cc. of absolute alcohol was treated as above with 10 drops of concd. hydrochloric acid. A strong odor of ethyl benzoate developed. The solution turned faintly yellow. Upon chilling there was obtained a solid mixture which upon fractional recrystallization was separated into two fractions which melted at 95 and 131°. Mixed melting points with authentic samples proved that these two fractions were the benzoate of the β-monoxime of the *p*-methoxybenzil and the β-*p*-methoxybenzil monoxime, respectively.

In order to establish the fact that these experiments did not involve hydrolysis to the oxime with subsequent rearrangement and esterification, the following experiment was carried out:

A solution of 1.0 g. of α-benzil monoxime and 0.6 g. of benzoic acid in 15 cc. of absolute alcohol was treated as above with 10 drops of concd. hydrochloric acid. There developed a strong odor of ethyl benzoate, but there was no trace of an oximino ester produced.

Summary

In this paper we have first established that a shift in the configuration of certain benzoyl derivatives of α-benzil monoxime does occur, and, second, we have pointed out the possible bearing which these findings may have upon the relation of oxime configuration to ring opening.

WASHINGTON, D. C. RECEIVED MARCH 11, 1938

[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES, HARVARD UNIVERSITY]

Contact Potentials of Stearate Films on Metal Surfaces

BY ELIOT F. PORTER AND JEFFRIES WYMAN, JR.

1. Introduction

Blodgett[1] and Blodgett and Langmuir[2] recently have described the building up of multilayer films of stearates on metal slides by successive dippings of the slides into aqueous solutions covered with a monomolecular layer of the stearate. These films are of two types, called *X* and *Y*, determined by the composition of the aqueous substrate from which they are obtained. Langmuir has suggested on the basis of the way in which they are deposited that in *X* films the molecules in successive layers are oriented in the same way, whereas in *Y* films the molecules in successive layers are oriented oppositely.

We have pointed out that if this hypothesis is correct the two kinds of film should produce quite different effects on the contact potentials of the slides, and have shown that this is in fact the case. A change of contact potential of 8.6 v. was obtained with 170 layers of an *X* film while the change remained constant at 0.12 v. from 10 to 220 layers of a *Y* film.[3]

On the other hand, recent X-ray studies by Holley and Bernstein[4] of the spacing of the Ca and Ba ions in built-up *X* and *Y* films provided by Langmuir and Blodgett seem to indicate that the orientation of the stearate molecules is the same in both, for they obtained the same spacing (48 Å.) for Ca in *X* films as for Ba in *Y* films. Clearly our results suggest that even though this spacing is the same, either the orientation of the molecules or the arrangement of the loci of the positive or negative charges is different in the two types of film. In order to throw more light on the whole problem, we have performed a series of experiments on the contact potentials of mixed *X* and *Y* films and on the effect of heat, X-rays, and ionic discharge on such potentials of *X* and *Y* films.

2. Materials and Methods.—The built-up *X* films were formed by the method of Blodgett[1] by depositing from a solution 10^{-3} molar in potassium bicarbonate, 10^{-4} molar in Ca ions, and adjusted with sodium or potassium hydroxide to a *p*H of about 9.4. Built-up *Y* films were formed (a) by depositing from a solution like that used for the *X* films but adjusted with carbon dioxide gas to a *p*H of 6.0–6.2 and (b) from solutions containing barium and copper as follows:

Solution 1 3×10^{-5} *m* $BaCl_2$, 2×10^{-4} *m* $KHCO_3$, 2×10^{-6} *m* $CuCl_2$ *p*H 7.4
Solution 2 3×10^{-5} *m* $BaCl_2$, 2×10^{-4} *m* $KHCO_3$, 2×10^{-6} *m* $CuCl_2$, 1 *m* KOH to *p*H 9.4
Solution 3 3×10^{-5} *m* $BaCl_2$, 2×10^{-4} *m* $KHCO_3$, 4×10^{-6} *m* $CuCl_2$, CO_2 gas to *p*H 6.2
Solution 4 3×10^{-5} *m* $BaCl_2$, 2×10^{-4} *m* $KHCO_3$, 4×10^{-6} *m* $CuCl_2$, 1 *m* HCl to *p*H 5.8

Solution 2 differs from Solution 1 only in *p*H and potassium concentration. Solution 3 contains twice the copper concentration of Solution 1 and the *p*H is lower due to increased carbonic acid concentration. Solution 4 is the same as Solu-

---

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

[2] Blodgett and Langmuir, *Phys. Rev.*, **51**, 664 (1937).

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

[4] Holley and Bernstein, *Phys. Rev.*, **52**, 525 (1937).

tion 3 except that the pH has been lowered by hydrochloric acid instead of carbon dioxide, whereby the bicarbonate concentration is the same as in Solution 1. All solutions were made up with water, redistilled through an all-Pyrex glass still and stored in Pyrex glass bottles. Two troughs were used, one for each kind of film, and the stearic acid monolayer on the liquid surface was kept under constant pressure with castor oil. The experiments were performed at room temperature, which varied between 22–26°.

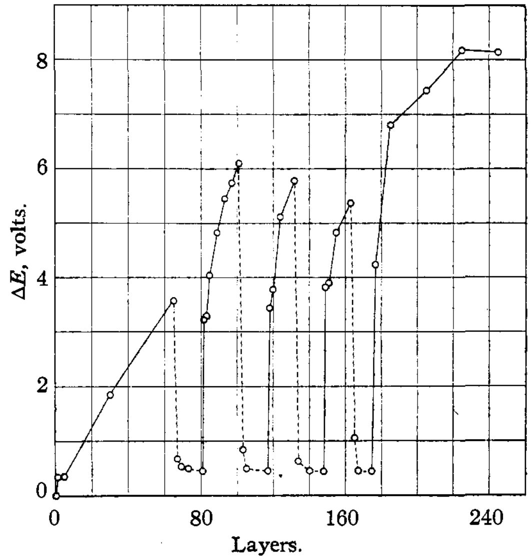


Fig. 1.—Effect of alternations of Y and X layers on the potential of an X film: - - -, Y layers; —, X layers.

The thickness of these films was determined, whenever the nature of the experiments necessitated it, by comparison of the color of the film with a standard step color gage of Y films.[1,2] This was accomplished by viewing simultaneously, through a polaroid screen, the unknown and the standard. These gages are satisfactory for determining the changes in thickness of X films even though the correlation between number of layers and color is not the same for X and Y films, the X layers being about 17% thicker than Y layers as judged by color. It is often convenient to express the thickness of X films in terms of the number of layers in a Y film of the same thickness by color and this is done in some of the experiments given below.

Contact potentials were measured by the vibrating plate method.[5,6] The polished stainless steel slides on which the films were built were placed beneath the vibrating gold plate in place of the liquid surface in earlier studies with the method. In what follows we will use the term potential to refer to the algebraic difference between the observed contact potential of the slide covered with film and that of the chemically clean steel slide. In this way the small differences between different slides are eliminated. These potentials are called positive when they correspond to an electric double layer with the negative surface toward the metal.

3. Complex Films of X and Y Layers

A. Case in which the Y Films are Deposited from a Substrate Containing Calcium Carbonate.—When a single Y double layer is deposited on a many-layer X film of high potential it causes a marked drop in potential which may amount to several volts (Fig. 1). Subsequent Y layers may produce a further decline in potential but never to a value below that of a built-up Y film. Subsequent deposition of X layers on such a Y depressed X film causes a steep rise in potential at a rate as high as 2 v. per layer. After 10 to 20 X layers have been deposited, the rate of increase diminishes to that of a straight X film, that is, to 80 mv. or less per layer. Such an alternation of potential apparently can be repeated indefinitely and the magnitudes of the X layer potentials obtained, when the rate of increase has become that of an uncomplicated X film, are generally in the neighborhood of the value to be expected for a pure X film of the same total number of layers.

Conversely when a single X layer is deposited on a many-layer Y film the potential rises sharply by as much as a volt (Fig. 2). If several more X layers are added, the rate of increase of the potential gradually diminishes, approaching the normal rate of 80 or less millivolts per layer as in the case described in the last paragraph. A Y double layer added at this point depresses the potential of the film, which may in turn be restored once more by further X layers. Such an alternation apparently can be repeated indefinitely as seen in Fig. 2, but in general the potentials following the deposition of X layers are not as great as would be expected for a pure X film of the same total number of layers. Nevertheless, in one case the deposition of 22 X layers on a Y film of 235 layers produced a potential rise of approximately 12 v.

---

(5) Zisman, *Rev. Sci. Instruments*, **3**, 7 (1932).

(6) Porter, This Journal, **59**, 1883 (1937).

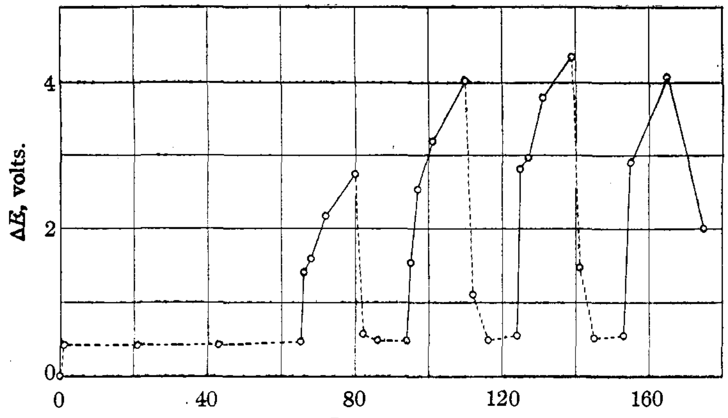


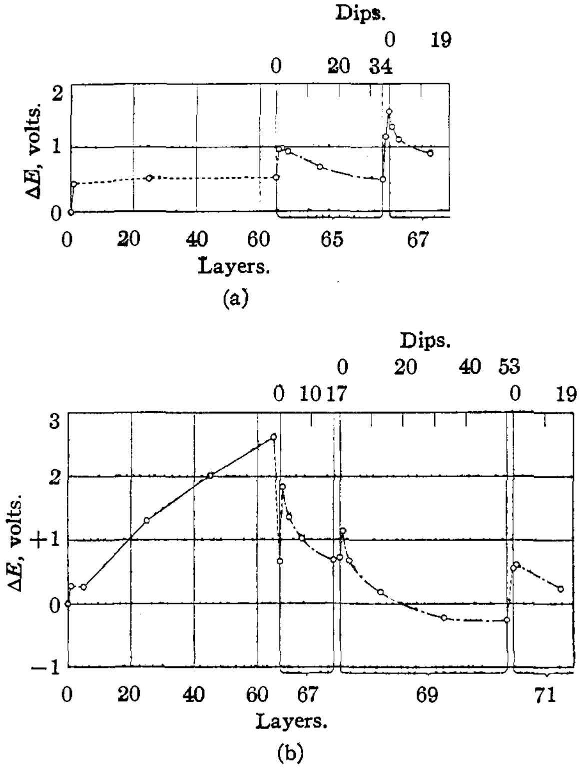
Fig. 2.—Effect of alternations of X and Y layers on the potential of a Y film: - - -, Y layers; —, X layers.

These two sets of results at once raise the question of how far the effects of depositing X layers on an underlying series of Y layers, or of depositing Y layers on an underlying series of X layers, are due to the added layers themselves and how far they may be due to the mere dipping into a different substrate, since the substrates from which X and Y films are obtained are necessarily different. In order to answer this question a number of experiments were performed on the effect of dipping simple X and Y films, as well as more complicated films involving alternations of X and Y layers, into various substrates. In view of possible changes of thickness of films by removal of layers by dipping the thickness of the films was checked throughout these experiments by color comparisons.

When a simple Y film is dipped once into the alkaline substrate used for forming X films there is a potential rise of about 0.5 v. Continued dipping, however, causes the potential to fall gradually until it attains its original value (Fig. 3a). Throughout the whole process there is no change of thickness as judged by color, although by the use of talc dusted over the surface of the substrate it may be seen that some of the film is actually removed. From this it may be concluded that although dipping in the substrate does augment the potential, it does so only at the first dip and then less than when an X layer is added, and moreover that the rise is not continued as in the case of the addition of successive X layers. It may be added that such dipping of Y films does not in any way alter the effects produced by the addition of X layers later.

When an X film is dipped in an alkaline X substrate the potential may or may not be raised slightly by the first dip. Continued dipping depresses the potential somewhat, but the process becomes progressively less effective as is seen in Fig. 4. As in the case of Y films, the use of talc shows that a small amount of film is removed by the process.[7]

When a Y depressed X film is dipped in an alkaline substrate, the potential may be raised by as much as 2 v. by the first dip (Figs. 3b, 4 and 5). However, subsequent dips lower this raised potential, whereas X layers continue to raise it as shown diagrammatically in the figures. Both Figs. 3b and 4 show the effect of continued dipping in alkaline solutions on a depressed X film where the potential after the initial rise drops back to the depressed level or below, even becoming negative on prolonged treat-



(a)

(b)

Figs. 3a, 3b.—Effects of dipping films in the alkaline X substrate (see text). In the bracketed regions the abscissa scale is in terms of dips instead of layers, since no layers are removed: —, X layers; - - - - -, Y layers; —-—-—, dips in alkaline substrate.

---

[7] While an X film is under the liquid, it is like a Y film of low contact potential as may be seen from measurements of the voltage of the combination X film/H_2O/Y film, which is always close to zero.

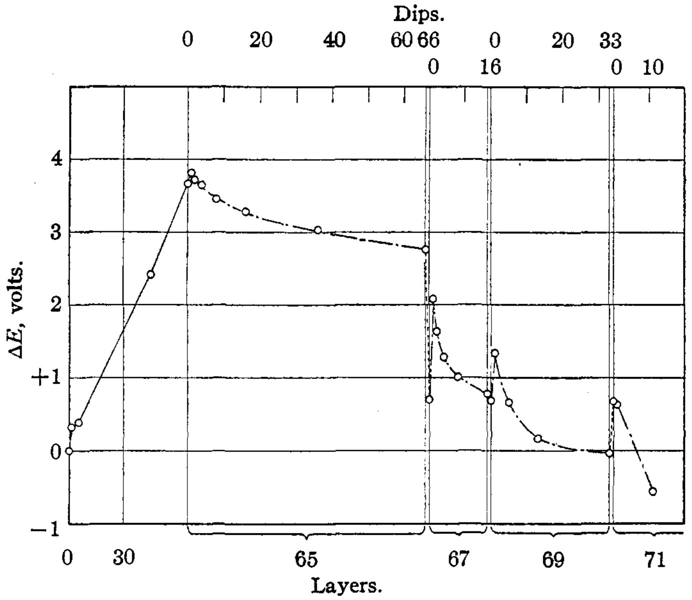


Fig. 4.—Effects of dipping films in the alkaline *X* substrate (see text). In the bracketed regions the abscissa scale is in terms of dips instead of layers, since no layers are removed: —, *X* layers; - - - -, *Y* layers; — - — - —, dips in alkaline substrate.

ment, *e. g.*, 53 dips (Fig. 3b) or 33 dips (Fig. 4). When a *Y* layer is deposited on a film treated in this way, the potential always returns to the *Y* film level. If the potential of the *Y* film has already been attained by dipping, no change occurs, but if the potential has been lowered below the *Y* film level a *Y* layer will raise it to this level, after which dipping depresses the potential without an initial rise.

An *X* augmented *Y* film is only slowly depressed by dipping in alkaline solutions (Fig. 5), as in the case of uncomplicated *X* films.

A phenomenon associated with the enhancement of the potential of a *Y* depressed *X* film by the deposition of *X* layers finds explanation in the effect of alkaline solutions on the potential. It has been observed repeatedly that the first *X* layer causes a very large potential rise, whereas the second *X* layer may cause only a slight rise (Figs. 1 and 2). The third and fourth *X* layers, however, again usually cause substantial increases in potential. The large effect associated with the first layer is the sum of the effects of the *X* layer itself and the alkaline substrate during the first dip, which both have an augmenting action on the potential of the underlying film. The unexpectedly slight rise associated with the second *X* layer is the sum of the positive effect of this layer itself and the negative effect of the alkaline substrate on the second dip. Since the depressing action of the alkaline solution during succeeding dips becomes progressively less, the total effect of subsequent *X* layers becomes greater again.

There remains to be considered the effect of acid substrates. When a film is dipped repeatedly into an acid substrate of *p*H 3.5–6.2 a number of layers (3–10) are removed. A layer may be removed by a single dip or again it may require several dips to remove a single layer, and as successive layers come off removal is retarded. For this reason the situation is different from alkaline dipping, and it is particularly important to follow the number of layers removed by color.

The effect of dipping a simple *Y* film in an acid substrate is shown in Fig. 6a. The potential remained essentially constant while three layers were removed.[8]

Figure 6b shows the effect of dipping a simple *X* film in the acid substrate. Here the potential rises with the removal of the first layer and then falls as another layer is removed. The removal of the third layer produces very little change. The effect of this treatment on the po-

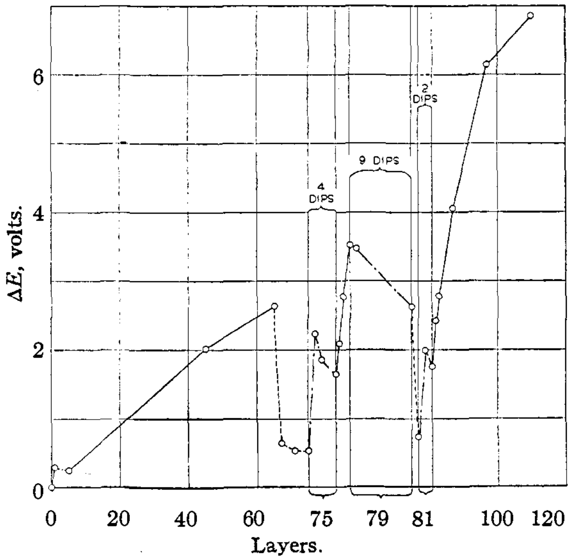
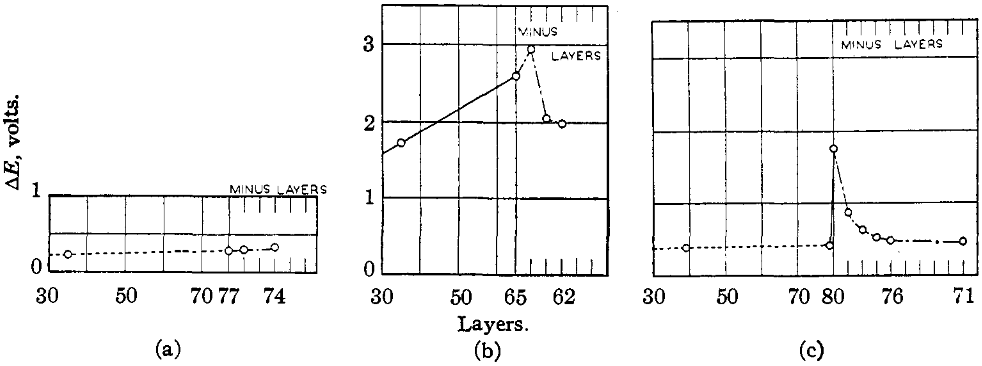


Fig. 5.—Effects of dipping films in the alkaline *X* substrate (see text). In the bracketed regions the abscissa scale is in terms of dips instead of layers, since no layers are removed: —, *X* layers; - - - - ,*Y* layers; — - — - —, dips in alkaline substrate.

---

[8] It should be noted that in Figs. 6a, b, c, and 7a, b, c, in which the effect of dipping in acid is shown, the scale for the removal of layers is four times the scale for the addition of layers.

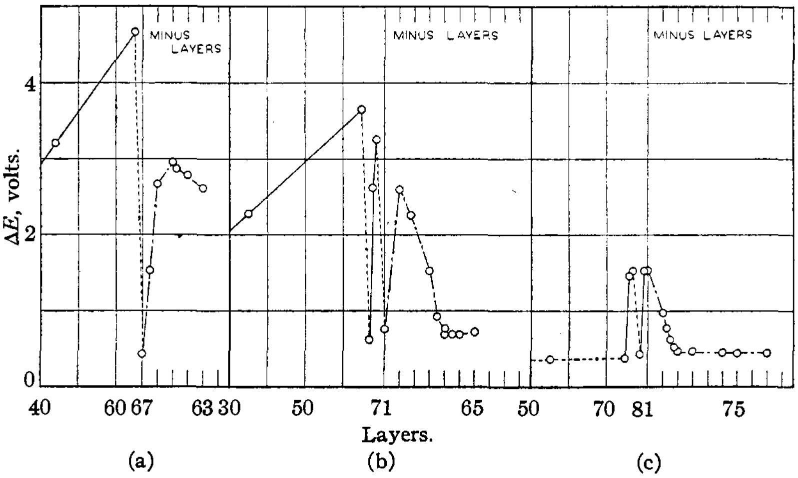


(a) (b) (c)

Figs. 6a, 6b, 6c.—Effects of removal of layers from simple and complex films. The scale for removal of layers is 4 times that for the addition of layers: —, *X* layers; - - - -, *Y* layers; — - — - —, removal of layers by acid substrate.

tential of an *X* film is very different from that produced by depositing *Y* double layers, of which the first reduces the potential to the *Y* film level.

When an *X* augmented *Y* film (Fig. 6c) or a *Y* depressed *X* film (Fig. 7a) is dipped in the acid substrate, the effect is that to be expected on removal of the modifying outer layer if it is assumed that the structure of the underlying film has not been irreversibly altered by this layer. Thus in Fig. 6c the potential of a *Y* film with one overlying *X* layer returns to the *Y* film value after apparent removal of 4 layers. In Fig. 7a the potential of a *Y* depressed *X* film rises to two-thirds of the original *X* film value after removal of two layers. If the layers could be stripped off systematically one at a time, the history of the films might be repeated more exactly in reverse order, but this is not possible for only 2 or 3 layers can be removed easily and pitting probably occurs, exposing several layers at once and changing radically the orientation of the molecules composing them. This difficulty is exemplified in the behavior of a film having a more complicated history. In Fig. 7b the history involving the effect of the top 4 layers has been retraced, while in Fig. 7c the effect of the top 2 layers only has been repeated.



(a) (b) (c)

Figs. 7a, 7b, 7c.—Effects of removal of layers from simple and complex films. The scale for removal of layers is 4 times that for the addition of layers: —, *X* layers; - - - -, *Y* layers; — - — - —, removal of layers by acid substrate.

B. Case in which *Y* Films are Deposited from a Substrate Containing Barium and Copper.—Most of the experiments described above have been duplicated with *Y* films deposited from the substrates containing barium and copper defined under Section 2.

Alternations of potential accompanying alternations of *X* and *Y* layers are of essentially the same character as with calcium stearate *Y* layers. There are, however, one or two minor differences. In the first place the initial one or two layers deposited from an *X* substrate on *Y* films containing barium and copper may be formed as *Y* layers and cause no increase in potential. When, however, *X* layers begin to be deposited the potential rises at a rate of 600 to 800 mv. per layer, which, although not as great as the initial rise without barium and copper, is still tenfold greater than the rate of increase of the potential in uncomplicated *X* films. In the second place *Y* layers deposited from the alkaline solution 2 depress the potential of an *X* film more slowly than the potential of an *X* augmented *Y* film.

Three or four layers may be necessary to bring the potential down to the Y level.

A difference due to barium and copper is seen in the behavior of Y films or Y depressed X films on dipping into the alkaline X substrate. This treatment produces, instead of the large potential increase characteristic of calcium stearate Y films, a relatively small drop in potential of 100–200 millivolts. Thus the copper and barium seem to stabilize the Y layers. This is also shown by dipping in the presence of talc, which reveals that only a barely appreciable amount of film is removed, less even than the small amount in the case of the alkaline substrate containing calcium. Indeed barium–copper substrates of whatever *p*H over the range studied fail to cause the removal of any considerable amount of film. The stabilizing effect of copper on Y films has been pointed out by Blodgett.[9]

Another difference appears on dipping pure X films in the Y film substrates 1 (*p*H 7.4), 3 (*p*H 6.2), and 4 (*p*H 5.8), containing barium and copper. This depresses the potential at the rate of 0.5 to 1 v. per dip, whereas acid substrates containing calcium have much less effect, although they do produce removal of layers. Even such large effects are, however, much less than the drop produced by one barium–copper stearate Y double layer, which will reduce the potential from any high value to the Y film level.

Solution 2, the alkaline substrate containing barium and copper, from which it is possible to form Y films, is ineffective in reducing film potentials, and in this respect resembles the acid substrate containing calcium.

In the case of dipping in barium–copper substrates, where no layers are removed, the magnitude of the effect seems to be due to the duration of contact with the substrate rather than to the number of dips. The potential of an X film can be reduced from a high value to less than 0.5 v. by remaining four minutes in a solution containing barium and copper at *p*H 7.4. At the same time the surface of the film acquires the property of shedding water very slowly. This change, probably associated with the adsorption of ions, alters the surface in such a way that the first few added layers are always Y layers even when deposited from an alkaline calcium carbonate substrate. Subsequently, however, X layers will deposit and the potential rises steeply. Blodgett states that in X films "a change takes place in the barium content of the film during the time that the film remains under water."[9]

4. Effect of Temperature on the Stability of Films

A. Room Temperature.—The potentials[10] of Y films formed from either a calcium carbonate substrate or a barium–copper substrate are essentially the same, *e. g.*, + 200 to + 400 mv., and persist for many weeks without appreciable change. The potentials of X films drop slowly in the course of time, but remain at a high value for many days as shown by the figures for an X film of 245 layers in Table I.

TABLE I

Time	0 hrs.	20 hrs.	2 days	4 days
Potential	+7.92	+6.87	+6.43	+6.02
Time	6 days	7 days	9 days	10 days
Potential	+5.63	+5.52	+5.19	+5.16

B. Higher Temperatures.—In order to determine stability at higher temperatures, the films were baked in an oven for ten-minute periods at various temperatures.

Y films formed from a substrate containing barium and copper, *p*H 7.0–7.4, when heated above 75°, gradually become opaque and the potential drops by 100–200 mv. If the temperature is not so high that the film loses all color the thickness can be determined by color, which reveals a decrease in thickness as has been shown by Blodgett.[1,9] This is illustrated by the two cases in Table II.

TABLE II

Temp., °C.	Thickness	Potential, v.
	Film 1, 81 layers	
Before heating	81 Y layers	+0.42
74–75	81 Y layers	+ .21
84–85	White, no color	+ .26
	Film 2, 85 layers	
Before heating	85 Y layers	+0.36
78–79	75 Y layers opalescent	+ .25

Y films formed from a substrate containing calcium carbonate, *p*H 6.8–7.0, do not become opaque when heated at any temperature between 80 and 150° for ten minutes, but remain almost completely transparent, though sometimes showing a slight opalescence. The thickness and po-

---

[9] Blodgett, *J. Phys. Chem.*, **41**, 975 (1937).

[10] The potentials reported in Section 4 are the observed contact potentials, no correction having been made for the small initial potentials of the clean slides.

tential diminish, however, as shown by the figures in Table III.

TABLE III

Temp., °C.	Thickness, Y layers	Potential, v.
Before heating	81	+0.34
94–95	79	+ .095
104–106	77	+ .090
115–117	71	+ .098
125–128	65	+ .053
137–140	61	+ .018
145–152	<60	– .033

X films formed from a calcium carbonate substrate, pH 9.4, behave somewhat differently on heating from the calcium stearate Y films. The potentials drop slowly, finally disappearing at high temperatures. Opacity gradually increases between 115 and 150°, the film becoming very opaque at the higher temperatures. The color thickness, instead of becoming less, increases considerably as the temperature is raised, as is shown by two examples (see Table IV).

TABLE IV[a]

Temp., °C.	Thickness, Y layers[b]	Potential, v.
	X Film, 70 layers	
Before heating	79	+2.59
115–117	80	+0.33
	Slightly cloudy	
117–119	80–81	+ .13
	Increased cloudiness	
120–121	81	+ .06
123–125	82	+ .02
	Further increased cloudiness	
129–132	85	+ .04
132–136	93–95	+ .06
	Opaque, coloring much reduced	
138–141	107	+ .06
	Very opaque, very little color	
	X Film, 65 layers	
Before heating	75	+2.17
63–64	75	+2.01
69–71	75	+1.79
77–78	75	+1.69
88–90	75	+1.49
110–114	75	+1.11
122–123	77	+0.77
	Transparent	
131–133	Opaque	+0.096

[a] Under the section on the effect of X-rays will be found a third example of the increase in the thickness of X films produced by heating. [b] We have for convenience expressed the thickness of these X films in terms of Y layers.

5. Effect of X-Rays

We have made a number of experiments on the effect of X-rays on the films. For this purpose the metal slides coated with film were exposed for ten minutes at a distance of 34 cm. from the tungsten target of a tube operated at 160 kv. drawing a current of 10 m. a. Under these conditions very large changes are produced in the contact potentials of both X and Y films. If the metal slides are insulated by placing them on a glass plate during irradiation the potentials may attain large positive or negative values and different parts of the same film may develop potentials of different sign amounting to many volts. If the metal slides are grounded by laying them directly on the lead shielding of the apparatus during X-raying the potentials developed are always negative, and have been observed to attain values as large as –50 v. in a film of 201 X layers. Both X and Y films appear to behave alike in this respect. The magnitude of the potentials developed in this way depends on the thickness of the films as may be seen from the figures in Tables V and VI.

TABLE V

POTENTIALS IN VOLTS OF X-RAYED Y FILMS

(Ba–Cu STEARATE)

	Initial layer	+1 Y double layer	+3 Y double layers	+7 Y double layers
Chemically clean slide	+0.06	+0.04	–0.04	0.00
Before X-ray	+ .36	+ .36	+ .34	+ .30
After X-ray	+ .33	– .09	– .38	–5.31
Difference	– .03	– .45	– .72	–5.61

TABLE VI

POTENTIALS IN VOLTS OF X-RAYED X FILMS

	Initial layer and 1 Y double layer	+1 X layer	+4 X layers	+8 X layers	+16 X layers
Chemically clean slide	–0.18	–0.14	–0.14	–0.13	–0.26
Before X-ray	+ .10	+ .22	+ .43	+ .66	+ .91
After X-ray	– .20	– .13	–1.17	–2.76	–7.19
Difference	– .30	– .35	–1.60	–3.42	–8.10
Heated 10 min. 79–80°	– .05	– .09	–0.93	–2.20	–5.93

The potentials obtained by X-raying Y film gradually drop, falling to less than half their value during a period of some sixteen hours, and appear to be in part at least due to the accumulation of charge on or in the film as a result of the X-radiation. The potentials of X-rayed X films drop by only a small fraction of the initial value in the same period. If Y films are dipped into the liquid substrate on which they were originally formed the potential returns to approximately its original value, *e. g.*, +0.200 v., immediately. On the other hand, if *X* films are treated in this way the potential does not return to its original positive large value but to a value only somewhat less negative than the X-rayed value, as shown by the examples in Table VII.

TABLE VII

	Potential, v.
40 *Y* double layers (Ba–Cu stearate)	
Before X-ray	——
After X-ray	−15.2
After 2 dips	− 0.15
After 12 dips	− .23
After 15 min. in the soln.	+ .14
75 *X* layers	
Before X-ray	+ 3.24
After X-ray	−17.4
After 1 dip	− 9.6
After 13 dips	− 7.1
After 30 min. in the soln.	− 5.2

Very much the same difference of behavior between *X* and *Y* films is observed when X-rayed films are heated (in our experiments for ten minutes) without melting. The potentials of *Y* films return to their original value, while those of *X* films rise but little from the X-rayed values, as shown by the figures in Table VIII.

It is clear from this that there is no permanent change produced in *Y* films as a result of X-radiation. It seems probable that the large changes in potential observed are due to the accumulation of charge on and in the film which at once leaks off when the film is dipped or heated. On the other hand, it is indeed significant that in the intense if temporary electrostatic fields existing in the films as a result of the potentials set up by X-rays, there is no change, or at least no permanent change, in the electrical structure of the *Y* films. In the case of a film 80 layers thick with a potential difference of 20 v. between the two sides, this field is over 10^6 v. per cm. Whether or not the persistent changes produced in the *X* films by similar treatment are due to alteration in the structure of the films, or to the fact that in these films accumulated charges in the interior of the film leak off more slowly due to a difference in film resistance, is a question not answered by these experiments. There is, however, one point of interest which is settled by these results: it is clear that X-raying *X* and *Y* films does not change them so that they are alike. As we shall see, this point is of significance in relation to the measurements of Holley and Bernstein.

TABLE VIII

	Y film, 81 layers Ca stearate *p*H = 6.2		*Y* film, 81 layers Ba–Cu stearate *p*H = 7.4		*X* film, 70 layers *p*H = 9.4	
Treatment	Potential, v.	Thickness	Potential, v.	Thickness	Potential, v.	Thickness
Before X-ray	+ 0.33	81	+ 0.63	81	+ 1.45	79–81
After X-ray	−13.6		−15.5		−16.1	
71–75°	+ 0.13	80	+ 0.198	81	−14.3	79–81
85–86°	+ .097	79	+ .25	No color opaque	−13.5	79–81
94–95°	+ .074	77			−11.5	81–85 Slight opalescence
104–106°	+ .070	75			−10.8	81–85 Slightly opaque
115–117°	+ .070	66			− 2.7	82–87
125–128°	+ .049	63 Transparent			+ 0.07	93–95 Very opaque color much reduced

When *X* or *Y* films, which have been heated for ten minutes at 140–150° to destroy the original structure, are X-rayed their potentials change from initial values of less than +100 mv. to only −0.5 to −1.0 v.[11] On dipping once in an acid calcium carbonate substrate these negative potentials are replaced by positive potentials of 300–400 mv.

6. Effect of an Electrical Discharge on *X* and *Y* Films

Attempts to produce alterations in *X* and *Y* films by placing them in electrostatic fields failed. To test this point two slides, one coated with a film and the other bare, were connected to the poles of a 500-v. battery and brought together almost to the sparking distance in air. No change in the potential of the film was produced. On the other hand, very large modifications of potential were produced by the passage of a

---

(11) The production of such potentials appears to be related to the structure of the films. By means of treatment with a glow discharge described in the next section, it was possible to produce large potentials in a thick film of solidified paraffin, but not in a thick film of liquid Nujol.

series of sparks distributed over the surface of the film. These results suggested the procedure of making the slide coated with film one electrode in a glow discharge. The slide was connected to one terminal of the secondary of a 5000-v. transformer designed for operating neon lamps from the 60-cycle 110-v. line and placed under a small bell jar which could be evacuated by a Hyvac pump. The other electrode, connected to the other terminal, was simply a piece of brass rod projecting through a rubber stopper closing the opening at the top of the bell jar and also carrying the glass tube for connection with the pump. The rod projected down to a distance of 7 or 8 cm. above the center of the slide. In general the visible discharge took place between the tip of the brass rod and a piece of light copper wire attached to the binding post of the slide, which was the nearest point.

When the discharge was unrectified and therefore alternated in accordance with the 60-cycle power supply, the effect on the contact potentials was much the same as when the films were X-rayed without the slides being grounded: large changes in potential were produced which were of different sign at different parts of the same film. By introducing a rectifier into the circuit the slide could be made either the anode or cathode of a unidirectional discharge. When the slide was made the positive electrode the potentials of both *X* and *Y* films always changed to large negative values as a result of the discharge, as if negative charges accumulated in the outer portions of the films; when the slide was made the negative electrode equally large changes of opposite sign resulted, as if positive charges accumulated in the outer portions of the films. The positive and negative values attainable in this way seemed to be equally great for *X* and *Y* films, and, as in the case of X-raying, to increase with the thickness of the films. The greatest effect observed was in the case of a film of 304 mixed *X* and *Y* layers which developed a potential of −156 v. This corresponds to a field in the film of about 2×10^6 v. per cm.

When the potential of a *Y* film is made negative by a glow discharge and the film is dipped, the potential immediately returns close to the original small positive value.[12] On the other hand, when *X* films are subjected to the same treatment, the potential remains several volts negative. The behavior of the two types of film is thus the same as when they have been X-rayed. Likewise if the potential of a *Y* film is made positive by a glow discharge and the film is dipped, the potential returns close to its original value. In the case of an *X* film treated in this way, the potential returns to a value somewhat greater than its initial positive value of several volts. These facts are illustrated by Table IX.

TABLE IX

Potential	Film 1, 81 *Y* layers	Film 2, 82 *Y* layers	Film 3, 70 *X* layers	Film 4, 71 *X* layers
Initial	+ 0.27	+ 0.26	+ 2.3	+ 2.5
After discharge	−13	+17	−16	+12
After dipping	+ 0.22 (1 dip)	+ 0.45 (1 dip)	− 3.2 (8 dips)	+ 2.9 (8 dips)

As in the case of the X-ray work, these results show a significant difference between the two types of film, but again it is not clear whether the enduring potential changes, positive or negative, produced in *X* films represent a change of structure or the persistence of free charges which do not leak off so easily in this type of film as in *Y* films.

7. Discussion

The task which confronts us is to consider these and any other phenomena in relation to the problem of the structure of the films. Do *X* and *Y* films really differ in the manner originally postulated by Langmuir, namely, are the successive layers of a *Y* film oppositely, those of an *X* film similarly, oriented? Certainly such a difference accords well with the contrast between the potentials of the two kinds of films. It is likewise suggested by the manner in which the two kinds of films are deposited. Moreover, some fundamental difference of structure seems to be required by a number of other phenomena, notably the difference of thickness of *X* and *Y* layers as indicated by color, the opposite way in which the thickness and appearance of *X* and *Y* films change during heating, and the different way in which the potentials produced by X-rays or a glow discharge are affected when *X* and *Y* films are dipped or heated.

On the other hand, it is hard to reconcile this picture with the X-ray studies of Holley and Bernstein, which show that the metal cations are equally spaced in the two types of films. Since we may suppose that these ions are close to the

---

[12] In the case of very thick *Y* films there is some indication that the potential does not return quite to its initial value on the first dip or two.

negatively charged carboxyl groups of the stearate molecules, we should certainly expect them to be differently spaced in X and Y films if Langmuir's view is correct. It might, of course, be objected to Holley and Bernstein's results that the very X-radiation by which the spacing is observed itself produces a change in the structure of the films, either converting X films into Y films or both to some different common form so that the measurements do not really give us a comparison of the films in the original condition in which we are interested. We have seen the profound effects produced by X-rays on the potentials of both X and Y films and called attention to the intense fields which they must set up. But to whatever these effects may be due, whether to the accumulation of charge or to a true alteration of the structure of the films, it is clear from their different behavior after radiation that the two types of films are not made alike by the treatment, and certainly there are great differences between films in which the spacing of the metal ions is the same as revealed by X-rays. Again, to be sure, the point might be raised that Holley and Bernstein have studied the effects of X-rays on films built on quartz plates, whereas our results are on films built on metal plates from which the secondary radiation would be different; but this interpretation is unconvincing. It must be admitted that the results of Holley and Bernstein are very strong evidence against Langmuir's hypothesis.

Certainly, nothing so specific as the difference of structure involved in Langmuir's picture is required to explain the phenomena discussed in earlier sections of this paper. Without regard to any hypothesis in detail, it is natural to attribute the high potentials of X films to some continued electrical asymmetry of internal structure, whereby these films differ from the electrically symmetrical Y films.[13] If we do so, we may regard each successive layer of an X film as an electric double layer whose moment points in the same direction as those of the other layers. It is instructive to consider the magnitude of these moments. The moment m of a layer per unit area may be calculated from the potential[14] ΔE of the layer by the relation

$$m = \Delta E\epsilon/4\pi \qquad (1)$$

where ϵ is the dielectric constant. If m is expressed in electrostatic units, ΔE in volts, and ϵ is taken as unity, this becomes

$$m = 2.65 \times 10^{-4}\Delta E \qquad (2)$$

In pure X films values of ΔE are of the order of 0.06 v. per layer, corresponding to a value of $m \sim 1.6 \times 10^{-5}$ e. s. u. If we divide this quantity by the number of stearate molecules per sq. cm., which we may take as 5×10^{14} on the basis of a cross section of 20 sq. Å. per molecule, we obtain as the moment associated with each molecule the value 3.2×10^{-20} e. s. u. This, like all moments calculated from contact potentials, is exceedingly small, something like 100 times smaller than the electric moments of most polar molecules determined from dielectric constant measurements, the moment of straight chain fatty acids being between 1 and 2×10^{-18} e. s. u. It is of the same order of magnitude as the apparent moments of stearate molecules in monomolecular films on liquid substrates calculated in the same way from the contact potentials. We have shown[15] that such moments have no apparent correlation with the true electric moments of the film molecules but rather with their state of ionization. We should probably think therefore of the value 3.2×10^{-20} in terms of the spacing of the negative charges of the stearate molecules and the associated positively charged metal cations in the films. If we divide 3.2×10^{-20} by the value of the elementary charge, we obtain for the mean distance between the loci of positive and negative charge in an X film the value 6.7×10^{-3} Å. This is a very small distance indeed, and shows what very small changes in the spacing of the charges in the films may account for profound differences of potential, regardless of any general theory as to the structure of the films.

Carrying out this general point of view that there is some real difference in internal structure between X and Y films, how shall we explain the enormous effects on film potentials produced by the addition of single X or Y layers? The effects are so large, amounting to several volts, that it seems possible they are due not to the intrinsic properties of the added layers, but to their influence on the structure of the underlying film. In this case if we were to accept Langmuir's original picture it might be supposed that under-

---

(13) Langmuir recently has pointed out to us in correspondence that it might be possible to interpret many of the phenomena in terms of free surface charges at the faces of the films rather than in terms of any difference of internal structure.

(14) We are, of course, using the term "potential" in accordance with the convention given at the end of Section 2.

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

lying layers are actually reoriented by added layers, *i. e.*, that when a *Y* layer is deposited on an *X* film every other underlying layer is inverted to produce a *Y* film and that there is a corresponding rearrangement when an *X* layer is added to a *Y* film. Nevertheless, any such radical change of structure seems unlikely. The closeness of packing of molecules would give an area of only about 20 Å.^{2}[16] per molecule for turning. It is also an argument against this interpretation that when a *Y* layer is removed from a simple *Y* film there is no change of potential, whereas when a *Y* layer is removed from a *Y* depressed *X* film there is a large rise of potential, which would not be expected if the *X* film had been converted into a *Y* film. It seems more likely, if there is actually a modification of the structure of the underlying film by added layers, that this is produced as a result of minor changes in the spacing of the positive and negative charges due to stresses set up in the film by the outermost *X* or *Y* layers. We have seen what small changes of distance serve to account for very large potential effects.

On the whole it seems to us that the facts are against any such difference of structure of *X* and *Y* films as that originally pictured by Langmuir. We suggest, rather, that the orientation of stearate molecules in successive layers of *X* and *Y* films is the same, and that the differences between the two types of film are based on much smaller scale differences of internal structure involving the details of the spacing of positive and negative charges, or, possibly, the presence of an excess of positive ions in *X* films. But in any case, the facts seem to demand a real difference of internal structure. This view has one or two consequences worth considering. Since the surface of both *X* and *Y* films is hydrophobic, we must suppose that the polar groups are never exposed. In both types of film the first dip results in the deposition of only a single layer and in this layer the polar groups must be oriented toward the metal slide. After this, in the case of *Y* films, the layers are formed in pairs, one pair for each dip, the polar surfaces of the two layers of each pair facing together. This corresponds to the spacing of 48 Å. between the metal ions observed by Holley and Bernstein. The case of *X* films is more complicated. If we neglect the outermost layer in *X* films with an even number of layers, the film will be like a *Y* film in respect to the orientation of layers. This follows from our picture and is in agreement with the observations of Holley and Bernstein. In these films, however, the outermost layer is without a partner, its polar side being toward the metal. If we represent the polar end of a molecule by a circle, the three outermost layers of the film will be arranged as follows, the metal slide being on the left

—○ ○— ○—

When now such a film is dipped and one additional layer is added, the unpaired layer must turn over so that its polar surface faces that of the added layer, which, of course, is inward. *X* films with an odd number of total layers are like *Y* films in regard to orientation of layers; in them the four outer layers are arranged as follows

—○ ○— —○ ○—

We should expect, therefore, if our picture is correct, that the properties of *X* films of an even number of layers should be different from those of *X* films of an odd number of layers. Now there is some evidence that this is so. If during the early stages of building an *X* film the potential is measured each time a layer is added, as has been done in six cases, it appears that the potential does not rise by the same amount for each added layer but increases in a stepwise manner. This was noticed in each of the six cases, but is seen most clearly in that represented in Fig. 8. In all these cases the two pairs after the initial

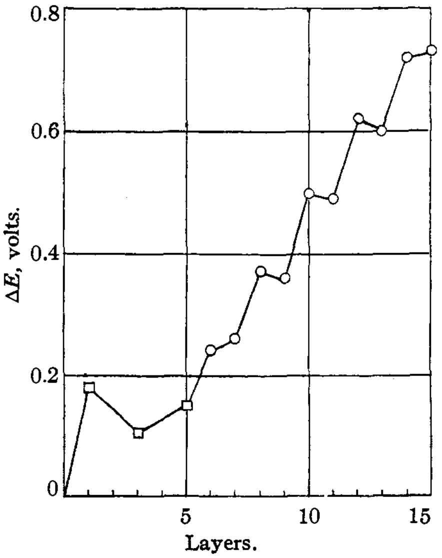


Fig. 8.—Potential rise in first few layers of an *X* film: ○, *X* layers; □, *Y* layers.

---

[16] Under the pressure of 15 dynes per cm. produced by castor oil this is approximately the cross section occupied by stearate molecules on a liquid substrate.

layer were *Y* layers, as so often happens. It has also been noted repeatedly in forming *X* films that the contact angle while the slide is being withdrawn from the solution shows an alternation of values over a series of dips, *e. g.*, <90°, 90°, <90°, 90° . . . . This effect, like the stepwise increase of potential, is only marked during the early stages of building *X* films. Later, apparently, the process becomes irregular.

Summary

Contact potentials of stearate *X* films increase with the number of layers and may attain values of many volts. Contact potentials of stearate *Y* films remain constant at a few hundred millivolts and are independent of the number of layers. Sudden very large jumps of potential can be produced by alternating the deposition of *X* and *Y* layers, one or two *X* layers producing large increases in *Y* film potentials and one or two *Y* layers large decreases in *X* film potentials. Such alternations of potential by alternations of *X* and *Y* layers can be continued indefinitely.

Control experiments are presented on the effect of dipping pure *X* and *Y* films and mixed *X* and *Y* films in the various substrates from which these films are deposited and in no case was it found that the substrates produced effects comparable with those of *X* or *Y* layers.

The stabilities of *X* and *Y* films are reported. At room temperature high *X* film potentials persist for many days. On the other hand, when barium-copper stearate *Y* films are heated between 74–85° the potentials decrease by about 200 mv. At about 85° the films begin to turn white and their optical thickness decreases. *Y* films containing only calcium stearate do not become white on heating but otherwise behave the same as those containing barium and copper. *X* films heated above 115° increase in optical thickness and gradually become opaque. The potentials drop to near zero. When heated at lower temperatures the potentials persist at high values.

The effect of X-rays on *X* and *Y* films is to produce large negative potentials, presumably due to the accumulation of charge on or in the film, the magnitude of which depends on the number of layers. *Y* films can be discharged very easily by dipping the slides in water or by heating to a temperature below that which changes the optical thickness. *X* films on the other hand cannot be readily discharged by dipping or by heating to temperatures which discharge *Y* films. Therefore, it is concluded that *X* and *Y* films are not made alike by X-ray treatment.

Very much the same results are obtained when *X* or *Y* films are made one pole in a glow discharge. In this case, however, it is possible to produce either positive or negative potentials according to the direction of the discharge. These *Y* film potentials are more readily reduced by dipping than are the *X* film potentials.

These results are discussed in relation to theories of film structure.

CAMBRIDGE, MASS. RECEIVED JANUARY 22, 1938

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Meaning and Standardization of the *p*H Scale

BY D. A. MACINNES, DONALD BELCHER AND THEODORE SHEDLOVSKY

According to almost universal practice *p*H values are computed using the formula

$$pH = \frac{E - E_0}{2.3026RT/F} \qquad (1)$$

in which R, T and F have their usual significance, E is the potential of a galvanic cell of the type

$$\text{(Pt), H}_2\text{; solution X} \underset{a}{:} \text{KCl (satd.) : reference electrode} \qquad \text{(A)}$$

and E_0 is a constant at a given temperature, which depends upon the nature of the reference electrode, and on other considerations which will be discussed in this paper.[1] In cell (A) "solution X" is the fluid the *p*H of which is desired. Although Sørensen[2] originally considered *p*H, as defined by equation (1), to be $-\log C_{H^+}$, in which C_{H^+} is the hydrogen ion concentration, that relation is no longer considered to be valid. It is, however, the basis for the E_0 values mostly used today. More

---

(1) The early work on the standardization of the *p*H scale cannot be summarized briefly. It is discussed by W. Mansfield Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928, 3d edition.

(2) Sørensen, *Compt. rend. trav. Lab. Carlsberg*, **8**, 1 (1909).