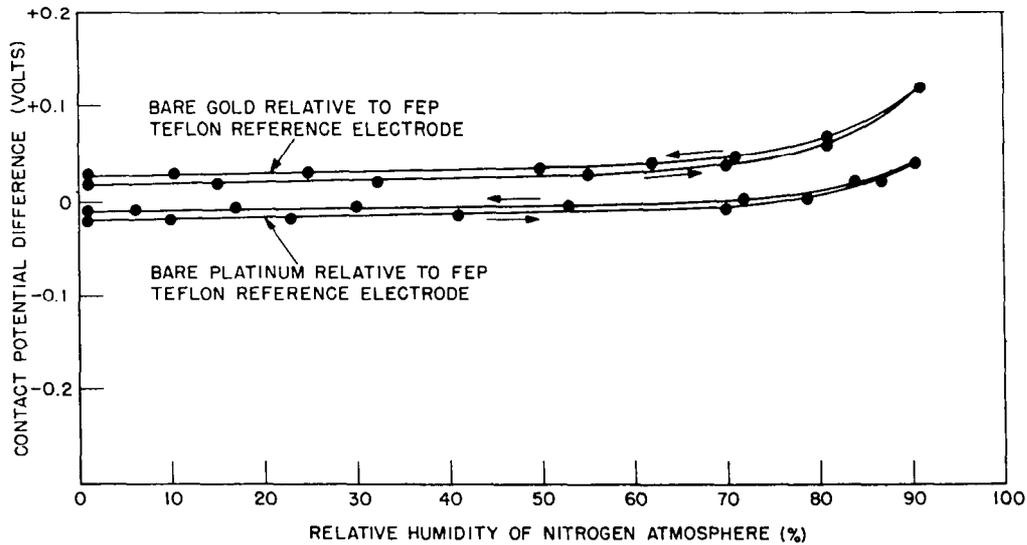


Fig. 4 - Contact potential difference of gold and platinum relative to FEP Teflon-gold reference electrode; total elapsed time 32 hours

Although the use of a low-energy plastic coating on the reference electrode can do much to aid in investigations of adsorption, there are definite limitations to this approach. In experiments lasting for days or weeks, water vapor and many other vapors will gradually penetrate the coating to alter the reference potential. Also gases (e.g., helium and hydrogen) which are much smaller than the pores between molecules of the plastic coating will diffuse rapidly through the coating to adsorb on the metal. This difficulty is illustrated by the two curves of Fig. 5 of ΔV vs time for platinum and gold in an atmosphere of pure hydrogen and helium (20). One curve gives the experimental results obtained with the bare electrodes, and the other those obtained when each metal was coated with FEP Teflon resin. Obviously, a coated noble metal cannot serve as a useful reference electrode in such a gaseous environment.

PREPARATION OF WELL-DEFINED ADSORBED MONOLAYERS

In attempting to establish the reliability and limits of using the contact potential difference between metals in detecting and studying adsorption, it was considered essential to study initially the adsorption of films on the active electrode which had known composition, surface concentration, and molecular orientation. To do so, the "retraction method" was used for preparing adsorbed monolayers of polar-nonpolar organic compounds on smooth, clean, high-energy surfaces (28,29). A condensed monolayer of each compound was usually adsorbed on the active metal electrode by using the retraction method with either or both a solution or a melt. Sometimes the wiping-down technique described by Hardy (30) was used; this method has been investigated fully and extended by Levine and Zisman (31).

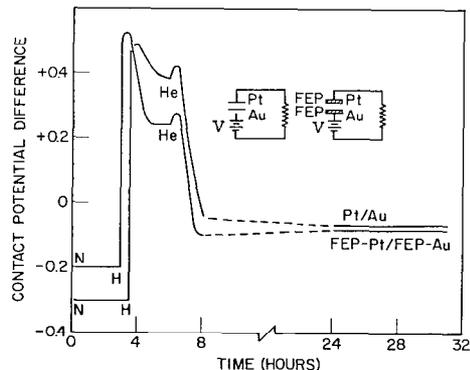


Fig. 5 - Contact potential difference of platinum relative to gold with and without FEP Teflon resin coating in hydrogen and helium gases

Because past research on the equilibrium contact angle and its relation to the surface chemical constitution of solids and liquids (28) had revealed the advantages of using the contact angle of various pure liquids to help characterize the surface composition and molecular packing of adsorbed organic films, the contact angle of methylene iodide (and sometimes that of water, glycerol, or hexadecane) was used frequently to verify the constancy of surface packing in the adsorbed films and obtain independent data on the nature and orientation of the adsorbed film. Used for these measurements were methylene iodide, which had been freshly percolated through a column of silica gel and alumina and had a surface tension of 50.8 dynes/cm at 20°C; triply distilled water (distilled the last two times in quartz) having a surface tension of 72.8 dynes/cm at 20°C; chromatographically analyzed n-hexadecane having a melting range of 18° to 19°C and a surface tension of 27.6 dynes/cm at 20°C; and U.S.P. glycerol which had been dried by percolation through a column of 4A Linde sieve and had a surface tension of 63.4 dynes/cm at 20°C. An example of the equivalence of an adsorbed monolayer of polar-nonpolar molecules prepared by retraction from the melt or from solution and of the use of the contact angle θ of methylene iodide to verify this equivalence is given in Table 1 for n-octadecylamine adsorbed on polished platinum (29).

Table 1
Equivalence of Various Retracted
Monolayers of Octadecylamine

Method of Isolating Adsorbed Film on Solid	Methylene Iodide Contact Angle at 25°C (degrees)
Retraction from molten amine	69
Retraction from hexadecane solution	70
Retraction from dicyclohexyl solution	68 (at 20°C)
Retraction from nitromethane solution	69
Retraction from aqueous solution of $C_{18}H_{37}NH_3Cl$	69

INTERPRETATION OF HELMHOLTZ EQUATION

The contact potential difference (ΔV) caused by the adsorption of a condensed monolayer of a polar-nonpolar compound results because each molecule in such a monolayer contains one or more oriented electrostatic dipoles. The Helmholtz equation

$$\Delta V = 4 \pi n \mu_p \quad (1)$$

relates ΔV to n , the number of molecules adsorbed per unit area, and to μ_p , the perpendicular component of all the dipole moments resulting from the adsorption process. In practice, the interpretation of μ_p is difficult because it is the vector sum of all dipole moments in or associated with the molecule and so includes (a) the permanent electrostatic dipoles present in the adsorbate molecules, (b) effects due to any induced polarization caused by the proximity of the molecule to the surface of the metal, (c) contributions due to a reorientation of adsorbed atmospheric gases present, and (d) polarization in the molecule arising from mutual inductive effects between neighboring adsorbed molecules. Thus, μ_p bears no simple relation to the dipole moment of the adsorbed molecule as determined in the gaseous state, although it may be approximately proportional.

The difficulties in relating the dipole moment in the gaseous state to the value of μ_p obtained in any experiment with an insoluble monolayer adsorbed on bulk water have led some investigators to doubt the applicability of the Helmholtz equation to these systems. But a recent investigation by Bennett, Jarvis, and Zisman of insoluble monolayers of an homologous family of ω -monohalogenated fatty acids (32) has given good evidence of the applicability of this relation to such studies and, therefore, by implication to the present related studies of adsorbed films on metals. In their work the group of atoms attached to the omega or terminal carbon atom had a large dipole moment which was far enough removed from the surface of the water to eliminate any contributions to its dipole moment caused by any water reorientation or ionic double layer effects. Hence, the Helmholtz relation enabled them to obtain more easily interpreted values of the ω -dipole moment contribution. Not only were reasonable moments so obtained, but good evidence was found for concluding that the terminal dipole moments were greatly altered by mutual laterally induced polarization. This result is of much help in interpreting the observed dipole moments of molecules adsorbed on metal surfaces.

SOME FUNDAMENTAL EXPERIMENTS ON ADSORBED POLAR MOLECULES

Levine and Zisman (31) have shown that a condensed monolayer of a fatty acid or amine containing 14 or more carbon atoms per molecule, when adsorbed on a smooth hard solid by retraction from the melt, acts like a solid film at 20°C in that it possesses remarkable durability upon being rubbed repeatedly under loads exceeding 100,000 psi. This is the justification for Sir William Hardy's (30) early method of preparing an adsorbed monolayer by "wiping down" an excess deposit of a fatty acid or alcohol on a metal or on glass. Bewig and Zisman (20) recently investigated further the durability of rubbed-down as well as retracted monolayers of octadecylamine. Measurements of the contact potential difference between a film-coated platinum electrode and a reference electrode of gold coated with FEP resin were made after first depositing the film on platinum and again after the various stages in rubbing down the retracted film by vigorously wiping the surface with clean and grease-free filter paper. For example, the active electrode was covered with a small amount of the amine which had been applied while molten and then allowed to solidify. The results in Table 2 reveal that the first wiping practically removed all of the octadecylamine in excess of a solid monolayer. Subsequent additional wiping did not alter the contact potential difference nor did it alter the contact angle of 68 degrees exhibited by methylene iodide. Such contact potential measurements resulted in a most convincing verification of the great durability of such a monolayer, as well as the identity of this monolayer with a retracted monolayer.

Studies of the contact potential changes caused by the adsorption on a metal of an homologous family of organic polar-nonpolar compounds have been productive, as in Bewig and Zisman's (21) investigation of the homologous family of primary n-aliphatic amines adsorbed on platinum. Figure 6 is a graph of ΔV as a function of N, the number of carbon atoms in the amine molecule. Figure 7 is a corresponding plot of the cosine of the methylene iodide contact angle, θ , as a function of N. Attention is called to the reproducibility of the measurements and to the close correspondence in the values of N at which the asymptotic maximum and minimum value is attained in each graph. Both Figs. 6 and 7 give corroborative

Table 2
Electrical Evidence of
Durability of Solid
Monolayer* (23°C; 50% R.H.)

Wipe No.	Contact Potential Difference (volts)
0	1.031
1	0.899
2	0.878
3	0.893
4	0.897
5	0.884
6	0.892

*Active electrode - Platinum coated with bulk C₁₈ amine. Reference electrode - Gold with FEP resin coating.

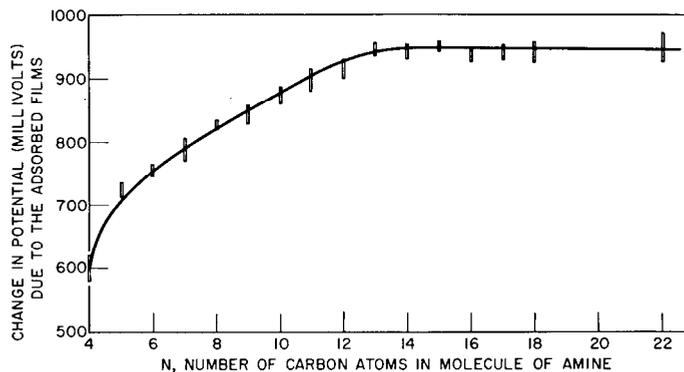


Fig. 6 - Contact potentials of homologous amines adsorbed on platinum from nitromethane

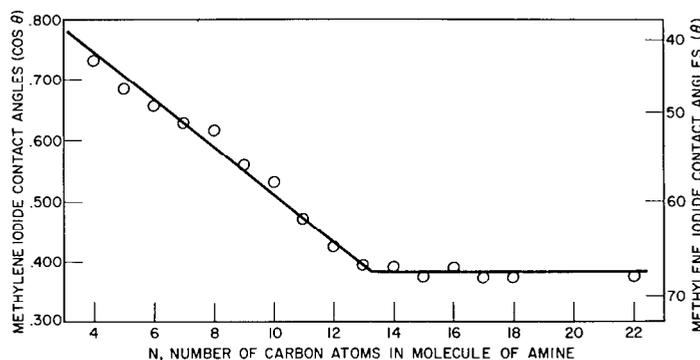


Fig. 7 - Contact angles of homologous amines adsorbed on platinum from nitromethane

evidence that the monolayers of compounds containing 14 or more carbon atoms per molecule are equally closely packed and oriented and cause the same contact potential change. Lower homologues show lower values of ΔV and θ because the number of terminal methyl groups per unit area decreases with N and because the principal molecular axis of the molecule is able to tilt and oscillate to a greater extent due to decreased intermolecular cohesion.

Figure 8 is a graph of ΔV as a function of the time allowed for solution adsorption on platinum before retracting an adsorbed film of octadecylamine from a solution of nitromethane or hexadecane. The dotted horizontal curve has the same value of ΔV as a close-packed adsorbed monolayer of octadecylamine adsorbed by retraction from the melt. This means that after very short times of immersing the electrode in the nitromethane solution, the retracted film was a close-packed monolayer of octadecylamine which was entirely free of solvent molecules. The lower curve results from analogous experiments using a solution of octadecylamine in *n*-hexadecane. It will be seen that if the time of adsorption is less than about six hours, the retracted film will contain some hexadecane molecules trapped in it. However, if sufficient immersion time is allowed so that adsorption equilibrium can be attained, the retracted film is entirely free of hexadecane because ΔV is practically identical with that observed on the film adsorbed from nitromethane or from the melt.

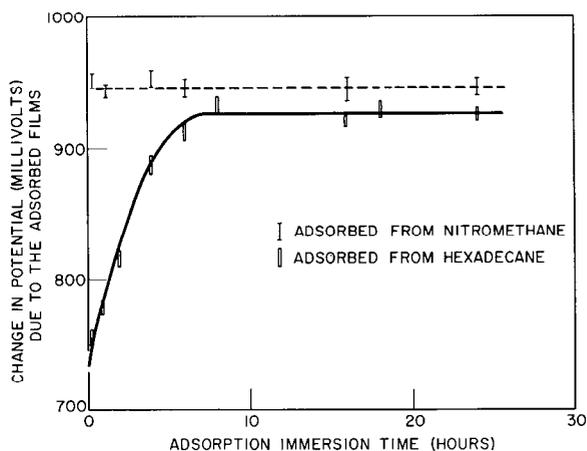


Fig. 8 - Contact potentials of octadecylamine adsorbed on platinum from nitromethane and hexadecane

A saturated alkane molecule has a zero dipole moment in the vapor state, and therefore a reasonable assumption is that it is negligible in the mixed adlineated adsorbed films described above. If the terminal methyl group of the alkane is in contact with the platinum electrode, it may become polarized inductively. However, if no contact is made, the induced polarization effect may become negligible. Assuming that the adlineated alkane molecules trapped in the film do not contribute to ΔV , it follows that ΔV is determined solely by the number of amine molecules adsorbed per unit area and by the perpendicular component of the dipole moment of the amine. If the alkane molecules are so located in the mixed film that the outermost methyl groups are situated approximately in the same plane as the methyl terminals of the amine molecules, then the surface density of outermost methyl groups in the mixed film would be the same as in the pure film because the cross-sectional areas of the amine or alkane molecules are nearly equal. Hence, unlike ΔV , the contact angle, θ , would not be effected by the presence of adlineated alkane molecules. Since the value of ΔV of 945 millivolts obtained from the study of octadecylamine in nitromethane is due solely to the oriented dipoles of close-packed amine molecules adsorbed on the platinum, this value can be used as a reference for computing the proportion of amine molecules to adlineated molecules in the mixed film. Thus, from the lower curve of Fig. 8 one can compute how the percentage of alkane molecules in the mixed film decreased as the time of immersion increased.

Similar studies of retracted films of amines in various solvents has made it possible to explain the conditions which limit the formation of mixed retracted films. In general, the largest effects were found when the length of the aliphatic solvent molecule was equal to that of the aliphatic amine. When the length of the amine and alkane differed by more than 4 carbon atoms per molecule, adlineation was decreased. No adlineation occurred when branches in either molecule were larger in size than a methyl group. It was also demonstrated that adlineated films were metastable in that they were prepared from a system which had not yet reached solution adsorption equilibrium. These results gave good evidence that contact potential measurements made in controlled atmospheres are a good means of studying adsorption from solution.

Among the many liquids reported by Hare and Zisman (33) in their study of "autophobic liquids," certain aryl phosphate esters, chlorinated aromatic hydrocarbons, and methylene iodide were also found to be nonspreading on high-energy surfaces no matter how much they were purified and, hence, were assumed to be autophobic also. Recently Timmons and Zisman (22) have used the contact potential method to demonstrate that these liquids were definitely autophobic. Certain by-products from that investigation have much interest here.

Table 3 gives the values of ΔV caused by the adsorption of a close-packed monolayer of each liquid adsorbed on platinum. The estimated value of μ_p is given for the adsorbed molecules assuming closest packing with the polar group as close as possible to the metal surface. The equal values of ΔV for tri-*p*-cresyl phosphate and the corresponding phosphite are good evidence of a reaction, or association, of the unpaired electrons in the phosphite phosphorus atom with oxygen atoms already adsorbed on the surface of the platinum, for there would then result an adsorbed molecular species identical with that of the phosphate and, thereby, would lead to the same apparent dipole moment. The Arochlor materials listed are mixed chlorinated biphenyls which average three, four, and five chlorine atoms per molecule, respectively. A reasonable explanation of their values of ΔV were also given in terms of the dipole moments and the location of the chlorine atoms in the biphenyl molecule. Methylene iodide is particularly interesting because the molecule, although having a polar-nonpolar structure, is not hydrophilic, and hence this liquid is being used in a number of current studies of adsorption on hydrophilic solid surfaces which will be reported subsequently.

Table 3
Contact Potential Differences
Resulting from Monolayers Adsorbed on Platinum
(20°-25° C; 50% R.H.)

Adsorbed Compound	Contact Potential Difference ΔV (volts)	Calculated Apparent Perpendicular Moment $\mu_p \times 10^{18}$ esu
Tri- <i>p</i> -cresyl Phosphate	0.620	1.65
Tri- <i>p</i> -cresyl Phosphite	0.619	1.65
Arochlor 1242	0.110	0.34
Arochlor 1248	0.053	0.18
Arochlor 1254	-0.020	-0.07
n-Octanol	0.140	-
n-Octanoic Acid	0.120	-
Methylene Iodide	0.120	0.11

The calculated dipole moments given in Table 3 are all considerably less than the values determined for each compound in the gaseous state; it is believed this is the result of the contributions to μ_p caused by induced polarization from the metal surface and from neighboring adsorbed molecules as well as from the effect of any water dipoles left adsorbed on the metal. The ΔV data are also interesting in showing that the studies of ΔV as a function of the chemical constitution of the adsorbed compound need not in any way be limited to simple compounds.

Most recently we have used the contact potential method to study the properties of adsorbed films of the homologous family of saturated, normal fatty acids (24). The results in Figs. 9 and 10 using platinum and NiO substrates are analogous to those obtained with the primary fatty amines on platinum, except for the minimum in Fig. 9 at $N = 3$. Remarkably interesting results were obtained, however, with the baser metals, iron, nickel, chromium, copper, silver, tungsten, molybdenum, niobium, aluminum, cadmium, magnesium, tin, and lead. Values of ΔV resulting from a given condensed fatty acid film on each metal were reproducible but varied with the nature of the metal; they are indicative of differences in the type or extent of the interaction with the metal surface. Contact potential

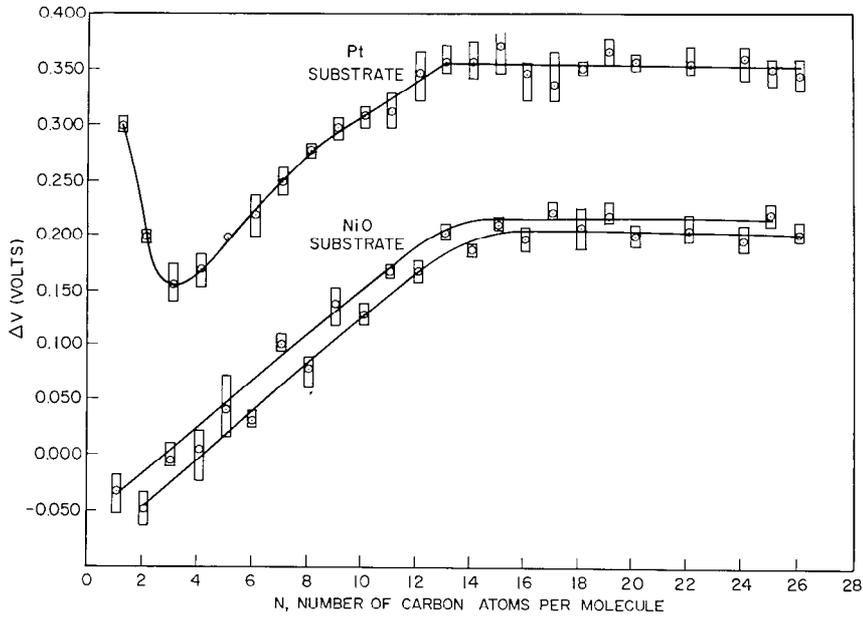


Fig. 9 - Contact potential differences (ΔV) of homologous fatty acids adsorbed on Pt and NiO

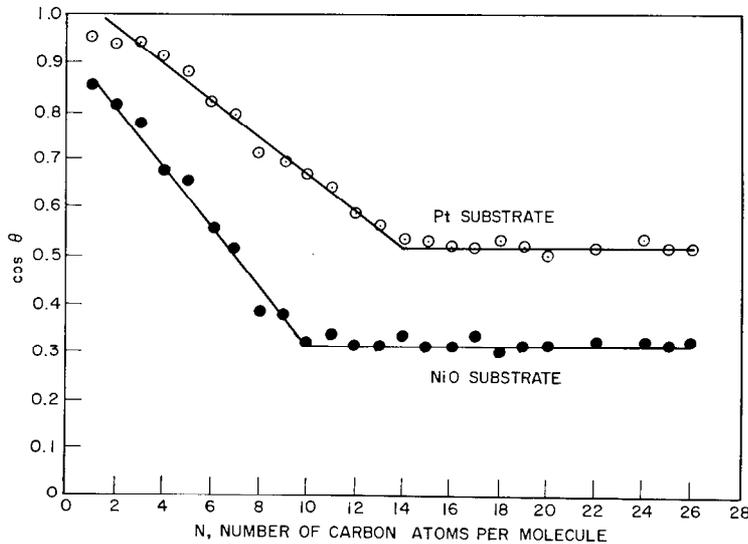


Fig. 10 - Methylene iodide contact angles (θ) on fatty acid monolayers (23°C ; 50% R.H.)

values varied greatly with the nature of the metal (see Table 4), and the extremes were as high as 365 millivolts for tungsten and as low as -95 millivolts for lead. Gold, which has much importance to us because it is used in reference electrodes, exhibited a value of 140 millivolts. On the noble metals the adsorption is physical; on some of the other metals chemisorption may have occurred.

Furthermore, the molecular packing of the adsorbed fatty acid films varied with the lattice spacing of the metal. Whereas films on beryllium, aluminum, iron, magnesium,

Table 4
 Contact Potential Difference and Methylene Iodide
 Contact Angle Data for Monolayers of Stearic and Nonadecanoic
 Acids Adsorbed on Various Metals (23°C; 50% R.H.)

Adsorbent Metal	Stearic Acid Monolayer		Nonadecanoic Acid Monolayer	
	ΔV (volts)	θ (degrees)	ΔV (volts)	θ (degrees)
Tungsten	0.365	59	0.415	59
Platinum	0.355	58	0.360	58
Molybdenum	0.350	65	0.380	64
Aluminum	0.300	68	-	-
Nickel	0.275	63	0.315	63
Chromium	0.260	61	0.305	62
Iron	0.240	71	-	-
Silver	0.235	61	-	-
Niobium	0.220	64	0.330	63
Gold	0.140	45	0.140	47
Cadmium	0.115	64	0.130	65
Tin	0.110	66	0.130	65
Copper	0.095	66	0.170	66
Magnesium	-0.070	68	-	-
Lead	-0.095	62	-	-
Beryllium	-	68	-	-
Zinc	-	68	-	-

and zinc exhibited closest packing of fatty acid molecules and a corresponding methylene iodide contact angle of 68 degrees, those on the other metals were less closely packed. Calculations revealed that these packings corresponded with the lattice spacings in the underlying metals so that in the latter group of metals the adsorption sites were too far apart for the fatty acids to come into closest packing. The fact that the spacings of fatty acid molecules were readily related to the metal lattice parameter rather than that of the oxide lattice may be evidence of epitaxy and a result of the extreme thinness of the oxides present. Unquestionably, other interesting and productive investigations can be made on the adsorptive properties of fatty acids on metals and metal oxides by the contact potential and contact angle methods.

SOME FUNDAMENTAL EXPERIMENTS ON ADSORBED NONPOLAR MOLECULES

In adsorption processes the induced moment μ_i is in the direction of the inducing electrical field of the adsorbing surface; it may not be negligible because of the strong polarizing effect of the electrostatic field in the immediate vicinity of the surface of every metal which serves to restrain escape of conduction electrons from the metal lattice. In

principle, it should be possible to calculate μ_i from a knowledge of the molecular polarizability of the adsorbed molecule and the intensity of the average electrostatic field (\bar{F}_0) existing in the region occupied by it. DeBoer (34) has pointed out that adsorbed molecules may develop large induced electrostatic moments caused by the polarizing action of the field of force of the solid, and Mignolet (35,36) has demonstrated experimentally by contact potential difference measurements that μ_i for xenon adsorbed on gold at extremely low temperatures is 0.276×10^{-18} esu.

In view of the reproducibility in ΔV obtained in the experiments with adsorbed condensed monolayers of polar fatty amine and acid molecules, it was believed possible, by using the same technique, to measure any polarization in adsorbed nonpolar molecules induced by the metal surface. This led to recent experiments (23) on films of the n-alkanes from hexane through hexadecane, carbon tetrachloride, cyclohexane, dicyclohexyl, benzene, toluene, and o-xylene adsorbed on platinum. As large contributions to ΔV can result through adsorption from the nonpolar liquid of a polar (or other more adsorptive) impurity sufficient to coat the metal with a monolayer or less, extreme care was required in purifying the nonpolar liquids for this investigation. Also, since each of the pure liquids studied always spread completely on the clean metal electrode surface, the retraction method of adsorbing a monolayer could not be used here to prepare an adsorbed condensed monolayer. Therefore, suitable adsorbed films of each liquid were prepared either by allowing a thick layer to evaporate on the metal electrode at room temperature or by using the wiping and rubbing-down technique. Furthermore, Fox, Hare, and Zisman (37) had shown earlier that a well-rubbed film of the nonpolar liquid, n-hexadecane, on platinum did indeed behave as an adsorbed condensed film on which a plot of the cosine of the contact angle of each liquid sessile drop plotted against the liquid surface tension γ_{LV} agreed reasonably well with the data obtained using a smooth clean block of polyethylene. They had concluded that in the residual adsorbed layer the molecules of n-hexadecane were lying flat on the surface, thus presenting to the liquid sessile drops a surface comprised essentially of close-packed CH_2 groups.

Regardless of whether the evaporation method or the wetting and rubbing-down technique was used, each of the residual films in the experiments was so durable that repeated and continued vigorous rubbing of the adsorbed film with grease-free, clean filter papers did not change the value of ΔV . When a platinum or gold surface, which was not covered by an organic film, was rubbed with this kind of paper in the same manner, the change in ΔV was always less than 10 millivolts. Furthermore, no significant adsorbed impurity was contributed nor surface change caused by the rubbing-down method using the other metal systems reported. Each one of the evaporated or rubbed-down liquid films was also studied by measuring under the same conditions the contact angles exhibited by sessile drops of four pure reference liquids: water, glycerine, methylene iodide, and n-hexadecane.

Measurements were made at 20°C of ΔV and θ for each of the four reference liquids on the adsorbed rubbed-down films and also on the evaporated films remaining on polished clean platinum for each of the n-alkane liquids having an even number of carbon atoms per molecule, from n-hexane to n-hexadecane. The first interesting result found was that ΔV , and also θ , had the same value for both evaporated and rubbed-down films. Table 5 summarizes the average values of ΔV and θ obtained for the homologous family of n-alkanes on platinum and shows that both ΔV and θ did not vary with the number of carbon atoms in the hydrocarbon molecule. Note also that the water, glycerol, and methylene iodide contact angles, which were about 78, 64, and 24 degrees, respectively, are all considerably smaller than the corresponding values of 102, 94, and 66 degrees obtained on close-packed films of octadecylamine (38) where the methyl groups were outermost; they are closer to but smaller than the values of 94, 79, and 52 degrees reported for solid polyethylene by Fox and Zisman (39). However, there is a better basis for comparison with the earlier measurements of 79, 69, and 52 degrees, respectively, by Fox, Hare, and Zisman (37) on

Table 5
 ΔV and Contact Angle θ of n-Alkanes Adsorbed
 on Platinum (20°C; 50% R.H.)

Compound Adsorbed	ΔV (volts) $\pm 0.010v$	Contact Angle θ (degrees)			
		Water	Glycerol	Methylene Iodide	Hexadecane
n-Hexane	0.215	74	64	24	0
n-Octane	0.220	75	63	24	0
n-Decane	0.220	78	64	23	0
n-Dodecane	0.205	79	63	23	0
n-Tetradecane	0.210	78	63	24	0
n-Hexadecane	0.215	78	63	23	0

rubbed-down films of n-hexadecane on platinum. The solubility of the adsorbed alkane films in methylene iodide was found to be causing the lower value of θ for this liquid than on solid polyethylene. The greater penetration of water molecules through the adsorbed film to the metal substrate lowered θ for water to a value lower than that for solid polyethylene. However, the larger molecules of glycerol could not so readily penetrate the film and the solubility of the alkane in it was negligible, hence the contact angles of glycerol were in reasonably good agreement with either those of solid polyethylene or of a well-rubbed hexadecane film.

The dependence of ΔV and θ on molecular structure was studied further by treating in the same way each of a variety of nonhomologous pure, nonpolar organic liquids and the results are listed in Table 6, n-hexane being included for purposes of comparison. Reasonably good agreement is found among the contact angles of 55, 52, and 40 degrees for water, glycerol, and methylene iodide, with the residual film of CCl_4 and those of 66, 56, and 34 degrees for a condensed adsorbed monolayer of perchloropentadienoic acid by Ellison and Zisman (40). Agreement would be expected since both films have exposed surfaces of closely packed covalent chlorine atoms. Again, ΔV and θ had the same values for evaporated and rubbed-down films. The conclusion is unavoidable that both types of residual films are condensed monolayers of the organic molecule having values of ΔV and θ which are characteristic. These residual adsorbed films of nonpolar organic liquids were by no means fugitive in character; even when the bulk liquids had high vapor pressures, the films were remarkably stable at 20°C. Thus, when a rubbed-down film of hexane (or dodecane) on platinum was stored in a clean atmosphere, the change in ΔV was only 15 millivolts after 2 hours; this is comparable to the change in ΔV of a fatty amine monolayer adsorbed on the same metal.

An alkane would be unlikely to chemisorb on platinum at 20°C, and one would expect the adhesion of the residual film to be through physical adsorption. A simple experiment was devised to establish this point firmly. The platinum electrode was rested in contact with one end of a massive cylinder of brass heated at the opposite end by a small electrical heater which was arranged to be outside of the stainless steel enclosure containing the reference and platinum electrodes. By this means it was possible to raise the temperature of the platinum gradually while measuring its contact potential difference with the reference electrode. The experimental procedure was to coat the platinum with the alkane liquid, allow evaporation to remove all but the residual adsorbed film, and measure ΔV as a function

Table 6
 ΔV and Contact Angle θ of Various Compounds Adsorbed
 on Platinum (20°C; 50% R.H.)

Compound Adsorbed	ΔV (volts) $\pm 0.010v$	Contact Angle θ (degrees)			
		Water	Glycerol	Methylene Iodide	Hexadecane
n-Hexane	0.215	74	64	24	0
Benzene	0.130	64	52	22	0
Toluene	0.130	64	50	20	0
o-Xylene	0.145	63	51	20	0
Cyclohexane	0.185	44	59	36	0
Dicyclohexyl	0.210	62	54	32	0
Carbon Tetrachloride	0.245	55	52	40	0

of time while the temperature of the platinum was gradually increased to some maximum temperature around 130°C and then cooled to 24°C. A similar procedure was followed with the platinum entirely free from the adsorbed alkane. In this way it was found that the n-hexane molecules could be removed completely by heating the system to 100°C and then the surface potential reverted to its original value as the system cooled. Hence the process was one of physical adsorption.

When adsorbate molecules do not have a permanent dipole moment, one would expect μ_p in Eq. (1) to be proportional to the average electrostatic field strength (\bar{F}_o) existing in the region occupied by the adsorbed molecule. If the normal component of the oriented molecular polarizability is α_p , then μ_p can be calculated by

$$\mu_p = \alpha_p \bar{F}_o. \quad (2)$$

Hence according to Eq. (1)

$$\Delta V = 4\pi n \alpha_p \bar{F}_o. \quad (3)$$

Therefore, ΔV for any one compound adsorbed on the different metals should vary as \bar{F}_o varies with the constitution of the metal. Experimental values of ΔV were obtained (23) for rubbed-down films of pure n-hexane and benzene adsorbed under the same conditions on nine different elemental metal surfaces (Tables 7 and 8). Attention is called to the constancy of θ and the large variation ΔV for either hexane or benzene in going from nickel to tin. The almost constant values of the contact angles of the liquids in Tables 7 and 8 are good evidence that the adsorbed film of hexane (or benzene) on the different metals has the same orientation and surface concentration.

Assuming the residual adsorbed film is a condensed monolayer, the Helmholtz relation in Eq. (1) can be used to calculate μ_p from the measured value of ΔV if n , the number of molecules adsorbed per unit area, is known. In the case of n-hexane, the value of n was taken as corresponding to closest packing of the horizontally arranged molecules. Since measurements of a Stuart-Briegleb molecular model indicate that an n-hexane molecule can be just contained in a rectangle 10.2Å long and 4.2Å wide, the area per molecule is

Table 7
 ΔV and Contact Angle θ of n-Hexane Adsorbed
 on Various Metals (20°C; 50% R.H.)

Metal Substrate	ΔV (volts) $\pm 0.010v$	$\mu \times 10^{18}$ (esu) Calc	Contact Angle θ (degrees)			
			Water	Glycerol	Methylene Iodide	Hexadecane
Nickel	0.216	0.246	71	58	27	0
Chromium	0.220	0.251	75	65	24	0
Platinum	0.215	0.245	74	64	24	0
Silver	0.155	0.177	73	59	25	0
Copper	0.135	0.154	70	61	24	0
Gold	0.130	0.148	70	63	23	0
Tungsten	0.207	0.236	69	60	23	0
Cadmium	0.123	0.140	71	62	22	0
Tin	0.100	0.114	72	59	23	0

Table 8
 ΔV and Contact Angle θ of Benzene Adsorbed
 on Various Metals (20°C; 50% R.H.)

Metal Substrate	ΔV (volts) $\pm 0.010v$	$\mu \times 10^{18}$ (esu) Calc	Contact Angle θ (degrees)			
			Water	Glycerol	Methylene Iodide	Hexadecane
Nickel	0.124	0.118	59	55	23	0
Chromium	0.115	0.110	65	56	24	0
Platinum	0.122	0.116	64	52	22	0
Silver	0.070	0.067	60	53	23	0
Copper	0.091	0.087	59	51	23	0
Gold	0.092	0.088	60	54	20	0
Tungsten	0.101	0.096	55	52	21	0
Cadmium	0.083	0.079	52	51	22	0
Tin	0.052	0.050	50	52	20	0

$43 \times 10^{-16} \text{ cm}^2$. Therefore, n equals 2.33×10^{14} molecules/cm². Table 5 shows that the change in the contact potential due to the induced polarization of hexane on platinum was 0.215 volts. The value of μ_p calculated from Eq. (1) is 0.245×10^{-18} esu., which is a reasonable value. The resulting values of μ_p for n-hexane and benzene on the different metals are given in Tables 7 and 8.

It is possible to calculate ΔV using Eqs. (2) and (3) provided that \bar{F}_0 and α_p can be computed for each system studied. Values of α_p were calculated by the use of the concept of the oriented molecular polarizability of Meyer and Otterbein (41,42) in which the polarization of each bond in the molecule is treated as a tensor; hence a polarization ellipsoid exists for each bond having axial symmetry about the bond direction. Wang (43) has determined the lateral (α_1) and transverse (α_t) components of the bond polarizabilities for a number of molecular structures. In the case of an oriented molecule, when the electric field makes an angle φ with a directed vector of the bond, the bond polarizability is given by

$$\alpha_{\text{bond}} \approx \alpha_1 \cos^2 \varphi + \alpha_t \sin^2 \varphi \quad (4)$$

as was shown in the work of Denbigh (44) and Hirschfelder, Curtiss, and Bird (45).

$$\alpha_p = \sum_{\text{all bonds}_p} (\alpha_1 \cos^2 \varphi + \alpha_t \sin^2 \varphi). \quad (5)$$

For the entire molecule (M) we can then write

$$\alpha_p = \sum_{\text{bonds}} [\alpha_{(\text{C-H})_p} + \alpha_{(\text{C-C})_p}] \quad (6)$$

where the subscripts (C-H) or (C-C) refer to the carbon-hydrogen and carbon-carbon bonds, respectively.

Figure 11 is a drawing of the Stuart-Briegleb ball model of the n-hexane molecule in its stretched-out configuration with the principal axis of symmetry at the equilibrium distance r_0 from the idealized plane metal adsorbing surface. In this geometry all of the carbon-carbon bonds are parallel to the adsorbing plane, and it was assumed this arrangement corresponds to a maximum of α_p and hence to a minimum of the energy. There are 5 carbon-carbon bonds and 14 carbon-hydrogen bonds in the n-hexane molecule. Bond angles assumed are those shown by the Stuart-Briegleb ball model (i.e., $109^\circ 21'$) for the carbon-hydrogen bond angle. In the situation prevailing here, the electrical field of the adsorbing surface is directed along the normal, and φ is the angle between the bond direction and the normal. From the orientation and bond angles of the model, the perpendicular component of the total induced polarizability of the adsorbed molecule is given by

$$\alpha_p = 5\alpha_{t(\text{C-C})} + 14\alpha_{1(\text{C-H})} \cos^2 \varphi + 14\alpha_{t(\text{C-H})} \sin^2 \varphi. \quad (7)$$

Wang (43) has shown that

$$\begin{aligned} \alpha_{t(\text{C-C})} &= 0.2 \times 10^{-25} \text{ cm}^3 \\ \alpha_{1(\text{C-H})} &= 7.2 \times 10^{-25} \text{ cm}^3 \\ \alpha_{t(\text{C-H})} &= 6.2 \times 10^{-25} \text{ cm}^3. \end{aligned} \quad (8)$$

Using these values in Eq. (7), the result is that $\alpha_p = 96.9 \times 10^{-25} \text{ cm}^3$.

In calculating n and α_p for benzene, it was assumed from the dimensions of the molecular ball model that benzene adsorbed as a monolayer lying flat on the surface with an area

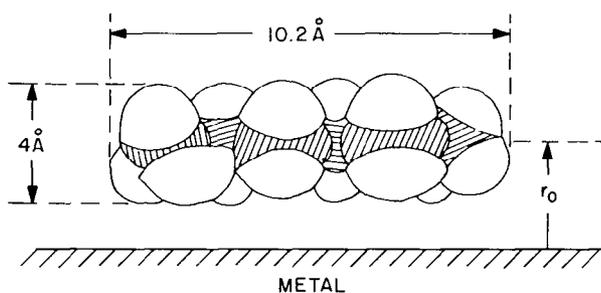


Fig. 11 - Elevation view of n-hexane molecule at equilibrium adsorption on a plane metal surface

per molecule of 36\AA^2 . Under such conditions of adsorption there are 6 C-H bonds, 3 C-C bonds, and 3 C=C bonds so that

$$\alpha_p = 6\alpha_{t(\text{C-H})} + 3\alpha_{t(\text{C-C})} + 3\alpha_{t(\text{C=C})}. \quad (9)$$

According to Wang

$$\begin{aligned} \alpha_{t(\text{C-H})} &= 6.2 \times 10^{-25} \text{ cm}^3 \\ \alpha_{t(\text{C-C})} &= 0.2 \times 10^{-25} \text{ cm}^3 \\ \alpha_{t(\text{C=C})} &= 9.6 \times 10^{-25} \text{ cm}^3. \end{aligned} \quad (10)$$

Finally, for benzene

$$\alpha_p = 66.6 \times 10^{-25} \text{ cm}^3.$$

Present knowledge of the field intensity just outside a metal surface is meager, and some assumptions must be made to treat it quantitatively here. Surface roughness will be ignored, despite its obvious importance, and the metal surface will be considered planar. When $r < r_0$, the intensity of the field of force attracting the molecule (M) to the metal will vary approximately as the inverse seventh power of r . When $r \gg r_0$, the attractive field can be calculated by the method of electrostatic images. Hence, the electrostatic force on that electron of charge e is $e^2/4r_0^2$, and the field intensity polarizing it is $e/4r_0^2$. Hence

$$\bar{F}_0 = \frac{e}{4r_0^2}. \quad (11)$$

Consider the adsorbed molecules of hexane having the principal axis parallel to the surface of the metal. The closest distance of approach from Fig. 11 corresponds to $r_0 = 2 \times 10^{-8}$ cm. Since $e = 4.77 \times 10^{-10}$ esu., it follows that $\bar{F}_0 = 0.3 \times 10^6$ electrostatic v/cm or 90×10^6 v/cm. On introducing this value of \bar{F}_0 as well as $\alpha_p = 96.9 \times 10^{-25}$ cm³ in Eq. (2), it follows that $\mu_p = 2.9 \times 10^{-18}$ esu. This calculated value of μ_p is to be compared with that of 0.25×10^{-18} esu. of Table 7 which was obtained with the Helmholtz equation from a knowledge of ΔV and n . In other words, our very approximate theoretical calculation is too large, but is of the same order of magnitude as the experimental value. Considering the oversimplified assumptions made in the calculation of \bar{F}_0 , the agreement is as good as could be expected.

Because of the roughness of even the most polished metal surfaces, and because oxides as well as some adsorbed oxygen and water were present in our measurements of ΔV , one would expect r_0 to be greater than 2×10^{-8} cm. To allow for these surface factors, we have adjusted r_0 so that the value of μ_p calculated from Eq. (2) would equal that calculated from Eq. (1). In the case of platinum, r_0 would have to be 6.8×10^{-8} cm; this is not an unreasonable value. Therefore, it is concluded that the experimental value of ΔV for hexane adsorbed on platinum did arise from the induced polarization caused by the electrostatic field of the metal surface.

Although current electronic theories of metals do not yet appear to give a quantitative basis for explicitly relating \bar{F}_0 to the constitution of the metal, some information is available concerning the effect of metal constitution on certain basic energies of the conduction electrons. Figure 12 is a conventional diagram (as well as certain essential definitions) of the electronic energy levels for a metal-vacuum boundary. The data available for the energy parameters E_F , E , and W of the metal studied have been collected and arranged in the order of decreasing values of E in Table 9. In the second column will be found the values of Z , the number of free electrons/cm³, calculated from the well-known relation

$$Z = (\text{Avogadro's number}) \frac{\text{specific gravity}}{\text{atomic weight}} \times (\text{number of conduction electrons per atom}). \quad (12)$$

As has been usual ever since the Drude-Lorentz electron theory of metallic conduction, it is assumed that for all the good conducting metals there is one conduction electron per metal atom. The Fermi energy (E_F) of the electrons in the metal are computed from the Fermi-Dirac-Sommerfeld degenerate function

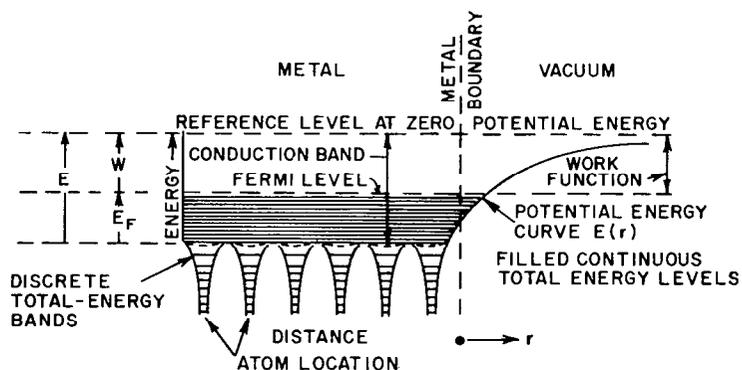
$$E_F = 3.64 \times 10^{-15} Z^{2/3} (\text{ev}). \quad (13)$$

Reliable values of W can only be obtained experimentally. Values given in the fourth column were obtained by arithmetically averaging the best experimental data for the photoelectric work function given in the Handbook of Chemistry and Physics (46) and by Michaelson (47). The photoelectric rather than the thermionic work functions were used because the latter were obtained at higher temperatures than in our experiments and under extreme degassing conditions. The values of E are calculated (see Fig. 12) from

$$E = E_F + W. \quad (14)$$

According to Table 9, W varied only 20% among the nine metals investigated. No graphical correlation was found on plotting W against ΔV for hexane or for benzene. However, a linear correlation was found in plots of ΔV against E (Figs. 13 and 14). In the series of metals examined, the contact angles of each liquid studied were constant on all of the hexane (or benzene) films. This constancy means that n in Eq. (1) was constant. From Eq. (3) it follows that \bar{F}_0 must also be proportional to E . Therefore, from Eq. (13) it follows that \bar{F}_0 will increase with the number of conduction electrons per unit volume of metal and will vary inversely with either the atomic volume or with the ionic lattice spacing of the metal. One would expect W also to vary among the metals with the atomic volume and density of conduction electrons and (in addition) with other parameters defining the surface state of the metal. Very likely the available experimental data on W are so much influenced by the effects of any oxides, adsorbed oxygen, water, and other impurities present on the surface as to be of little value for our purposes here. Possibly, data on W obtained under more ideal conditions would also show a linear variation with ΔV .

Thus the contact potential changes caused by adsorbed films of nonpolar liquids were always of the sign and magnitude to be expected if molecules on the surface were polarized by the electrostatic field of force of the metal substrate. From the evidence given by (a) the contact angles of the 4 reference liquids used as sessile drops, (b) the equality of the



E_F = FERMI ENERGY OF FREE ELECTRONS IN THE METAL CONDUCTION BAND

W = SURFACE WORK FUNCTION OF METAL

$E = E_F + W$ = MAXIMUM ENERGY NEEDED TO EXTRACT A CONDUCTION ELECTRON

Fig. 12 - Energy diagram for a metal-vacuum boundary

Table 9
Electronic Properties of Metals Investigated

Metal	$Z \times 10^{-22}$ (electrons per cc)*	E_f (electron volts)	W (electron volts)	E (electron volts)
Nickel	9.15	7.32	5.0	12.32
Chromium	8.35	7.00	4.4	11.40
Platinum	6.65	5.97	5.4	11.37
Silver	5.88	6.79	4.3	11.14
Copper	8.47	7.03	4.0	11.03
Gold	5.91	5.62	4.9	10.52
Tungsten	6.33	5.79	4.4	10.19
Cadmium	4.62	4.70	4.1	8.80
Tin	2.92	3.46	4.3	7.76

*Assuming (as usual) that there is one conduction electron per atom.

contact potential differences obtained for evaporated and rubbed-down films, and (c) the predicted behavior of homologous adsorbed compounds, it can be concluded that the residual films causing the change in surface properties were condensed monolayers of the adsorbed nonpolar compounds. Molecules of these residual adsorbed films are presumed to conform as closely as possible to the hills and valleys of the metal surfaces.

One would expect the residual field of force emanating from the metal to polarize less strongly the adsorbed molecules of liquid beyond the nearest (or first) monolayer,

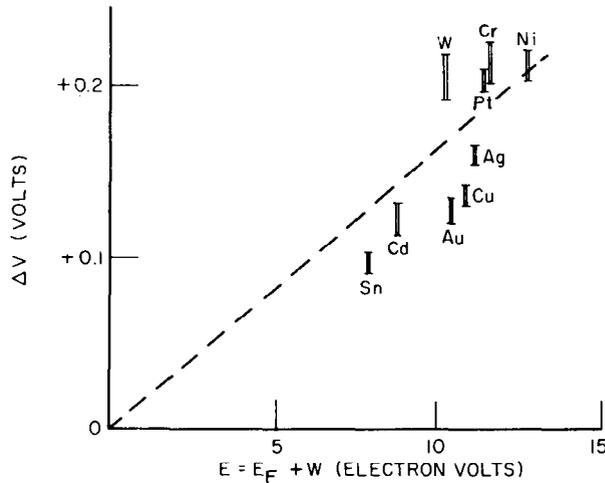


Fig. 13 - ΔV plotted against E for n-hexane on various metals

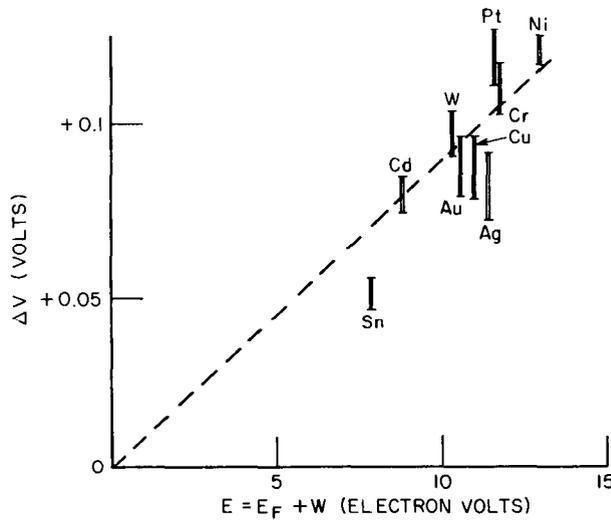


Fig. 14 - ΔV plotted against E for benzene on various metals

but our results with the liquids investigated reveal that such an effect was so weak that in the evaporation process at room temperature all but the first monolayer was removed. Furthermore, the shearing stresses created in the rubbing-down process also were effective in removing all but the first condensed monolayer. These points are of fundamental interest, and further experiments on the subject are in progress.

GENERAL REMARKS

Many investigators have attempted in the past 50 years to use the great sensitivity of the contact potential differences between metals as a quantitative tool for studying the

adsorption of gases and vapors, and other changes in surface composition or properties, but little success has been reported. Our results make evident many neglected experimental conditions for the successful use of contact potential measurements in gaseous atmospheres.

The major important effect of the adsorption of water on the contact potentials has been known for many years, but it has not been recognized that by controlling the relative humidity, temperature, and surface preparation, one could obtain reproducible and useful data in a gaseous atmosphere. Control of the relative humidity is necessary but is not critical when in the range between 1% and 75% at ordinary temperatures; however, it does become critical at lower (or higher) values of the relative humidity. Hence, if one desires to study contact potentials in the complete absence of adsorbed water, it is necessary to go to such extremes in drying the system that it is questionable whether this can be done under conditions other than those obtainable in a properly designed high vacuum system.

In the past five years Gottlieb (48), Fowkes (49), Intorre, Kwei, and Peterson (50), and Haydon (51) have reported investigations on the use of the contact potential differences between metals as a tool for studying adsorption. Their emphasis was on the adsorption on the metal of various polar-nonpolar organic compounds from solution in an organic solvent (usually nonpolar). Application of the results and techniques described here should do much to guide in planning such experiments and certainly in interpreting the experimental data. In general, in addition to their difficulties arising from the lack of a reference electrode, their work suffered from neglect of the effects of (a) the polarization induced in the solvent by the metal adsorbing surface, (b) the retention of a residual solvent monolayer by the solid surface after evaporation of the pure solvent, (c) the conditions required to avoid mixed film formation, and (d) the effect of impurities on the solvent and/or solute.

In past investigations of cleaning, friction, adhesion, adsorption, corrosion prevention, or other surface properties of metals, it has been assumed usually that a final solvent cleaning or degreasing of a surface was satisfactory provided a sufficiently pure or volatile solvent was used. Our results prove this supposition is incorrect even if the solvent is nonpolar. Many past surface studies have been greatly confused by the effects of such residual films. Where complete freedom from adsorbed organic material is desired, it is better to avoid using any organic solvent in the last stage of cleaning the solid surface.

The contact potential difference is very sensitive to the presence of adsorbable contaminants in the atmosphere (52), and the sensitivity is greater the longer the average lifetime (τ) of the adsorbed molecules and the greater the dipole moment (μ_p) of the adsorbed molecule. Hence, the sensitivity to a given pollutant in the atmosphere is greatest if the active metal electrode is selected to be such that τ is large or is surface-chemically treated to be so. Development of a general detecting system based on the contact potential method appears very difficult because all chemical contaminants do not have large values of τ , nor are they likely to be made so with any single surface-conditioning treatment. A different and more general approach is to pass the polluted atmosphere through a device which separates the pollutants into distinct chemical classes which may be detected and characterized separately. Here, the contact potential method offers much promise. For example, it could serve as a very sensitive, quick-response detector for a gas-liquid partition chromatograph, an approach which is being investigated.

REFERENCES

1. Volta, A., Gehler's Worterbuch, IV, 616 (1801); Ann. de Chemie I ser. XL:225 (1801)
2. Lodge, Sir Oliver, Phil. Mag. 19:153, 254, 340 (1885)
3. Herring, C., and Nichols, M.H., Rev. Modern Phys. 21:185 (1949)
4. Suhrmann, R., "Changes in Conductivity on Adsorption of Gases on Metal Films," in "Chemisorption," W. E. Garner, editor, London:Butterworths, p. 106, 1957
5. Culver, R.V., and Tompkins, F.C., "Surface Potentials and Adsorption Process on Metals," in "Advances in Catalysis," Vol. XI New York:Academic Press, p. 67, 1959
6. Patai, I.F., and Pomerantz, M.A., J. Franklin Inst. 252:239 (1951)
7. Schulman, J.H., and Rideal, E.K., Proc. Roy. Soc. A130:259 (1931)
8. Bewig, K.W., Rev. Sci. Instr. 35:1160 (1964)
9. Zisman, W.A., Rev. Sci. Instr. 3:367 (1932)
10. Yamins, H.G., and Zisman, W.A., J. Chem. Phys. 1:656 (1933)
11. Zisman, W.A., and Yamins, H.G., Physics 4:7 (1933)
12. Porter, E.F., and Wyman, J., Jr., J. Am. Chem. Soc. 60:1083 (1938)
13. Frost, A.A., and Hurka, V.R., J. Am. Chem. Soc. 62:3335 (1940)
14. Frost, A.A., Trans. Electrochem. Soc. 82:259 (1942)
15. Uhlig, H.H., J. Appl. Phys. 22:1399 (1951)
16. Koga, S., J. Sci. Research Inst. (Tokyo) 47:172 (1953)
17. Hackerman, N., and Lee, E.H., J. Phys. Chem. 59:900 (1955)
18. Rädlein, G., and Honrath, M., Zeitsch. fur Elektrochem. 63:397 (1959)
19. Phillips, G., J. Sci. Instr. 28:342 (1951)
20. Bewig, K.W., and Zisman, W.A., "Low Energy Reference Electrodes for Investigating Adsorption by Contact Potential Measurements," Advances in Chemistry Series, No. 33, Washington, D.C.:American Chemical Society, p. 100, 1961
21. Bewig, K.W., and Zisman, W.A., J. Phys. Chem. 67:130 (1963)
22. Timmons, C.O., and Zisman, W.A., J. Phys. Chem. 68:1336 (1964)
23. Bewig, K.W., and Zisman, W.A., J. Phys. Chem. 68:1804 (1964)

24. Timmons, C.O., and Zisman, W.A., "Investigation of Fatty Acid Monolayers on Metals by Contact Potential Measurements," NRL Report 6208, In press
25. Ende, W., Phys. Zeits. 30:477 (1929)
26. Checkel, R.L., Modern Plastics 36 (No. 2):125 (1958)
27. Bewig, K.W., "Improvements in the Vibrating Condenser Method of Measuring Contact Potential Differences," NRL Report 5096, Feb. 4, 1958
28. Zisman, W.A., "Relation of Equilibrium Contact Angle to Liquid and Solid Constitution," Advances in Chemistry Series, No. 43, Washington, D.C.:American Chemical Society, p. 1, 1964
29. Shafrin, E.G., and Zisman, W.A., J. Phys. Chem. 64:519 (1960)
30. Hardy, Sir William B., "Collected Scientific Papers," Cambridge:Univ. Press, 1936
31. Leviné, O., and Zisman, W.A., J. Phys. Chem. 61:1068 (1957)
32. Bennett, M., Jarvis, N.L., and Zisman, W.A., J. Phys. Chem. 68:3520 (1964)
33. Hare, E.F., and Zisman, W.A., J. Phys. Chem. 59:335 (1955)
34. DeBoer, J.H., "Adsorption Phenomena," in "Advances in Catalysis," Vol. VIII, New York:Academic Press, p. 38, 1956
35. Mignolet, J.C.P., Disc. Faraday Soc. 8:105 (1950)
36. Mignolet, J.C.P., J. Chem. Phys. 21:1298 (1953)
37. Fox, H.W., Hare, E.F., and Zisman, W.A., J. Colloid Sci. 8:194 (1953)
38. Shafrin, E.G., and Zisman, W.A., J. Colloid Sci. 7:166 (1952)
39. Fox, H.W., and Zisman, W.A., J. Colloid Sci. 7:431 (1952)
40. Ellison, A.H., and Zisman, W.A., J. Phys. Chem. 58:260 (1954)
41. Meyer, E.H.L., and Otterbein, G., Physik. Z. 32:290 (1931)
42. Otterbein, G., Physik Z. 35:249 (1934)
43. Wang, S.N., J. Chem. Phys. 7:1012 (1939)
44. Denbigh, K.G., Trans. Faraday Soc. 36:936 (1940)
45. Hirschfelder, J.O., Curtiss, C.F., and Bird, R.B., "Molecular Theory of Gases and Liquids," New York:Wiley, p. 948, 1954
46. Handbook of Chemistry and Physics, 44th Ed., Cleveland, Ohio:Chemical Rubber Publ. Co., p. 2655 (1962-1963)
47. Michaelson, H.B., J. Appl. Phys. 21:536 (1950)
48. Gottlieb, M.H., J. Phys. Chem. 64:427 (1960)

49. Fowkes, F.M., J. Phys. Chem. 64:726 (1960)
50. Intorre, B.J., Kwei, T.K., and Peterson, C.M., J. Phys. Chem. 67:55 (1963)
51. Haydon, D.A., Kolloid-Z. 188:141 (1963)
52. Zisman, W.A., "Fundamental Factors in Detecting Chemicals as Adsorbed Films,"
NRL Report 6168, Oct. 29, 1964

DOCUMENT CONTROL DATA - R&D		
<small>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</small>		
1. ORIGINATING ACTIVITY <small>(Corporate author)</small> U.S. Naval Research Laboratory Washington, D.C. 20390		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
		2b. GROUP
3. REPORT TITLE CHANGES IN CONTACT POTENTIALS OF METALS CAUSED BY ADSORBED MONOLAYERS		
4. DESCRIPTIVE NOTES <small>(Type of report and inclusive dates)</small> An interim report on one phase of the problem.		
5. AUTHOR(S) <small>(Last name, first name, initial)</small> Bewig, K.W., Timmons, C.O., and Zisman, W.A.		
6. REPORT DATE February 12, 1965	7a. TOTAL NO. OF PAGES 30	7b. NO. OF REFS 52
8a. CONTRACT OR GRANT NO. NRL Problem C02-10	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6200	
b. PROJECT NO. RR 001-01-43-4751	9b. OTHER REPORT NO(S) <small>(Any other numbers that may be assigned this report)</small>	
c.		
d.		
10. AVAILABILITY/LIMITATION NOTICES Unlimited availability. Copies available from Clearinghouse for Federal Scientific and Technical Information (CFSTI) Sills Building, 5285 Port Royal Road, Springfield, Virginia 22151.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Dept. of the Navy (Office of Naval Research)	
13. ABSTRACT A classic problem in the physics and chemistry of surfaces has been the successful utilization of changes in the contact potential difference between two metals as a means of studying surface properties and adsorption. Recent advances in experimental techniques, especially the use of a fluorocarbon coating on the reference electrode, have made possible a number of advances in the study of the surface potential changes resulting from the adsorption of monolayers of nonpolar liquids and of the higher molecular weight polar compounds. Studies have been made of adsorbed nonpolar liquid compounds including the various hydrocarbons and carbon tetrachloride. Polar-nonpolar compounds, such as the homologous families of the fatty acids and amines as well as certain aromatic phosphate esters, have also been investigated with the new techniques. Reproducible and interesting results have been obtained, even though the measurements were made in the presence of atmospheric oxygen, nitrogen, and water vapors as well as any surface oxide development on the metal at ordinary temperatures; however, it was necessary to control the relative humidity and air temperature carefully, to use an atmosphere entirely free of organic vapors or polar inorganic compounds, to take great care in cleaning the metal surfaces, and to employ compounds of extremely high purity.		

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Contact potential Adsorbed monolayers Contact angle Surface chemistry Adsorption on metals Polar and nonpolar monolayers						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.