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## Hydrogen Ion Concentration and the Behavior and Measurement of Monomolecular and Polymolecular Films on Water

WILLIAM D. HARKINS AND ROBERT J. MYERS, *University of Chicago, Chicago, Illinois*

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### 1. INTRODUCTION

IN view of the great importance of hydrogen ion concentration in chemical equilibria in chemical and biological systems, several attempts have been made to examine the effect of the hydrogen ion concentration of the substrate upon the behavior of monomolecular films of polar substances on water surfaces. Up to the present time the results obtained by various investigators possess little more than qualitative significance for one or more of the following reasons:

1. Substances chosen as showing the most marked effects, and hence studied in detail, such as proteins, have been of a doubtful purity and uncertain chemical constitution.
2. In many cases there is considerable doubt that a true monomolecular film was obtained; the films may have consisted of polymolecular aggregates enmeshed in a monomolecular layer.
3. Capillary-active buffers, such as citrate, acetate and borate, have been used and the results have obviously been affected by the adsorbed film of the buffer constituents.
4. The rate of compression of the films has been purely arbitrary. No detailed analysis of the effect of the rate of compression has yet been made by any investigator in the field. As shown below this is very important since new phenomena appear upon slow compression.

These objections indicate that a reexamination of the phenomena under controlled conditions should yield results of more quantitative character and of value in the solution of biological problems. For this reason an investigation was undertaken to determine if there exists any simple relationship between the character of the force-area curve and the state of ionization of the film. The above objections were avoided as follows:

1. The substance used was myristic acid, a crystalline material of high purity and definite chemical composition, which yielded expanded films which withstand considerable compression whether spread from solvent or from the crystals.
2. The results of many investigators have left no doubt that the film obtained from myristic acid is truly monomolecular, at least when first spread.

3. Noncapillary active substances, such as hydrochloric acid, potassium phosphate, sodium hydroxide and sodium bicarbonate were used in the preparation of the substrates.

4. The rate of compression of the film was varied, with equal time intervals between points, to determine the effect of the rate on the character of the  $F$ - $A$  curve. A suitable rate was chosen to allow equilibrium to be established after each pressure increment, yet such as not to allow the film to dissolve more than was necessary.

5. An apparatus of high precision and an improved technique of spreading were employed since small differences in behavior might easily be overlooked with apparatus of the usual degree of precision.

The work done thus far indicates some of the difficulties still to be overcome in a problem of this character, and seems to point to a more desirable method of attack. Inasmuch as small differences may be important, a new improved film balance of high precision was constructed and an improved technique of spreading from a volatile solvent was employed. These are described in detail.

### 2. APPARATUS AND PROCEDURE

The apparatus consists essentially of a trough of glass as used by Agnes Pockels,<sup>1</sup> together with an improved torsion balance, which is a modification of that used by Adam.<sup>2</sup> In Fig. 1, the trough  $ABA$  may be indicated as  $ABA1$ , and the balance as  $G1$ . This abbreviated system of designation is followed throughout the paper.

The trough, as indicated by the figure, is set on three adjustable supports of brass and amber ( $O1$ ) inside a tight box of plate glass, with a heavily galvanized cold-rolled steel flat as a base, supported by screws which are used to adjust the level of the base. The glass box is inside a thermally insulated metal box, which serves as an air thermostat. In a later model this air thermostat is inside a water thermostat which totally incloses it except for a large enough opening in front to allow the trough to be removed.

<sup>1</sup> A. Pockels, *Nature* **43**, 437 (1891).

<sup>2</sup> N. K. Adam and G. Jessop, *Proc. Roy. Soc. A* **110**, 423 (1926).

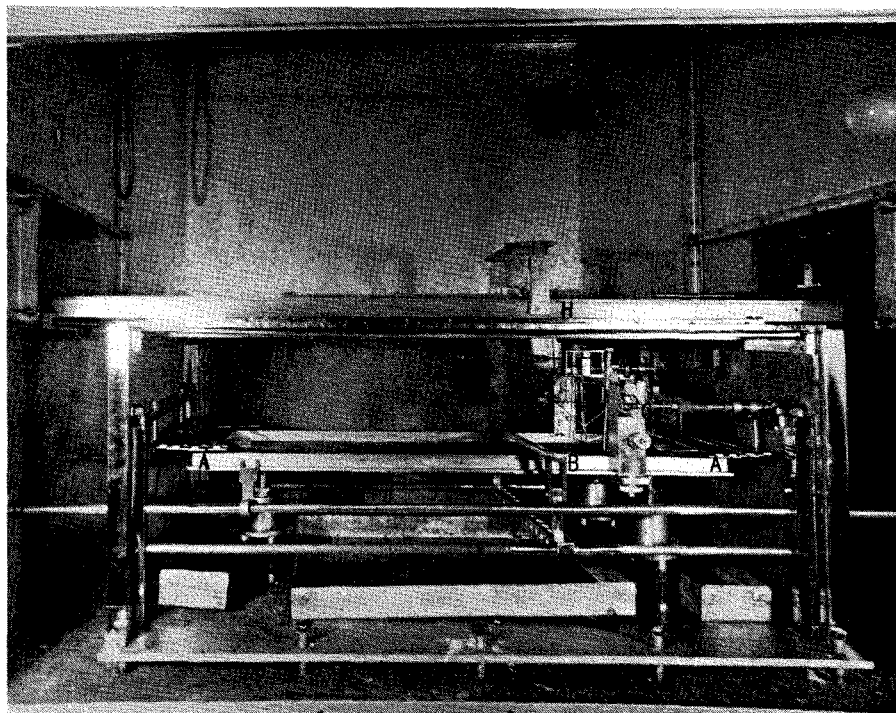


FIG. 1. Trough and film balance inside glass box with front removed. The copper netting is for electrical shielding. The outer box of metal is the air thermostat.

The trough *ABA1* is filled with conductivity water, or with an aqueous solution with a known *pH* made from water free from organic matter. The film is held between a barrier of glass, the front end of which is at *B1*, and a float of phosphor bronze attached to the film balance. The glass barrier is moved by two forks, the front one at *B1*, attached to a slide *E1* underneath the balance. The slide is driven by a screw of known pitch, which is turned by a wheel (*K2*) outside the right end of the thermostat. The number of whole turns of the screw is registered by the counter *M*, and the partial turns by marks on the wheel. By this means the position of the barrier may be read to 0.1 mm. Since all films examined are from 100 to 300 mm in length, the precision here is better than 0.1 percent.

Before the film is put on the surface of the water, and while the glass barrier is still on the left shelf at *A1*, the forks *B1* are set in line with the film balance, and the surface of the water is swept by the use of paraffined brass sweepers which lie on the shelves at *A1*. To pick up a

sweeper a handle outside the left end of the thermostat is pushed and turned. This moves the rods *DD1* and the attached forks at *C1*. In this way any sweeper may be removed from the shelf, brought against the edge of the film balance without touching the surface of the liquid, and then lowered into the surface. The sweeper may then be moved along the surface to the corresponding end of the trough. The surface is thoroughly cleaned by several sweepings while the whole apparatus is kept closed. Also the right end of the trough, which has no film at the surface, may be swept at any time to determine if it has become contaminated.

A more sensitive method for the detection, but obviously not for the removal of uncleanness, is to compress the contamination film against the float by the use of one of these barriers.

When desired the whole surface of the liquid may be swept by barriers from *A1* before the film balance is lowered into its place.

The worm gear device which turns the end of the torsion wire is driven by the rod *G1* which contains an insulating section of amber,

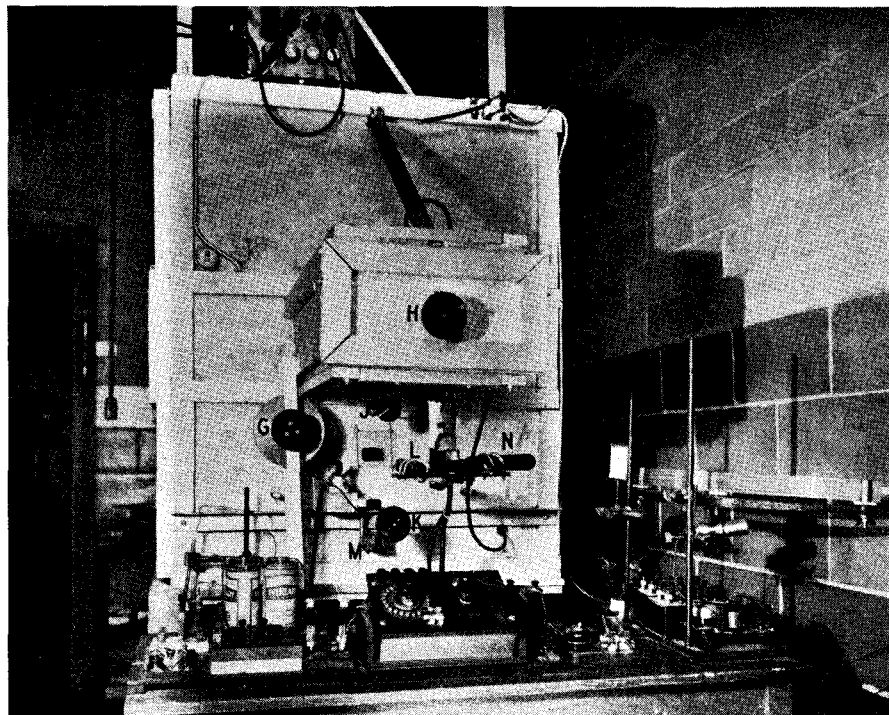


FIG. 2. Right end of air thermostat with controls for film balance, barrier, and electrodes (*H*). The controls for the sweepers are at the left end.

and is turned by the hard rubber disk at *G2*. The bright circle of brass at *G2* has a graduated circle, read by a vernier on its edge. The circle and rod *J2* are used to raise and lower the balance support shown in the photograph (Fig. 3).

The telescope *L2* is used to read the graduated scale in the mirror of the film balance, while that at *N2* is used to read the graduated circle and vernier in the mirror.

The hard rubber circular disk *H2* is used to turn a screw which moves a set of four or more electrodes supported in the brass cover *H1* at the top of the glass box which incloses the apparatus. These electrodes are used to determine the surface contact potentials.

The electrical equipment in Fig. 2 is for the determination of the hydrogen ion concentration of the solution used in the trough. The apparatus used for the determination of the surface potential consists of a potentiometer, a Compton electrometer, and silver electrodes coated with polonium, as described by Harkins and Fischer.<sup>3</sup>

<sup>3</sup> W. D. Harkins and Fischer, *J. Chem. Phys.* **1**, 852 (1933).

### 3. FILM BALANCE

The details of the film balance itself are shown in the photograph (Fig. 3) and the drawing (Fig. 4). The description, the letters of which refer to Fig. 4, gives particular attention to the improvements or changes which have been made in the new design.

The measurement of film pressure is carried out, as heretofore, by a determination of the torque in the torsion wire *A4* which is necessary to return the float *B4* to its zero position.

1. The gold ribbons *C4* are 3 mm high, 0.01

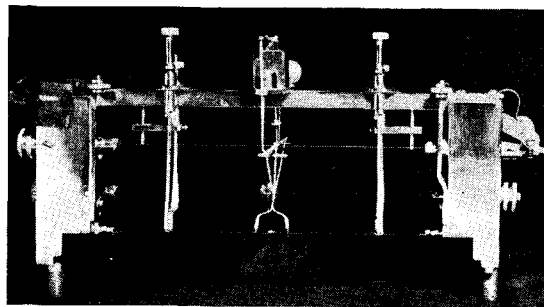


FIG. 3. Film balance.

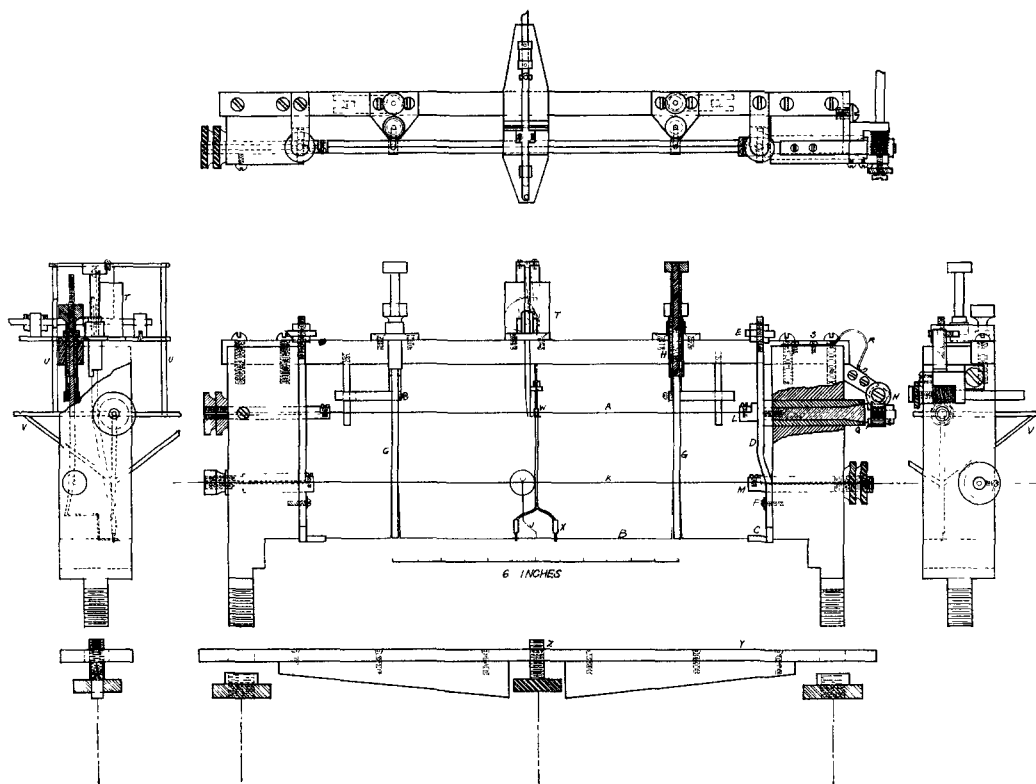


FIG. 4. Details of the film balance.

mm thick, 1.5 cm long, but are buckled to give a horizontal distance of 1 cm. They are attached to vertical strips *D4*, rather than to the posts of the torsion head. These strips *D4* may be adjusted in a vertical direction by means of screws *E4*, to bring the float and ribbons into the same horizontal plane, in order to adjust for differences in level of the liquid in the trough. The vertical strips are clamped tightly to the posts by means of screws *F4* to prevent leaks between the strips and the posts. This type of construction is very important in the prevention of leakage of the film past the float.

2. The gold ribbons *C4* are attached to the float and to the vertical strips by means of Wood's metal, which obviates the use of corrosive fluxes, high temperatures and ordinary solders, all of which destroy the flexibility of the gold ribbons.

3. The float *B4*, of rolled phosphor bronze strip, is supported when not in use by two clamps, *G4*, rather than the single-acting device of Adam. The clamps operate independently.

The lower half of each clamp raises the float, the upper half presses down by an enclosed spring, *H4*, and this construction does not allow the float to be raised and stored in a cramped position, as may sometimes occur if the two arms of Adam's single device are not exactly in line.

4. The small wire *J4* which connects the float to the mirror is one mil silver wire, carefully soldered at each end.

5. The torsion wire *A4*, as well as the lower wire *K4*, both of phosphor bronze, are clamped at each end by clamps *L4* and *M4*, the details of which are shown in the drawing. The wires pass through the clamps as shown. These screw clamps make it unnecessary to solder the phosphor bronze wires at their ends. This is important since such soldering often destroys the temper of the wires, thus causing them to lose their elasticity.

6. The torsion wire is driven by a worm-gear device *N4*, operated by a shaft leading to the exterior of the apparatus. Fractions of a degree

of arc are read on a drum and vernier on the outside shaft, which enables the pressures to be determined while the entire apparatus is enclosed and in total darkness. The wire is calibrated in terms of the outside drum, and hence any slack or irregularities in the worm-gear device are included in the calibration.

7. The end of the torsion wire next to the worm-gear is clamped to a conical piece of stainless steel *P4* which fits into a brass sleeve *Q4*. This enables the wire to be drawn taut from the other end, and the worm-gear end of the wire is centered automatically.

8. A phosphor bronze spring *R4* which may be adjusted by a screw *S4* allows the worm to be fitted neatly into the worm-gear without undue friction of the gear teeth.

9. The attachment *T4*, shown more plainly in Fig. 3, *T3*, operates like the eccentric beam elevator of a balance, and is a valuable aid in both the calibration of the torsion wire and when working with the balance in the determination of film pressures. In its use, the vertical arms *U4* may be raised to such a position that they exert a very slight vertical pull on the float, which is thus clamped into its "zero" position. In this position weights may be attached to the ends of the triangular stirrup *V4* without a disturbance of the float and ribbons. We have found the disturbance of the float and ribbons to be very considerable without the use of this device, and this often leads to an erroneous calibration. Again, after a determination of film pressure, it is advisable to check the "zero point" of the balance, that is, the position of the float without any film on the water surface. In the earlier technique, the film was swept away, while an attempt was made to turn the wire back through its arc without a loss of equilibrium. As often happened, the float would shoot forward and exert undue torque on the wire. With the elevating device the wire can be clamped in the central position while the surface is swept several times, the drum may be turned to the zero reading, and the stirrup slowly released to check the zero-point reading. With this device we have never failed to check the zero point after adequate sweeping, whereas without the device, undue torque would disturb the float so that the zero position could not be obtained.

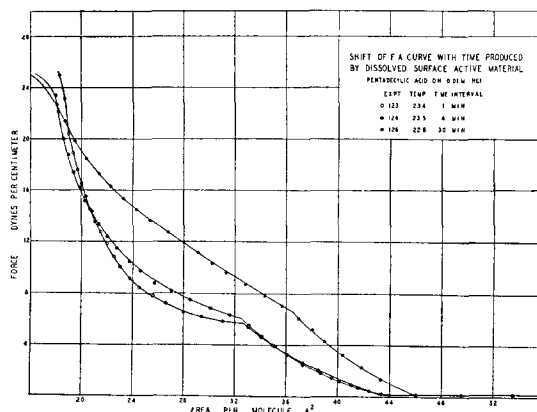


FIG. 5. Effect of dissolved surface active material.

10. All parts other than the float, ribbons, stirrup and stainless steel conical shaft were made of brass, then nickel- and chromium-plated, to resist corrosion.

11. The triangular stirrup or balance beam *V4* was produced from a sheet of Dow metal in which the open spaces were made by drilling out the metal and filing the edges. The beam was fitted with a brass ring *W4* bolted to the beam and the phosphor bronze wire was soldered to this brass tube. Great care is necessary in soldering the wire; the heat is applied as little as possible, since the temper of the wire may be destroyed at this spot. On very acid solutions the Dow metal was attacked, due to its magnesium content, hence brass sleeves were fitted over the fingers *X4* which pass through slots in the float. The whole beam is lightly paraffined to prevent corrosion from the acid fumes.

12. The torsion head is clamped to the trough by a bar *Y4* which acts as a spring when the thumb screw *Z4* is turned. This enables the torsion head to be removed directly from the trough, without injury to the paraffin surface.

#### 4. ADJUSTMENT OF VAPOR PRESSURE

In the production of polymolecular films a mixture of a surface-active substance with an inactive oil is used. Often this oil is moderately volatile, so to reduce its evaporation, shallow troughs filled with the oil are kept inside the glass box, and a slow stream of nitrogen is bubbled through the oil to keep the pressure of the vapor more nearly that of saturation.

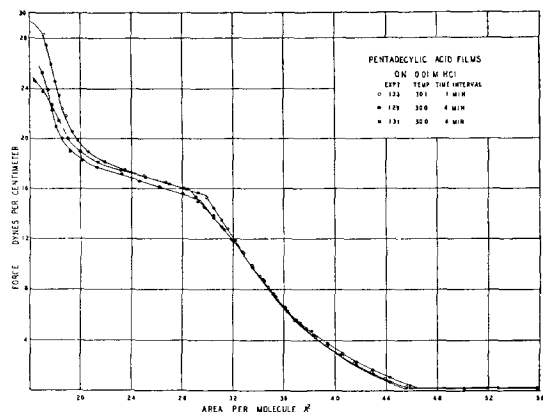


FIG. 6. Reproducibility of force-area curves.

To prevent undue evaporation of the solution in the trough during extended experiments, a second stream of nitrogen passes through a beaker of the same solution as that in the trough. This saturates the atmosphere above the film with water vapor.

## 5. WATER

Since the pressure of a film is a function of the hydrogen ion concentration, and because ordinary tap and distilled water often contain organic impurities, it is important to use only very pure water as the substratum for the film. The method of purification now employed in this work is that of Ellis and Kiehl.<sup>4</sup>

The effect of poor water is illustrated by Fig. 5. Films of pentadecylic acid on a 0.01 molar solution of hydrogen chloride in ordinary distilled water as used in the laboratory for analytical work were used. The film pressure was determined with time intervals between successive readings of 1, 4, and 30 minutes, respectively. While the film pressure is a function of the time, the wide spread between the curves in this figure is due largely to impurities in the water. With very pure water the curves with 1 and 4 minute intervals are almost identical in the region of the expanded film (Fig. 6), and a shift to lower areas with longer time intervals, is observed, as to be expected.

## 6. CLEANLINESS

Before each experiment the trough is freed from paraffin and cleansed by holding it very

close to a jet of hot steam. The paraffin emulsifies and is carried away. The barriers are cleaned by the same procedure. The trough is then coated with paraffin while warm by painting with a solution of paraffin in a low boiling paraffin oil (ligroin) free from active materials. Care is taken not to allow the hands to touch the barriers or any part of the trough which later comes in contact with the aqueous solution with which the trough is filled.

In some laboratories more than one film is spread on the same aqueous solution. While moderately good results may be obtained in this way, our experience indicates that a higher degree of accuracy is attained if a new aqueous solution or fresh water is used for each film.

The air in the box which contains the trough and film balance should not be stirred since motion of the air brings its impurities into the surface of the liquid. In our apparatus, as already described, the moving air of the air thermostat, when this is used, is kept away from the trough and film balance by the inner box of plate glass.

## 7. SPREADING THE FILM

In work on equilibrium pressures monomolecular films are spread from crystals of the solid or lenses of the liquid, or the solid may be spread from its coating on a glass plate or rod.

In work upon the pressure-area relations the film is usually spread over a large molecular area by the use of a dilute solution of the film forming substance in a highly volatile paraffin oil, in benzene, or in chloroform if the substance is not soluble in the other solvents.

The high volatility of the solvent is essential for its removal from the film, but is a source of error in weighing the amounts of solution used. Obviously this particular error may be reduced by the use of a more dilute solution, so the accuracy given below refers to solutions of the concentration usually employed.

The error in weighing solutions of the ordinary concentration (order of 5 percent as given by Adam,<sup>5</sup>) is reduced to about 0.25 percent by the use of the weight-pipette shown in Fig. 7. The bottle consists of two necks, one for filling, one for dropping, each fitted with two caps, with

<sup>4</sup> S. B. Ellis and S. J. Kiehl, *J. Am. Chem. Soc.* **67**, 2145 (1935).

<sup>5</sup> N. K. Adam, *The Physics and Chemistry of Surfaces* (Clarendon Press, 1930).

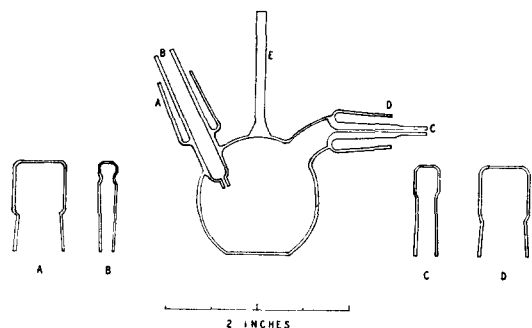


FIG. 7. Weight pipette for spreading solutions. Good tight joints on all caps. C-flat (drop-weight) capillary tip.

tightly fitted ground joints. The dropping tip is a fine capillary, the end of which is ground flat, according to the directions given by Harkins and Humphrey,<sup>6</sup> for the preparation of tips for the determination of surface tension by the drop-weight method. It is essential that this tip be as flat as possible. When properly made, the tip will prevent the solution from "climbing" around the edge of the tip-face, the drops form easily and cut off neatly as they fall.

The bottle is filled with a small funnel fitting into the left neck, the caps are placed in position and the bottle weighed, preferably with a similar bottle for a counterpoise, to five decimals, on the balance mentioned below. The cap joints must be dry during weighings. The solution is dropped on the surface by removing the two caps over the capillary tip, and tipping the bottle to allow the solution to flow into the capillary.

Slight warming with the fingers on the cloth by which the weight-pipette is held usually suffices to form four or five drops which fall slowly from the tip. When the bottle is returned to its normal position, the solution flows back into the large chamber, and leaves an almost negligible quantity on the tip-face. The caps are quickly replaced and the bottle reweighed. The bottle is handled with a clean cloth, and wiped carefully before each weighing. No correction is made for the quantity which evaporates from the tip-face, since various experiments have shown this to be of the order of 0.03–0.05 mg, while the total quantity delivered is 40–50 mg. *This precision can be attained only with a very flat tip-face.*

<sup>6</sup> W. D. Harkins and E. C. Humphrey, J. Am. Chem. Soc. 38, 228 (1916).

## 8. ACCURACY

The screw, which measures the length of the film, may be read to 0.1 mm, or better than 0.1 percent. The graduated drum used to read the pressure on the film balance is geared 20–1 to the torsion wire, which was a high pressure wire (0.0125 inch diameter), and is never turned through more than 30°. The drum is fitted with a vernier, and is read to 0.02 dyne per centimeter although pressure differences less than 0.01 dyne per centimeter are easily detected. Resetting of the drum can be checked to within 0.04 dyne per centimeter. The temperature was controlled to less than 0.1°C but this will soon be improved to 0.005°. The precision of the area and force recording devices might be easily increased, but the error in weighing, as in all work of this character, limits the accuracy. To reduce this error, a special Ainsworth balance weighing to five decimal places was used, whereby the error in the area per molecule was reduced to about 0.25 percent. Assuming all errors to be additive, the accuracy is probably of the order of 0.5 percent.

An important feature of the apparatus, which increases the accuracy, is the moderately tight plate glass box, which incloses the trough and film balance. This decreases greatly the evaporation of the volatile constituents on the surface, and greatly reduces the contamination from vapors, liquid droplets, and dust.

Curves which illustrate the accuracy of the apparatus are exhibited in Fig. 6, which gives two determinations of the pressure-area relations at 30°. Here the time interval between successive readings is 4 minutes. A third curve, Expt. 133, gives similar values at 30.1° with time intervals of 1 minute.

With smaller torsion wires the apparatus may be made to show differences of pressure of about 0.001 dyne per cm, but the accuracy will seldom be so great.

With these improvements considerable ease and precision have resulted. The apparatus was constructed by Mr. R. Kittel, instrument maker of the Department of Chemistry, University of Chicago. Deepest thanks are due him for valuable suggestions throughout the construction of the instrument.



## 9. RATE OF COMPRESSION

A study of the effect of the rate of compression on the character of the  $F$ - $A$  curves of pentadecylic acid films was made. The results of a few experiments are shown in Fig. 8. Time intervals of one to four minutes give essentially the same force-area curve, with collapse at somewhat lower pressures associated with the slower compressions, but intervals of ten minutes or longer cause considerable shift of the curve in its upper portion, probably due to solution of the film in the substrate. An arbitrary time interval of two minutes was selected in the preliminary experiments as suitable. This allowed the film to come to equilibrium under each pressure increment, and the total time was short enough to overcome any appreciable solution of the film. As a further precaution against dissolution, the substrates were made 2 molar in sodium chloride (fused, grease-free). The sodium chloride apparently causes only a slight shift in the curve, *in toto*, to somewhat larger areas, without affecting the other characteristics. In this connection the shift with time caused by dissolved substances, shown in Fig. 5, may be mentioned again as an indication of the care to be exercised in the examination of a time effect.

## 10. EFFECT OF HYDROGEN ION CONCENTRATION

The effect of the hydrogen ion concentration of the substrate upon the force-area curve of myristic acid films at 22° is shown in Fig. 9. Upon substrates which ranged from  $pH$  2 to  $pH$  6, practically no difference in the  $F$ - $A$  curve was observed. Upon a solution of  $pH$  6.5 the film is expanded at low pressures but approaches the curves given on lower  $pH$ 's as the pressure is increased. With further increase in alkalinity to  $pH$  7.3 the film becomes very expanded at low pressures, the kink disappears, and a smooth hyperbolic curve which extends to very small areas with no definite collapse point, is obtained. Upon 0.01 *m* NaOH, the film becomes quasi-gaseous in character, but the film contracts throughout the compression, probably due to both dissolution and collapse on this alkaline substrate. There appears to be no simple relationship between the character of the  $F$ - $A$  curve and the  $pH$  of the substrate, other than an increased

expansion on solutions of  $pH$  6.5 and above. This may be attributed qualitatively to repulsion of the more highly ionized heads, but no quantitative correlation is immediately apparent. It is worthy of note that the  $F$ - $A$  curve remains quite unchanged from  $pH$  2 to  $pH$  6, although there should be a considerable ionization of the head groups in the region  $pH$  4-6.

## 11. COLLAPSE PRESSURES

The collapse pressure of the film is largely dependent upon the rate of compression. A slow compression results in a lower collapse pressure. There seems to be no simple relationship between the collapse pressure and the hydrogen ion concentration of the substrate. However, upon slow compressions (of the order of four-minute time intervals, and longer), the second curved portion of the  $F$ - $A$  curve, above the kink-point, is not observed. The films then collapse at pressures but slightly above the kink-point. This suggests that the kink may possibly be at the pressure necessary to remove the fatty acid molecule from the water surface, and may not be a phase transition or an intraphase aggregation as has been postulated by various investigators. This will be studied further.

## 12. EQUILIBRIUM PRESSURES

The equilibrium pressures of myristic acid crystals upon substrates of  $pH$  2 to 8 was determined by immersing a glass rod in a melt of the acid, allowing the liquid to solidify, and

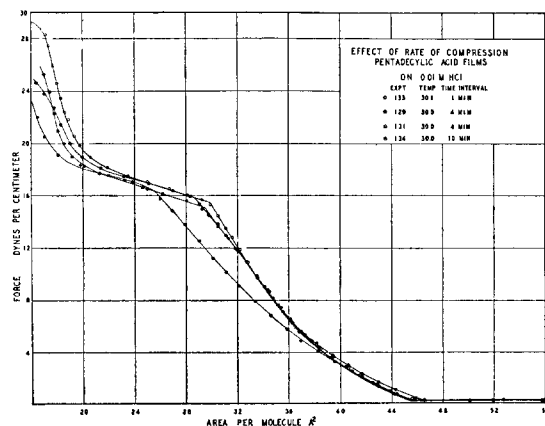


FIG. 8. Effect of time on the pressure-area relations of films of pentadecylic acid on water.

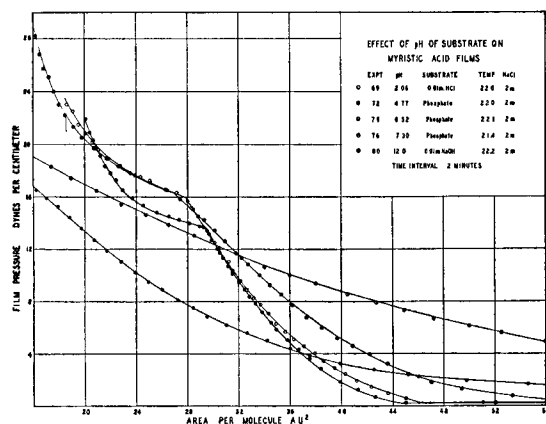


FIG. 9. Effect of hydrogen ion concentration on the pressure-area relations of films of myristic acid.

inserting the rod into the surface of the liquid in the film trough. The film pressure built up by the crystals, after reaching a maximum, fell to lower values when alkaline solutions were employed. The results are shown in Fig. 9. The equilibrium pressures were quite constant through the range  $pH$  2–4.5, then fell rapidly with further increase in alkalinity. On 0.01  $m$  sodium hydroxide (+2  $m$  NaCl) the equilibrium pressures rose again to 12.1 dynes, but there was no inflection point in the region  $pH$  5, as might be expected if the film behaved as a fatty acid in bulk. There appears to be no relationship between the  $pH$  and the equilibrium pressures of the crystals which would yield information concerning the amount of ionization of the film material.

The variation of equilibrium pressure with temperature is also shown in Fig. 9. The value of  $dF/dT$  is 0.575 on  $pH$  2.05, in good agreement with the value 0.568 given by Cary and Rideal.<sup>7</sup>

Though these results are not so striking as with proteins, they indicate a different method of attack, which should yield results of a more definite nature. A consideration of the spreading coefficient,

$$S = \gamma_1 - \gamma_2 - \gamma_{12} = P_{\text{collapse}},$$

where  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_{12}$ , represent the surface tensions of the water, oil and interface re-

<sup>7</sup> E. Cary and E. K. Rideal, Proc. Roy. Soc. **A109**, 318 (1928).

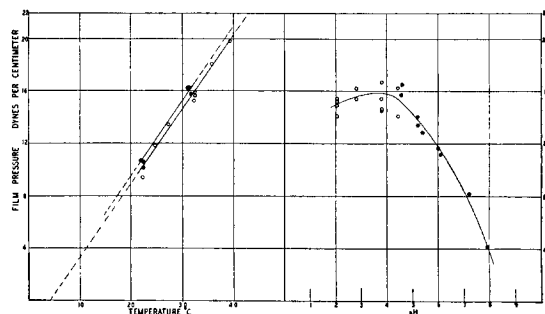


FIG. 10. Equilibrium pressure of myristic acid on water as affected by temperature and by hydrogen ion concentration. Left, equilibrium pressure of myristic acid crystals at various temperatures. Open circles,  $pH$  2.05; black circles,  $pH$  2.82. Right, equilibrium pressures of myristic acid crystals at 31°. Open circles, HCl; black circles, phosphate; half circles, bicarbonate.

spectively, indicates that the collapse pressures of liquid fatty acid films, when they collapse in a reversible manner, should be a function of the interfacial tension, which in turn has been found by several investigators to be a function of  $pH$  of the water phase, in an oil-water system when there are active molecules in the oil. Thus there should be some relationship between the collapse pressure of the film and the  $pH$  of the aqueous phase. In the above experiments this proved not to be the case, but it must be remembered that this was a solid fatty acid, and the collapse does not take place reversibly. However, with films at the interface oil-water, collapse should take place in a reversible fashion, since the fatty acid molecules can enter the oil phase with ease and then spread again when the film pressure is reduced. Ordinary oils possess too high an attraction for fatty acids to be used in this way. It will be essential that such an oil possess:

1. A relatively high interfacial tension against water.
2. A negative spreading coefficient.
3. A density greater than that of water.
4. Very slight solubility in water and hydrocarbons.

The apparatus described in this paper may be used to examine fatty acid films at such an interface, and preliminary experiments indicate that such films form with ease at the interface trichlorethane water, by spreading from a crystal on a glass rod. The trough has been modified to study such films and the work is being continued.