

TABLE II

	B. p., °C.
Methyl mercaptan	7.2
Methyl sulfide	38
Phenyl mercaptan	169.5
Phenylmethyl sulfide	188
Methyl alcohol	64.5
Methyl ether	- 24.9
Phenol	182
Anisole	155.8

boiling point than methyl sulfide; similarly phenyl mercaptan has a lower boiling point than phenylmethyl sulfide; on the other hand, the reverse is true for the oxygen analogs. This indicates that phenyl mercaptan as well as alkyl mercaptans is unassociated or at most forms very weak S-H←S bonds. This is in agreement with previous work³ which showed that a sulfur atom is an ex-

tremely poor donor atom for the bonding of a hydrogen on a carbon.

Summary

The heats of mixing of *n*-heptyl and phenyl mercaptans with *N,N*-dimethylacetamide, ethyl ether, acetone, and benzene have been measured. The results afford evidence of hydrogen bonding to donor oxygen and nitrogen atoms by phenyl mercaptan, but not by *n*-heptyl mercaptan. The failure of aryl mercaptans to show association is a result of the weak donor ability of the sulfur atom for hydrogen bonding and not from any lack of acceptor ability on the part of the hydrogen of the S-H link. It is pointed out that whenever a hydrogen is attached to another atom by a sufficiently ionic link, hydrogen bonding is possible.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

Electrical Characteristics of Molecular Films

BY FRANCIS J. NORTON

1. Introduction

It has been shown by Blodgett and Langmuir^{1,2} that single layers of molecules on water surfaces can be transferred to polished metal slides by dipping the slide through the water surface. When one molecular layer goes on the slide as it is dipped downward, but none as the slide is withdrawn, this transferred layer is called an X film. When one layer is transferred on the down dip and one on the up dip, they are called Y films.

Porter and Wyman^{3,4} found that X films of calcium and barium stearates, deposited from baths of pH above 9, possess a potential which increases with the number of molecular layers. The Y films of calcium and barium stearates, on the other hand, do not show this growth of potential with successive dips.

The experimental results of Porter and Wyman have been repeated and confirmed, using both the vibrating plate method and also a polonium-air electrode to measure surface potential. The interpretation of certain of our experiments indicates, according to the theory given by Langmuir,⁵

that the principal portion of the charge on calcium and barium stearate X films may be due, not to molecular orientation within the films, but to a surface electrification.

2. Apparatus

The vibrating plate method is that described by Zisman⁶ and Porter.⁷ A beat frequency oscillator (RCA type TMV 134-A) was used to produce the audio frequency which was amplified and fed to a loud speaker element in a sturdy support. This element vibrated an insulated polished nickel disk just above the film. When a potential exists between the disk and film, this vibration plate condenser feeds an alternating current into an audio-frequency amplifier. An opposing potentiometer and voltmeter was used to balance out the surface potential to a minimum of sound in earphones.

The polonium-air electrode affords an independent method of measuring surface potentials. The use of radioactive material for measuring contact potentials was described by Lord Kelvin shortly after the discovery of radioactivity. The polonium method has been used by Guyot, Frumkin, Rideal and others. Old radon tubes were crushed and soaked in 4 *N* hydrochloric acid. A buffed disk of nickel 0.5 cm. in diameter, 0.025 cm. (10 mils) thick was welded to a nickel wire. When this is rotated for a few minutes in hydrochloric acid extract from radon tubes, polonium is deposited on the nickel disk. The disk was then washed in distilled water and dried.

(1) Blodgett, *THIS JOURNAL*, **57**, 1007 (1935).

(2) Blodgett and Langmuir, *Phys. Rev.*, **51**, 964 (1937).

(3) Porter and Wyman, *THIS JOURNAL*, **59**, 2746 (1937).

(4) Porter and Wyman, *ibid.*, **60**, 1083 (1938).

(5) Langmuir, *ibid.*, **60**, 1190 (1938).

(6) Zisman, *Rev. Sci. Instruments*, **3**, 367 (1932).

(7) Porter, *THIS JOURNAL*, **59**, 1883 (1937).

The polonium ionizes the air in the neighborhood, and this polonium-air electrode can be used to explore the potentials existing between the disk and the metal slide, or the surface of thin insulating films on the slide.

One essential feature of the method was a guard sleeve around the disk, so the ionized air was confined to the immediate region of the film being measured, and stray currents did not flow to other parts of the apparatus. The slide was held on a small adjustable table. It was brought 2 mm. from the polonium disk and 1 mm. from the protecting sleeve. The whole was enclosed in a grounded metal box, as was the amplifier and lead to the grid of the tube.

By a d-c. amplifier using an FP-54 tube⁸ the small ionization currents were amplified and put into a photoelectric recording micro-ammeter.⁹ This had a coil resistance in the primary galvanometer element of 1200 ohms, and a damping resistance of 20,000 ohms across the meter terminals. By putting various known values of grid resistances, from $R_g = 10^9$ to $R_g = 10^{11}$ ohms, into the amplifier circuit, currents down to 10^{-13} ampere could be continuously recorded. The resistors were made by the S. S. White Dental Mfg. Company. Care was taken not to touch the resistor element with the fingers, and the air in the amplifier box containing resistor and tube was kept at low humidity by phosphorus pentoxide. The usual grid resistor used was 10^9 ohms, which was near the value of resistance of the ionized air constituting the polonium-air electrode. Where these two resistances are of the same order, best sensitivity is obtained. The usual range of current was 10^{-8} to 10^{-11} ampere. As shown in Fig. 1, a potentiometer and voltmeter enabled various potentials to be applied so as to bring the current to zero on the recording microammeter, and the surface or contact potentials existing between the film surface and the nickel-polonium disk could thus be determined. The calibration of the recording galvanometer to give actual currents was made by putting a known high resistance externally in place of the polonium-air electrode. Then various voltages were applied by the external potentiometer, and for each applied voltage a reading was obtained on the galvanometer. A circulating current is obtained in the circuit: external resistance, voltmeter, ground, grid resistor. The galvanometer reading represents the amplification of this current. Knowing the values of voltage and of the two resistors in the circuit, the value of the current for each galvanometer reading can be calculated from Ohm's law.

The procedure for obtaining the resistance of the polonium-air contact was as follows. The nickel slide was buffed so as to offer the same type of surface as the small polonium coated disk. After a time, the value of surface potential between disk and slide became nearly zero as measured on the external potentiometer circuit. Then various values of voltage were applied by the potentiometer to give various readings on the galvanometer. These were translated into current readings by the calibration described in the preceding paragraph, and the value of total resistance obtained in the circuit: polonium-air electrode, voltmeter, ground, grid resistor. Knowing the value of the grid resistor, and using various resistors as a check, the resistance of the polonium-air

electrode was calculated. It was found to be ohmic in the range of voltages used.

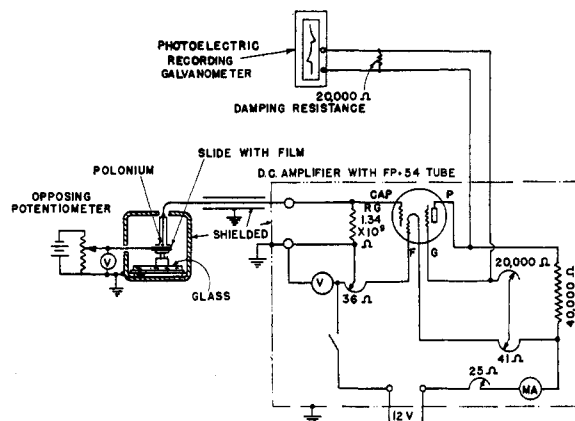


Fig. 1.

The two methods, vibrating plate and polonium-air electrode, gave substantial agreement in values of surface potential. The obvious difference is that a film left in the ionized air loses its charge, as the surface is continually short-circuited. This behavior is discussed later.

The principal baths used were:

- Solution 1: for Ca stearate Y films pH 7, 10^{-4} m CaCl₂, 3×10^{-4} m KHCO₃
- Solution 2: for Ca stearate X films pH 10, 10^{-4} m CaCl₂, 10^{-3} m KHCO₃, raise pH by adding NH₄OH
- Solution 3: Ba baths like Ca
- Solution 4: for Cu stearate Y pH 5.0, 10^{-4} m Cu acetate, 3×10^{-5} m HCl
- Solution 5: for Pb stearate X pH 5.7, 10^{-4} m PbCl₂, 2×10^{-6} m HCl
- Solution 6: for Pb stearate Y pH 5.7, 10^{-4} m PbCl₂, 2×10^{-6} m HCl, 10^{-5} m SnCl₂·2H₂O

The pH values were measured by a glass electrode pH meter.

Effect of pH of Bath.—The surface potential of calcium stearate films put on by 20 round-trip dips was found to vary with the bath pH in the manner shown in Fig. 2. At pH 9, the layers are definitely of the X type; at pH 7, definitely Y. The transition region may give a mixture.

It is interesting to note that the region where charged X films are formed on dipping is one of change in sign of electrical potential of stearic acid films on the bath surface. When stearic acid is spread on a water of pH 6, the surface becomes more positive by +250 mv.¹⁰ At pH 7 this change is about +160 mv., but near pH 9, spreading stearic acid on water causes no change in its surface potential. Above 9 the surface becomes negative with respect to the clean water surface, and it is in this region that the greatest surface charges on the transferred films are found.

(8) Metcalf and Thompson, *Phys. Rev.*, **36**, 1489 (1930).

(9) LaPierre and Carson, *Gen. Elec. Rev.*, **36**, 271 (1938).

(10) Porter, *THIS JOURNAL*, **59**, 1883 (1937).

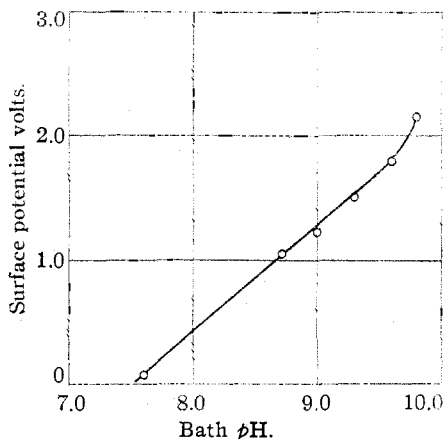


Fig. 2.

Age of Film on Bath Surface.—Another factor influencing the voltage acquired by calcium stearate X films on dipping is the age of the stearic film spread on water. If the film is transferred immediately after spreading, a higher charge per dip results than if an interval of ten or twenty minutes elapses between the time of spreading and the time of dipping. This is illustrated in Fig. 3 and was observed many times. The data of this figure also confirm the result of Porter and Wyman—that one Y dip will take away the charges resulting from X dips.

Various Types of Films.—Dr. Blodgett has found that stearic acid ($C_{17}H_{35}COOH$) spread on a bath 10^{-4} molal in lead chloride, pH 5.5, will yield an X type film when transferred to metal. If arachidic acid ($C_{19}H_{39}COOH$) is used on this same bath a Y type of film results. This affords an excellent opportunity to find out if the surface potential depends on the film type.

Surface type	Potential volts	ΔE
Bare Cr	+0.25	
55 mol. layers Pb arachidate Y films	+ .38	+0.13
Bare Cr	+ .43	
40 mol. layers Pb stearate X films	+ .55	+ .12

This would indicate that X films of lead stearate do not possess the high surface charge which calcium and barium X films show, or else lose the charge much more quickly.

Another test involving X and Y films deposited from a bath at the same pH is afforded by Dr. Blodgett's discovery that adding a small amount of stannous chloride (10^{-5} molal in bath) to a lead

bath of pH 5.5, causes Y films to be deposited, whereas without the tin, X films are deposited.

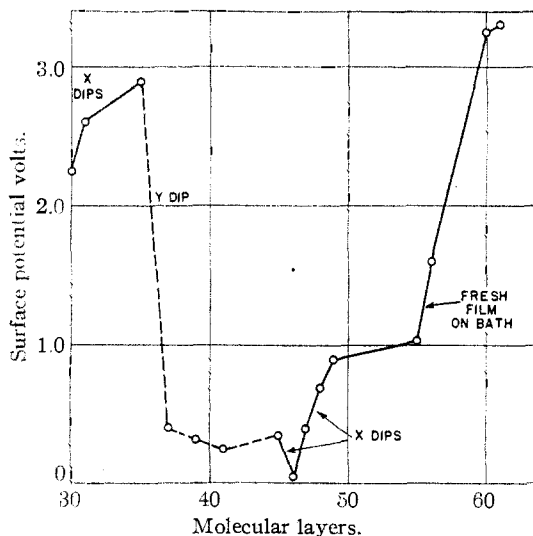


Fig. 3.

When this was tried, the measurements being made within a minute of completing the film transfer, the results indicated two things: first, lead stearate X films can build up an initial potential at about a tenth of the rate for calcium stearate X films; second, these lead X films have this potential even though they are made from a bath of pH 5.5, whereas Y films do not have the charge. The stannous chloride enabled both X and Y films to be made from a bath of the same pH.

Experiments to be presented in detail in a subsequent publication indicate that lead stearate films have lower electrical resistance than calcium stearate films and hence do not hold their surface charges so well.

Dipping into Various Solutions

The effect of dipping various films into clean water at different pH values indicated the composition of the bath and especially pH governed the magnitude of the charge developed on the surface.

A calcium stearate X film, 30 round-trip dips in bath pH 8.8, with stearic acid spread on it, gave 31 molecular layers (counting the initial layer on the rubbed slide) and a surface potential $E = +2.20$ volts, measured by the vibrating plate method. This was then dipped into baths which had no stearic film on. The successive changes in surface potential upon successive dips are:

Bath	pH	ΔE
		+2.20 as made
Clean Ca bath	9.4	+2.40
Clean Ca bath	8.25	+2.30
Distilled water	6.7	+1.70
Distilled water	6.1	+0.50
Clean Ca bath	9.4	+1.30

Successive dips into a bath of pH 9.4 will, as Porter and Wyman report, make the X films more negative after the first dip. On the other hand, Y films became consistently more negative on dipping into an alkaline bath, as shown below.

ΔE	Dips	
+0.27		Bare Ni surface
+ .08		37 Ca stearate Y layers, bath pH 7.5
+ .046	1	Clean Ca bath pH 9.5
+ .022	2	Clean Ca bath
- .15	7	Clean Ca bath
		Left in Po to discharge
0	..	Start
- .20	1	Clean Ca bath pH 9.5
- .22	2	Clean Ca bath
- .54	7	Clean Ca bath

These films all came out dry. If they are dipped into solutions containing aluminum or thorium ions, the surfaces are made hydrophilic, they emerge wet and the surface charge is near zero.

Solutions were made from sodium chloride, barium chloride, aluminum sulfate, thorium nitrate and hydrochloric acid with the pH values given below; 21 calcium stearate X layers were then dipped and held for thirty seconds in each with the results shown in Table I.

TABLE I
21 CA STEARATE X LAYERS ON NICKEL

Bath 0.001 N	pH	ΔE			Surface emerged
		Initial	1st dip	2nd dip	
Na	6.1	+1.2	+1.0	..	Dry
Ba	5.95	+1.7	+1.15	+0.85	Dry
Al	4.5	+1.45	0	0	Wet
Th	3.4	+1.15	+0.13	- .15	Wet
HCl	3.45	+1.0	+1.15	+ .78	Dry

This illustrates the importance of the composition of the solution on changes of surface potential on dipping. In every case it has been found that when the film surface comes out wet, the surface charge has been lost. Sometimes the drying takes place very quickly as the film is being raised out of the water.

Surface Potential of Films on Glass.—To find out whether the metal surface on which Y films were deposited was essential to their possessing a surface potential, the following experi-

ment was devised. A glass electrode was made from very thin special glass of high conductivity such as is used in pH electrodes. A portion was made flat, and on this X films of Ca stearate were deposited. The interior of the glass electrode was filled with 0.1 N hydrochloric acid and contact made to this by a platinum wire. This flat thin glass with calcium stearate film on the top surface and hydrochloric acid beneath was then made the lower plate, and the surface potential measured by the vibrating plate method.

It was found at the start that the clean glass had a potential relative to the vibrating nickel plate of near zero, ≈ 0.005 v. This was raised to +0.80 v. by 25 X dips of calcium stearate on glass and with more layers finally a potential of +1.5 v. was attained. This value was checked by the ionized air method.

Through ionized air, 10 v. was applied, so the surface potential of these calcium stearate X films was raised to +6.2 v. The surface was then taken out of the ionized air and the next day was +3.3 v. Upon dipping the glass with the film into a solution of citrate-phosphate buffer of pH 7, the film was displaced from the glass and floated on the solution as iridescent fragments.

Application and Decay of Surface Potential in Ionized Air.—As described, the air-polonium electrode was so arranged that voltage could be applied with a potentiometer arrangement, and the small current resulting recorded continuously. Upon applying and maintaining a voltage, a relatively high initial current flows. This then decays exponentially, as the charges accumulate on the insulating surface film. These charges create an opposing potential, the magnitude of which is given by Equation 2, in Langmuir's paper⁵

$$V = 4\pi\sigma et/D$$

where σ = surface intensity of electrification

e = elementary charge = 4.77×10^{-10} e. s. u.

t = thickness of film = 24×10^{-8} cm. per layer

D = dielectric constant = 2.56

If the film is a good insulator, the initial charging current drops to zero, if a poor insulator, to a constant value of current, the conduction current of the insulator. The automatic record is shown in Fig. 4. At "a," 5.0 v. were applied to 41 calcium stearate X layers. The initial current was "b" which decayed to "c." At "c" the external voltage was taken off and the current "d" resulted from the surface charge. This then decayed along "de."

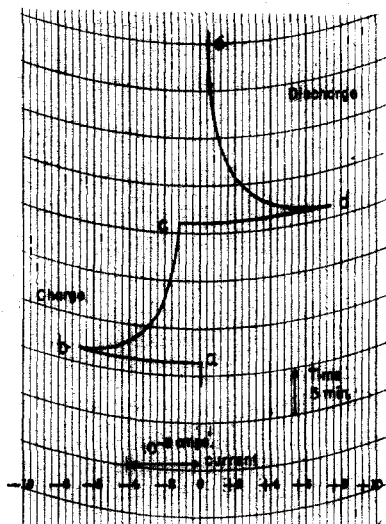


Fig. 4.

Thus when a charged film is put into ionized air, with no voltage applied, but the nickel slide and polonium electrode grounded, the ionized air short circuits the charges on the film surface, and the voltage decays exponentially to zero.

The magnitude of surface intensity of electrification is interesting, especially when considered as number of charges relative to the number of surface molecules.

On 41 calcium stearate Y layers a surface potential was built up by putting it into the ionized air beneath the polonium-air electrode and applying 0.5 v. for sixteen minutes. On taking off the voltage, a surface potential of 0.48 v. was found. This, left in the ionized air, decayed to $1/e^{\text{th}}$ of its value in one hundred and eighty seconds.

First can be calculated σ from the equation given above, remembering to convert the ordinary volts to e. s. u. and putting in the proper film thickness. The surface intensity comes out 7×10^{10} elementary charges per square centimeter. The cross sectional area of the stearate molecule is 20 square Ångströms, or 20×10^{-16} sq. cm., a total of 5×10^{14} molecules per sq. cm. Hence to produce the surface potential of 0.48 v., there need be only one elementary charge per 7000 surface molecules, and if distributed in a square array, two charges would be separated by some 84 molecules.

The 7×10^{10} elementary charges per sq. cm. amount to 1.11×10^{-8} ampere-second, or coulomb, per sq. cm. Since the area of the polonium-air electrode is 3.14 sq. cm., the total amount of electricity in that area is 3.5×10^{-8} coulomb.

The recording meter gives amperes \times seconds, so by graphically integrating the area under the decay curve, the total amount of electricity discharged is found. This integration gave 5.3×10^{-8} coulomb, compared to the 3.5×10^{-8} calculated from the voltage equation. This discrepancy undoubtedly is due to a difference between the actual effective area of the polonium-air electrode and that calculated from its dimensions.

The capacitance of this 3.14 sq. cm. of charged film is $C = AD/4\pi t$ (where A is the area) = 6.5×10^4 cm. or 7.2×10^{-8} farad. The time constant of a condenser discharge in seconds is $\tau = CR$. The resistance in this circuit is the polonium-air gap, of 0.9×10^9 ohms, and that of the grid resistor, 1.34×10^9 ohms. Hence

$$\tau = 7.2 \times 10^{-8} \times 2.24 \times 10^9 = 161 \text{ sec.}$$

This is to be compared to the observed value of 180 sec.

From these calculations three results emerge which seem to indicate that the surface potential on molecular films can be regarded as a surface electrification.

(1) The value of σ , the surface intensity of electrification, is reasonable, and when thought of in relation to the total number of molecules on the surface, it is surprising what a low density of charge population will account for the observed surface potentials.

(2) The total amount of electricity as observed in the charge decay curve is approximately the same as that calculated from the voltage equation of Langmuir's paper.

(3) The time constant of decay observed is near that calculated, regarding the charged film simply as a charged condenser.

By the corona discharge from a spark coil leak tester, a surface potential of 4.0 v. was put on 5 molecular layers of calcium stearate X films. This is a gradient through the film of 3,300,000 v./cm., and the surface intensity of electrification can be calculated as 4.7×10^{12} elementary charges per sq. cm. There is thus one charge for a hundred molecules on the surface, and this represents some type of saturation value for this particular film.

Application of Surface Potential by Corona Discharge.—The sharp point of a portable spark coil leak tester was held 7 cm. above a film on a grounded nickel slide, so a corona discharge but not actual sparks occurred in the air just above the film. It became charged to a value

which depended on the number of molecular layers in the film, and on the time in the corona atmosphere, up to saturation. This is shown in Table II.

TABLE II
EFFECT OF CORONA

Mol. layers Ca stearate X	After			
	1/2 Minutes in corona,	1	1 1/2	2
2	+0.685	1.1	1.2	1.25
3	1.5	2.0	2.3	2.3
5			3.85	4.0
10				9.3

The gradient in these films of various thicknesses is high, and of the same order of magnitude, as Table III shows.

TABLE III

CA STEARATE X, CHARGE PUT ON BY CORONA

Mol. layers	Surface potential, v.	Volts per layer	Gradient volts/cm.
2	1.25	0.63	2,600,000
3	2.3	.77	3,200,000
5	4.0	.80	3,300,000
10	9.3	.93	3,700,000
50	23.5	.47	2,000,000

Corona was also produced by high voltage d. c., and it was found that the film collected a positive charge on its surface when the underlying nickel slide was made negative relative to the sharp point from which the corona was proceeding. With the nickel slide positive, a negative charge accumulated on the surface of the insulating film, presumably the negative ions attracted to the positively charged slide.

As discussed in a communication by Norton and Langmuir¹¹ corona from high voltage a. c., as near an unlighted Coolidge X-ray tube, caused a negative charge to accumulate on the surface film of a grounded slide, as though there were a preponderance of negative ions in the neighborhood or a higher mobility of the negative ions. The film becomes negative, even though there are no X-rays. Experiments involving X-rays will be presented in a subsequent paper. The results are, briefly, that when air is rendered conducting by X-rays, surface charges of either sign can be put on the film by applying the appropriate field.

Loss of Charge in Air.—As Porter and Wyman have indicated, calcium stearate X films can maintain their surface potentials for a surprisingly long time. I have found that the charges put on by

ionized air, as well as the potentials on the film by dipping, persist after a rapid initial drop.

The fact that the charge stays on for weeks must mean that the calcium stearate films are extremely good insulators. How then is the loss of charge to be explained? An examination of the rate is of interest.

One film of 71 molecular layers had a surface potential of 1.22 v. at twelve days, and 0.97 v. at forty-eight days, a loss of 0.25 v. in thirty-six days when kept out in the air, away from radioactive material. From the voltage equation, it can be calculated that this represents a loss of 6750 elementary charges per second from each square centimeter, or a current of

$$6750 \times \frac{4.77 \times 10^{-10}}{3 \times 10^9} = 1.07 \times 10^{-15} \text{ ampere per sq. cm.}$$

In an article on "Ionization of the Atmosphere" Koller¹² states that for the gradient existing in the earth's atmosphere of some 100 v./m., the air conductivity leads to a current of 2×10^{-16} amp./sq. cm. constantly flowing toward the earth. It will be observed that this is near the order of magnitude of the leakage of charge from the molecular films, where a similar gradient exists to the bare metal near-by.

Similarly, Porter and Wyman⁴ find on a 245-layer film a potential 6.02 v. at four days and 5.19 v. at nine days, a leakage of 0.16 v./day. This represents a loss from each sq. cm. of 3.9×10^4 elementary charges per second or 6.2×10^{-15} amp./sq. cm. Since the voltage gradient is about six times greater on Porter and Wyman's slide, their results reduce to the same value as mine, 1×10^{-15} amp./sq. cm., and the loss of charge can be explained as being due to normal air conductivity.

The following three examples illustrate the loss of charge in the air, away from radioactive material. These surface potentials were all measured by the vibrating plate method.

(1) On 20 Ca stearate Y layers were put 51 Ca stearate X layers, a total of 71 molecular layers on a nickel slide

Time, days	0	4	12	15	18	22	23	48
Potential	+3.20	+1.90	+1.22	+1.40	+1.15	+1.08	+1.07	+0.97

(2) 21 Ca stearate X layers. Slide made positive and 90 volts applied through air ionized by Po for half an hour, then slide taken out

Time	0	30 min.	5 days	8	11	15 days
Potential	-6.88	-4.3	-2.42	-2.25	-2.25	-2.17

(3) 21 Ca stearate X. Slide made negative and 90 volts applied through air ionized by Po, 15 min. then slide taken out

(11) Norton and Langmuir, *THIS JOURNAL*, **60**, 1513 (1938).

(12) Lewis R. Koller, *Jour. Franklin Inst.*, **214**, 543 (1932).

Time, min.	0	2	5	14	24
Potential	+6.9	+6.5	+6.2	+5.5	+5.0
Time, hr.	1½	4	5		
Potential	+4.0	3.3	3.0		
Time, days	5	8	11	15	
Potential	+1.74	+1.65	+1.51	+1.45	

It is apparent that the usual potentials acquired by dipping, or potentials of either sign put on by ionized air, all behave in a similar manner.

Summary

Surface potentials can be put on X or Y stearate multi-films by applying a voltage while the films are in a conducting medium as air ionized by po-

lonium. With voltage off, the films lose their charge exponentially. The coulombs represented by the area under the automatically registered discharge curve agree with Langmuir's equation which calculates potential resulting from surface charges.

The slow leakage of charge from X films left in ordinary air can be explained by the natural electrical conductivity of air.

Surface potentials were found to exist on calcium stearate X films deposited on glass.

SCHENECTADY, NEW YORK

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Measurements on Hexaphenyldigermane

BY P. W. SELWOOD¹

The molecular weight of hexaphenyldigermane has been reported by Morgan and Drew² as 560 to 566 determined ebullioscopically in benzene. They interpret this as evidence for "no recognizable dissociation" although the value obtained is slightly lower than the molecular weight (606.8) computed for the compound.

A sample of this compound was obtained through the courtesy of Professor Warren C. Johnson of the University of Chicago.

Experimental Part

Magnetic Measurements.—The magnetic susceptibilities were measured by means of the Gouy balance previously described.³ The only modifications were (1) the use of a magnetically damped microbalance, and (2) a modified temperature control. In previous work the temperature of the sample had been maintained through careful injections of liquid air into a lead block surrounding the sample. In the present work oxygen was liquefied by passing it through a condenser surrounded by liquid nitrogen. The oxygen was then allowed to fall, drop by drop, into the lead block. Through control of the rate of flow of oxygen into the condenser, a high degree of temperature control was possible.

All measurements were referred to freshly boiled distilled water, the specific susceptibility of which was assumed to be -0.7200×10^{-6} at 20°.

Preparation of Materials.—Measurements were made on powdered hexaphenyldigermane and on a solution of the digermane in benzene. Some rather interesting experiences were encountered in preliminary tests on the powder, and are described.

(1) The author is indebted to the National Research Council for funds for the construction of a magnet, and to the National Academy of Sciences for a research grant from the Joseph Henry Fund.

(2) Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

(3) Haller and Selwood, *THIS JOURNAL*, **61**, 85 (1939).

The substance gave evidence of having a magnetic susceptibility markedly dependent on field strength. The apparent susceptibility varied from $+1.45 \times 10^{-6}$ at 1000 oersteds to -0.10×10^{-6} at 11,000 oersteds. This behavior strongly suggested the presence of a ferromagnetic impurity. The digermane was therefore recrystallized from benzene, after which the susceptibility became normal, that is, constant, from about 1000 to 17,000 oersteds. A small insoluble residue was found to contain a very few almost microscopic specks of some highly magnetic substance, presumably magnetic oxide of iron. These results are illustrated in Fig. 1 in which Δw , the apparent change in weight on application of the field, is plotted against i , the current through the magnet. While these results have no bearing on the main problem, yet they do show the extraordinary sensitivity of the magnetic method for detecting ferromagnetic impurities and the necessity for excluding iron-bearing laboratory dust from samples under investigation.

The benzene solution used in this work was prepared by shaking the powdered digermane with redistilled thiophene-free benzene. No effort was made to exclude air. The solution was analyzed by evaporating to dryness at 125° and weighing the residue. The density was determined pycnometrically.

Results

The susceptibility of the powdered hexaphenyldigermane at several temperatures is given in Table I.

These results follow the relationship $\chi = A + (C/T + \Delta)$ where χ is the susceptibility, A is the constant diamagnetic part of the susceptibility, C is the Curie constant of the paramagnetic part, T is the absolute temperature, and Δ is the "molecular field constant." In the above relationship $A = -0.47 \times 10^{-6}$ and this is believed