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# Surface Potentials and Induced Polarization in Nonpolar Liquids Adsorbed on Metals

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# Surface Potentials and Induced Polarization in Nonpolar Liquids Adsorbed on Metals

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The contact potential difference between a metal and a suitably coated metal serving as a reference electrode can be used in clean air as a sensitive and reliable tool for studying adsorbed monomolecular films of polar compounds. The change ( $\Delta V$ ) in the contact potential difference resulting from the adsorption on a metal of a film is reported for each of the following pure, nonpolar liquid compounds: hexane, octane, decane, dodecane, tetradecane, hexadecane, cyclohexane, dicyclohexyl, benzene, toluene, xylene, and carbon tetrachloride. Clean polished surfaces of Pt, Au, Ag, Cu, Ni, W, Cr, Sn, and Cd were the adsorbing metals. Contact angles of water, glycerol, methylene iodide, and hexadecane on the same adsorbed films supplied information about their nature, packing, and orientation. The following conclusions can be made: (a) evaporation of the liquid always leaves on the metal an adsorbed monolayer oriented so that the maximum number of atoms contact the surface; (b) when excess liquid is wiped off the metal by rubbing with clean filter papers, a monomolecular adsorbed film remains whose properties are identical with those obtained by evaporation; (c) the electrostatic image field of the adsorbed molecule is not sufficient to cause the observed values of  $\Delta V$  and the parameters involved include the lattice spacing and atomic volume of the metal. Values of  $\Delta V$  obtained were reproducible and characteristic for each compound and metal. Theoretical calculations of  $\Delta V$  in terms of the molecular polarization induced in the adsorbed liquid molecules by the electrostatic field just outside of the surface of the metal agreed in order of magnitude with experimental data. As theory predicted,  $\Delta V$  for any compound increased linearly with the electrostatic field intensity in the vicinity of the adsorbed molecules or the total energy necessary to extract a conduction electron from the metal.

## INTRODUCTION

In previous reports (1, 2) a method of measuring the contact potential difference ( $V_1 - V_2$ ) between a clean, polished, metal surface and a stable reference electrode of platinum or gold coated with FEP Teflon was described, and various examples were given (2) of the reproducible values of the change in the contact potential difference ( $\Delta V$ ) arising from the adsorption on a metal surface of a condensed monomolecular film of a polar-nonpolar organic compound. Such monolayer coatings were prepared by using the retraction method (3-5) employing either a dilute solution of the polar compound in a nonpolar solvent or the pure polar compound in the liquid state. More recently the results have been reported of a similar study of the values of  $\Delta V$  arising from the adsorption on platinum of a condensed monolayer of each member of the homologous family of pure fatty amines (6).

The observed change in the contact potential difference between the metal electrodes under such circumstances is caused by the adsorption of a monolayer of oriented molecules having permanent electrostatic dipoles; hence, the Helmholtz relation

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

may be applied. Here  $\mu_p$  is the perpendicular component of  $\mu$ , the total electrostatic dipole moment per molecule, and  $n$  is the number of molecules adsorbed per unit area. In general,  $\mu$  is the vector sum of the permanent moment ( $\mu_0$ ) and the induced moment ( $\mu_i$ ). In adsorption processes,  $\mu_i$  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  $\mu_i$  from a knowledge of the molecular polarizability of the adsorbed molecule and the intensity of the electrostatic field (F)

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existing in the region occupied by it. Lippert (7) has frequently 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 (8) has demonstrated experimentally by contact potential difference measurements that  $\mu_i$  for xenon adsorbed on gold at extremely low temperatures is 0.276 debye.

In view of the reproducibility in  $\Delta V$  obtained in our recent experiments on the adsorption on a metal of a condensed monolayer of polar fatty amine molecules (2, 6), it was believed that by using the same techniques it would be possible to measure any polarization induced by a metal surface in an adsorbed film of nonpolar molecules. This is to report results of our experiments on films of the n-alkanes from hexane through hexadecane, carbon tetrachloride, cyclohexane, dicyclohexyl, benzene, toluene, and o-xylene adsorbed on nine metals.

### EXPERIMENTAL MATERIALS AND TECHNIQUES

Although some measurements of  $\Delta V$  were made using the vibrating electrode apparatus described previously (1, 2), an ionization method has been used more frequently because it could be adapted to continuous recording on a chart-type dc millivoltmeter. Surface potential measurements were always made using plane disk electrodes of the pure metal 3/8 inch in diameter and 1/16 inch thick. Methods used for controlling the relative humidity, temperature, and purity of the air in the vicinity of the electrodes have been described earlier (5, 6). Platinum, gold, and chromium electrodes were of 99.999% purity as indicated by the supplier; the other metals (nickel, tungsten, copper, cadmium, tin, and silver) were 99.9% purity or better. The vibrating condenser reference electrode used throughout these experiments was a pure gold disk uniformly coated with a 5-mil-thick layer of FEP Teflon resin by a method described earlier (1, 2). The ionization method reference electrode was a 6-mm-square foil activated with radium 226 sandwiched between a silver base-plate and a gold overlayer having an activity of 5 microcuries.

The plane surface of each electrode studied was prepared by abrasion under flowing, grease-free, distilled water, using a graded series of

carborundum metallurgical papers to a final grit size of 600-C (Minnesota Mining and Manufacturing Company "Wet or Dry Tri-M-It Paper"). Each metal was then given a mirror finish on a polishing wheel covered with a Buehler Selvyt cloth using Linde alumina abrasive having an average particular size of 0.3 micron. Finally, the polished surfaces were scrubbed under flowing, grease-free, distilled water on a clean Selvyt cloth, rinsed in doubly distilled water, and dried in clean air. This method of surface preparation was used because each of the metals investigated reacted differently and sometimes unreproducibly to etching, flaming, and chemical polishing techniques. Degreasing with solvents in a Soxhlet extractor was abandoned because a film of the solvent remained adsorbed on the metals as indicated by large water contact angles and finite values of  $\Delta V$  after the extraction treatments. Our criterion of sufficient freedom from organic contamination was that just before each surface potential experiment, the polished metal surface should exhibit a zero contact angle with water. When metal surfaces were not flamed or heated but were polished and cleaned at room temperature in this way, there was insignificant drift in  $\Delta V$  with time after surface preparation. For example, if a freshly cleaned gold or platinum electrode showed a change in  $\Delta V$  of over 10 mv in 2 hours exposure to the clean humidity-controlled atmosphere in the apparatus used, it was always found to have adsorbed contamination from the air.

As large contributions to  $\Delta V$  can result through adsorption from the nonpolar liquid of polar (or other more adsorptive) impurity sufficient to coat the metal with a small fraction of a monolayer, it was difficult to prepare nonpolar liquids pure enough for this investigation. Each of the n-alkane liquids used was analyzed by chromatography and shown to be 99.5 mole percent pure by the producer (Lachat Chemicals Company, Inc., of Chicago), the melting point range of each compound always being within 1°C of the literature values (9). However, trace impurities of a polar nature were detectable in some instances and for further purification each liquid was slowly percolated through a long, narrow, adsorption column containing a layer of activated silica gel and another of alumina. Three successive percolations just prior to use in an experiment were sometimes necessary. Finally the liquid was percolated through a column of Linde 4A sieves to

remove any dissolved water. Benzene from three sources was used; one particular source of benzene produced an anomaly in the data until it was purified by gas/liquid chromatography. The resulting material had less than one part per million of hydrocarbon impurities. Measured values of  $\Delta V$  on this material agree well with those taken on percolated specimens of 99 mole percent benzene from Phillips Petroleum Co., Matheson, Coleman, and Bell Co., and Baker Chemical Co., as well as a sample of anhydrous benzene of better than 99.99 mole percent purity obtained from Dr. A. Glasgow of the National Bureau of Standards. The other aromatic compounds used were Eastman white label grade o-xylene and Phillips Petroleum Company toluene, minimum 99% mole purity grade. The carbon tetrachloride used was Fisher Certified Reagent.

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 platinum electrode at room temperature or by using the wiping and rubbing technique first employed by Sir William Hardy (10) in his classic experiments on boundary friction. Levine and Zisman (11) in their investigation of adsorbed monolayers of polar-nonpolar compounds had covered the solid surface with the liquid phase, or else exposed it to the vapor phase, and then had removed any excess adsorbed material by vigorously wiping and rubbing the surface with carefully selected clean, grease-free, tissue papers or adsorbent cotton. The wetting and frictional properties of the resulting rubbed-down films of polar compounds had agreed with those obtained on condensed monolayers of the same compounds adsorbed and retracted from the melt (4) or from solution in appropriate nonpolar solvents. We had successfully used these same methods in recent studies of the electrical properties of adsorbed monolayers of fatty acids (2) and amines (6). Furthermore, Fox, Hare, and Zisman (12) 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  $\gamma_{LV}$  agreed reasonably well with

the data obtained using a smooth clean block of polyethylene (13). They had concluded that in the residual adsorbed layer, the molecules of n-hexadecane were lying flat in the surface thus presenting to the liquid sessile drops a surface comprised essentially of close-packed  $\text{CH}_2$ -groups.

Regardless of whether the evaporation method or the wetting and rubbing-down technique was used, each of the residual films in the experiments reported here 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  $\Delta V$ . 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  $\Delta V$  was always less than 0.010 volt. Furthermore, no significant surface change was caused by the rubbing-down method using the other metal systems except silver (to be discussed later).

All measurements of  $\Delta V$  were made in air freed of dust or organic materials while maintained at 50% R.H. and 20°C. Since the final step in the cleaning procedure for each of the polished metals involved rinsing it in distilled water and then drying in the room atmosphere, obviously some water always remained adsorbed on the clean surfaces. Bowden and Throssell's (14, 15) microbalance studies had shown that at adsorption equilibrium from one to forty molecular layers of water remained adsorbed on clean platinum foil in an atmosphere containing water vapor at a pressure of 15 mm of mercury, the lower value resulting only in the absence of any hygroscopic surface deposits such as salt. Our measurements of the changes in  $\Delta V$  caused by adsorbed liquid films were always made on metal surfaces on which had adsorbed a film of water in equilibrium with the atmosphere at 50% R.H. and 20°C. However, under such controlled conditions the adsorbed water vapor and any adsorbed oxygen or nitrogen would each be expected to make a constant additive contribution to the surface potential of the adsorbed hydrocarbons. Despite the possible complications caused by the presence of such adsorbed gases, the study of the effect on  $\Delta V$  of adsorbed films of liquid hydrocarbons is of interest and is both informative and useful as will be demonstrated here.

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. The slowly advancing drop method was used by techniques described elsewhere (5, 6, 13). For these measurements we used 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; triple-distilled water (distilled the last two times in quartz) having a surface tension of 72.8 dynes/cm at 20°C; chromatographically purified 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 sieves and had a surface tension of 63.4 dynes/cm at 20°C.

### EXPERIMENTAL RESULTS ON ADSORBED FILMS

Measurements were made at 20°C of  $\Delta V$  as well as the contact angle  $\theta$  exhibited by 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 (n-hexane to n-hexadecane). The first interesting result found was that  $\Delta V$  and  $\theta$  had the same value for both evaporated and rubbed-down films. Table 1 summarizes

the average values of  $\Delta V$  obtained for the homologous family of n-alkanes on platinum as well as the corresponding contact angles exhibited by each of the four reference liquids. Table 1 shows that both  $\Delta V$  and  $\theta$ , within the experimental uncertainty, 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 (5) 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 (13). However, there is a better basis for comparison; the earlier measurements of 79, 69, and 52 degrees, respectively, by Fox, Hare, and Zisman (12) on 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  $\theta$  than that on solid polyethylene. The greater penetration of water molecules through the adsorbed film to the metal substrate lowered  $\theta$  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

TABLE I  
 $\Delta V$  and Contact Angle  $\theta$  of n-Alkanes Adsorbed on Platinum  
(All data at 20°C and 50% R.H.)

Compound Adsorbed	$+\Delta V^*$ $\pm 0.010$ (volts)	Contact Angle $\theta$ (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

\*Positive sign before  $\Delta V$  means that outermost charge in the equivalent dipole is positive.

either those of solid polyethylene or of a well-rubbed hexadecane film

Dependence of  $\Delta V$  and  $\theta$  on molecular structure was studied further by treating in the same way each of a variety of pure nonpolar organic liquids, and the results are listed in Table 2, n-hexane being included for purposes of comparison. Reasonably good agreement is found between the contact angles of water (55 degrees), glycerol (52 degrees), and methylene iodide (40 degrees), with the residual film of  $\text{CCl}_4$  and those of 66, 56, and 34 degrees, respectively, for a condensed adsorbed monolayer of perchloropentadienoic acid by Ellison and Zisman (16); this would be expected since both films have exposed surfaces of closely packed covalent chlorine atoms. Again  $\Delta V$  and  $\theta$  had the same values for evaporated and rubbed-down films. It is difficult to avoid the conclusion that both types of residual films are condensed monolayers of the organic molecule having characteristic values of  $\Delta V$  and  $\theta$ . Furthermore, these residual adsorbed films of nonpolar organic liquids were by no means unstable 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  $\Delta V$  after two hours was only 0.015 volt; this is quite comparable to the stability of a fatty amine monolayer adsorbed on the same metal (6).

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 outside of the stainless steel enclosure containing the reference and platinum electrodes. By this means it was possible to raise gradually the temperature of the platinum 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  $\Delta V$  as a function of time while the temperature of the platinum was gradually increased to some maximum temperature around 130°C and then allowed to cool to 24°C. A similar procedure was followed with the clean platinum (entirely free from the adsorbed alkane). The results are charted in Fig. 1. It is evident that  $\Delta V$  decreased monotonically from an initial value of + 0.215 volt at 23°C to - 0.030 volt at 135°C; on cooling the platinum,  $\Delta V$  increased slowly attaining an equilibrium value of + 0.020 volt. When no hexane was present at the start of the experiments,  $\Delta V$  changed by only a few hundredths of a volt during the temperature rise to 135°C, and on

TABLE 2  
 $\Delta V$  and Contact Angle  $\theta$  of Various Compounds Adsorbed on Platinum  
(All data at 20°C and 50% R.H.)

Compound Adsorbed	+ $\Delta V^*$ $\pm 0.010$ (volts)	Contact Angle $\theta$ (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

\*Positive sign before  $\Delta V$  means that the outermost charge in the equivalent dipole is positive.

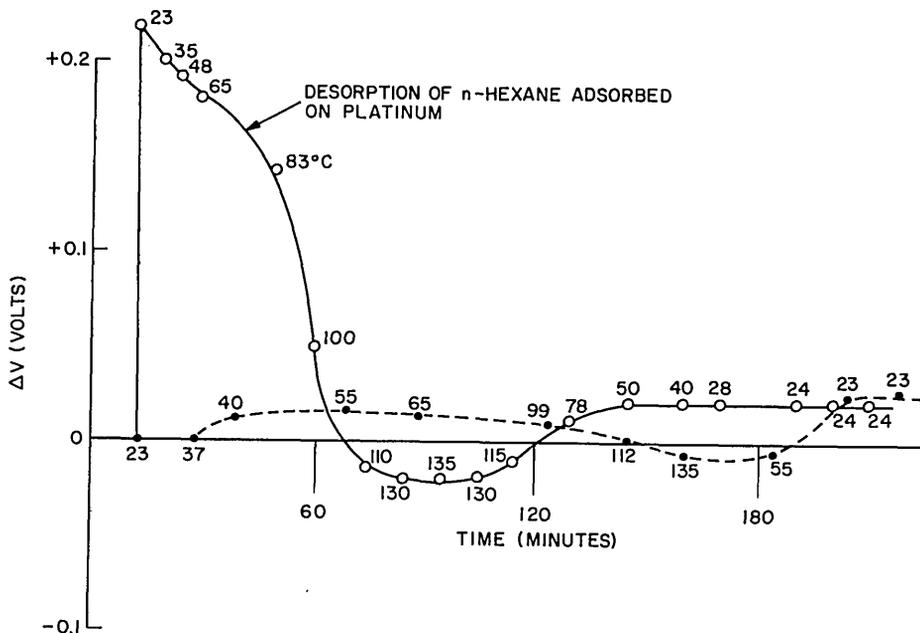


Fig. 1 — Effect of heating and cooling of n-hexane adsorbed on platinum

returning to 23°C, the equilibrium value was about + 0.030 volt.

The principal cause of the initial rise in  $\Delta V$  of clean platinum with temperature is perhaps in the reversible desorption of physically adsorbed water; however, there appears to have been a small irreversible change in  $\Delta V$  of a few hundredths of a volt in the heating and cooling cycle or else the apparent change was caused by the experimental error in measuring  $\Delta V$  in this apparatus. If one uses the difference in the two curves of Fig. 1 to find the effect of desorbing the n-hexane monolayer on  $\Delta V$ , the conclusion follows that the effect of heating to 135°C and cooling to room temperature is to return  $\Delta V$  to the value to be expected for clean platinum; in other words, the n-hexane molecules were adsorbed physically and could be removed by heating the system enough to overcome an energy barrier corresponding to a change in temperature of about 100°C.

When adsorbate molecules do not have a permanent dipole moment, one would expect  $\mu_p$  in Eq. (1) to be proportional to the average electrostatic field strength ( $\bar{F}_0$ ) existing in the region occupied by the adsorbed molecule. If the normal component of the oriented polarizability is  $\alpha_p$ ,

then  $\mu_p$  can be calculated by

$$\mu_p = \alpha_p \bar{F}_0 \quad (2)$$

Hence, according to Eq. (1)

$$\Delta V = 4\pi n \alpha_p \bar{F}_0 \quad (3)$$

and  $\Delta V$  for any one compound adsorbed on the different metals should vary as  $\bar{F}_0$  varies with the constitution of the metal. Experimental values of  $\Delta V$  were obtained for rubbed-down films of pure n-hexane and benzene adsorbed under the same conditions mentioned earlier on nine different metal surfaces, and the results are summarized in Tables 3 and 4. In each instance  $\Delta V$  was reproducible within the previously indicated experimental uncertainty. Attention is called to the constancy of  $\theta$  and the large variation in  $\Delta V$  for either hexane or benzene in going from nickel to tin. The almost constant values of the contact angles of the liquids in Tables 3 and 4 give good evidence that the adsorbed film of hexane (or benzene) on the different metals has the same orientation and surface concentration. Therefore,  $n$  and  $\alpha_p$  are the same for each metal and  $\Delta V$  varies because  $\bar{F}_0$  varies for each metal surface.

TABLE 3  
 $\Delta V$  and Contact Angle  $\theta$  of n-Hexane Adsorbed on Various Metals  
 (All data at 20°C and 50% R.H.)

Metal Substrate	$+\Delta V^*$ $\pm 0.010$ (volts)	$\mu \times 10^{18}$ (esu) Calc.	Contact Angle $\theta$ (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

\*Positive sign before  $\Delta V$  means that the outermost charge in the equivalent dipole is positive.

TABLE 4  
 $\Delta V$  and Contact Angle  $\theta$  of Benzene Adsorbed on Various Metals  
 (All data at 20°C and 50% R.H.)

Metal Substrate	$+\Delta V^*$ $\pm 0.010$ (volts)	$\mu \times 10^{18}$ (esu) Calc.	Contact Angle $\theta$ (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

\*Positive sign before  $\Delta V$  means that the outermost charge in the equivalent dipole is positive.

Assuming the residual adsorbed film is a condensed monolayer, the Helmholtz relation (Eq. (1)) can be used to calculate  $\mu_p$  from the measured value of  $\Delta V$  once  $n$ , 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 because the material was applied to the metal surface from the liquid state. Since the molecular model can be just contained in a rectangle 10.2Å long and 4.2Å wide, the area per molecule is  $43 \times 10^{-16} \text{cm}^2$ . Therefore,  $n$  equals  $2.33 \times 10^{14}$  molecules/cm<sup>2</sup>. Table 1 shows that the change in electrostatic potential due to the induced polarization of hexane on platinum was 0.215 volt. The value of  $\mu_p$  calculated from Eq. (1) is  $0.245 \times 10^{-18}$  esu, which is a reasonable value. The resulting values of  $\mu_p$  for n-hexane and benzene on the different metals are given in Tables 3 and 4.

### THEORETICAL CONSIDERATIONS

It should be possible to calculate  $\Delta V$  using Eqs. (2) and (3) provided that  $\bar{F}_0$  and  $\alpha_p$  can be computed for each system studied. Values of  $\alpha_p$  can be calculated by several methods from available literature data on either the atomic or bond polarizabilities. The most appropriate approach for this study was Meyer and Otterbein's (17) concept of the oriented molecular polarizability. 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 (18) has determined the lateral ( $\alpha_l$ ) and transverse ( $\alpha_t$ ) 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  $\Phi$  with a directed vector of the bond, the bond polarizability is given by

$$\alpha_{bond} = \alpha_l \cos^2 \Phi + \alpha_t \sin^2 \Phi \quad (4)$$

as was shown in the work of Denbigh (19) and Hirschfelder, Curtiss, and Bird (20).

$$\alpha_p = \sum_{\text{all bonds } p} (\alpha_l \cos^2 \Phi + \alpha_t \sin^2 \Phi) \quad (5)$$

For the entire molecule (M), the perpendicular component of  $\alpha$  is

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

when the subscripts refer to the carbon-hydrogen (C-H) and carbon-carbon (C-C) bonds.

Figure 2 is a drawing of the Stuart-Briegleb ball model of the n-hexane molecule in its stretch-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 is assumed this arrangement corresponds to a maximum of  $\alpha_p$  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.*,  $109^\circ 20'$  for the carbon-hydrogen bond angle. In the situation prevailing here, the electrical field of the adsorbing surface is directed along the normal, and  $\Phi$  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

$$\alpha_p = 5\alpha_{(C-C)} + 14\alpha_{(C-H)} \cos^2 \Phi + 14\alpha_{(C-H)} \sin^2 \Phi \quad (7)$$

Wang (18) has shown that

$$\alpha_{(C-C)} = 0.2 \times 10^{-25} \text{cm}^3$$

$$\alpha_{(C-H)} = 7.2 \times 10^{-25} \text{cm}^3$$

$$\alpha_{(C-H)} = 6.2 \times 10^{-25} \text{cm}^3$$

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

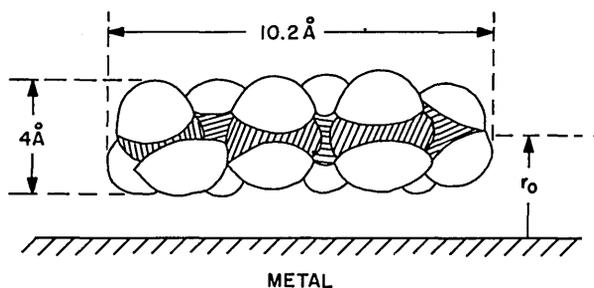


Fig. 2 — Elevation view of n-hexane molecule at equilibrium adsorption on a plane metal surface

In calculating  $n$  and  $\alpha_p$  for benzene, it is assumed from the dimensions of the molecular ball model that benzene is adsorbed as a monolayer lying flat on the surface with an area per molecule of  $36\text{\AA}^2$ . Under such conditions of adsorption there are 6 C-H bonds, 3 C-C bonds, and 3 C=C bonds so that

$$\alpha_p = 6\alpha_{t(C-H)} + 3\alpha_{t(C-C)} + 3\alpha_{t(C=C)} \quad (8)$$

According to Wang (18)

$$\alpha_{t(C-H)} = 6.2 \times 10^{-25}\text{cm}^3$$

$$\alpha_{t(C-C)} = 0.2 \times 10^{-25}\text{cm}^3$$

$$\alpha_{t(C=C)} = 9.6 \times 10^{-25}\text{cm}^3$$

Finally, for benzene

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

Present knowledge of the field intensity just outside of 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  $r \ll r_0$ , the intensity of the field of force attracting the molecule (M) to the metal will vary approximately as the inverse seventh power of  $r$  (7). When  $r > r_0$ , the attractive field can be calculated by the method of electrostatic images. It will be assumed that the average polarizing field acting on each orbital electron in the adsorbed molecule (M) at distance  $r_0$  from the surface is given to a good enough approximation by its electrostatic image field. Hence, the electrostatic force on that electron of charge  $e$  is

$$\frac{e^2}{4r_0^2}$$

and the field intensity polarizing it is

$$\frac{e}{4r_0^2}$$

Of course  $r$  varies rapidly with time in each orbit and there are mutual forces between neighboring orbiting electrons which should not be neglected. But we will assume that the time-averaged normal

component of  $\bar{F}_0$  in the region of space occupied by M will be given by neglecting the forces between neighboring orbiting electrons or arising from their images. Hence,

$$\bar{F}_0 = \frac{e}{4r_0^2} \quad (9)$$

Consider the adsorbed molecule of hexane having the principal axis parallel to the surface of metal. The closest distance of approach from Fig. 2 corresponds to  $r_0 = 2 \times 10^{-8}\text{cm}$ . Since  $e = 4.77 \times 10^{-10}\text{esu}$ , it follows that  $\bar{F}_0 = 0.3 \times 10^6$  electrostatic volts per cm or  $90 \times 10^6$  volts/cm. On introducing this value of  $\bar{F}_0$  as well as  $\alpha_p = 96.9 \times 10^{-25}\text{cm}^3$  in Eq. (2), it follows that  $\mu_p = 2.9 \times 10^{-18}\text{esu}$ . This calculated value of  $\mu_p$  is to be compared with that of  $0.25 \times 10^{-18}\text{esu}$  of Table 3, which was obtained with the Helmholtz relation (Eq. (1)) from a knowledge of  $\Delta V$  and  $n$ . In other words, our very approximate theoretical calculation is too large but is 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 surface, and because oxides as well as some adsorbed oxygen and water were present in our measurements of  $\Delta V$ , one would expect  $r_0$  to be greater than  $2 \times 10^{-8}\text{cm}$ . To allow for these surface factors,  $r_0$  was adjusted so that the value of  $\mu_p$  calculated from Eq. (2) would equal that calculated from Eq. (1). In the case of platinum,  $r_0$  would have to be  $6.8 \times 10^{-8}\text{cm}$ . This is not an unreasonable value. Therefore, it is concluded that the experimental value of  $\Delta V$  for hexane adsorbed on platinum did arise from the induced polarization caused by the electrostatic field of the metal surface.

The experimental data of Table 3 for n-hexane and of Table 4 for benzene adsorbed on a variety of metals reveal that  $\Delta V$  decreases regularly in going from nickel to tin with the extreme values differing by a factor of from two to three. If  $\bar{F}_0$  were simply the electrostatic image force field as assumed in the preceding approximate calculation,  $\Delta V$  for a given adsorbed compound would be the same for all metals. Therefore, the electrostatic image force field method cannot be a correct basis for estimating  $\bar{F}_0$  and  $\mu_p$  at distances of approach as close as from 2A to 7A.

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. Fig. 3 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 metals studied have been collected and arranged in the order of decreasing values of  $E$  in Table 5. The value of  $N$ , the number of free electrons per  $\text{cm}^3$ , in Table 5 were calculated from the following:

$$N = (\text{Avogadro's Number}) \left( \frac{\text{Specific Gravity}}{\text{Atomic Weight}} \right) \quad (10)$$

(Number of conduction electrons per atom)

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

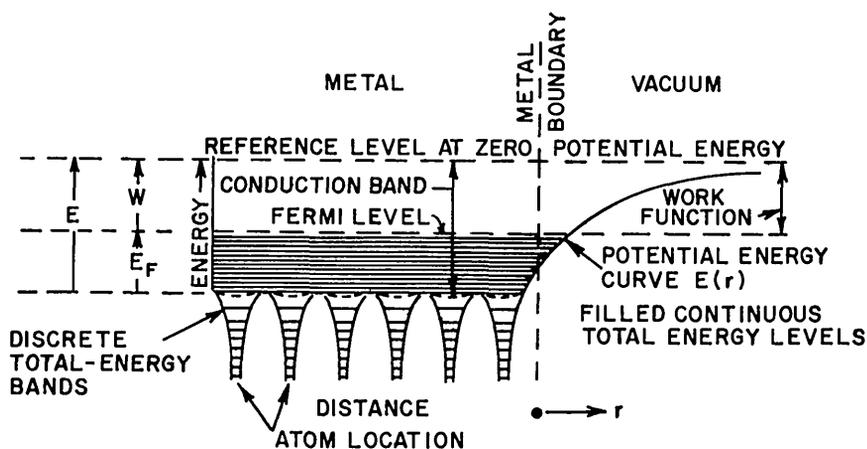
metal were computed as usual from the Fermi-Dirac-Sommerfeld degenerate function:

$$E_F = 3.64 \times 10^{-15} N^{2/3} \text{ in electron volts.} \quad (11)$$

Reliable values of  $W$  can only be obtained experimentally. Values given for  $W$  in Table 5 were obtained by arithmetically averaging the best experimental data for the photoelectric work function given in the Handbook of Chemistry and Physics (21) and by Michaelson (22). 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  $E$  were calculated as usual (see Fig. 3) from

$$E = E_F + W \quad (12)$$

According to Table 5,  $W$  varied only 20% among the 9 metals investigated. No graphical correlation was found on plotting  $W$  against  $\Delta V$  for hexane or benzene. However, a simple linear correlation was found in plots of  $\Delta V$  against  $E$  (Figs. 4 and 5). Early in the experiments the values obtained for hexane and benzene adsorbed on



$E_F$  = 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. 3 - Energy diagram for a metal-vacuum boundary

TABLE 5  
Electronic Properties of Metals Investigated

Metal	$N \times 10^{-22}$ (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	4.63	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.

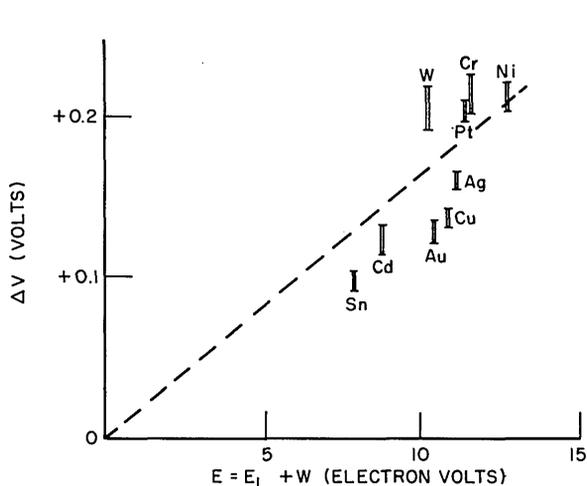


Fig. 4 -  $\Delta V$  Plotted against  $E$  for n-hexane on various metals

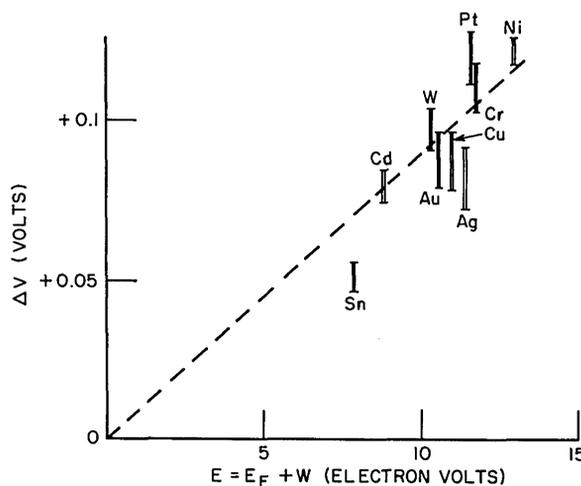


Fig. 5 -  $\Delta V$  Plotted against  $E$  for benzene on various metals

silver were far below the values shown on Figs. 4 and 5. As it was realized that these films had been formed on the silver by the rubbing-down method and that a thin film of silver sulphide might have formed before wetting the silver with the hydrocarbon, it was considered possible that the rubbing action might have removed or rearranged the sulphide. Hence, the experiments were repeated using the evaporation method only; the resulting values of  $\Delta V$  agreed well with

the linear graphs of Figs. 4 and 5, and therefore these values were considered significant. A straight line from the origin through the group of graphical points is not a bad fit as the dotted line shows. After all, if  $\Delta V$  were a direct function of  $E$ , one would expect the curve to pass through the origin. Hence, it is suggested that  $\Delta V$  may be simply proportional to  $E$ . In the series of metals examined, the contact angles of each liquid studied were constant on all of the hexane (or benzene)

condensed films. From Eq. (1), this constancy means that  $n$  was constant. Therefore, we can conclude that  $\mu_p$  is also simply proportional to  $E$ . From Eq. (2) it follows that  $\bar{F}$  at  $r = r_0$  (or  $\bar{F}_0$ ) must also be proportional to  $E$ .

It is not unreasonable for  $\bar{F}_0$  to be proportional to  $E$  because Eq. (10) would then imply 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 also expect  $W$  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  $\Delta V$ .

### GENERAL DISCUSSION

Although the experiments reported here were all carried out in clean and controlled air at atmospheric pressure rather than under the high vacuum conditions usually considered essential for productive research of contact potential differences between metals, the results obtained are reproducible and useful in revealing new and fundamental information about the properties of the metal substrates and adsorbed liquid films. 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 four reference liquids used as sessile drops, (b) the equality of the 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 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, 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.

The study of one compound adsorbed on a series of metals has made evident large, reproducible, and specific polarizing effects on the adsorbed molecules which are believed to arise from differences in  $\bar{F}_0$ . Good evidence has been found for inferring that there is an approximately linear correlation of the induced moment with the energy  $E$  to remove an electron from the metal. However, further research is needed on the effect of the thickness of surface oxides and adsorbed water on  $r_0$ .

Many investigators have attempted in the past 50 years to use the great sensitivity to surface changes of the contact potential differences between metals as a quantitative tool for studying the adsorption of gases and vapors, but little success has been reported. Our results make evident some of the many experimental conditions necessary for the successful use of contact potential differences at ordinary gas pressures or in evacuated systems. It is hoped that the necessity for controlling these conditions has been made clear in this and in preceding papers (1-6). The necessary techniques do not require the adoption of new or complex equipment but are especially concerned with prevention of atmospheric pollution in the vicinity of the electrodes by any organic compounds whatsoever, with the importance of exercising extreme care in preparing, cleaning, and handling the solid surfaces as well as with the value of thoughtful applications of the appropriate selective adsorption techniques such as liquid/solid and liquid/gas chromatography to purity adequately even the best available compounds. The important effect on surface potentials of the adsorption of water has been known for some time, but it has not been recognized that by controlling the relative humidity and temperature in a gaseous atmosphere, one could obtain reproducible and useful data. As previous papers (1, 2, 6) have shown, control of the relative

humidity is necessary but is not difficult when in the range between 10% and 80% at ordinary temperatures; however, it becomes critical at lower (or higher) values of the relative humidity. Hence, if one desires to study surface potentials in the complete absence of adsorbed water, it is necessary to go to such great extremes in drying the system that it is questionable whether this can be done under conditions other than those obtainable in a high vacuum system properly designed.

In the past five years Gottlieb (23), Fowkes (24), Intorre, Kwei, and Peterson (25), and Haydon (26), have also published 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 help plan such experiments and to obtain interpretable experimental data.

In past investigations of cleaning, friction, adhesion, corrosion prevention, and other studies or uses of the surface properties of metals, it usually was assumed that a final solvent cleaning or degreasing of a surface was satisfactory provided that a sufficiently pure or volatile solvent was used. Our results prove that this supposition is incorrect even if the solvent is nonpolar, and is capable of greatly confusing or interpreting the experiments. 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 surfaces.

In general, the neglect of the effects of: (a) the polarization induced in the solvent by the metal adsorbing surface, (b) the retention of a residual film by the solid surface after evaporation of a pure solvent, and (c) the conditions required to avoid mixed film formation (6) are all sources of difficulty which should be avoided in research in this field.

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