

[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES, HARVARD UNIVERSITY]

**Further Studies on the Electrical Properties of Stearate Films Deposited on Metal**

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**I. Introduction**

In two previous communications<sup>1,2</sup> we have discussed a variety of phenomena associated with the contact potentials of multilayer stearate films built on metal slides by dipping the slides through stearate monolayers spread on liquid surfaces. Langmuir<sup>3</sup> recently has pointed out the advantages of interpreting these phenomena on the hypothesis that the potentials are due to the production of surface charges. He also has outlined a mathematical analysis of the electrostatic forces brought into play in consequence of the potentials while the films are being dipped. This analysis suggests that by introducing an arbitrary voltage between the submerged metal slides and the liquid it should be possible to modify the behavior of the films and to control the potentials which they develop, and Langmuir refers to observations pointing to this. Thus, speaking in terms of the surface charge hypothesis, he states that "By applying potentials of a few volts between the plate and the metallic tray during the deposition of stearate monolayers it has been found possible to alter the surface charge  $\sigma$  on X or Y films and to obtain either positive or negative values of  $\sigma$  over wide ranges of  $pH$ ."

In the present paper we describe a variety of experiments which reveal new phenomena associated with the films, and which have a bearing on the problem of the source and nature of the potentials, particularly in relation to the surface charge hypothesis.

**II. Effects of Liquids on Potentials Associated with the Films**

In this section we discuss studies on the effect of dipping films into various liquids, as well as electromotive force measurements involving films covered with liquids. In these electromotive force measurements, owing to the very high resistance of the circuits due to the films themselves and in some cases to the liquids as well, it was impossible to make direct measurements with a potentiometer. For this reason we employed a

bridge circuit of the type described by Du Bridge,<sup>4</sup> involving an F. P. 54 Pliotron.

We already have pointed out<sup>2</sup> that dipping an X film of high contact potential into water or the aqueous substrates from which films are obtained does not greatly alter its subsequent contact potential in air. Nevertheless while the film is under the liquid its electrical behavior is like that of a film of zero potential. The same is true of Y films and X films of lower potential. Thus the e. m. f. of the arrangement

X or Y film/liquid/X or Y film

is always very close to zero, irrespective of the contact potentials of the films. This is illustrated by the case of two X films of potentials 1.79 and 0.175 v. separated by a few drops of a solution used for forming X films. The voltage of the combination was close to zero, *i. e.*, 0.055–0.075. If we think of the potential as due to internal charges, or to the orientation of dipoles within the film, the effect may be interpreted as due to the accumulation of a layer of compensating free charge, or of oriented dipoles, at the outer face of the film while it is in contact with the liquid. On the other hand, if we regard the potential as due to the presence of a layer of free charge on the surface, we may think of this effect as due to the surface being discharged by contact with the liquid. It is then, of course, necessary to assume that the surface of the film is recharged by the act of separating it from the liquid, since contact potentials persist after the slides are dipped into aqueous solutions. This result at once raises the question whether a similar neutralization takes place when other liquids are substituted for water or aqueous solutions. We have made a number of observations to answer this question.

When films are immersed in benzene there is no evidence of neutralization of the potentials. This is illustrated by the case of an X film originally of potential 5.6 v. separated from a Y film of potential 0.19 v. by a layer of benzene. The voltage from left to right<sup>5</sup> of the combination

X film (5.6 v.)/C<sub>6</sub>H<sub>6</sub>/Y film (0.19 v.)

(4) Du Bridge, *Rev. Sci. Instruments*, **4**, 532 (1933).

(5) *I. e.*, the voltage of the metal plate coated with film on the right minus that of the plate on the left. This convention is used throughout in expressing the voltage of such combinations

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

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

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

varied from +5.4 to +4.0 over a period of three hours, showing some tendency to fall, but rising each time the benzene was renewed close to the initial value. The sign of the voltage agrees with the orientation of the films. After the observation was over the potentials of the two films were measured in air and found to be 4.9 and 0.29. In this and all following cases we adopt the convention that the number in brackets following the word "film" refers to the original contact potentials of the film in air. Measurements of other pairs of films all gave the same results, *e. g.*

X film (3.10 v.)/C<sub>6</sub>H<sub>6</sub>/X film (0.18 v.)

Voltage varied between +2.7 and +1.3 over a period of about fifty-two minutes, showing some tendency to drop but returning close to the original value when the benzene was renewed. After the measurements the potential of the left-hand X film in air was about 2.70.

When chloroform is substituted for benzene, neutralization is complete as in the case of water and aqueous solutions. For example the voltage from left to right of the combination

X film (4.9 v.)/CHCl<sub>3</sub>/Y film (0.29 v.)

was -0.14. The potentials of the films in air after the measurements were 1.8 and 0.29. The same type of neutralization is produced by mixtures of chloroform and benzene containing about 60% or more by weight of chloroform but not by those containing less, as may be seen by the following three examples:

- (1) X film (2.8)/C<sub>6</sub>H<sub>6</sub> + CHCl<sub>3</sub> (25%)/X film (0.34)  
Voltage +2.3 -- +2.2 over a period of twenty-five minutes  
Potentials of films after measurements 2.5 and 0.35
- (2) X film (2.6)/C<sub>6</sub>H<sub>6</sub> + CHCl<sub>3</sub> (50%)/X film (0.35)  
Voltage +2.1 -- +1.0 over a period of forty-five minutes  
Potentials of films after measurements 1.7 and 0.16
- (3) X film (1.9)/C<sub>6</sub>H<sub>6</sub> + CHCl<sub>3</sub> (59%)/Y film (0.22)  
Voltage fell quickly from 0.73 and reached a value of 0.01 in twenty-five minutes  
Potentials of films after measurements 1.0 and 0.20

Other observations were made by placing small drops of mercury on films and making contact with them by means of a fine platinum wire. The voltages of the combination

Film/Hg/Pt

are always small and independent of the potentials of the films, as may be seen by the following examples, in which the different values of the voltage belong to different parts of the film

X film (2.6)/Hg/Pt, voltage +0.25, +0.15, +0.13, +0.19  
Y film (-0.20)/Hg/Pt voltage 0, +0.20, 0

Contact with mercury has little or no effect on the subsequent potential of the films. This point was tested by dipping films into a beaker of mercury the surface of which had been scraped clean. After an X film having an initial potential of 3.0-3.2 v. was dipped repeatedly its potential was found to be 3.4-3.7 v. A color comparison showed that none of the film had been removed. In another case several layers were found to have been removed by continued dipping but there was no significant change in the potential. The same result is obtained when Y films are dipped in mercury. On the other hand, it may be seen from the data given above that prolonged contact with chloroform reduced the potentials of X films considerably. Contact with benzene, however, reduces the potentials only slightly.

If warm moist air is blown over the films so as to produce water condensation on the surface while the contact potentials are being measured there is no appreciable change, although, as we have pointed out, immersion in water leads to neutralization of the potential.

We have referred to the fact that when X and Y films are made electrodes in a glow discharge, they develop very large contact potentials. These are positive or negative according to the direction of the discharge. In the case of Y films these "discharge potentials" are abolished by dipping the films into water and aqueous substrates; in the case of X films a residual potential, amounting to several volts or more, always remains after dipping and seems to have the same degree of permanence as the native potentials of X films. Like the spontaneous potentials, these potentials are neutralized while the films are under water. Dipping into benzene wholly fails to reduce such "discharge potentials" in the case of both X and Y films. The same is true of dipping into mercury, although when several of the outermost layers are removed there is some reduction in the "discharge potentials," *e. g.*, in one case when 4 layers were removed from an X film a reduction from +13 to +7.4 v.; in another when several layers were removed from a Y film a reduction from about +15 to +4 or 5 v. The same results are obtained when the potentials are negative. Such removal of layers generally occurs the first time a slide is dipped; if subsequently a new "discharge potential" is impressed on the film and

it is dipped in mercury no film is removed and there is no reduction of potential. When Y films are dipped in chloroform the "discharge potentials" are at once reduced to zero, although no film is removed. On the other hand "discharge potentials" of X films are completely unaffected by dipping in chloroform. Nevertheless, measurements of the voltages of combinations like those discussed above show that while X and Y films are in contact with mercury and chloroform the "discharge potentials" are always neutralized.

### III. Effect of Applied Voltages

In this section we shall present a detailed investigation of the effects of applying a voltage between the plate and the liquid subphase while films are being built. Under the conditions of our experiments such voltages give rise to currents of the order of several milliamperes which may be read easily by placing a milliammeter in series with the voltage source. In accordance with Langmuir's hypothesis such currents might be expected to have a marked effect on potentials by modifying the density of the surface charge. Langmuir has referred to observations suggesting this.<sup>6</sup> In any case, quite apart from the concept of surface charge and its relation to the current flowing, simply on the basis of Langmuir's general analysis of the electrostatic forces acting during the formation of films, it would be expected that applied voltages would alter the contact angles and the upper limiting potentials of the films, and perhaps also the slope of the potential-thickness curves throughout the whole process.

Since it is well known that metallic ions even at very low concentrations have marked effects on the properties of built-up stearate films,<sup>7</sup> an attempt was made to eliminate as far as was conveniently possible all sources of contamination of the solutions by traces of metallic ions. For this reason glass trays and glass barriers were substituted for the usual metal trays and barriers. Water for making up solutions was redistilled through a Pyrex glass still. In the earlier experiments the films were built on stainless steel slides, but in the greater part of the work a platinum slide was substituted to avoid complications due to possible electrolytic effects under the influence of applied voltages. Contact with the solution was made with a platinum wire. The source of

voltage applied between the slide and solution was either a storage battery or dry cells.

To prevent large changes in pH, especially when working in the alkaline range, the solutions were buffered with borates.<sup>8</sup> The following solutions were used:

- (1)  $1.33 \times 10^{-3} M H_3BO_3$ ;  $1.33 \times 10^{-3} M NaOH$ ;  $0.12 \times 10^{-3} M Ca (Ac)_2 \cdot 2H_2O$ ; pH = 10.9; for X layers
- (2)  $1.87 \times 10^{-3} M H_3BO_3$ ;  $0.93 \times 10^{-3} M NaOH$ ;  $0.4 \times 10^{-3} M HCl$ ;  $0.12 \times 10^{-3} M Ca (Ac)_2 \cdot 2H_2O$ ; pH = 8.6; for X layers
- (3) Same as (2) but with the addition of  $2.0 \times 10^{-6} M CuCl_2 \cdot 2H_2O$ , for Y layers
- (4)  $1.33 \times 10^{-3} M H_3BO_3$ ;  $0.67 \times 10^{-3} M NaOH$ ;  $0.67 \times 10^{-3} M HCl$ ;  $0.12 \times 10^{-3} M Ca (Ac)_2 \cdot 2H_2O$ ; and with or without  $2.0 \times 10^{-6} M CuCl_2 \cdot 2H_2O$ ; pH = 7.4-7.7; for Y layers
- (5)  $1.33 \times 10^{-3} M H_3BO_3$ ;  $0.67 \times 10^{-4} M NaOH$ ;  $0.67 \times 10^{-3} M HCl$ ;  $0.36 \times 10^{-4} M BaCl_2 \cdot 2H_2O$ ;  $2.0 \times 10^{-6} M CuCl_2 \cdot 2H_2O$ ; pH = 7.4; for Y layers

During the deposition of X layers, unless otherwise indicated, the slides were kept submerged in the solution for ten seconds on each dip. This procedure usually favors the deposition of more uniform X layers than can be obtained by more rapid dipping. Castor oil was used to keep the monolayer under constant compression. The experiments were conducted at room temperature, which varied between 19-24°.

**A. Effects on X and Y Films Deposited on Stainless Steel.**—If stainless steel slides are used for deposition of the film with an applied voltage, reproducible results can be obtained only for a certain length of time which seems to depend to some extent on the magnitude as well as on the polarity of the voltage. Invariably, however, in time the slide begins to show signs of electrolytic action such as small pits and there may even be an evolution of gas while the slide is submerged with an applied voltage in the course of depositing films. This occurs most rapidly when the voltage is high—22 v. was the highest voltage used in the work—and when the slide is attached to the positive pole of the battery. A slide affected in this manner is useless for further work without repolishing. The potentials of X films deposited on such slides fail to rise in the usual way with increase in number of layers, perhaps due to metallic ions escaping from the steel and becoming incorporated in the stearate films. It was pos-

(8) Sørensen's borate buffers given by W. Mansfield Clark in "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 3d edition, 1928.

(6) See quotation, p. 2855.

(7) Langmuir and Schaefer, *THIS JOURNAL*, **69**, 2400 (1937).

sible, however, by using new steel slides for only one or two films and working at relatively low voltages to obtain very consistent results.

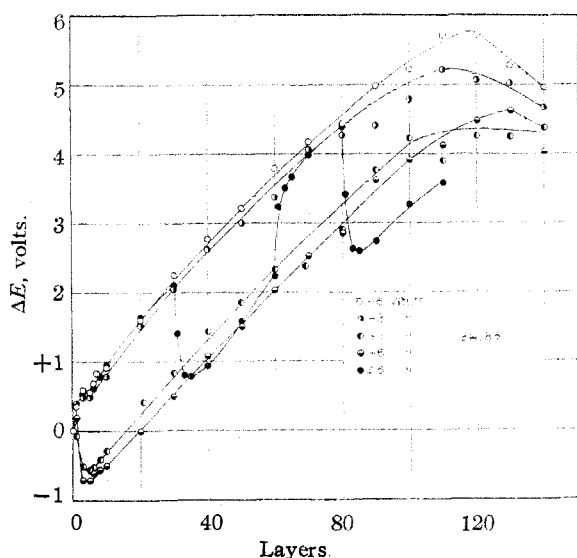


Fig. 1.

Figure 1 shows the change of contact potential with increase in number of layers for X films formed from solution (2), pH 8.6, on stainless steel at four different applied voltages, +3, +6, -3, -6 v. It should be noted that in all cases discussed in this paper we call the applied voltage positive when the positive pole of the battery is attached to the slide. The most striking characteristic of these curves is that from layer 5 to layer 90 they are parallel, *i. e.*, have equal slopes. Between 0 and 5 layers, however, the curves obtained with positive and negative applied voltages behave quite differently. The potentials of films made with positive voltages drop sharply, *e. g.*, to -0.6 v. for a voltage of +3, and to -0.7 v. for a voltage of +6. On the other hand, the potentials of films made with negative voltages rise, *e. g.*, to +0.5 for a voltage of +3 v. and to +0.5 for a voltage of +6. This initial behavior gives rise to the separation of the two parallel sets of curves.

The potential curve for a film formed without an applied voltage is not shown in this figure, but a typical curve lies between the positive and negative curves, although not necessarily parallel to them, usually more nearly coinciding at the start with the negative voltage curves and as the number of layers increases crossing over to the positive voltage curves. The curve for +6 v. in the figure was obtained by changing the direction of

the applied voltage at 30, 60 and 80 layers. From 0-30 layers, with -6 v. applied, the curve is coincident with the -6 v. curve. On reversing the polarity the potential drops rapidly to the +6 v. level and becomes approximately coincident with the +6 v. curve. On changing back to -6 v. the potential rises steeply and this time coincides with the -3 v. curve. On reversing the polarity once more at 80 layers the curve drops below the +6 v. curve but becomes parallel with it at a lower potential level. Similar results have been obtained on substrates containing carbonates instead of borates.

In Fig. 2 are plotted the potential changes due to the X layers alone of the first four curves of Fig. 1, the contribution to the potential of the first five Y layers being in each case eliminated by subtracting from the actual potential the potential observed after the deposition of the last Y layer. The resulting curves are all the same within the experimental variation.

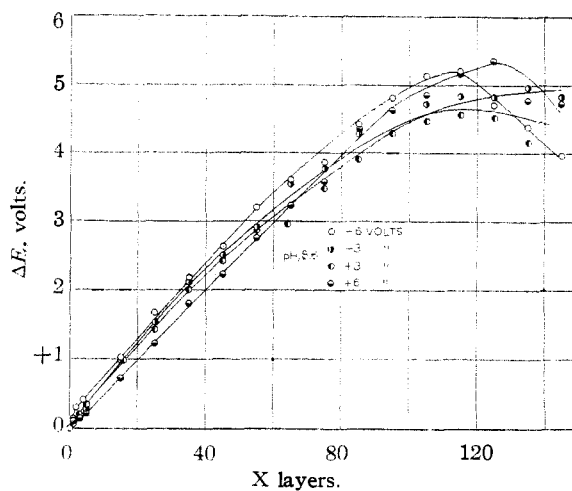


Fig. 2.

The effect of an applied voltage on Y films formed from solution (5), pH 7.4, is shown in Fig. 3.

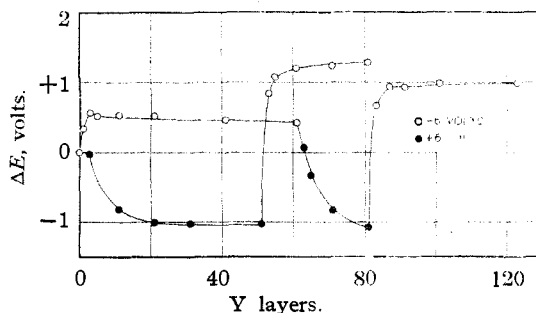


Fig. 3.

With  $-6$  v. the potential rises to a maximum of  $+0.6$  v. at three layers and declines from then on slightly as the thickness of the film increases to 61 layers. At this point the voltage is reversed and the potential drops rapidly to  $-1.1$  v. at 81 layers. Return to the original voltage causes a sudden rise in potential to an approximately constant value of  $+1.0$  v. from 87–123 layers. If we start with  $+6$  v. the sequence is reversed as may be seen from the figure.

The separation of the two curves in Fig. 3 before reversing the polarity of the applied voltage amounts to 1.5 v., which is approximately the magnitude of the separation of the  $+6$  and  $-6$  v. curves for X films in Fig. 1. In both the curves of Fig. 3 there is an over-compensation when the polarity of the applied voltage is changed from  $+6$  to  $-6$  v. This may be a phenomenon similar to the over-compensation observed in Fig. 1 after the last change in polarity from  $-6$  to  $+6$  v. in the  $\approx 6$  volt curve.

**B. X and Y Films Deposited on Platinum.**—Essentially the same results are obtained with a platinum slide. However, in this case it is possible to work with higher applied voltages. In Fig. 4 potential curves are given for two X films deposited on platinum from solution (2),  $pH$  8.6.

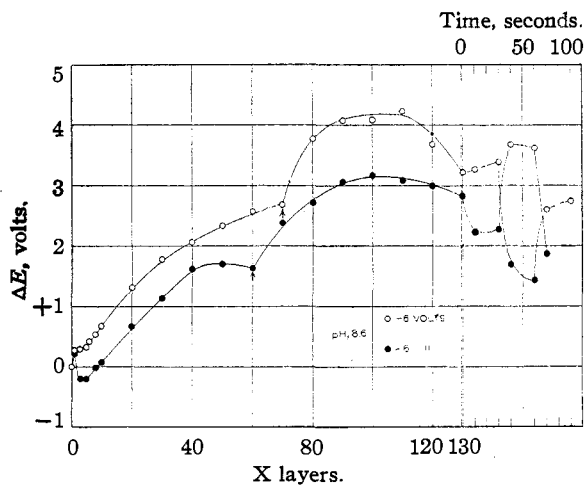


Fig. 4.

The first four layers after the initial layer are Y layers. The curves for  $+6$  and  $-6$  v. are very nearly linear and parallel between 5 and 40 layers. At thicknesses greater than 40 layers the curves cease to be linear but have the same general configuration. The two arrows in the figure indicate points after which a fresh monomolecular layer was spread on the substrate in the tray used

for building the films. The increase of slope following renewal of the monomolecular layer in the tray is like what is always observed when there are traces of contaminating ions in the subphase. Apparently such ions slowly diffuse into the surface layer and impair its ability to form X films of high potential.

Figure 5 shows potential-layer curves for four films deposited on platinum from solution (1) at  $pH$  10.9 with applied voltages of  $+6$ ,  $-6$ ,  $+22$  and  $-22$  v. The curves are in every way very similar to those in Fig. 4 at  $pH$  8.6.

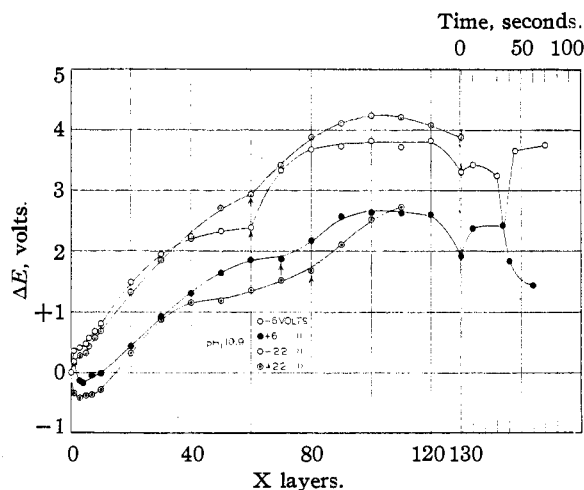


Fig. 5.

In Fig. 6 the six lower curves show the potential change due to the first 55 X layers of the films represented in Figs. 4 and 5. The point for the last Y layer in each case is taken as the origin. The six curves all fall together and the slopes are all the same, within the random variation among the films. This is like the situation shown in Fig. 2 for films on steel slides. In both cases the average slope is 58 mv. per X layer. Thus the increase of potential due to the addition of each successive X layer, at least up to a total of 55 layers, is independent of the metal on which the films are deposited, the  $pH$  of the substrate, and the sign and magnitude of the applied voltage.

As we have already pointed out, reversal of the applied voltage during the deposition of X or Y layers causes a sudden shift of contact potential from a value on the characteristic potential layer curve for the original voltage to a value on the curve for the reversed voltage. This shift, however, does not depend on the deposition of layers, but can be brought about equally well by reversing the applied voltage and dipping the slide into

the substrate through a clean surface free of the monolayer. A few seconds in the liquid with reversed voltage is sufficient to establish the new

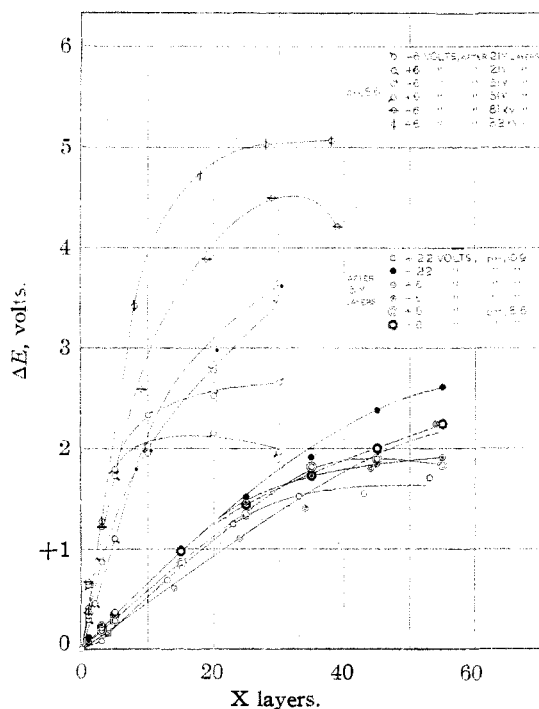


Fig. 6.

value. The potential can be changed back and forth from one curve to the other many times in this manner, just as when layers are being deposited. If the applied voltage is not reversed there is practically no change in contact potential when the slide is submerged in the substrate, as the first two points indicate. At the right-hand sides of Figs. 4 and 5 are given what we will call potential-time curves illustrating this phenomenon. In these curves "time" refers to the total length of time that the slides were submerged with the applied voltage.

Potential-layer curves for Y films on platinum with applied voltages of +6 and -6 v. are shown in Fig. 7. Two different solutions were used: solution (3), pH 8.6, with copper; solution (4), pH 7.7, without copper. The small initial differences between the two pairs of curves from solutions (3) and (4) are due probably to the difference in pH rather than the copper content of the solution, for curves similar to the pair without copper at pH 7.7 are ob-

tained at the same pH with copper. Comparison of these results with those for steel slides given in Fig. 3 shows that the nature of the underlying metal has only a slight effect on the shapes of potential curves of Y films, the curves for steel becoming horizontal, those for platinum continuing to rise or fall slightly. It is significant that the separation of the two Y film curves at 5 layers for applied voltages of +6 and -6 is about 0.6-0.7 v., which is also the separation of the parallel portions of the curves for X films on platinum obtained with the same applied voltages, shown in Figs. 4 and 5.

Potential-time curves for Y films submerged with an applied voltage are given at the right-hand side of Fig. 7. These are in general similar to those in Figs. 4 and 5 for X layers, which we have already described. The bracketed points are identical, the origin of the time curve having been displaced to the right merely for convenience in plotting.

It may be recalled that during the first dip of a chemically clean slide into a substrate covered with a monolayer, only a single layer is deposited on the slide under all conditions. This layer is formed when the slide is withdrawn from the liquid and seems to be different from either an X or a Y layer. Germer and Storck<sup>9</sup> have shown that the polar groups of this layer are attached to the metal surface of the slide. The effect of an applied voltage on the potential associated with

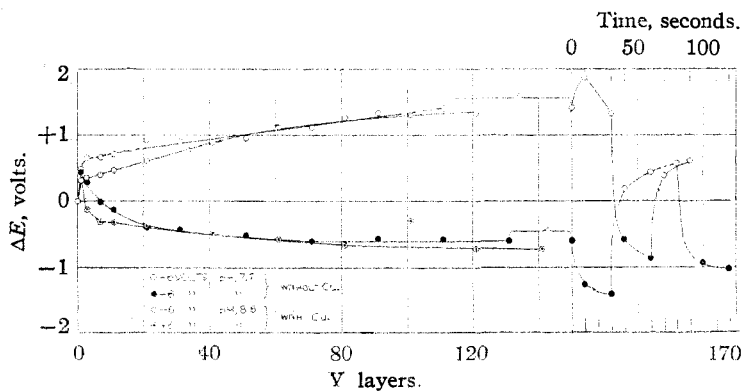


Fig. 7.

such layers is somewhat different from that observed in the case of X and Y films. If the applied voltage is between +6 and -6 v., the initial layer always causes an increase in the contact potential but by a somewhat smaller amount for positive than for negative voltages. We have

(9) Germer and Storck, *Proc. Natl. Acad. Sci.*, **23**, 390 (1937).

not investigated applied voltages between +6 and +22 v. but at +22 v. the initial layer produced a decrease in contact potential. These effects are apparent in certain of the figures already presented. Presumably there is some critical positive voltage, for any given set of conditions of substrate and temperature, at which the initial layer produces no change in contact potential.

### C. Composite Films Deposited on Platinum.

—It will be recalled that the addition of X layers to a Y film causes a steep rise of potential to values characteristic of a pure X film of the same total thickness, that the addition of Y layers to an X film causes a sudden drop of potential to the Y film level and that by alternating blocks of X and Y layers it is possible to shift the potential back and forth between the curves for pure X and Y films. The question arises as to the effect of an applied voltage on these phenomena.

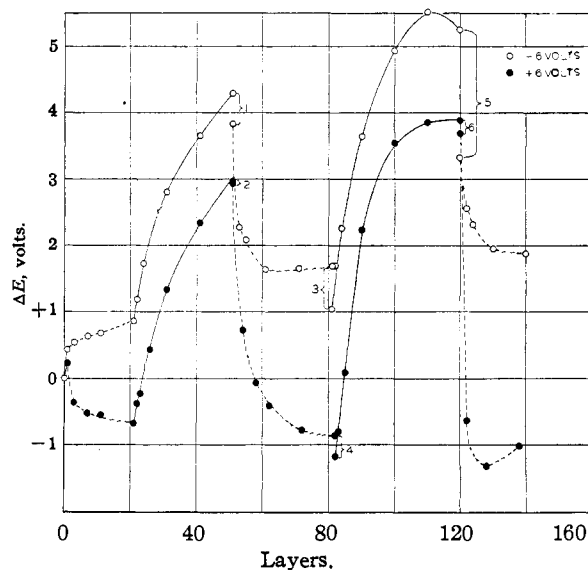


Fig. 8.— - - - Y layers; — X layers.

Two sets of results bearing on this question are given in Figs. 8 and 9. The X layers were obtained from solution (2); the Y layers from solution (4), with copper. Two curves are shown in each figure, one for +6 v. and one for -6 v. In each case Y layers were deposited first and the potential curves obtained were in every way similar to those already described. In the experiment shown in Fig. 8 after 21 Y layers had been laid down X layers were deposited. During this process the potentials rose steeply, the curves for +6 and -6 v. being very nearly parallel. After a total of 51 layers, Y layers were again de-

posited and the potentials dropped sharply to approximately the values for pure Y films of the same total thickness formed with the corresponding applied voltages. At a total of 81 to 82 layers X layers were added once more. This time the potential rose considerably more steeply and to a higher value than before, after 21 Y layers. Finally, after a total of 120 layers, one more block of Y layers was deposited with much the same results as before. In the experiment shown in Fig. 9, 51 Y layers were deposited before the addition of X layers. The X layers then produced a steeper rise of potential than the first block of X layers at +6 or -6 v. in Fig. 8.

From these results it appears that with an applied voltage the alternation of blocks of X and Y layers is accompanied by a shift of potential back and forth between the curves for pure X and Y films obtained with that voltage. The situation is like that observed in the absence of such a volt-

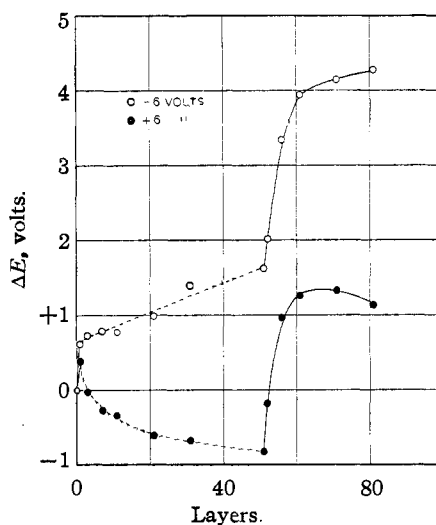


Fig. 9.— - - - Y layers; — X layers.

age. The rate of increase of potential when X layers are deposited on underlying Y layers is greater the greater the total thickness of the film but it does not depend on the applied voltage. This point is shown by the upper group of curves in Fig. 6. These curves are obtained by plotting the potential against the number of layers for each block of X layers in the experiments shown in Figs. 8 and 9. In each case the origin is the point corresponding to the last preceding Y layer. The curves for a block of X layers added to a Y film of 21 layers are the same for applied voltages of +6 and -6 v., and have an initial slope of 240 mv. per layer. Those for a block of X layers

added to a Y film of 51 layers at +6 and -6 v. have a slope of 360 mv. per layer; those for a block of X layers added to a film of 81 or 82 total layers at +6 and -6 v., a slope of about 430 mv. per layer or greater.

the potentials of Y films on steel quickly attained a constant value under the influence of an applied voltage, whereas the potentials of Y films on platinum continued to rise or fall, depending on the direction of the voltage, as the films increased in thickness.

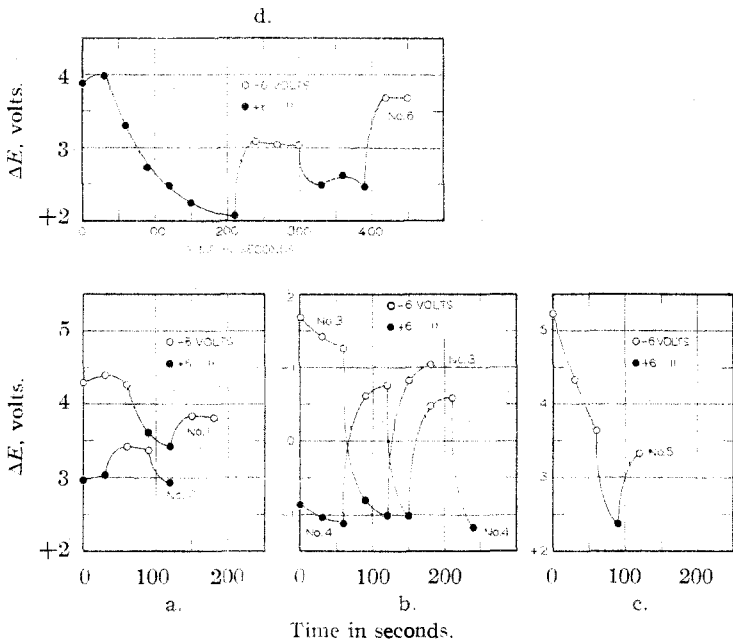


Fig. 10.

The treatment of the films represented in Fig. 8 between the numbered, bracketed points involved submerging them in the substrates with an applied voltage without the deposition of layers. During this treatment the behavior of these composite films is much like pure X or Y films. A complex film always resembles a film made up entirely of the kind of layer last deposited, as shown by Fig. 10.

The composition of the substrates used had no detectable influence in these phenomena.

**IV. X and Y Films Deposited from Substrates Containing Iron and Lead**

In the last section we described phenomena observed with films deposited on stainless steel and on platinum. Although the major effects were the same for both kinds of film, nevertheless there were certain minor differences: the potentials of simple X films on steel rose more nearly linearly and attained higher values than the potentials of X films on platinum (cf. Figs. 2 and 6);

Since it is known that the properties of films are greatly affected by certain ions, even at very small concentrations, it seemed possible that these differences were due to the influence of ferric ions arising from the steel slides. In order to test this possibility, X films were deposited on platinum from solution (2) which had been made  $1.4 \times 10^{-5}$  molar in ferric chloride. The potential-layer curves of these films, which are given in Fig. 11, are quite similar to those of X films deposited on platinum from solution (2) without iron, except for a somewhat greater slope, the initial slope of these calcium-ferric stearate films being about 80 mv. per layer. Also the potential-time curves when these films are submerged in the subphase with an applied voltage are like those of films without iron. It

appears then that no considerable effects are produced by the presence of ferric ions in the concentration we have used, and there must therefore be

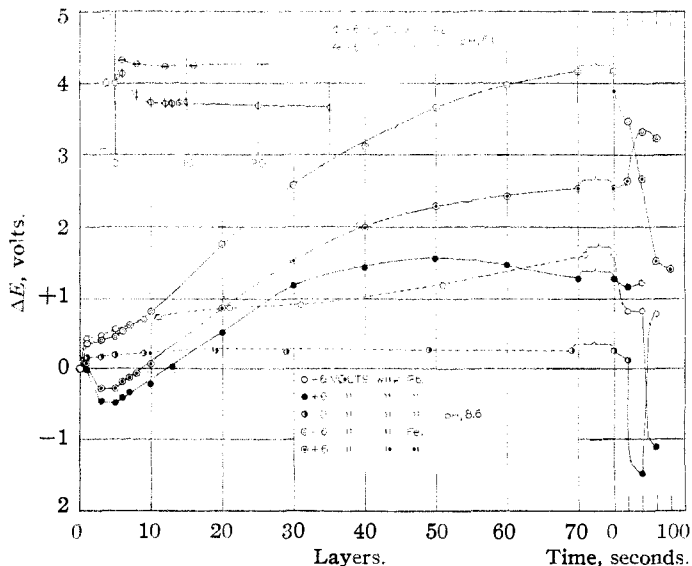


Fig. 11. --- Y layers; — X layers.

some other basis for the differences in behavior between films deposited on steel and on platinum.



On the other hand, the properties of films are greatly altered by small concentrations of lead. Langmuir<sup>3</sup> has reported that in the presence of lead acetate X films may be formed at  $pH$  6, and that the potentials of such films are like those of Y films. On this basis he has suggested that the  $pH$  of the subphase is the primary factor which determines film potentials. Other observations of our own show certain curious effects of lead at other values of  $pH$  and with an applied voltage.

It will be recalled that films deposited from solution (2),  $pH$  8.6, are always X films regardless of the applied voltage. However, when this solution was made  $2 \times 10^{-6}$  molar in lead acetate the films deposited on platinum were Y films with applied voltages of 0 and  $-6$  v. and X films with a voltage of  $+6$  v. The potential-layer curves of these films are given in Fig. 11. The initial slope of the X film curve (after the deposition of the last underlying Y layer) is about 80 mv. per layer, but the curve flattens out before reaching the higher values characteristic of X films without lead. The two Y film curves are much like those of other Y films formed with the same applied voltages without lead. The potential-time curves of these films, giving the effect of an applied voltage on films submerged without deposition of layers, are those characteristic of the respective types of film, X or Y.

In the insert in Fig. 11 are given the potential-layer curves for two films formed on platinum from a pure sodium acetate buffer of  $pH$  6.0 containing lead acetate,  $2 \times 10^{-5}$  molar, with applied voltages of  $+6$  and  $-6$  v. Just as at  $pH$  8.6, the film obtained with the positive voltage was an X film, the other a Y film. As in the case of the X film reported for  $pH$  6 by Langmuir, the potential of this X film failed to rise above the characteristic Y level. It was noted while this film was being deposited that the contact angle as the slide was withdrawn from the liquid was considerably less than  $90^\circ$ , somewhat approaching the angle for a Y film. This accords with the observation based on many cases that large contact angles are associated with high contact potentials; for example, if under conditions otherwise favorable for the production of high potentials in X films, the slide is dipped too rapidly, the contact angle is small and the film fails to develop a high potential.

Curiously enough, when films are formed on stainless steel under these same conditions, *i. e.*,

with a sodium acetate buffer of  $pH$  5.9–6.0 and a concentration of lead acetate  $2 \times 10^{-5}$  molar, X layers are deposited at both  $+6$  and  $-6$  v. The potential of the film formed with the positive voltage becomes constant, after a few layers, at  $-0.5$  v.; that of the film formed with the negative voltage, constant at  $+0.4$  v. These potentials are the same as those of Y films obtained with the same applied voltages in the absence of lead.

The question arises whether these X films of low potential are in other respects like X or Y films. In one respect they show a striking difference from any other films, X or Y which we have studied. All other films when made electrodes in a glow discharge or subjected to X-ray treatment develop very large contact potentials, generally exceeding any values developed spontaneously by X films in the course of their formation. These low potential X films containing lead entirely fail to develop high potentials under such treatment. Two such X films of 35 layers, one formed with a positive voltage and having an initial potential of about  $-0.5$  v., the other formed with a negative voltage and having an initial potential of about  $+0.4$  v., gave, respectively, potentials of only  $-0.35$  and  $-0.04$  v. after the usual treatment with X-rays. When similar films were subjected to a rectified glow discharge the potentials failed to change by more than a small fraction of a volt, regardless of the direction of the discharge. There appears to be some curious feature in the structure of these lead containing X films which prevents the development of high potentials. Whether or not this may be related to the resistance of the films we will consider later.

#### V. Potentials Observed during the Early Stages of the Formation of X Films

It already has been observed,<sup>2</sup> when measurements are made after each dip during the early stages of building an X film without an applied voltage, that the potential increases in a stepwise manner, and that the contact angle alternates between  $90^\circ$  and values less than  $90^\circ$ . This effect we have attributed to the condition at the outer surface of the films where at the end of every other dip there must be an unpaired layer, presumably with its polar surface inward. As a result of the succeeding dip each such unpaired layer receives a partner, and we have suggested that during this dip it turns over so that its polar surface

comes to face that of the partner, which is inward, an interpretation which accords with the X-ray spacing of the metallic ions, and the hydrophobic character of X films.

This stepwise increase of potential, which appears so significant in relation to events at the surface of the film, becomes blurred and lost as the thickness of the films increases beyond about 15 layers in the case of films formed without an applied voltage, perhaps in consequence of different areas of the same film falling out of step. When, however, the phenomenon is investigated in the case of X films formed with applied voltages, it shows up much more clearly and persists much longer. Certainly it remains undiminished up to thicknesses of 26 layers, which is as far as we have carried the measurements. The applied voltages seem to have a steadying effect on the films.

Two films were studied in this connection, both deposited on platinum from solution (2), pH 8.6, one with an applied voltage of +6, the other with -6 v. The results are shown in Fig. 12. X

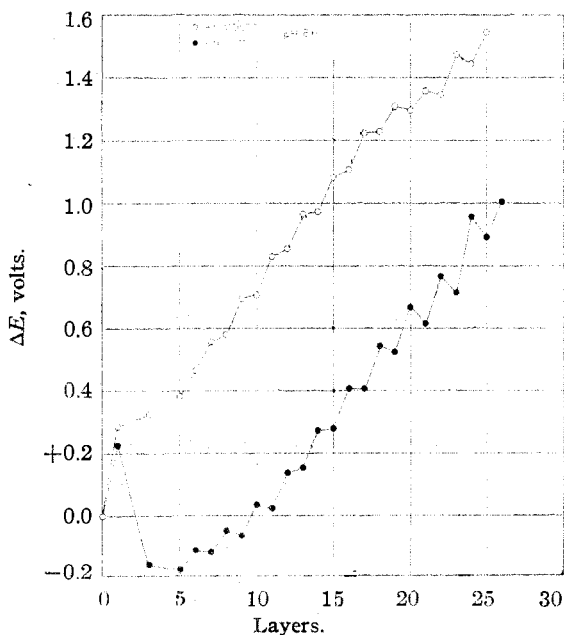


Fig. 12.

layers were formed after the fifth layer. As a result of the behavior at the addition of the seventh layer the two curves fall out of step. Corresponding to the stepwise increase of potential there was observed initially an alternation of contact angle. The rise of potential occurred with an angle of  $90^\circ$ . During the addition of

alternate layers, when the potential failed to rise, or dropped, the angle was always less than  $90^\circ$ . After about 20 layers, this alternation of contact angle disappeared and the angle was always close to  $90^\circ$ , although the stepwise increase of potential continued undiminished.

The parallel course of the two curves, after X layers begin to be formed, is very striking. It is also striking that the applied voltage has very little effect on the potential of the initial layer, and the separation of the curves for +6 and -6 v. is realized during the deposition of the two pairs of succeeding Y layers.

## VI. Impedance of Films and Related Phenomena

We have referred in passing to the possibility of the resistance being different for different types of films. For example, this would be a possible reason for the fact that the large potentials produced by the X-ray treatment or a glow discharge, provided they are due to internal charges in the film, are abolished by dipping the films into aqueous solutions in the case of Y films but not in the case of X films. Again the fact that the lead films deposited at pH 6 never develop high potentials might be laid to a relatively low resistance. On the other hand, from attempts to measure voltages of circuits involving films in contact with conducting liquids (section II) it is evident that the d. c. resistance of all types of films must be very high. These considerations point to the importance of direct evidence on the resistance of the films, and in this section we discuss measurements bearing on this question.

An initial attempt was made to measure the impedance of the films by placing a small drop of mercury on the film, with which contact was made with a platinum wire. The binding post of the slide and the platinum wire were connected to the terminals for the unknown on an a. c. bridge and measurements attempted at 800 cycles. The results were not very satisfactory, but it was at once apparent that with high signal voltages the resistance of the films was very low, less than 1 ohm, whereas with signals of 1 or 2 v. the resistance was of the order of megohms. Evidently, the higher signals exceeded the breakdown voltages of the films.

Much more satisfactory measurements were obtained at radio frequencies with a General Radio Co. radio frequency bridge, by using as be-

fore the device of placing a small drop of mercury on the surface of the film. Two sets of measurements were made, one at a frequency of 1 megacycle ( $\lambda = 300$  m.), the other at a frequency of 0.244 megacycle ( $\lambda = 1230$  m.). The strength of the signal did not exceed a fraction of a volt. At the higher frequency the bridge was balanced by a condenser and power factor dial; at the lower frequency by a condenser and a series resistance. The capacity settings were very sharp; the power factor or resistance settings less so, particularly with the thicker films. A number of different mercury drops were used, but all the results given below were obtained with 3 different drops, all of very nearly the same size, 1.5–1.8 mm. in diameter. The same drop could be rolled from one place to another on a given film or from one film to another. There was considerable variation in the results obtained on the same film with different drops, or with the same drop in different places, due apparently to differences in the size of the drops and in the exact area of contact of a given drop with a film in different places. This variability was much greater for the power factor and resistance settings than for the condenser settings. Results on X and Y films deposited on stainless steel slides are given in Tables I and II. These are expressed in terms of parallel capacity,  $C_p$ , and resistance,  $r_p$ . Bracketed results were obtained with the same drop. The Y films were copper-barium stearate films formed at pH 7.4; the X films, of which the first four

TABLE I

Frequency $0.244 \times 10^6$ ( $\lambda = 1320$ m.)					
$n =$ No. of layers	$C_p, \mu\mu F$	$r_p \times 10^{-3}$	$nC_p$	$r_p/n$	
Y Films (Cu-Ba Stearate, pH 7.4)					
No. 1	7	1,680	47	11,800	6,700
	17	775	200	13,200	11,900
	31	515	400	16,000	13,000
No. 3	35	468	470	16,400	13,300
	71	220	1,360	15,600	19,100
No. 2	141	97	22,200	13,700	158,000(?)
Av. 14,500					
X Films (Ca Stearate, pH 9)					
No. 2	9	1,530	83	13,800	9,200
	13	1,000	213	13,000	16,000
	21	650	504	13,700	24,000
	37	362	1,300	13,400	35,000
	37	423	951	15,700	26,000
	69	218	2,240	15,000	32,000
	133	112	4,550	14,900	34,000
Av. 14,200					

TABLE II

Frequency $10^6$ ( $\lambda = 300$ m.)					
$n =$ No. of layers	$C_p, \mu\mu F$	$r_p \times 10^{-3}$	$nC_p$	$r_p/n$	
Y Films (Cu-Ba Stearate pH 7.4)					
No. 2	35	323	117	11,200	3,300
	71	167	415	12,100	5,800
	141	96	2760	13,500	19,000
No. 3	35	570	39	20,000	1,100
	71	260	153	18,500	2,160
	141	133	660	18,800	4,700
Av. 15,800					
X Films (Ca Stearate, pH 9)					
No. 2	37	395	101	14,600	2,700
	69	224	338	15,500	4,900
	133	114	2080	15,200	11,400
Av. 15,100					

layers after the initial layer were Y layers, were calcium stearate films formed at pH 9.

It is evident from the data in these two tables that there is no significant difference between X and Y films in respect to either capacity or resistance. Other measurements on X films of low potential deposited from a sodium acetate buffer of pH 6,  $2 \times 10^{-5}$  molar in lead, gave substantially the same results. In both types of film the capacity decreases with thickness, as would be expected, but the capacity multiplied by the number of layers is the same, within the experimental variation, for all the films and at both frequencies, as shown by the fourth column. Since

$$C_p = A\epsilon/4\pi nt \quad (1)$$

in which  $\epsilon$  denotes dielectric constant,  $n$  number of layers,  $t$  the thickness of a layer and  $A$  the area of the drop in contact with the film, and since  $t$  is the same for X and Y films, this result implies that the dielectric constant is also approximately the same and approximately independent of frequency. The known size of the drops agrees with a value of the dielectric constant of approximately 2.5, or a value close to that obtained for stearate in the bulk phase. Thus on the basis of  $t = 24 \text{ \AA.}$  and  $\epsilon = 2.5$  the average value of  $nC_p = 14,500$  gives for the radius of the area of contact of the drop with the film a value of 0.72 mm. The over-all diameter of the drops, which should be somewhat more than twice this value, was 1.5–1.8 mm., as well as could be estimated. This estimate of the dielectric constant is of some interest in relation to the question of possible water of hydration in the films.

The fifth columns of both tables give average

values of the resistance per layer. Although these values probably do not differ significantly between X and Y films, they show a definite increase with the thickness of the films. Moreover, the values obtained at 1 megacycle are definitely less than those at the lower frequency. It may be noted that a value of 20,000 ohms per layer corresponds to a specific resistance of about  $2 \times 10^9$  ohms, having regard to the size of the drops and the thickness of the layers. The resistance of the films measured at both frequencies is far less than would be judged from the experience of measuring the electromotive force of circuits involving films covered with mercury (section II). Evidently there is a phenomenon of power absorption in the films, increasing with frequency over the range studied.

In view of this, and also to explore the question of the breakdown of the films under high voltages, various d. c. measurements were undertaken. X and Y films of different numbers of layers were covered with a drop of mercury and subjected to a variable measured voltage in series with a galvanometer, which, with the shunt turned on full, gave a deflection of 1 mm. for a current of  $4.37 \times 10^{-9}$  ampere. The readings of the galvanometer were followed as the voltage was increased. With films of about 30 layers and thicker there was no observable deflection of the galvanometer until a certain critical breakdown voltage was reached. To determine values of this voltage it was unnecessary to make use of the galvanometer. As soon as it was reached the relatively low resistance voltmeter placed in parallel with the film was automatically shorted and the needle immediately fell to zero. With thinner films there were appreciable currents almost from the start. Values of the breakdown voltage for various X and Y films are given in Table III.

TABLE III

X Films <sup>a</sup> (Ca Stearate, pH 9)						
Layers	11	15	23	39	71	135
Voltage	0.5	0.5	2.0	9.10	27.34	60.90
Voltage per layer	0.05	0.03	0.09	0.2	0.4	~0.5
Y Films (Cu-Ba Stearate, pH 7.4)						
Layers	7	17	35	71		
Voltage	0.1	0.6	11	29		
Voltage per layer	0.01	0.03	0.3	0.4		

<sup>a</sup> The first six layers after the initial layer were Y layers.

Apparently the breakdown voltage per layer

rises sharply at a thickness of about 20 layers. It may be pointed out that a value of 1 v. per layer corresponds to a field of about five million volts per centimeter. Below the breakdown voltage the resistance of the films is very high. In the thicker films where there is no observable galvanometer deflection up to the breakdown voltage (0.4 v. per layer) the resistance between the drop and the plate must be at least  $10^8$  ohms per layer, corresponding to a specific resistance of the order of  $10^{13}$  ohms. In thinner films, where there is a deflection of a fraction of a mm. with fields as low as  $10^{-2}$  v. per layer, the resistance cannot be more than about  $10^7$  ohms per layer. This is suggestive of the bridge measurements, in which the resistances per layer, though all of a different order of magnitude, are found to be less for the thinner films.

In view of these values of the breakdown voltage and the very high d. c. resistances observed below these voltages, it would appear hard to explain the magnitude of the current (of the order of a milliampere or two) observed when films are submerged in aqueous liquids with an applied voltage. The answer to this paradox is found in observations like those we have just described but with a drop of tap water substituted for the mercury drop. In this case, much as in the case of the mercury drop, there is no deflection of the galvanometer until a certain "breakdown" voltage is reached; at this point a current begins to flow which soon shoots up and rises almost vertically as the voltage is further increased. There is, however, the striking difference between these and the results obtained with mercury, that the critical voltage at which the current suddenly rises is very nearly independent of the thickness of the films: for the thin films it is higher, for thick films lower, than with mercury. The behavior of X and Y films<sup>10</sup> is shown in Fig. 13; they are not very different. For both, however, there is a difference in the voltage-current curves depending on the direction of the voltage. When the positive pole of the battery is connected with the slide the curve shoots up more steeply than in the opposite case, in which, though the curve begins to rise at about the same voltage, it does so more slowly until it passes over a kind of shoulder. It seems likely that this difference is due to an electrical asymmetry in the film, probably asso-

(10) Y films containing lead were not significantly different from Cu-Ba stearate Y films.

ciated with the initial layer (see for example Fig. 9). Below these breakdown voltages, the d. c. resistance of the films covered with water is, so far as we can say, as great as that of films covered with mercury. There is another contrast between the results obtained with water and mercury. With mercury drops the film seems to be ruptured permanently when the breakdown voltage is exceeded, and the resistance remains low. With water drops this is not the case, and subsequent curves obtained with the same drop in the same place on the film are about the same as the initial curve.

This very striking difference between the results obtained with films covered with water and with mercury may be due to a difference in the affinities of the two liquids for the surface, although neither water nor mercury wets the surface. It is suggestive to recall in this connection that Y films which have acquired large contact potentials as a result of a glow discharge completely lose these potentials as a result of being dipped in water, whereas the potentials remain unaffected or are only partially abolished when the films are dipped in mercury, even though several layers may be removed by the process. It is as if the water were able to penetrate the films.

## VII. Discussion

In view of the spacing of the metallic ions revealed by the X-ray studies of Holley and Bernstein,<sup>11</sup> it is clear that the basic structure of X and Y films is the same: the layers, apart from the first layer, occur in pairs, with the polar surfaces together. On the other hand, there must be some structural differences to account for the very different properties and behavior of the two kinds of film. As a result of the great effects often produced by very small changes in the character of the substrate it seems likely that these differences are closely connected with the ionic composition of the films. If we accept the surface electrification hypothesis it would be such differences which determine whether or not the films acquire a charge when withdrawn from the substrate rather than the fact that the layers are deposited singly or in pairs. This accords with the fact that lead X films formed at pH 6 do not develop high potentials although the layers are deposited only one at each dip. Evidently, however, it is not the character of the whole film, but

only that of the outermost layer or two which is the determining factor, since when one or two X layers are deposited on a Y film it develops the potential characteristic of an X film of the same total thickness and conversely when one or two Y layers are deposited on an X film. Moreover, when layers are successively removed from composite films the films appear to retrace their past history in respect to potential. We have seen that the characteristic potentials of all films disappear while the films are in contact with various polar liquids, but redevelop when the films are withdrawn from the liquids. Evidently the original surface charge is restored by the work of separation from the liquid, and the sign and magnitude of the charge depend on the character of the surface of the film rather than on the nature of the liquid, *e. g.*, whether chloroform, water or mercury.

On the other hand, certain other phenomena clearly depend not on the nature of the surface layer but upon that of the whole film, for example, the optical thickness of the films, the temperatures at which they soften and the change of optical thickness which accompanies softening. In all these respects X and Y films differ, and the experiments show that X augmented Y films and Y depressed X films behave like simple Y and X films, respectively.

It seems probable that, unlike the "natural" potentials of the films, potentials produced by the X-ray treatment or a glow discharge are due to the development of an internal charge in the body of the films as a result of the penetration of ions into the films. Otherwise it is hard to understand how these potentials, whether positive or negative, can persist as they do after X or Y films are dipped into mercury and several layers are removed. Even on the basis of this view, however, certain points remain obscure. Why are these potentials, whether positive or negative, abolished in the case of Y, but not of X, films as a result of dipping the films into water and chloroform? By what mechanism are they neutralized while the films are in contact with polar liquids, supposing that the internal charge is not removed? These phenomena, together with the curious behavior of the lead films, which fail to develop large potentials under any conditions, remain a difficult problem.

Consider now the experiments on the effect of a voltage applied between the slide and the liquid subphase while films are being deposited. The

(11) Holley and Bernstein, *Phys. Rev.*, **52**, 525 (1937).

data show clearly that for all types of film an applied voltage does not affect the shape of the potential-layer curves (except for the first three layers of simple X and Y films, as in Fig. 12), but simply serves to displace the curves by a constant amount up or down depending on its direction. The absolute magnitude of the shift is nearly if not quite independent of the magnitude of the applied voltage, as well as of the type of film. From this it appears, in terms of the surface charge hy-

its being otherwise altered. But on either interpretation it is the charge  $\sigma$  which determines the character of the potential-layer curves, and it follows, somewhat unexpectedly, that  $\sigma$  is wholly unaffected by the applied voltage.

It now remains to consider why the up or down displacement of the curves is independent of the magnitude of the applied voltage. An explanation of this is to be found in the results represented in Fig. 13. Evidently when a voltage  $V$  is applied between a point in the liquid and the submerged metal slide a voltage  $V_f$  at once begins to build up across the film. However, it may be seen from Fig. 13 that before  $V_f$  attains the value  $V$  (if  $V$  be sufficiently high) the critical point will be reached when the resistance of the film suddenly drops, and a current begins to flow. Equilibrium is then established when the current reaches such a value that the resulting voltage drop in the liquid is equal to  $V - V_f$ . Since after the attainment of the critical voltage, the current through the film rises sharply (see Fig. 13) it is evident that  $V_f$  should be very nearly independent of  $V$ , as it is found to be. This explanation has nothing to do with the nature of the reversible "breakdown" associated with the sudden rise of current in the film in contact

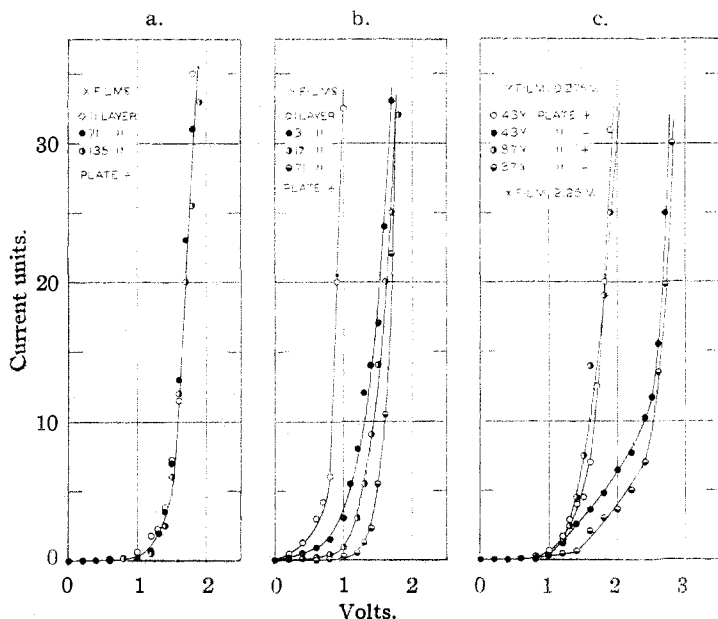


Fig. 13.—Voltage-current curves of X and Y films in contact with water.

pothesis, that when the films, of whatever type, are withdrawn from the liquid they acquire the same charge as in the absence of the applied voltage, but that in addition to this there is superposed an effect due to the voltage. This effect might be interpreted as due either to a polarization, possibly involving a reorientation of an underlying layer, or to the accumulation of a subsidiary charge on the surface of the film. In accordance with the latter interpretation we may think of the film as a condenser of capacity given by equation (1). Then, under the influence of the applied voltage  $V_f$  effective across the film, the film will accumulate a charge per unit area given by

$$\sigma' = \epsilon V/4\pi nt$$

This charge, over and above the charge  $\sigma$  acquired by the film independently of the applied voltage at the time it is withdrawn from the liquid, would account for the displacement of the potential-layer curve by an amount  $V$ , without

with the liquid when the applied voltage reaches a certain value, but depends simply on the fact that such a process occurs.

### Summary

Voltage measurements of circuits involving X and Y films in contact with polar liquids indicate that the potentials of the films are neutralized by contact with the liquids, although they reappear after the films are separated from the liquids. Similar measurements of films in contact with benzene show that in this case the potentials are not neutralized.

Contact potentials induced in X and Y films by exposure to a glow discharge are not abolished as a result of dipping the films in mercury even when several layers of the film are removed, but are abolished in the case of Y films by contact with water and chloroform.

The effect of applying an arbitrary voltage between the slide and the liquid while films are being

built is to displace the potential-layer curves up or down without altering their shape subsequent to the first three layers. The absolute magnitude of the displacement is independent of the type of film and of the magnitude of the applied voltage but the direction of displacement, up or down, depends upon the direction of the voltage. Similar shifts of potential are produced when films are immersed in the liquids under the influence of an applied voltage without the deposition of layers.

X or Y films containing lead fail to develop large contact potentials under all conditions and show certain unusual properties.

Impedance measurements at frequencies of 1

and 0.244 megacycles show no significant difference between X and Y films. They indicate a dielectric constant of about 2.5 and give evidence of power absorption. Breakdown voltages of X and Y films are the same. Breakdown voltages of films in contact with mercury increase with the thickness of the films, and correspond to fields of the order of  $10^6$  v./cm. Apparent breakdown voltages of films in contact with water are nearly independent of thickness and depend on the direction in which the voltage is applied. The specific d. c. resistance of both X and Y films is of the order of  $10^{13}$  ohms.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

## The Volumetric Oxidation of Iodide and Bromide by Periodic Acid<sup>1</sup>

BY HOBART H. WILLARD AND LUCIEN H. GREATHOUSE

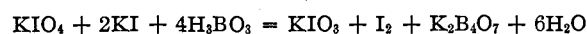
Periodic acid and periodates of the alkalis are powerful oxidizing agents in dilute aqueous solution and usually stable enough for use in volumetric analysis.

Reactions of periodates as oxidizing agents have been investigated from an early date.<sup>2</sup> The reaction between periodate and iodide with excess of the former



is of particular interest.<sup>3</sup>

The excess of periodate may be determined accurately in the presence of iodate by titrating with standard arsenite the iodine liberated from iodide in neutral solution, thus



This principle was first stated by Péchard<sup>4a</sup> but the method was developed by Müller and his asso-

ciates.<sup>4b</sup> For this purpose the solution is buffered preferably with boric acid-borax mixture.

Titration based on these reactions have been used recently to identify polyhydric alcohols.<sup>5</sup>

### Periodates Suitable as Reagents

**Potassium Periodates.**—The metaperiodate,  $\text{KIO}_4$ , commercially available, contained 79.51% of  $\text{I}_2\text{O}_7$  compared with the theoretical value of 79.52% and was free from iodate by test with silver nitrate.<sup>2a,6</sup> It may be used as a primary standard for iodimetry.

The solubility of potassium metaperiodate in water was found to be as follows, in grams per 100 ml. of the saturated solutions

0°	25°	35°	45°	55°	65°
0.1546	0.5112	0.785	1.190	1.75	2.51

The specific gravity at 25° of the solution saturated at 25° was 1.00125. If the solubility at 25° as determined by Hill<sup>7</sup> is recalculated to grams per 100 ml. a value of 0.5106 is obtained.

The metaperiodate decomposes in solution with a strong odor of ozone. Dipotassium paraperiodate,  $\text{K}_2\text{H}_3\text{IO}_6$ , is much more soluble than the meta salt and more stable in solution and hence better suited for standard solutions.

**Sodium Periodates.**—The paraperiodates precipitated by the reaction of chlorine on iodate in alkaline solution vary in composition between  $\text{Na}_3\text{H}_2\text{IO}_6$  and  $\text{Na}_2\text{H}_2\text{IO}_6$ .<sup>7</sup>

(1) From a dissertation presented in partial fulfillment of the requirements for the degree of doctor of philosophy at the University of Michigan by Lucien H. Greathouse in 1917.

(2) (a) Ammermüller and Magnus, *Ann.*, **11**, 18-24 (1834); (b) Bengieser, *ibid.*, **17**, 254-260 (1836); (c) Langlois, *ibid.*, **83**, 153-175 (1852); (d) Selmons, *Chem. Centr.*, [3] **18**, 502-504 (1887); (e) Grütznier, *Arch. Pharm.*, **234**, 634-640 (1896); (f) Péchard, *Compt. rend.*, **128**, 1101 (1899); (g) Brunner and Mellet, *J. prakt. Chem.*, [2] **77**, 33-42 (1908); (h) Willard and Greathouse, *THIS JOURNAL*, **39**, 2366 (1917).

(3) (a) Phillip, *Bull. soc. chim.*, [2] **12**, 350 (1869); (b) Péchard, *Compt. rend.*, **130**, 1705 (1900); (c) Garzarolli-Thurnlackh, *Monatsh.*, **22**, 955-975 (1901); (d) Müller, *Z. Elektrochem.*, **9**, 584-594, 707-716 (1903); (e) Bray, *Z. physik. Chem.*, **54**, 463-497 (1906); (f) Auger, *Bull. soc. chim.*, [4] **11**, 731 (1912).

(4) (a) Péchard, *Compt. rend.*, **128**, 1453 (1899); (b) Müller and Friedberger, *Ber.*, **35**, 2652 (1902); and Jacob, *Z. anorg. Chem.*, **82**, 308-314 (1913); and Weglin, *Z. anal. Chem.*, **52**, 755 (1913).

(5) (a) Malaprade, *Compt. rend.*, **186**, 382 (1938); *Bull. soc. chim.*, [4] **43**, 683-696 (1928); *ibid.*, [5] **1**, 833-852 (1934); (b) Fleury and Lange, *J. pharm. chim.*, [8] **17**, 107-113, 196-208, 313-326, 409-427 (1933); (c) Fleury, *ibid.*, [8] **18**, 476-481 (1933); (d) Rappaport, Reifer and Weinmann, *Mikrochim. Acta*, **1**, 290-299 (1937); Rappaport and Reifer, *ibid.*, **2**, 273 (1937).

(6) Willard and Thompson, *THIS JOURNAL*, **56**, 1827 (1934).

(7) Hill, *ibid.*, **50**, 2678 (1928).