AN INVESTIGATION OF THE ORIENTATION OF CERTAIN LONG-CHAIN FATTY ACIDS AT THE AIR-WATER INTERFACE.

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A Thesis submitted in part fulfilment of the requirements for the Degree of Master of Science of Rhodes University.

By

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A C K N O W L E D G E M E N T S.

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C O N T E N T S .

I. INTRODUCTION.

When a small quantity of insoluble and non-volatile material is placed on the surface of a liquid (usually water which has a high surface tension), with which it does not react chemically, this may either remain as a coherent solid mass leaving the surface of the liquid clean, or spread and cover the whole surface. In what follows it will be assumed that the liquid to be used is water, but it should be noted that similar procedures may be used for any not-too-volatile, non-hygroscopic liquid.

The condition for spreading is that the molecules of the material should attract those of the water more strongly than they attract one another, that is, the molecules should possess polar groups, for example, $-CH_2OH$ or -COOH groups. Examples of such spreading materials are certain long-chain fatty acids and alcohols. Many of these are solids at ordinary temperatures, but they can be made to spread as thin films on aqueous surfaces by placing small quantities of a solution of the substance in a volatile solvent, such as benzene or petroleum ether, on the water surface and allowing the solvent to evaporate.

If the condition for spreading is fulfilled, as many of the molecules of the spreading substance as possible will endeavour to get into direct contact with the water surface. On compressing these molecules which are scattered over the surface, between barriers, a surface film is formed on the substrate. Depending on the structure of the molecules, the surface film may be composed of a single layer of molecules or a multimolecular layer.

In monomolecular films the molecules are usually arranged in a simple manner, and from a study of such films one can readily obtain data regarding the shape and orientation of individual dimensions, molecules or polar groups.

Monomolecular surface films (monolayers) have been found to have measurable effects on the mechanical, optical and electrical properties of the surfaces on which they are spread. The method usually employed for studying such films is to measure the outward force exerted on a boundary which confines the film within a definite area on the surface. By gradually diminishing the area covered by the film until it resists further compression, it is possible, by a graphical method, to calculate the

- area occupied -

area occupied per molecule in the closely packed monlayer.

The method described above is based on results obtained with Langmuir's original surface pressure balance. This consists of a rectangular trough for containing the substrate liquid and a set of barriers for confining the surface film. The force on the film is usually measured by the torsion of a wire which is connected to a more or less mobile barrier in the surface of the substrate.

Another method whereby molecular cross-sectional areas may be obtained, is with the aid of a Wilhelmy vertical pull surface balance. This technique uses a small glass slide dipping into the substrate liquid. The contact angle which the slide forms with the substrate is zero. The substrate surface exerts a vertical downward pull on the slide which in turn is connected to one arm of an analytical balance or to a torsion device. The difference between the downward force, exerted by a clean surface, and that of a film-covered surface, gives the total force exerted by the film. The area of the substrate may be altered, as in the case of Langmuir's design, by means of mobile barriers. From a plot of the force exerted by the film and the area covered by the film it is possible to obtain data relating to the cross-sectional areas and hence orientation of individual molecules.

However, the present research concerns itself mainly with the horizontal type of surface balance as originated by Langmuir and only passing attention will be paid to the Wilhelmy method.

II. HISTORICAL REVIEW OF THE DEVELOPMENT AND APPLICATIONS OF THE SURFACE FILM BALANCE.

Soon after the concept of surface tension had been introduced, Lord Rayleigh, among others, discovered that contamination due to a film of oil or grease on the surface of water, lowered the surface tension of the water quite markedly.

The origin of the first surface pressure balance may be traced back to 1891, for it was in May of that year that Rayleigh received a letter from a German lady, Fraülein Agnes Pockels[1]. In this letter Fraülein Pockels described a simple method, which had been employed by her, for handling surface films by pushing them in front of barriers extending the whole width of the trough.

She made use of a rectangular tin trough 70 cm long 5 cm wide and 2 cm high, which could be filled with water up to its brim. A strip of tin about 1.5 cm wide was placed across the trough so that the lower edge of the strip made contact with the surface of the water. This barrier, serving as a partition for dividing the trough in two, could be shifted along the length of the trough thus shortening or lengthening the surface on either side in any desirable proportion. The extent of displacement of this mobile partition could be read off from a scale held along the front of the trough.

The apparatus suffered from leakage between the partition and the sides of the trough, particularly during the process of shifting the barrier along the length of the trough edge.

The surface tension could be measured in any part of the trough by means of the force that was necessary to separate a small disc, about 6 mm in diameter, from the substrate surface. In order to determine this, a small balance, with unequal arms and a sliding weight was utilized. Fraülein Pockels found that the surface tension of contaminated water varied to a certain extent with the size of the surface. She spread vegetable oils and "spirits of wine" (ethyl alcohol) on the substrate surface, stirred up waves at the one end of the trough and studied the effect of contamination on the number of wave passages.

In order to clean the surface, the partition was placed at one end of the trough and moved along towards the middle. The surface, thus formed

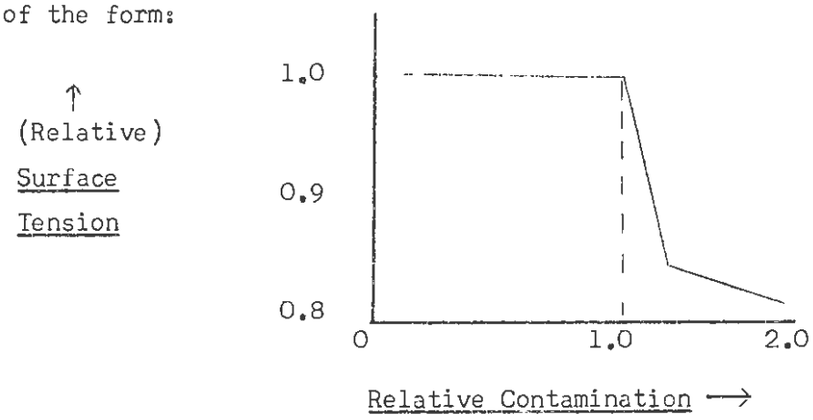
on the one side, was found to be reasonably clean.

The effects of solid bodies, for instance glass, tinfoil and wax on the water surface were also studied. It was found that all these substances lowered the surface tension of the water and a "contamination current" was set up. This could be rendered visible by sprinkling Lycopodium powder or sulphur flowers on the surface.

A typical experiment which was carried out by Fraülein Pockels consisted of dipping a glass plate into the substrate surface on one side of the barrier and a metal plate on the other. The surface was then dusted with Lycopodium powder and the partition removed - a decided current set in from the glass contaminated side towards the metal contaminated side.

In 1893 Fraülein Pockels[2] published a further article on the relation between the surface tension and relative contamination of water surfaces. However, instead of placing a partition across the surface, she used a floating wire in order to find some relation between the relative contamination and the decrease in the surface tension. The method employed for measurement of the surface tension was by separating the weight of a ring of thin wire, with a circumference of 114 mm from the surface. This wire was cleaned by ignition to enable it to be moistened entirely by the liquid contained in the trough.

She spread tallow, poppy and olive oils on the substrate surface and then compressed the films between mobile barriers while measuring the surface tension by the method described above. On plotting the surface tension versus the relative contamination of these oils, she obtained typical graphs of the form:



However, when the surface of the water was contaminated by soap, resin or palmitic acid, the surface contracted, the surface tension first decreased sharply and then gradually increased, while the surface area remained

- constant. -

constant. Stearic acid was found to render the surface more or less solid as soon as the surface tension decreased.

Fraülein Pockels found these various phenomena rather complicated and could not satisfactorily explain the results she had obtained.

Lord Rayleigh[3] repeated many of the experiments initiated by Fraülein Pockels and made further applications of the methods she had devised. He put forward the theory that olive oil molecules spread on the surface of water until they form a single layer of molecules touching one another over the entire surface, at a certain critical pressure.

Rayleigh's apparatus consisted of a long narrow trough to contain the substrate liquid. The oils were prevented from spreading over the whole surface by barriers consisting of strips of glass placed across the tray and resting on its edges. By sliding these barriers along, the area of water surface could be varied at will. He measured the surface tension by the Wilhelmy plate technique.

During 1917 Irving Langmuir[4] published his now historic manuscript on "The Constitution and Fundamental Properties of Liquids" in which he described a surface balance used for determining the cross-sectional areas of various long-chain acids and other related compounds.

The balance consisted of an enamelled tray 60 cm long by 15 cm wide. Above this trough a small balance was erected with a knife edge resting on a glass plate. One end of the balance beam had a counter-weight, while the other had a small knife edge from which a pan was suspended. Two glass rods, which were cemented to the knife edge, extended downwards and passed through two small holes in a strip of waxed paper which floated on the substrate surface. The strip was so arranged that it did not come into contact with the sides of the trough. Any leakage past this paper barrier was effectively prevented by having two jets of air directed against the surface of the water between the edges of the trough and the barrier.

He dissolved oils and certain long-chain fatty acids in benzene and spread these on the surface of the substrate liquid by means of a pipette.

These surface films were then compressed between barriers and the force required to do this, was balanced against weights on a pan attached to the balance beam. The water in the tray was heated to the required temperature with the aid of Bunsen burners.

- In order to -

In order to determine the cross-sectional areas and lengths of molecules of certain selected substances, Langmuir dissolved these purified materials in freshly distilled benzene (usually 50 mg per litre) and by means of a calibrated dropping pipette, he placed a few drops of the solution on the clean water surface in a photographic tray.

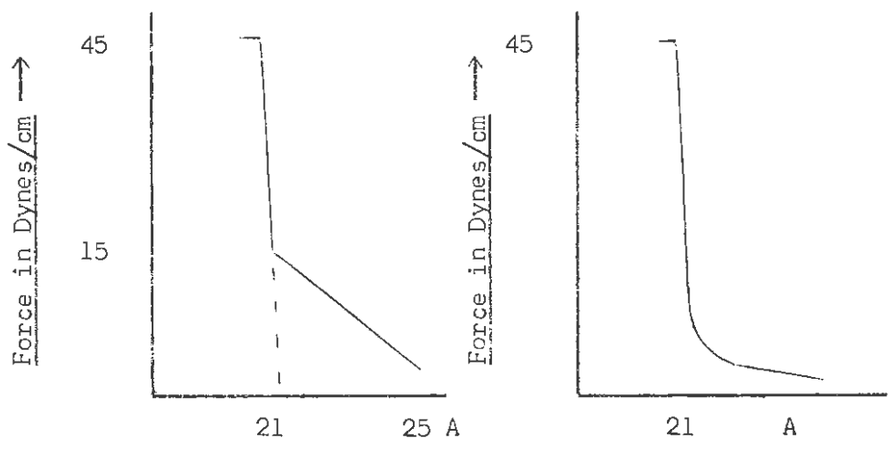
For these selected substances, Langmuir obtained the following representative results regarding their dimensions:

Substance.	Cross-sectional area/molecule.	Length of Chain.
Palmitic acid	21×10^{-16} cm^2	24×10^{-8} cm
Stearic acid	22×10^{-16} "	25×10^{-8} "
Cerotic acid	25×10^{-16} "	31×10^{-8} "
Tristearin	66×10^{-16} "	25×10^{-8} "
Oleic acid	46×10^{-16} "	11.2×10^{-8} cm

From these results Langmuir concluded that the chains of these materials should be regarded as extremely flexible.

During 1921 Adam[5] started an investigation of the properties and molecular structure of thin films of palmitic acid spread on water surfaces. He used Kahlbaum's K quality palmitic acid which had a m.p. of 62.5°C after recrystallization from aqueous alcohol. The benzene employed for spreading the palmitic acid, was free from thiophene and had been twice distilled in an apparatus free from cork or rubber.

He found that the film gave a distinctly different force-area curve when the acid was spread on a neutral water surface from that when it was spread on a slightly acidic substrate.



On Dilute HCl Soln. On Neutral Water Surface.

Adam's experiments proved conclusively that the palmitic acid molecule formed a monomolecular layer with the carboxyl group oriented towards the

- water and -

water and the hydrocarbon chain more or less normal to the surface.

Adam[6] further studied the effect of increasing the temperature on the spreading of films of several surface active agents and found that when the temperature was sufficiently high, a definite change took place in the properties of the monolayer with a considerable increase in the area occupied per molecule. This change appeared to be due to a separation of molecules from one another in the surface. This was probably brought about by the thermal agitation in the surface becoming so violent that the lateral attractions of the molecules, which constitute the main stabilising influence, were overcome.

He also distinguished between "expanded" and "condensed" films. In the former case, the molecules behaved similarly to a gas in two dimensions, while in the latter case, the molecules appeared to be in direct contact over the whole surface area.

Adam pointed out the analogy between surface films and gases. The equation:

$$F.A. = n.R.T.$$

holds for surface films in 2 dimensions, where F is the force in dynes per cm which is necessary to counteract the film pressure; A is the area covered by the film; n is an integer; R the Universal Gas Constant, and T the temperature in degrees absolute. The above equation is very similar to that of the General Gas Equation for gases in 3 dimensions:

$$P.V. = n.R.T.$$

where P = pressure exerted by the gas, V = volume occupied by the gas and the other symbols having the same significance as above.

He found that palmitic, pentadecylic, margaric, stearic, heneicosanoic and behenic acids gave essentially similar curves. Lauric and tridecylic acids were found to be too soluble in water, while cerotic acid would not spread satisfactorily from a benzene solution.

Adam made use of distilled water which had been left in the trough for several days and he measured the temperature of the substrate by means of a thermometer placed in the trough.

In 1926 Adam[7] modified his surface balance somewhat. The same trough 60 x 14 x 1.5 cm was used as in his previous work, but the design of the float was altered. It was made from copper foil, about 11 cm long,

the ends of which carried small vertical strips of copper. To these were soldered strips of gold ribbon about 2 mm wide and having a thickness of about 0.009 mm bent into a $\backsim$ - shape and fixed with its width perpendicular to the water surface.

The torsion head assembly consisted of two phosphor-bronze wires, the lower one carrying a mirror which served to indicate the position of the float. The upper torsion wire was controlled by a head which carried a vernier arm moving over a 180° scale. The torsion head assembly was mounted approximately 10 cm from the one end of the trough and had a microbalance arrangement soldered to it.

He used light sheet-aluminium covers, with windows of thin glass fitted to the front and rear, to exclude draughts and dust from the apparatus. The following procedure was used for cleaning the trough: It was first cleaned with very fine emery cloth under running water, then rinsed with boiling water. It was then coated with paraffin wax, using a solution of this in benzene. The float and upper sections of the vertical gold ribbons were also paraffined in a similar way.

Leakage past the barriers and ribbons was prevented by pushing these down into the water a couple of times.

In order to clean the substrate surface, Adam moved paraffined glass barriers across the surface a number of times and collected the contamination behind these barriers at the one end of the trough.

He made use of an optical system for indicating movement of the float and put the films on to the surface with the aid of a very fine, calibrated dropping pipette. It was generally possible to obtain steady pressure readings within one minute of spreading the film.

Adam found that benzene and toluene, which had been carefully purified by distillation, apparently did not evaporate immediately after spreading. Thus he put forward the theory that this was due, not to the presence of non-volatile impurities but rather to the slight solubility of these solvents in water. Petroleum ether of b.p. 60 - 70°C was found to be slightly better in this respect.

In order to estimate the amount of contamination, he reduced the area of the "clean" surface to one quarter of its original area by moving the barrier along the trough. On a freshly cleaned surface he found

this increase in the pressure was less than 0.03 dyne /cm, and hence he concluded that the amount of contamination was so small as to be negligble.

Woog[8] investigated the orientation of certain oils and fatty acids on aqueous surfaces. He came to the conclusion that the orientation of monomolecular films of these materials was in some way dependent on the number of surface active groups in each molecule. At low surface pressures, the molecules were spread at random on the subphase, but as compression was increased, the film attained a rigid structure with the molecules arranged in the characteristic vertical position.

Woog[9] also carried out some work on the resistance to rupture, lateral compression and on the equilibrium states of monomolecular films spread on water surfaces from various selected solvents.

Towards the close of 1925 Harkins and Morgan[10] published their investigations on polymolecular and monomolecular surface films. They were concerned particularly with the orientation of phenanthrol, but also carried out research on stearic acid films spread on water and salt solutions.

The surface film balance used by Harkins et al.[11], consisted of a glass trough similar to the one used by Fraülein Pockels. The torsion head assembly resembled that used by Adam with minor modifications. The trough was erected on three adjustable supports, and kept inside a box made of plate glass. A heavily galvanised cold-rolled steel sheet served as a base. This base-plate could also be levelled by means of adjusting screws. The entire apparatus was enclosed in a thermally insulated metal container, which served as a thermostat.

Harkins used conductivity water or aqueous solutions of a known pH value, made from water which was rendered free from organic matter. The films were confined between a glass barrier and a float made from phosphor-bronze sheeting. All the accessories of the balance could be manipulated from outside the thermostat.

The torsion wire was twisted by a worm-gear connected to a circular graduated scale and could be read by means of a vernier attachment along its circumference. A telescope and a complex system of mirrors formed part of the optical null indicator.

The measurement of film pressures was determined by torque in the torsion wire necessary to return the float to its zero position.

- To prevent -

To prevent leakage past the ends of the float, Harkins made use of gold ribbons, 3 mm wide, 0.01 mm thick and 1.5 cm long, which were buckled up to give a horizontal length of 1 cm. These ribbons were attached to the torsion wire assembly with the aid of vertical strips of metal, one on either side, using Wood's metal, which does not require any corrosive fluxes during soldering, which would destroy the flexibility of the gold ribbons.

The float was made from rolled phosphor-bronze strip and was connected to the mirror, located on the upper torsion wire, by a thin silver wire. This torsion wire was clamped at each end in an adjustable screw clamp. This method was adopted because it obviated the use of solder which could possibly destroy the temper of the torsion wire.

All parts of the balance, except the float, ribbons and stirrups were made of brass which was heavily nickel and chromium-plated to resist corrosion.

Before each experiment the trough was cleaned by holding it in front of a jet of super-heated steam. The paraffin coating was emulsified and washed away. Then the trough was thoroughly cleaned and re-paraffined, ready for the next experiment.

In order to spread solutions of oils and other materials, Harkins and his co-workers used a weight-pipette to measure small volumes of liquid.

During 1927 Müller[12] carried out an X-ray investigation of certain long-chain compounds and, amongst other things, found that the cross-sectional area for the stearic acid molecule was 20.5$\AA^2$. This value compared very favourably with areas which had been obtained by investigators for this particular acid up to that time. For instance, Adam found the cross-sectional area of stearic acid to be 21$\AA^2$.

In the early 1930's a few Japanese workers showed a keen interest in surface phenomena, especially in the orientation of molecules on aqueous solutions. Tamamishi[13] spread such compounds as lauric acid, palmitic acid, cetyl alcohol, cetyl and myricyl-palmitate on water and several other aqueous solutions and determined the areas occupied per molecule for each of these compounds. Typical substrate liquids were: 3% sucrose solution, 0.5 N HCl, 0.5 N KCl, 0.5 N KBr, 0.5 N KI, 0.5 N KCNS, 0.5 N LiCl, 0.5 N NaCl and 0.5 N $MgCl_2$ solutions.

Sameshima and Sasaki[14] studied monomolecular layers by means of the ripple method. Ripples were generated on the surface of the substrate liquid in the trough by an electrically-maintained tuning fork which caused approximately 50,000 vibrations per second.

The height of waves, created by this method, was measured using the reflected light on the wave surfaces. Monochromatic light was passed through a system of lenses and prisms in order to obtain incident light which was absolutely vertical to the surface of the substrate. The beam of light was reflected onto a scale as a band of light of width approximately proportional to the amplitude of the wave.

The trough, used to contain the substrate liquid, and the mobile barriers were made of metal and were heavily paraffined. Two sizes of trough were used, one measuring 14" x 20" for films of constant surface area and multimolecular layers, while the other measured 14" x 15" for films containing a constant quantity of material at different areas.

Tap water was employed and was either made alkaline (pH = $\pm$ 8) or acidic (with 0.04 N HCl) according to the solubility of the substance in water.

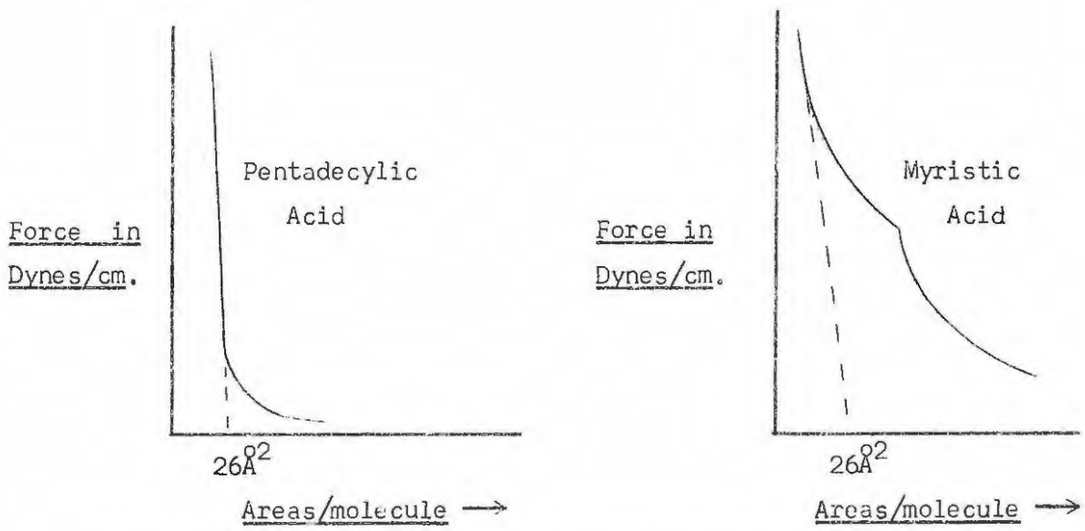
Sameshima and Sasaki found fair agreement, by this method, with values for the cross-sectional areas of certain fatty acids as obtained by previous investigators.

They put forward the suggestion that the larger areas obtained for palmitic acid, stearic acid, myristic acid, oleic acid and tetradecanol on HCl solutions, were due to the fact that the molecules did not orient themselves vertically to the substrate surface during compression until a certain critical pressure had been exceeded. After this point had been passed, the chains attained their vertical orientation.

Havinga and de Waal[15] in 1937 carried out research work on the salts of fatty acids. They employed a Langmuir-type of trough which was paraffined to render it hydrophobic. The entire balance, with its accessories, was enclosed in a thermostatically controlled, thick-walled cabinet with heavy plate glass windows. The mobile barrier and sweepers were controlled by knobs from the outside of the cabinet. They also determined surface potential measurements with the aid of a polonium-calomel cell. This cell consisted of polonium source, which was used to ionise the air

just above the substrate surface and could be moved about on the surface, and a calomel electrode dipping into the substrate liquid. A slight potential difference was set up between these two electrodes and this surface potential could be measured by means of a voltmeter in the circuit. The electrodes could be positioned at any point on the substrate surface from the exterior of the thermostat.

Pentadecylic and myristic acids were spread on a 0.1N HCl substrate and yielded cross-sectional areas of the order of 26Å^2 at a temperature of approximately $20^\circ C$. However, in contrast to the pentadecylic acid isotherm, the myristic acid curve showed an expanded as well as a condensed state.



During the period 1938 to 1939, several Russian scientists, amongst them Achmatov[16], Trapeznikov[17], Pankratov[18], Rehbinder[19] and Frumkin[20] investigated the mechanical properties of, and sorption of long-chain aliphatic compounds from surface films. Achmatov made use of a series of fatty acids to study the adsorption of these materials by charcoal on aqueous substrates. Contrary to the established method of measuring the force exerted on the film, he employed an electromagnetic tensimeter for measuring the two-dimensional pressures.

The apparatus consisted of two coils of wire connected with the aid of a straw rod to the float of a more or less conventional Langmuir-type of trough and barriers. The larger outer coil was fixed rigidly above and below, while the smaller coil was suspended on a thin wire and was thus capable of rotating about a vertical axis. The magnetic axes of these 2 coils were arranged to be at right angles to each other and the torque on the float was proportional to the square of the current passed through the coils. The one end of the smaller coil was attached to the float

assembly.

The measurements were conducted with the aid of a null-indicator. The zero position of the float was recorded by an optical system.

In the final stages of the compression, the pressure was counter-balanced by the electromagnetic field alone.

The sensitivity of the balance was found to be of the order of thousandths of a dyne/cm. However, this sensitivity was rather limited by the impurities of the materials and the surface contamination.

The dimensions of the trough were as follows:
60 x 2.0 x 13.2 cms, and the edges were carefully bevelled and smoothed. To render it non-wetting, paraffin wax was coated evenly over the entire trough.

Trapeznikov studied the mechanical properties of adsorption layers of certain fatty acids and alcohols on aqueous sub-phases and also investigated the influence of the pH of the substrate liquid on these properties.

He made use of a circular corrugated disc suspended from a torsion wire arrangement. This disc was positioned in the substrate liquid which was contained in a Langmuir trough.

The torsion was measured by an optical mirror-cum-scale system. From his measurements, Trapeznikov was able to calculate the film strength, surface concentration, viscosity and elasticity of monomolecular layers.

Pankratov, on the other hand, investigated the adsorption of ions on films of organic compounds and also the influence of this adsorption on intermolecular forces.

All surface pressure measurements were made with a torsion balance similar to the one used by Adam and Jessop, while surface potential measurements were carried out with the aid of a Compton electrometer and a radioactive air-electrode.

All chemicals were of C.P. quality. He spread films of ethyl palmitate on such varied electrolytes as 1 N K_2SO_4, 3.3 N $CaCl_2$, 1 N KBr, 3.3 N KCl, 3.3 N Nacl, 3.3 N KBr, 8 N $CaCl_2$ and 3.3 N KI solutions.

According to Frumkin, inorganic electrolytes charged the solution-air interface negatively, while Pankratov discovered that the increase of the negative charge of the substrate surface, by these electrolytes, could be arranged in the following order:

$$SO_4^{2-} < Cl^- < Br^- < I^-$$

- This -

This sequence also gave the order of decreasing hydration of the electrolytes.

Trapeznikov[21] further ascertained that the previously observed high stability of palmitic acid films on neutral substrate surfaces, was due to the formation of a soap film with polyvalent cations. On surfaces devoid of cations, the palmitic acid monolayers remained slightly viscous right up to the point of collapse. Furthermore he found that the length of the hydrocarbon chain and the polar hydrophilic group determined the mechanical properties of the film.

Washburn and Wakelham[22] determined the flow of unimolecular surface films of stearic acid. The stearic acid used had a m.p. of 68.9°C. This compared favourably with the mp. of 69.3°C listed in "International Critical Tables." Reagent grade benzene was ued as solvent for the acid. Redistilled water, buffered with citric acid and Na_2HPO_4, was employed as substrate. The pH of this buffer was measured by a colorimetric method on a "Wulff" pH tester.

The film balance bore a similarity to the Adam balance and was erected inside a small glass-sided, wooden cabinet to keep it free from dust.

A study of the pressure-area relations for stearic acid films indicated that the transition, from viscous to solid form, took place at a pressure of approximately 27 dynes/cm for pH values of the substrate liquid between 3.8 and 7. The collapse of the film occurred at about 40 dynes/cm on the more acidic solution, while on the neutral substrate it was found to take place at the much higher pressure of about 60 dynes/cm.

Adam[23], in his article on "Molecules and Surfaces" written in 1939, reviewed the ideas on orientation of monomolecular layers up to that date, and attempted to explain certain curious phenomena associated with films of long-chain compounds. His surface film balance was again used to gather data relating to such monolayers.

In the same year, Nutting and Harkins[24] studied the pressure-area relations of certain fatty acids and alcohols. All films were spread on 0.01 N sulphuric acid solutions at temperatures ranging between 20 and 25°C. The solvents employed for dissolving the materials, usually consisted of benzene or petroleum ether of b.p. 60 - 80°C. They found that benzene spread fairly slowly on H_2SO_4 solutions.

Monolayers of stearic acid were also spread on 0.01 N HCl solutions with either 0.01 M $Cu(NO_3)_2$ or 0.01 M $Zn(NO_3)_2$. The isotherms were found to be no different from those of stearic acid spread on the HCl solution alone.

McBain and Perry[25] applied the surface balance technique to materials spread on solutions of various salts. The torsion wire of the balance was of 0.33 mm diameter phosphor-bronze and this enabled the readings to be reproducible to 0.03 dyne/cm. The balance was housed in a cabinet made of glass and was lined with cheesecloth strips dipping into water trays. This enabled the operators to maintain the relative humidity inside the cabinet between 95-100%.

The interaction between adsorbed substances and insoluble monolayers was studied by Adam, Askew and Pankhurst[26] in 1939. They employed a silica trough for doing surface potential measurements; otherwise a brass trough, which was paraffined, was used.

They spread myristic acid monolayers on butyl alcohol, butyric acid and 0.02 N HCl solution. Both myristic acid and palmitic acid were also tried on a substrate consisting of an aqueous solution of phenol at 22°C.

McBain, Vinograd and Wilson[27] effected an improvement in their balance, by making use of a 12 cm strip of Pt-irridium, which was folded longitudinally, as a float. They used conductivity water as substrate liquid and they swept the surface at least five times before attempting any spreading. The variation of the solubility of unimolecular films with surface pressure, and the effect on the true pressure was investigated by Sebba and Briscoe[28]. These workers made use of a subphase having a pH = 7 by adding Na_2CO_3 to slightly acid distilled water.

The benzene used as solvent for the materials which were to be spread, was purified by shaking with H_2SO_4, then NaOH solution, dried over sodium wire and finally distilled under partial vacuum.

They found the palmitic acid to be slightly soluble in substrate liquids of pH = 7. However, on 0.01 N HCl solutions the acid was insoluble. Also the solubility of a homologous series of fatty acids decreased from C_{12} to C_{18}. Above C_{20} the acids were found to be virtually insoluble in pure water.

During their studies of solutions of hydrocinnamic acid and lauryl sulphonic acid in water, McBain and Spencer[29] modified their balance slightly. The float, as related before, was made from a strip of Pt-iridium bent longitudinally in the form of an inverted V. The top portion of this fold was coated with dicetyl and the lower section was caused to dip deeply into the body of the substrate liquid. Gold foil, 0.0025 mm in thickness, was used as ribbons for attaching the float to the sides of the trough. These ribbons were also covered by a thin film of dicetyl.

The torsion wire was of 0.18 mm diameter phosphor-bronze. Fused silica barriers, 1 cm square and 26 cm long were used and these were completely coated with bakelite lacquer.

Boyd and Harkins[30] pointed out the importance of the film balance as an analytical tool for food and biological research. They employed various solvents such as pentane, hexane, benzene, hydrocarbons plus alcohols and chloroform for spreading purposes. They were mainly concerned with the Wilhelmy vertical-pull type of balance, but also spread films of proteins on aqueous solutions in a trough of the horizontal type of surface balance.

Pankhurst[31] was one of the originators of a simple single-wire film balance. The torsion wire was of phosphor-bronze, 20 cm long and situated about 5 cm above the surface of the substrate. A mirror, mounted in the centre of this wire, formed part of an optical null-indicator device.

The float, a strip of paraffin-coated mica, was joined to the sides of the trough by means of silk threads which were lightly vaselined. The trough was manufactured from silica. The remainder of the apparatus was of brass, which was nickel-plated.

Soon after, in 1946, Puddington[32] described another surface balance which could be readily constructed by a worker with minimum of effort.

The device could be termed a "two-dimensional Bourdon gauge" and floated on the surface of the substrate liquid. It enclosed a clean area and film pressures exerted on the gauge from the outside, were observed from the way in which the gauge became distorted. Thus, in a

way, the instrument was a modification of Marcelin's "two-dimensional aneroid" which was developed in 1925. The gauge was manufactured from 0.02 mm hard brass shimming having a width of 5 mm. It was placed in position on the cleaned substrate surface, and the force exerted on the instrument by the film spread around the gauge, was observed by a mirror-and-scale optical system. Vibrations in the movement of the mirror were damped by means of a vane which was mounted on the mirror and dipped into a cup of viscous oil. The guage itself, was lightly waxed to render it hydrophobic. He used "Lucite" and Plexiglass" troughs which were also slightly waxed around the rim.

In their article on the interaction between long-chain compounds and certain polycyclic materials in monolayers, Dervichian and Joly[33] reviewed work done by Rideal and Schulmann, Stenhagen and Pillet on monolayers by means of the surface balance technique. They spread the more soluble substances on substrate liquids of pH = 8. This pH was obtained by dissolving sodium bicarbonate or disodium phosphate buffer in pure water. Oleic acid, which was insoluble in pure water, was spread on a dilute HCl solution having a pH = 3. They found that the pH seemed to have very little effect on the sodium salts of cleic and palmitic acids. They further studied the solubility, the physical structure, the probable composition of the complexes and the three-dimensional orientation of such compounds as palmitic acid, cetyl alcohol, cholesterol, oleic acid, trimyristin, tripalmitin and triolein.

The year 1948 marked the advent of an entirely new era in the study of surface films. Certain advances in the techniques developed for the study of adsorbed monolayers at the liquid-air interface were described by Fox and Zisman[34] at the beginning of that year. Up to 1949, all parts of a surface balance, in contact with the water or aqueous substrate liquids, for instance the trough, mobile barriers, floats or flexible ribbons for connecting these floats to the sides of the trough, had to be coated with some form of water - repellent material. Many workers on the Langmuir-type of film balance made use of high melting-point paraffin wax or some such hydrophobic substance to prevent the water from coming into contact with metallic parts of the balance. Also the process

of rendering the trough hydrophobic, enabled the water level to rise above the edges of the trough in order to facilitate the cleaning of the substrate by means of the sliding barriers.

Several investigators found that the slight metallic impurities, in the water, which resulted from the use of metal troughs and barriers, even though these had been waxed, seriously affected their results. Thus they resorted to silica or "Pyrex" glass troughs. As already seen, McBain[29] made use of a coating of hydrophobic "Bakelite" lacquer. However, even these protective coatings were not permanent and proved to be permeable to certain ions. In addition to these difficulties no satisfactory way had been found to contain organic liquids at a level above the rim of the trough.

Fox and Zisman, working at the Naval Research Laboratory, Washington, found that polymers of tetrafluoroethylene which had been developed by the Du Pont Company during the war, and which became commercially available after the war, were admirably suited to the use in surface work. The properties of polytetrafluoroethylene (Teflon) will be described later, but let it suffice here to recount some of its properties which make it such an ideal material for the construction of parts of surface film balances. Teflon was found to be virtually inert chemically, thus enabling the sections of the balance made from it to be cleaned by various organic solvents or by immersion in chromic acid. It was very stable thermally and exhibited hydrophobic and oleophobic surface properties. One disadvantage, however, was the difficulty encountered in the bonding Teflon to itself or to other materials. This objection has only been solved as recently as 1959.

Fox and Zisman used samples of Teflon, obtained by them during the war, to manufacture accessories for their film balance. For instance, they made very flexible and durable ribbons, for connecting the float to the edges of the tray, by shaving 0.0005" thick sections from a cube of Teflon by means of a microtome. Because of the difficulty encountered in bonding Teflon, they had to "rivet" these ribbons to the float. This process consisted of making holes in the float and ribbons with the aid of a needle and applying a nitrocellulose cement on both sides thus effective-

ly "rivetting" the two sections together. They used film balances, after the war, in which the troughs were constructed entirely of Teflon. The troughs were supported on a steel base to prevent distortion of the Teflon which is prone to "cold-flow." During the course of their studies of the force-area curves of selected materials on the surfaces of organic liquids the usual sliding barriers could not be used because of leakage past these barriers due to the capillarity of the substrate liquid. Thus they were forced to resort to the original method of using jets of air or nitrogen between the barriers and the sides of the trough as employed in Langmuir's film balance.

Mibashan-Saraga[35] studied isotherms of monolayers of lauric acid on acidified aqueous substrates. Due to the solubility of lauric acid in acidic solutions, the usual technique had to be modified. Hence she measured the surface pressure as a function of the molecular area at certain points on the film with the aid of a suspended pressure gauge, similar to the one employed by Guastalla[36]. She deposited a certain quantity of lauric acid, dissolved in a volatile solvent, on the surface and after an interval of 2 to 3 seconds, compressed the film thus formed. The surface pressure was found to vary with temperature and solubility of the acid. Benzene and petroleum ether, of boiling point 60-70°C, were used as solvents. The experiments were carried out at 20 ± 2°C on 0.01 N HCl substrates.

Mibashan-Saraga compared these isotherms with curves obtained for myristic acid, which proved less soluble under the same circumstances, and found significant differences. Hence she put forward the theory that the molecules of benzene remained on the surface of the water and only evaporated after a short while. This tended to give surface pressures which were initially high but soon decreased to the more normal values.

Alexander[37] developed a new technique for the measurement of force-area curves of adsorbed and insoluble monolayers at the air-water interface. He utilized a torsion strip instead of the more normal phosphor-bronze torsion wire and claimed a distinct advantage over the latter method because the zero position of the float was automatically located. The leakage past the ends of the float was prevented by using vaselined silk

threads lying on the surface. However, contrary to the normal practice where the loops of the threads both face the same direction, the ribbons were so arranged that the loops faced in opposite directions.

The movement of the float under compression was amplified by an optical system which operated from the torsion assembly and projected a small spot of light on a scale running along the side of the trough. Thus the graduated scale served a dual purpose as indicator for the position of the mobile barrier, and to measure optically the deflections of the float. The float movement was deliberately restricted to less than 1 mm by choosing a torsion strip of the required rigidity. The strip was either made from a thin steel watch spring or a phosphor-bronze strip (1/16" x 0.008" thick) and was mounted about 2 cm above the substrate surface. Thus a movement of the float of 1 mm gave a deflection of approximately 20 cm at a distance of 2 meters from the torsion strip. The float was constructed from a thin duralmin sheet turned up at the edges. It was screwed to a duralmin bar which was vertically located and clamped to the torsion strip at its upper section. To avoid contact of the metal with the water surface, a thin mica strip could be attached by means of paraffin wax, to the lower section of the float. A rectangular "Pyrex" dish or a glass dish, of the type used in refrigerators, served as a trough. Calibration was performed by hanging small weights from a pan which was attached to the duralmin bar. Alexander also employed the de Nouy tensiometer technique in determining the force-area curves for insoluble monolayers at the oil-water interface.

In 1949 Kalousek[38] developed a torsion microbalance for the measurement of very low surface pressures of monomolecular films. The microbalance made use of the "loop" technique. Films were spread both inside and outside the loop area. If the film inside the loop had a greater surface pressure, the loop became more circular in order to enclose the maximum area and if the film inside the loop had a lower surface pressure, the loop tended to be compressed into an elliptical shape. The loop was anchored at one point and could be moved around this point in a semi-circle by a torsion assembly at some other position opposite the first . An optical system also served to zero the balance.

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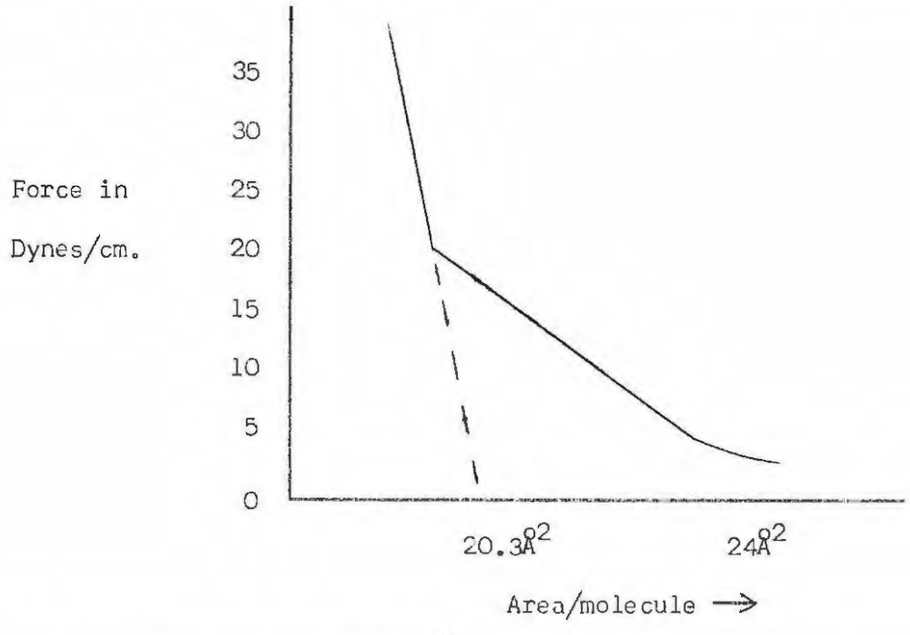
He cleaned the surface of the trough by blowing the contamination into one corner and removing it by means of suction. The trough, itself, was of silica and was freed from contamination by heating it to a dull red-heat before use. The water employed was twice distilled from all all-glass apparatus, the second distillation being from a dilute $Ba(OH)_2$ solution. Kalousek used light petroleum ether, b.p. 70°C, as a solvent for the materials and found that it required one minute to evaporate completely. Benzene, on the other hand, sometimes persisted for about five minutes after spreading, while alcolhol and acetone traces were detected after the passage of one hour. A solution which was 0.01 N with respect to HCl was used as a subphase for myristic acid films, due to the fact that the acid is slightly soluble in pure water.

Seelich and Hendler[39] investigated the effects of temperature and concentration on the structure of molecular layers of arachidic and stearic acids. These fatty acids were purified by recrystallization from alcohol. The melting points were determined by a micro-technique as originated by Kofler. Decalin was used as spreading solvent and was purified by shaking up with H_2SO_4, washed with water, neutralised and then treated with sodium or $CaCl_2$. The water used as substrate liquid was twice distilled from "Jena" glass. Arachidic and stearic acids were spread on phosphate buffers.

Another improved spreading apparatus was described by Heynis and Maaskant[40] in 1949. They used a balance similar to the one which had been constructed by Gorter and Seeder[41], but improved upon it in several details. In the latters' apparatus the surface pressures were transmitted to the torsion assembly via a waxed metal strip which floated on the substrate surface. This float or "swimmer" was connected to the edges of the trough by two thin, finely rolled flexible platinum strips. The pressure exerted on the float was counteracted by the torsion on a spring connected to a circular scale and the deviations of the float, from its zero position, were detected by an optical system consisting of slit, mirror and scale system. They modified the optical system in such a way that the device for zero-ing the balance, and the position of the mobile barrier were brought into one plane in front of the apparatus

where they could be readily seen by the operator. The balance was also enclosed in a cabinet thus minimising the ingress of dust and keeping the apparatus, to a certain extent, at constant humidity. In order to slow down the movement of the float, an oil-damper was inserted in the torsion head assembly. The balance was calibrated in the usual way by placing small weights on a scale with the aid of a small hook. The sensitivity of the balance was found to be 0.02 dyne/cm/degree of torque. To facilitate the draining of the substrate liquid in the trough, this could be tilted through an angle of about 45° from horizontal. Thus the liquid could be run out through an opening into the gutter which surrounded the trough.

Anderson and Evrett[42] described an automatic recording surface pressure balance in 1952, which could record the pressure-area, pressure-time and area-time characteristics of monomolecular films automatically on a special recorder. Basically, the balance consisted of a null-deflecting device which was incorporated in a Langmuir-type of film balance. It thus retained the sensitivity and range of a typcial film balance, and was also capable of following the rate processes continuously. A synchronous motor and a photoelectric tube-relay circuit were embodied in the design. A typical force-area curve for stearic acid on 0.01 M HCl at $21^{\circ}C$, as drawn by the recorder, is shown diagramatically below:



During the same year Few and Pethica[43] built a double electrode electrometer in order to investigate surface potentials of certain monomole-

- cular films. -

cular films. The radio-active source was suspended on a few millimetres above the substrate surface and ionised the air in that region. The calomel electrode dipped into the liquid in the trough some distance behind the float. This instrument was used mainly for studying myristic acid films at the air-water interface. In this way they obtained isotherms for the force-area, as as electrode potential-area on 0.01 M HCl at 18°C. The latter method proved more accurate.

Giles and Neustadter[44], during their researches on monolayers, studied the molecular areas and orientation of about twenty aromatic azo-compounds containing long alkyl chains. The film balance they used was based on Alexander's[37] design, with a trough (30 x 25 x 5 cm) of "Pyrex" glass. This trough was coated with paraffin wax to make it hydrophobic. Distilled water was used as substrate liquid. The surface active compounds were dissolved in solvents such as benzene and spread by means of an "Agla" micrometer syringe. All measurements were carried out at room temperature and were reproducible to $\pm$ 1Å^2 for the cross-sectional areas of the materials which were employed. By using Stuart-type molecular models, they were able to determine the orientation of these azo-compounds at the air-water interface. It was also discovered that these materials formed contact angles varying between 65° and 90° with the water surface.

During the latter part of 1952 Ellis[45] published his Ph.D., thesis on "A Study of the Properties and Reactions of Monolayers of Collagen and Other Proteins." He used a surface film balance similar to the one which was described by Guastalla[36]. In this balance, the float was pivoted about the one end and could be returned to its zero position by twisting a vertical torsion wire. The torsion wire was calibrated with the aid of a brass bob-weight which was placed at various points on a horizontal beam attached to the torsion wire. In order to clean the substrate Ellis made us of the "blow and suck" method whereby all contamination was gently blown into one corner and then removed by a suction pump. The apparatus was used in a thermostatically controlled room and the temperature of the subphase was kept between the limits 18 to 22°C.

Allen and Haigh[46] studied the isotherms for monolayers of impure stearic acid on acidic substrates which contained additional salts.

The stearic acid which was used was prepared from commercial stearic acid with a m.p. = 50°C. This was converted to the methyl ester and then fractionated under vacuum. The fraction boiling between 162 - 170°C at 3 mm of mercury was reconverted to the acid form and recrystallized several times from alcohol solutions and finally from ether. The melting point of the purified acid was found to be 65.6°C. The pH of the substrate was varied by the addition of HCl to the water in the presence of several buffer solutions. The experiments were all carried out at a room temperature of about 20°C. Substrates containing various salts, such as $CoCl_2$ and $CuCl_2$, dissolved in slightly acid solutions, were also used.

During 1953 Inokuchi[47] described an improved film balance for which he claimed very high accuracy. It was designed specially for the measurement of low film pressures and consequently a sensitivity of the order of millidynes per cm could be obtained. The apparatus described, was of the usual horizontal variety having a vertical torsion wire which was connected to a torsion head assembly. Above the torsion wire a circular scale was situated so that it was coaxial with the torsion head. This scale was equipped with a pointer and the torsion head could be manipulated from outside the cabinet, enclosing the apparatus, by remote control. The torsional angle could be read to 0.1° by means of a vernier scale. A paraffin-waxed mica strip served as float, and was supported by an arm extending above the surface of the water parallel to the length of the trough. This arm was attached to the float with the aid of two pins which fitted through two holes in the float. The fit was loose enough to allow for the up and down movement of the float, due to variation of the substrate level, but tightly enough to follow lateral movements of the float due to variation in film pressures. Thin silk threads, treated either with vaseline or paraffin wax, prevented leakage past the ends of the float. An optical system served to indicate variations in the position of the float assembly. Inokuchi used a torsion wire of phosphor-bronze, 0.273 mm in diameter and about 8 cm in length. He cleaned the surface by sprinkling talcum powder on the substrate and driving the contamination, plus the powder, towards one

side of the trough where it could be kept behind barriers. He also used the powder to test for leakage past the silk ribbons attached to the float.

During their studies on monomolecular layers, Allingham, Giles and Neustadter[48] made use of a surface balance to investigate dyeing processes. The balance used has already been described.

Experiments in connection with the "Influence of Salt on the Spreading Pressure of Films of Long-chain Weak Acids" were conducted by Payens[44] of the Philips Laboratoria in Holland, who spread monolayers of surface-active weak electrolytes on subphases of various ionic concentrations. The method of Alexander and Teorell was used whereby the surface concentration of the material was gradually increased by injecting the surface-active substance into the oil/water interface with the aid of an "Agla" micrometer syringe. The interfacial tensions were measured either by the ring or plate method.

Allan and Alexander[50] investigated monofilms at low surface pressures by using a horizontal type of film balance. A thin mica float was used in conjunction with vaselined ribbons. Later a nylon monofilament with a diameter of about 0.05" was used. Finally this was replaced by terylene threads with a diameter of 0.01". The float was connected to the torsion head assembly by an inverted Y-shaped metal plate which was suspended either on hardened steel points resting on shallow brass grooves or on rounded steel points resting on glass. Absence of appreciable contamination was shown by allowing the clean surface to stand for approximately 10 minutes and then compressing it to a fifth of its original area. If this resulted in a surface pressure not exceeding 0.02 dynes per cm the surface was taken to be free from contamination. For spreading solutions of the materials on the substrate, they used a microsyringe with a very fine, obliquely cut glass tip. The tip of the syringe just touched the substrate surface during the spreading process. Redistilled petroleum ether of b.p. = 60 - 80°C was used as a solvent. The more soluble materials were usually spread on substrates containing approximately 35% $(NH_4)_2SO_4$ by weight. The sulphate was first purified by heating with active charcoal and filtered before use.

- In 1955 the -

In 1955 the force-area properties of monolayers of certain poly-fluoroquaternary ammonium compounds, on hydrocarbon substrates, were studied by Ellison and Zisman[51]. They utilised the film balance described earlier[34], and found that the surface-active properties of such polar compounds at the air/oil interface could be used to examine the formation of peroxides, with ageing, in various types of vegetable and mineral oils.

In an article on the surface isotherms of unimolecular layers of arachidic and behenic acids on acidic and basic supports, Daguerre[52] described a film balance which was based on Guastalla's[36] original design. The trough was of a T-shaped design, while the float was of [- section, and connected with ribbons to the sides of the trough. The float, itself, was connected to the torsion head assembly by means of a very delicately constructed system of rods and pins. The behenic acid was prepared by the hydrogenation of erucic acid, and purified by recrystallization from acetone. Arachidic acid, on the other hand, was obtained by condensing malonic acid with octadecyl iodate. The pH of the substrate liquid varied between 11 and 16. These values were obtained by the addition of potassium phosphate, boric acid and KCl solutions to the substrate water.

During 1955 Bruun[53, 54] carried out a study of the expansion of condensed monlayers of normal long-chain fatty acids when mixed with isodestropimaric acid. The investigation was conducted with the aid of a continuously recording surface balance of the Wilhelmy-Dervichian variety. Typical acids which were used were palmitic, myristic, stearic, arachidic, behenic and lignoceric. He determined the molecular areas of these normal fatty acids containing traces of isodestropimaric acid on subphases containing dilute HCl at 20°C. In addition he obtained a series of isotherms for molecular areas of isodextropimaric acid films containing traces of fatty acids under the same conditions.

Towards the end of 1955 Durham[55] published an article on the interaction of monolayers of certain branched-chain fatty acids with calcium ions in the substrate liquid. He used α-substituted fatty acids and showed that, on introducing an ethyl group in the α-position of lauric, myristic and palmitic acids, the calcium ions were prevented from causing the films of these acids to become solid and brittle at a pH = 7.5.

A Langmuir-Adam-type of trough was constructed of Monel metal. The balance, as well as the mobile barriers, were heavily paraffined. The balance was housed inside a double-walled wooden cabinet which contained heaters and a thermostat so that the air temperature and hence that of the water in the tray were maintained at a temperature of $20 \pm 0.5^{\circ}C$. All manipulations of the barriers and accessories of the balance were conducted from the exterior of the cabinet. A modified Wilhelmy plate technique was used to measure the force/area isotherms. Conductivity water was utilised as substrate. The fatty acids were dissolved in redistilled A.R. benzene and spread with the aid of an "Agla" micrometer syringe. All glass apparatus employed, was cleaned by soaking in a 50/50 mixture of concentrated H_2SO_4, and concentrated HNO_3 and then rinsed with water.

In their report on the surface activity at the organic-liquid/air interface, Ellison and Zisman[56] described a "Teflon" film balance as first used by Fox and Zisman[34]. The trough was manufactured from polytetra-fluoro-ethylene because of its non-wetting properties, extreme durability and chemical inertness. A paraffin-coated mica strip served as a float in the case of aqueous substrates, while a strip of aluminium (0.02" thick) with a "Teflon" coating 0.0015" thick served as a barrier for organic liquids. Due to the difficulty encountered in cementing any material to "Teflon", they spot welded 3 short rods to the upper surface of the aluminium float before coating it with "Teflon". After coating, the "Teflon" was scraped off the end of these rods leaving the metal surface exposed. This procedure enabled the usual cemented connection to made with the torsion head assembly. The oil-repellent character of the "Teflon" surface of the trough was greatly aided by buffing the surface with a cloth to impart a shiny finish. A commercially available "Cenco Hydrophil" torsion head was used in conjunction with fine jets of nitrogen to prevent leakage past the float. This method of containing the film between barriers was only employed for organic-liquid subphases. For water substrates, the normal ribbons were preferred. The trough, barriers and float were usually cleaned by soaking for 30 minutes in a detergent solution. Thereupon they were scrubbed with a camel's hair brush and finally rinsed under tap water. In order to spread solutions of the

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materials on the surface, they made use of a micrc-pipette which was attached to a hypodermic syringe.

Cook and Ries[51] investigated the "Effects of the Spreading Solvent on Monolayers as determined by the Pressure-area and Radio-activity area Isotherms." They carried out experiments with stearic acid and solvents such as benzene, n-hexane and chloroform and showed that these solvents caused no measurable differences in the intermediate and high-pressure regions of the curves. At low pressures, however, both the force/area and radio-activity/area graphs showed a non-homogeneous distribution of the film. The uncompressed layer seemed to consist of "large clusters of extremely small islands." During compression, these islands tended to aggregate and finally a continuous film was formed. Thus they found that the solvent could impart a definite structure, packing or deformation to the film in the low-pressure region.

Nakagaki and Iida[58] studied the uptake of metallic ions from aqueous solutions by unimolecular layers of stearic acid. The stearic acid was spread on aqueous solutions of Sr and Co containing radio-labelled cations. The object was to determine the binding energy of the Sr and Co atoms adsorbed onto the monolayer. They found that the number of Sr and Co atoms bound to one molecule of stearic acid, increased with increasing pH of the subphase, as well as the concentration of these ions in the subphase. NH_4OH was utilised to adjust the pH of the substrate to the required value.

In their article on "Radioiodine exchange between Iodostearic acid monolayers and Substrate Iodide" in 1956, Robertson, Winkler and Mason[59] described their surface balance. The stainless steel trough, which was carefully coated with paraffin wax before use, was enclosed in an air thermostat. The temperature of the thermostat was regulated by pumping water from external thermostats through copper coils into the cabinet in which the apparatus was housed. By this means they were able to control the temperature to within $0.2^{\circ}C$ of that of the thermostat. In order to saturate the atmosphere inside the cabinet with water vapour, they placed a reservoir of water inside it. Into this bath strips of filter paper were hung. The balance was of the Wilhelmy-Harkins vertical-pull type,

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and included an optical system, consisting of a hairline image reflected from a small mirror mounted at the main knife edge of the balance, to indicate the zero position of the slide. The mobile sweepers and Geiger-tube mounting were operated by remote control from the exterior of the thermostat. They claimed a sensitivity of 0.48 dyne/cm/scale division of optical lever.

Unimolecular films of myristic acid were studied at low surface pressures by Semeluk, Hahn and Morrison[60]. These investigators used a horizontal type of film balance of the familiar Langmuir variety. They modified their balance so that the head and mica float could be moved vertically by a cam in order to sweep the entire surface area in one operation. The trough was bakelite-coated and small stirrups were used to hold the gold-foil ribbons against the side of the trough. The other ends of the S-shaped ribbons were attached to the mica float. Phosphor-bronze torsion wires were used to measure the forces acting on the float while an optical system registered movements of the float. Surface potential measurements were effected with the aid of a polonium-coated air-electrode and a calomel half-cell. The entire surface balance was enclosed in a double-walled copper box, the temperature of which was regulated to about 20°C. A small door in the plexi-glass front of the apparatus, provided entry to the balance for adjustment and calibration. The myristic acid samples were recrystallized three times from absolute alcohol and finally gave a sharp melting point of 58°C. Ine spreading solvents were petroleum ether (b.p. 30 - 35°C) and thiophene-free benzene. These solvents were refluxed over P_2O_5, and then fractionally distilled. The substrate consisted of 0.01 N HCl solution prepared from conductivity water. A micropipette was employed to spread the solutions of myristic acid on the subphase.

Dieu[61] determined the molecular weights of proteins and certain polymers by the monolayer technique. He employed a modified Guastalla balance for measurements in the lower pressure region, and a Wilhelmy-type slide balance or Marcelin-type in the high pressure regions. The influence of several variable factors such as pH, ionic strengths of substrate liquids, addition of surface-active agents and the effect of

- temperature were -

temperature were investigated. He utilised a micropipette, graduated in thousandths of a cc, for spreading solutions of proteins and polymers on aqueous surfaces. A plexiglass box enclosed the whole balance while the temperature inside could be varied between $0^{\circ}C$ and $30^{\circ}C$. Pepsin and certain proteins were spread on phosphate buffers of pH = 5.5 or on solutions of pH = 2 obtained by adding HCl to the substrate.

While investigating monomolecular films of dicetyl-fumarate and maleate and their reactions with bromine and iodine, Shereskefsky found that Br_2 and I_2 lowered the surface potentials of the maleate-ester films, while fumarate monolayers seemed unaffected. He put forward the theory that the maleate films formed a strongly polar interface, while the fumarate layer lacked such an interface. All surface potential measurements were carried out with the aid of a polonium air-electrode used in conjunction with a Lindeman electrometer.

In an interesting paper on the determination of molecular characteristics by means of the surface technique, Guastalla[63] described his surface film balance which was based on Marcelin's apparatus which was in turn a derivation of Langmuir's original horizontal trough design. A balance which was essentially similar to Guastalla's had already been described by Daguerre[52]. It incorporated a T-shaped trough and a highly complicated connection between the float and the torsion head assembly.

Guastalla indicated how a new structural formula for cholesterol was derived by means of data obtained from surface area measurements. He also stressed the effects of purity of certain long-chain compounds on their molecular areas. A contemporary of Guastalla, by the name of Michel[64], carried out an extensive survey of surface potentials of long-chain fatty acids. She described the methods of surface potential measurements as pioneered by Guyot in 1913, and subsequently developed by Langmuir, Schulman and Rideal, Adam and Harding, Harkins and Fisher and Dervichian. The surface potentials of myristic acid monolayers were determined on 0.01 N HCl substrates at $17^{\circ}C$ in a Langmuir-type trough.

In 1957, Few[65] studied the properties of monomolecular films of tyrocidin and gamacidin cyclic decapeptides at the air/water interface. A Langmuir-Adam-type of film balance was used. The sensitivity

was quoted at about 0.1 dyne/cm. The entire apparatus was enclosed in a metal covered wooden box. Temperature stability was maintained by means of circulation of water from an external thermostat through coils within the box and glass trough of the balance. Temperatures in the region of 12 - 12.5°C were employed for experiments. 70% ethyl alcohol was used to spread samples of these decapeptides on water substrates and about 5 minutes were allowed for the solvent to evaporate.

Cameron and Giles[66] during their investigations on monolayers, made use of a film balance which was developed from the one described by Allan and Alexander[50]. The trough and mobile barriers, which served to compress the film, were manufactured from solid blocks of polythene. The trough was bolted to a heavy brass plate to ensure rigidity. Thus a paraffin-wax coating was only required to cover up the countersunk bolt-heads. The floating barrier was made of "Teflon" and attached by fine polythene threads to the sides of the trough. The torsion head swung on agate knife-deges and carried the usual mirror for the optical lever system.

La Mer and Robbins[67] studied the effects of the spreading solvent on the properties of monolayers and found that the resistances exhibited by fatty acid monolayers to evaporation of aqueous substrates were sensitive to the type of solvent and the particular technique used in the spreading procedure. They used stearic acid (m.p. 68.8 - 69.3°C), recrystallized thrice from petroleum ether, as solute, and "analar" benzene as the solvent. The limits of the non-volatile impurities of the benzene were found to be 0.0005%. A microburette was used for spreading the solutions, and it was calibrated with mercury. A precision of 0.1% was claimed for this burette. The substrate consisted of 0.01 M HCl solution.

A sandblasted "Pyrex" dish served as trough. The edges were rendered hydrophobic by rubbing with paraffin wax, while the interior of the trough was kept free from contamination by the wax. "Pyrex" glass tubing carried water, which was kept at 25°C in a thermostat, to the trough and served to keep the temperature of the substrate liquid at 25° ± 0.05°C. The Wilhelmy plate method was employed to measure the surface pressure. The sensitivity of this balance was estimated at better than 0.1 dyne/cm. The entire apparatus was enclosed in a hood, the walls of which were coated

with vaseline to prevent dust from settling on the surface of the substrate.

The molecular structure in surface films of saturated monoglycerides on water surfaces, related to the the three-dimensional states of these compounds, was discussed by Merker and Daubert[68]. All molecular areas were calculated from density and X-ray data for the 3-D crystals. They found these areas to agree very well with those obtained for liquid condensed monolayers. The following formula was employed by them for calculating the average cross-sectional areas from X-ray data:

$$\text{Average cross-sectional area/molecule} = \frac{\text{Molecular wt. x 10 x 2}}{\text{Density x 6.023 x long spacing of molecule.}}$$

All force-area measurements were recorded on a Langmuir-type of film balance which was housed in an air thermostat that controlled the temperature of the substrate, film and surrounding atmosphere to within $0.1^{\circ}C$. The temperature was measured with the aid of thermocouples and a Leeds-Northrup potentiometer. Benzene which was employed as solvent, was purified by washing with concentrated H_2SO_4, dried and finally distilled from a mixture of Zn and caustic soda.

Boyd[69] studied the energy relations during the formation of monolayers, in particular, the spreading of long-chain fatty acids on aqueous surfaces. The temperature variations and spreading pressures of such acids as tridecylic, myristic, pentadecylic and palmitic on aqueous subphases were measured and from this data, Boyd was able to estimate the molar latent heat, entropy, free energy and the changes in enthalpy during the formation of these unimolecular films. He purified a series of these fatty acids (C_{13}-C_{16}), by means of sublimation in vacuo at temperatures a fraction above their melting points. The water, which was used to prepare the 0.01 N HCl substrates, was twice distilled from alkaline permanganate solutions and then condensed in a block-tin condenser. He used a thermostated surface film balance of the horizontal variety as described by Nutting and Harkins[24], and maintained the substrate temperature to within $0.1^{\circ}C$ of the required temperature. Two single-junction copper-constantan thermocouples, one placed in the air about 1 mm above the film

- and the other -

and the other 1 mm below the film in the substrate liquid, were used to measure the temperature. The monolayers of the acids were spread from purified ligroin using a constant volume pipette.

While continuing his investigations on the molecular interaction in mixed monolayers of fatty acids, Durham[70] obtained force-area isotherms for mixed layers of arachidic acid and α ethyl-stearic acid. This mixture was spread on conductivity water and also on 0.00025 M $CaCl_2$ solutions of pH = 7.5. The arachidic acid was purified by recrystallization and melted at 75.0°C. Durham used a Langmuir-Adam trough assembly with a torsion wire having a sensitivity of 0.05 dyne/cm. The silica trough and movable barrier were coated with a high melting-point paraffin wax. The entire balance was enclosed in a wooden cabinet which was kept at 20 ± 0.5°C. The fatty acids were spread from light petroleum ether-ethanol mixture (4:1)on distilled water. The trough and all glassware were cleaned by soaking in a 50/50 mixture of concentrated H_2SO_4 and HNO_3 and rinsing in pure water.

A very interesting series of experiments were carried out by Cook and Ries[71] on the pressure/area isotherms for stearic acid. This acid was spread on aqueous substrates without the aid of a solvent. A sensitive helical quartz spring was used to weigh a single crystal of pure stearic acid. The water in the "Teflon"-coated trough was heated to about 71°C, which is slightly above the m.p. of stearic acid. The crystal was placed on the surface between the mobile barrier and the float. The hot water caused the crystal to melt and spread over the surface between the two barriers. After the water had been allowed to cool, the force-area isotherms were determined in the usual way. The reproducibility was found to be excellent and the value obtained for the molecular area agreed fairly well with those areas observed for stearic acid spread from solvents such as benzene, n-hexane and chloroform. They also discovered that the collapse of the film occurred at slightly higher pressures and was less abrupt than for films formed from evaporation of solutions.

Rabinovitch, Robertson and Mason[72] studied the "Relaxation of Surface Pressure and Collapse of Unimolecular Films of Stearic Acid." This investigation included a study of time variations of force-area

- isotherms for -

isotherms for stearic acid films at the air/water interface. They used an automatic recording surface balance of the Wilhelmy vertical plate type. The balance incorporated a null-detector which was activated by an electronically controlled servo-mechanism. The dipping plate was hung by a thin nichrome wire from the lower edge of the left hand pan of a chainomatic balance. A galvanometer mirror was cemented to the fulcrum of the balance beam and reflected the light beam from a source on the twin cathodes of a photo-electric tube. This tube converted the minute displacements of the balance arm into an electrical voltage with the correct polarity. This voltage was fed into the input of an amplifier and a corresponding output current was obtained. The current was led through a solenoid and magnet system which operated on the right hand pan of the balance. A chart recorder was employed to plot the force/area curves. The trough, barriers and thermostat were essentially the same as before[59]. The area occupied by the film, could be varied either manually or mechanically by means of a motor.

Gaines[73] carried out certain observations on monomolecular films of carbon-14 labelled stearic acid. He deposited such films on a variety of solids, for example, Cu, Al, Pt, Cr, mica and glass. Two main methods were used - firstly the transfer from water surfaces and secondly by adsorption from cetane and nitromethane solutions of the acid. The stearic acid was labelled in the carboxyl group and purified by first dissolving in reagent grade n-hexane and then extracting with 1 N HCl and finally with water. The solvent was thereupon evaporated and the acid dried. It finally gave a m.p. of 68 - 68.5°C. The force/area isotherms for ^{14}C labelled stearic acid were comparable with curves for the normal acid. A "Cenco Hydrophil" balance with a torsion wire giving 0.35 dyne/cm/degree of rotation, and a paraffin waxed brass tray were used in the investigation. The water was redistilled from quartz. All counting measurements were performed with the aid of an end-window Geiger-Müller tube having a mica window.

Stewardt[74] prepared certain surface-active alcohols containing the anthracene nucleus. He examined their physical properties, particularly the surface activity and fluorescence. The surface behaviour was

investigated by means of a surface film balance consisting of a lightly paraffined trough and "Perspex" barriers. Experiments were carried out at room temperature. The monolayers were spread from light petroleum ether (b.p. 80 - 100°C) or benzene solutions by means of an "Agla" micrometer syringe. The Wilhelmy technique was employed to calculate the surface area per molecule for these alcohols.

During 1960, Stewardt[75, 76] carried out some further research on the spreading of unimolecular films of anthracene derivatives and discussed the molecular configurations of these compounds at the air/water interface. The experimental technique was essentially the same as before, except for a modification made to the null-detecting apparatus. Initially an optical system was employed, but later in the research program, he developed a capacitance-operated null-detector for following the movement of the Wilhelmy glass plate. This detector made use of the capacitance change of a variable condenser which had its moving plate attached by some way to the balance beam.

The circuit was contained in a small metallic chassis and attached to the frame of the balance by means of brackets.

III. THE DESCRIPTION OF THE APPARATUS.

A. THE DESIGN AND CONSTRUCTION OF THE SURFACE FILM BALANCE. (See Fig. 1).

The surface film balance employed during the investigation, was designed by and constructed under the supervision of Dr. W. F. Barker at the Case Institute of Technology, Cleveland, Ohio. In its final form, it offered a number of improvements on the film balances used by most earlier investigators.

Basically, the film balance consisted of a trough, to hold the substrate liquids upon which films were spread, a mobile barrier to confine these films and a float which served to transmit the film pressures to a torsion wire for measurement as torque.

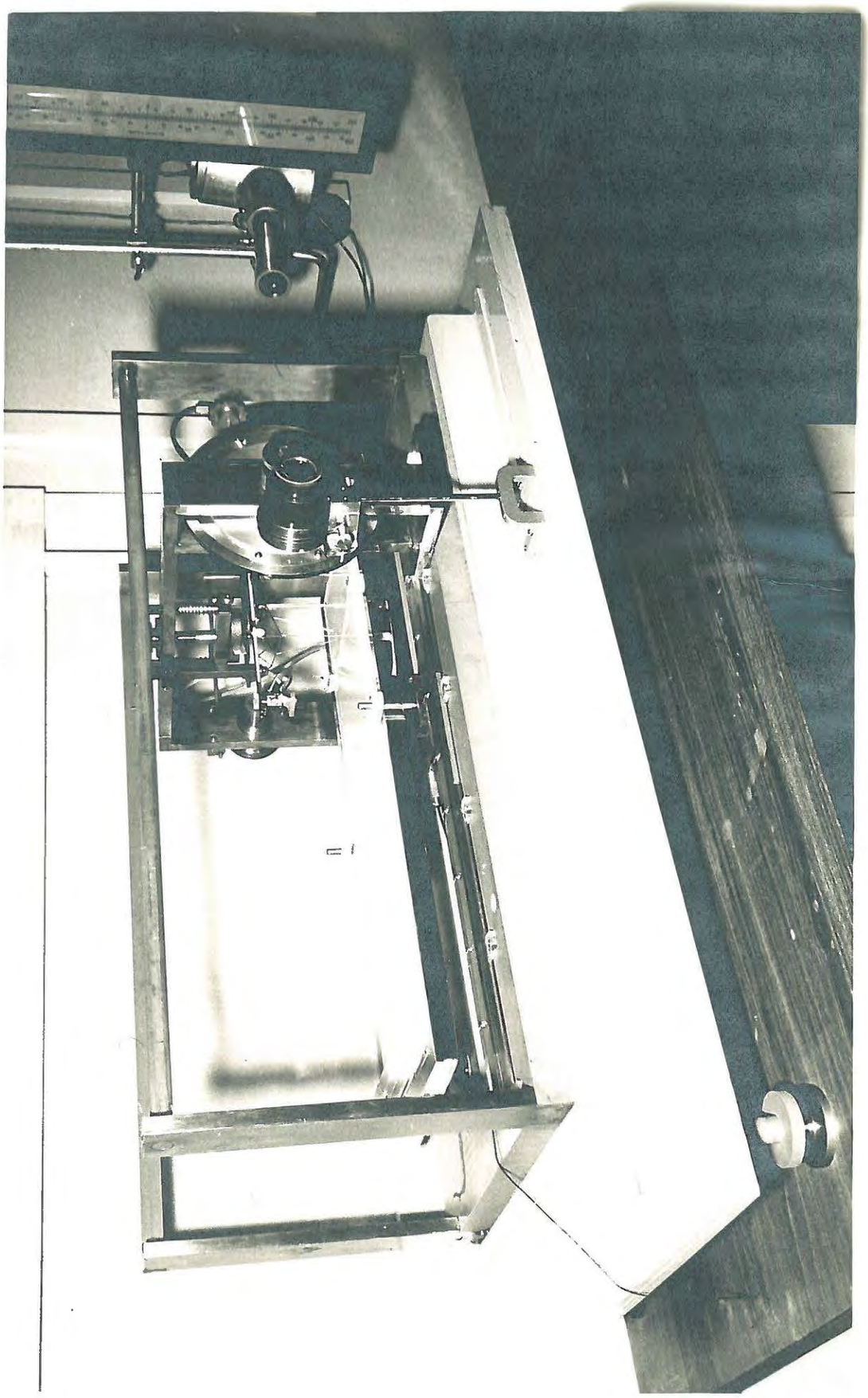
The trough was machined from a single, rectangular piece of polytetrafluoroethylene, as were the mobile barriers which were used to compress the surface films and clean the substrate surfaces. The floating barrier was made of thin "Teflon" film with "Teflon" ribbons attached to it by a specialized technique. All exposed steel surfaces and those subjected to wear, were covered with a thin "Teflon" coating. The method used for this procedure will be described, in detail, later.

The remaining sections of the framework were made from brass and received a generous coating of varnish to resist corrosion.

One of the foremost requirements for surface work is stability and freedom from vibration of the apparatus. In order to achieve this end, the following method was adopted:- the entire balance, apart from certain electrical components, was assembled on a heavy, rigidly constructed table (106 x 60 x 94 cm). The legs of the table were firmly bolted to the floor of the room. In addition to this measure, the rear edge of the table top was attached to the one wall of the constant temperature room which housed the apparatus. A strip of heavy duty "Dexion" angle iron was used for this purpose. In this way a very stable structure was obtained for accommodating the film balance. Only exceptionally severe knocks or vibrations, transmitted through the floor, were noticed during the process of conducting experimentswith the balance.

- (1) The Wooden Base: -

1. SURFACE BALANCE.



(1) The Wooden Base.

A heavy wooden base (96 x 56 cm) rested on the table and could be levelled with the aid of three levelling screws. These screws were attached to the lower surface of the base-plate and consisted of 4 parts each - a threaded screw, firmly attached to the base, a knurled nut, fitting on the thread and resting on a ball-bearing, and stationary socket placed on the table. The threaded screw was cut from brass and attached by means of brass screws to the base-plate. The knurled nut and socket were of steel and coated with a thin film of "Teflon" to resist wear and corrosion. The ball-bearing was liberally greased in order to attain a smooth and virtually frictionless adjustment of the level of the base-plate (Fig. 4.).

This wooden base supported the entire film balance on a polyurethane foam pad (81 x 41 cm), of a density determined by the load, so as to give proper damping. This pad was contained in a rectangular metal framework which was fixed to the base-plate. The object of the pad was to absorb shocks and vibrations, and to prevent these from being transmitted to the more delicate parts of the balance.

(2) The Steel Base.

The balance framework consisted of a "Teflon"-coated steel base-plate (75 x 36 cm), on to which was fitted a brass structure and torsion head assembly. Along the front edge of the base, running parallel with the length of the trough, a centimeter scale was attached to enable the operator to determine the longitudinal position of the mobile barrier along the trough.

Three "Perspex" plugs were fitted into holes in the metal base. These plugs supported the levelling screws for the trough and were triangularly disposed so as to give a stable three-point suspension. The rounded heads of the screws fitted into grooves beneath the trough assembly and were also equipped with lock-nuts to enable them to be fixed in any predetermined position. Between the perspex plug and lock-nut a thin "Teflon" washer was inserted to eliminate friction between the screw and the steel base during levelling operations.

(3) The Mobile Undercarriage. (Fig. 3.).

Running below the trough was a small brass undercarriage which slid along a longitudinal V-shaped groove which had been machined in the metal base parallel to the centimeter scale. At the rear, the undercarriage ran along the flat base-plate on a roller-bearing. Due to this arrangement the movement of the undercarriage was exceptionally smooth and it was also very positively located since it could only move longitudinally to the trough. At the extremities of the undercarriage two upright brass pins were affixed, one on either side of the trough. The mobile barrier, which slid along the edges of the trough, had two elongated slots into which these brass pins could fit. The barrier was merely slipped over these pins and were press-fitted over the edges of the tray. Hence by moving the undercarriage along, by means of two cords attached, one at either end, the barrier could be swept along the length of the trough to clean the substrate or to compress the film upon the substrate.

The brass pins could be adjusted in a horizontal plane by means of two screws, one at each end, in order to locate the barrier exactly at right angles to the long edges of the trough. A small vernier scale was attached to the lower part of the under-carriage and this moved along the steel centimeter scale running along the length of the trough in front of the apparatus. This centimeter scale was encased in "Perspex" and was firmly bolted to the steel base-plate. Thus the position of the mobile barrier, in relation to the float, could be obtained quite readily. The scale was divided into fractions of 0.5 mm and with the aid of the vernier, it could be read to 0.05 mm provided that care was taken to avoid errors of parallax.

(4) The Trough.

The trough was made from a solid, rectangular block of "Teflon" (61.2 x 20.4 x 0.8 cm). It was decided to make use of this polymer because of its chemical inertness and excellent non-wetting properties (see section (13) for further details.).

A metal base, which was used to provide support for the trough during machining operations, and also subsequently to prevent any move-

ment in the finished trough, was made from brass. Before the "Teflon" block was fixed in position for machining, the brass trough was plated first with nickel, and then with chromium. The section of "Teflon" was firmly bolted to this base by means of coarse-threaded shallow plug-bolts at short regular intervals, about one every 6 cm to prevent warping of the "Teflon" stock during the milling operation. This was necessary because of the well-known fact that "Teflon" tends to cold-flow when handled.

The trough was carefully and slowly machined in a milling machine, leaving the corners rounded and the edges square and flat. The cuts of the mill were deliberately restricted to 0.001" in depth to avoid thermal distortion of the surface. The milling operation took several days for completion. After the machining operation, a buffing followed, for which purpose a clean, dry cloth wheel was used without buffing compound. The buffing imparted a smooth, shiny surface which enhanced the water-repellent character of the "Teflon" stock and also served to seal any pores in the surface.

To the lower surface of the metal base-plate of the trough, two strips of metal had been fixed, at right angles to each other, and on the opposite ends of the trough. Into these strips V-shaped grooves had been cut to position the three levelling screws. This ensured the positive location of the trough on these screws and allowed it to be safely and easily replaced after cleaning. The final dimensions of the trough, after machining, were as follows: 56.5 x 17.5 cm on the outside. The inside width was 15.2 cm while the edges were 1.2 cm wide. It was 0.5 cm deep and the corners were left rounded in order to avoid pockets which might be difficult to clean.

(5) The Mobile and Barrier and Sweeper.

The mobile barrier was 29.5 cm long, 1.6 cm wide and 0.95 cm high at its thickest section. Near the extremities of the barrier two slots were cut, one at either end, to allow the brass pins of the carriage to pass through.

The barrier was also machined from a solid length of "Teflon"

- stock. -

stock. On either end, the section in contact with the trough was milled to fit firmly over the edges of the trough so that the barrier dipped about 0.2 cm below the level of the rim into the substrate liquid in the trough. Thus by moving the undercarriage along, with the aid of the dial-cords attached to it, the barrier was swept along the surface of the substrate and the film was prevented from leaking past the barrier due to the excellent fit over the edges of the trough.

A solid "Teflon" sweeper, which was essentially similar to the barrier, just described, was employed to clean the surface of the substrate. It facilitated the removal of contamination by confining it near the one side of the trough from which it could easily be removed by applying suction to the confined area via a fine nozzle connected to a filter pump.

(6) The Torsion Head Assembly. (Fig. 2.).

The entire torsion head assembly was permanently bolted to the steel base-plate which formed part of the framework of the balance. The assembly consisted of a brass structure to which various sections of the torsion head were attached. The brass structure was varnished to resist corrosion.

Facing the operator, in front of the framework, was a circular dial with graduations in degrees of arc. This dial also incorporated vernier attachments for the scale. It recorded the angle of twist of the torsion wire and had been salvaged from a theodolite. The dial was fitted into the brass framework with the aid of a well lubricated metal-to- metal bearing.

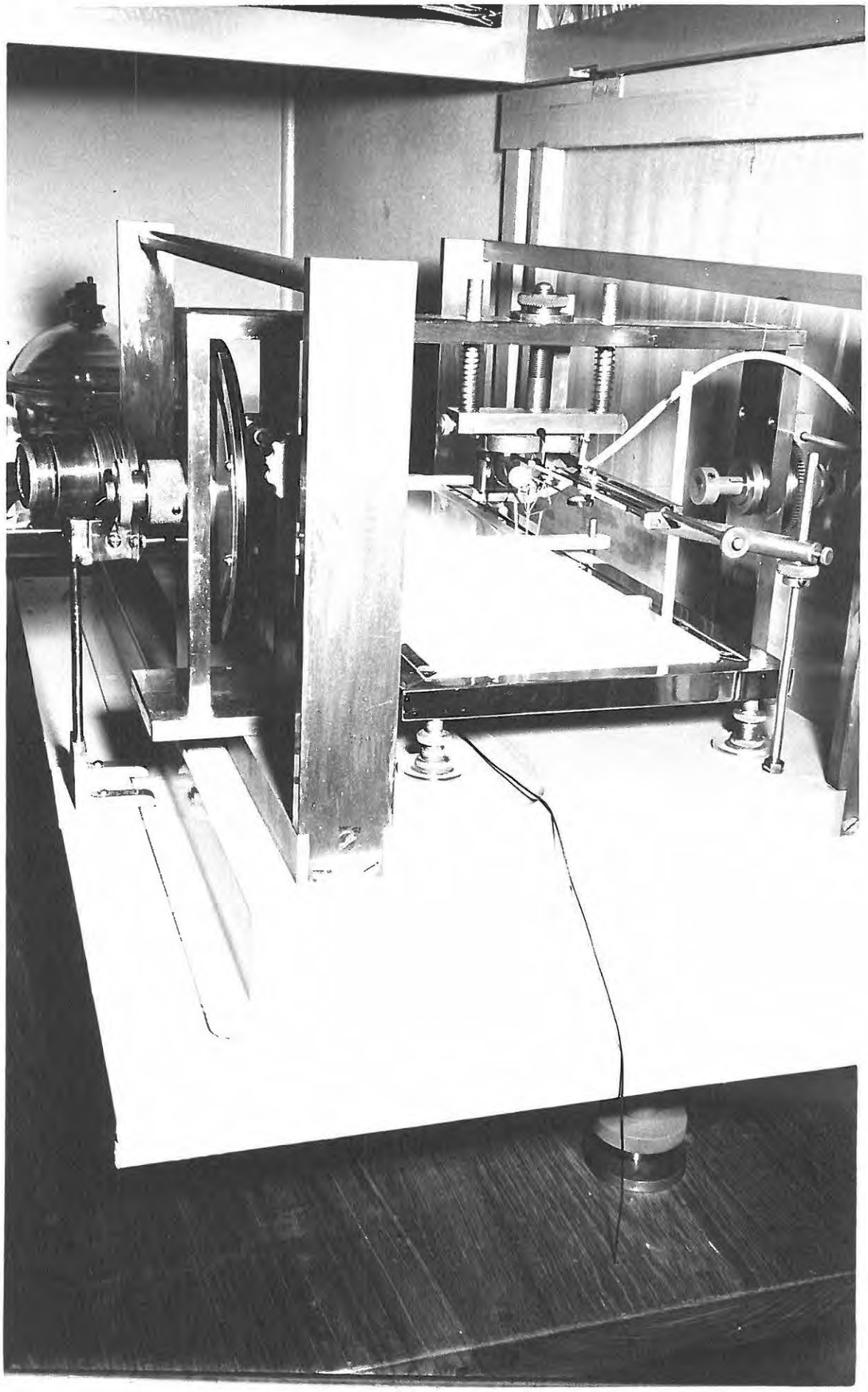
A magnifying lens was used for reading the very fine graduations on the circular dial and its vernier scales. Although this magnifier was situated inside the dust cover, the graduations could be readily seen through the transparent cover, particularly if use was made of a small external light source to illuminate the dial at an appropriate angle.

The graduations on the dial could be read to 2 decimal places with the aid of the vernier scale.

The torsion wire was of tungsten, 0.007" in diameter and about 25 cm long. It was stretched across the trough at a height of

- approximately -

2. TORSION HEAD ASSEMBLY.



approximately 9 cms. On either side it was clamped between two hemispheres recessed in a large bolt with a small hole drilled through its centre and a key along the outside which could slide into a corresponding keyway in the bearing (see Fig. 5.). The front bearing, facing the operator, was attached to the theodolite dial, thus enabling the dial and bolt to turn without backlash. At the rear, a similar bolt was passed through a slotted bearing and had a spring and lock-nut device attached to it. This arrangement enabled the torsion wire to be drawn tautly across the trough.

The hemispheres, one of which was permanently fixed in the bolt-head, were held in position by means of Allen-screws and the torsion wire was clamped between these two sets of hemispheres.

Both the front and the rear bearings were geared to adjusting knobs by means of worm gears acting on pionions attached to the journals. The front adjuster thus drove the dial through the worm-gear and simultaneously the bolt, which fitted into the slot of the bearing, would the twist torsion wire through a certain angle which could be read off from the revolving circular dial and its stationary verniers.

The worm-gear at the rear could also exert a torque on the torsion wire by turning the rear adjuster. The spring-lock-nut assembly could be utilised to tighten up or slacken off the tension in the torsion wire simply by screwing the lock-nut in or out respectively.

A small saddle-shaped fitting (see Fig. 7) manufactured from the agate knife-edge housing of an old assay balance beam, was cemented to the centre of the torsion wire. This fitting, in turn, was screwed into the balance beam with the aid of "Samsonite" cement. The beam was salvaged from an old brass assay balance. It was considerably lightened in weight by careful machining. A crescent-shaped aluminium vane with an adjustable bob-weight was screwed into the upper end of the beam. When the torsion wire was in position, the vane fitted into an aperture between two small but powerful horseshoe-magnets suspended from the framework of of the torsion head assembly. These magnets set up "Eddy-currents" in the vane when it moved and thus served to damp out oscillations of the balance beam. The bob-weight screwed into the thread of the vane and

- was used to -

was used to adjust the meta centre of the entire beam plus accessories to correspond with the centre of the torsion wire.

To the lower end of the brass beam a glass attachment was cemented (see Fig. 6.). This attachment was in the form of a T-shaped "Pyrex" glass rod, 1 mm in diameter, with two side arms to render the structure more rigid. A special jig, which will be described in greater detail later, was utilised to cement this glass T-piece in its correct position in relation to the beam.

When the torsion wire was clamped into position, the horizontal section of the glass attachment was suspended a few millimetres above the surface of the substrate in the trough. It fitted into a central slot cut in the "Teflon" floating barrier. The substrate liquid, which did not wet the "Teflon", rose up through this slot and adhered to the glass rod due to the surface tension effect. This method was found admirably suited to surface pressure measurements because it offered an excellent way of connecting the float to the balance beam and torsion wire system, and also it exhibited very little lost motion during compression and expansion procedures.

A horizontal brass cross-member, suspended from a small vertical pillar which was clamped to the torsion head assembly by means of a bracket retained by Allen screws, carried a horizontal scale and slider. The slider was able to move alongside the one arm of the brass balance beam. It incorporated a small fitting which enabled the operator to place a small platinium rider at various positions on the beam and to read off this position from the scale fixed below it. This method was used for the calibration of the apparatus (see Section V for calibration procedure.).

The two horseshoe magnets, which acted upon the aluminium-alloy vane fixed to the top of the beam, were suspended from the framework supporting the torsion head assembly. These magnets could be moved in a horizontal plane, at right angles to the vane, with the aid of threaded screws. This provided a means of adjusting the gap into which the vane fitted and served also to increase or decrease the damping action as required. The magnets could be adjusted in a vertical plane by means

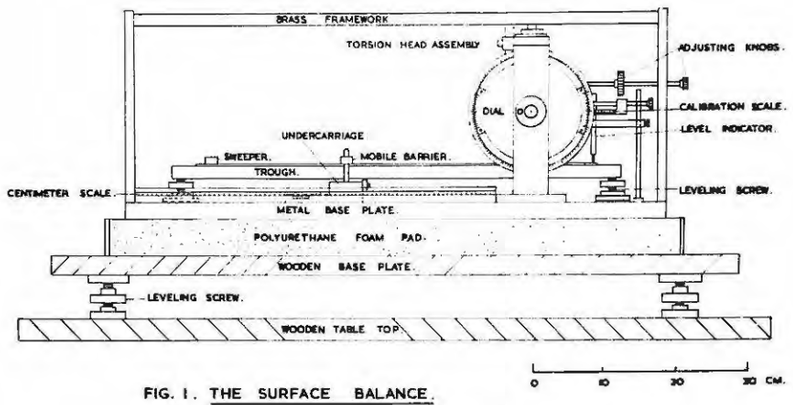


FIG. 1. THE SURFACE BALANCE.

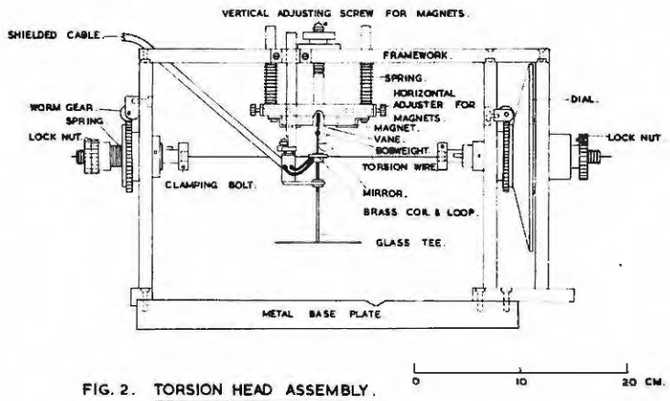


FIG. 2. TORSION HEAD ASSEMBLY.

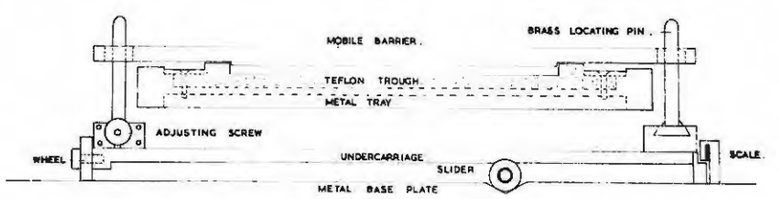


FIG. 3. TROUGH & UNDERCARRIAGE.

of a brass screw with two additional sliders equipped with spring-washers. (See Fig. 2.)

(7) The Floating Barrier. (See Fig. 9.)

The floating barrier or float, has always been the weakest point in the Langmuir-type of surface film balance. The requirements of a good float are threefold: firstly, it must be sufficiently rigid to withstand quite a powerful sideways thrust yet low in mass to ensure adequate sensitivity of the apparatus; secondly, it must be easily detachable from the trough and torsion head assembly for cleaning purposes; and thirdly, the most important property of all, the float must prevent leakage between the barrier and the edges of the trough.

After an extended period of experimentation, this problem was surmounted in a novel way. A fairly rigid float was developed, and was attached to the edges of the trough with the aid of thin ribbons which effectively prevented any leakage of the film past the barrier. The floating barrier was made from "Teflon" film 0.005" in thickness and as such, was of exceptionally low mass. A rectangular section of film was used having the following dimensions: 12 cm long by 1 cm wide with a central slot, 8.5 cm long by 0.15 cm wide, cut in it.

This "Teflon" sheet was found to be sufficiently rigid in structure for use as a float.

In order to attach the float to the sides of the trough, use was made of two "Teflon" ribbons, made from 0.003" film. Two clips served to clamp these ribbons to the trough edges. The ribbons were carefully cut from "Teflon" film and were approximately 12 x 0.3 cm originally. This thickness of film was found to be ideal since it imparted some rigidity to hold the ribbon upright in the substrate, yet was sufficiently flexible to follow the movement of the float without exerting any undue force on it.

A narrow slot, about 0.007" in width, was cut in the centre of each ribbon to enable the float to fit through it. Small holes were drilled through the ends of the float, about 1 mm from the edges, and the ribbons fitted into position. This was done by placing the float on a small

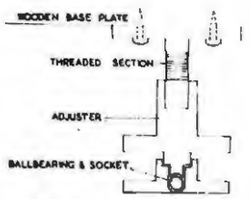


FIG. 4. LEVELING SCREW.

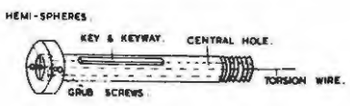


FIG. 5. CLAMPING BOLT.

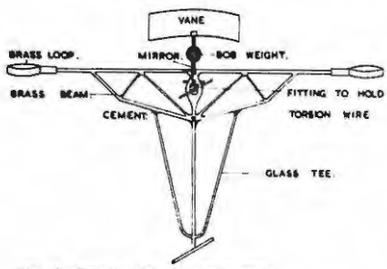


FIG. 6. BRASS BEAM ASSEMBLY.

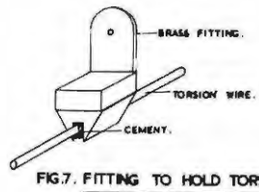


FIG.7. FITTING TO HOLD TORSION WIRE.

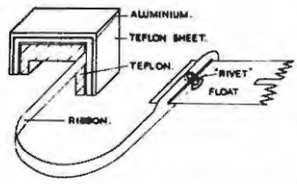


FIG.8. CLIP FOR ATTACHING RIBBONS TO THE EDGE OF THE TROUGH.

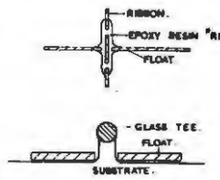


FIG.9. THE FLOAT.

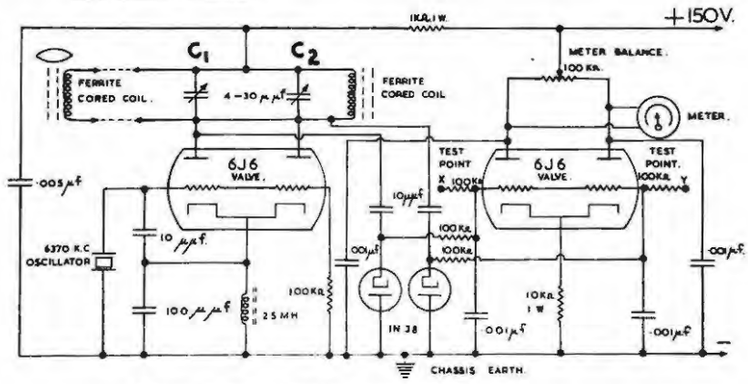


FIG.10. CIRCUIT FOR NULL INDICATOR.

wooden block with a small hole drilled in it. A hand-drill was used to drill a hole, about 1 mm in diameter, through the "Teflon" sheet at the appropriate positions. The jagged edges, due to the drilling operation, were trimmed very carefully with a sharp blade and this resulted in exceptionally neat holes in the sheet.

The float and ribbons were aligned at right angles to one another in a specially made jig (see Section III A (12)). The ribbons had also had small holes drilled through the centres. In this jig the ribbons were "rivetted" to the float with the aid of epoxy resin "rivets". This method had to be resorted to in view of the difficulty of bonding anything to the "Teflon". Epoxy resin was utilised because of its resistance to organic solvents, and non-wetting properties. The ribbons were attached to the edges of the trough by means of two clips, one on either side. The ribbons formed semi-circular loops between the float and the sides of the trough. Each clip consisted of two sections; an inner "Teflon" ⌐¬-shaped clip which fitted firmly over the edges and a similar stainless steel outer clip which fitted over the former. (See Fig. 8.).

The section of the stainless steel clip, in contact with the substrate liquid, was covered with "Teflon" sheet to avoid contamination of the liquid by metallic ions. The ribbons were fitted firmly in position between these clips, and the composite assembly was then press-fitted over the edges of the trough at a distance of approximately 10 cm from the one end. This resulted in the float resting on the substrate surface. The water was caused to adhere to the glass T-piece through the central slot and thus formed a frictionless link between float and torsion wire.

(8) Devices used for zeroing the Balance Beam.

(a) (i) The Optical Null-Indicator:

Initially an optical system was employed for zeroing the balance beam. A small circular mirror about 1 cm in diameter, was cemented at right angles to the brass beam at a distance about 1 mm above the torsion wire. To compensate for this extra weight on the one side of the beam, an equal weight was placed on the opposite side by fitting the clamping device for the torsion wire in such

a way that the heavier section of the clamp was on this side. The meta centre of the balance beam assembly was arranged with the aid of the bob-weight which screwed into the vane attached to the brass beam. By adjusting the position of the bob-weight, the meta centre was adjusted until it coincided with the point at which the torsion wire passed through the beam.

A narrow beam of light was shone from a galvanometer lamp on the mirror, from which it was reflected on a galvanometer scale situated at a suitable distance away from the mirror. The beam passed through a small aperture with a thin wire in its focal plane. This cast an image on the galvanometer scale. Hence the oscillations of the beam could be followed by the upward or downward displacement of the black hair-line in the centre of the spot of light, and the degree of displacement could be read from the scale. The balance could thus always be brought back to its reference or zero position merely by twisting the adjusting knob of the rear worm-gear device and setting the spot at such a position on the scale that the fine black line was superimposed on the zero mark of the scale. However, this arrangement was found to be lacking in certain refinements and also suffered from obvious limitations. For instance, the lamp could not be housed inside the dust cover fitting over the balance, due to the heat generated. This heat was undesirable not only with regard to the temperature control, but also because of the convection currents which would result and the attendant difficulties in the control of the surging dust particles.

Thus the galvanometer lamp and scale had to be housed outside the cover at some distance away and this entailed sending the beam of light through the polythene cover twice, with the resultant decrease in the intensity of the light and blurring of the image. Another difficulty was the relatively low sensitivity of this optical system, particularly when dealing with very small displacements of the float on the substrate surface.

For reasons outlined above, it was decided to adopt an electronic method of obtaining the zero position of the balance beam. For

this reason a null indicator was constructed for the torsion balance.

(a) (ii) Method used for making Silver Mirrors on Glass.

The method used for making small silver mirrors for the optical system was as follows: 2 ml of dilute $AgNO_3$ solution were placed in a clean vessel. One drop of a 10% solution of NaOH was added and then dilute NH_4OH added drop by drop until the precipitate formed by the caustic soda, was just not redissolved. Then one one or two ml of glucose solution was added and the vessel placed in a beaker of hot water at $50^{o}C$. Meanwhile, the microscope coverslide, which was used to deposit the mirror on, had been cleaned with chromic acid solution and rinsed with copious amounts of distilled water.

This slide was placed in the vessel containing the mixture and a silver mirror was deposited in about 2 minutes. It was then removed and allowed to dry. The mirror on the one side was removed by gentle rubbing, while the one on the surface was left intact. When it was completely dry, a coat of paint was put on the rear of the mirror and finally it was cemented in position on the beam by means of a pin which had been bent at right angles.

(b) (i) The Capacitance-operated null detector for the Surface Balance.

Fig. 10 illustrates the circuit for the null-detector. The instrument was based on a circuit designed by Benade[77] in 1957. A ferrite-core pickup coil was mounted at such a distance from the torsion head assembly that a copper foil loop, attached to the one end of the balance beam, could move up or down, over the coil, vertically. This process tended to change the Q value of the coil. A similar coil was mounted on the chassis of the detector unit. The Q value of the latter coil did not change. Both these coils were insulated from the chassis by small blocks of "Perspex". A shielded cable served to connect the first coil to the main chassis unit.

A 6370 Kilocycle quartz oscillator crystal induced oscillations

in two 4-30μF variable condensers, after amplification by 6J6 double triode valve. These variable condensers were adjusted to give maximum response and fed the voltage, due to the change in Q value of the coil, into a circuit containing two IN 38 Germanium diode rectifier crystals, thus giving D.C.

This D.C. voltage was fed into a Wheatstone bridge arrangement and the voltmeter included in this circuit indicated the change in the Q value of the ferrite coil, due to the movement of the beam, as a change in voltage.

(b) (ii) Adjustment of the Circuit.

A 20,000 ohm per volt meter was connected between the point X and earth. This was reached through a grommetted hole in the case. The resonance point of the first condenser C_1 was found by varying the pressure applied to the plates by means of a screw-driver. It was set so that C_1 was detuned half-way down the resonance peak on the high capacity side. This resulted in a D.C. voltage of about 20 volts at point X.

The procedure was repeated with condenser C_2 by connecting the meter between point Y and earth, but it was set off the resonance point on the low capacity side. The meter balance adjuster then zeroed the voltmeter near the middle of its range.

The range 0 - 40 volts was usually employed and thus the null-point became the 20 volt mark.

An automatic voltage stabiliser served to eliminate fluctuations in the 250 A.C. mains voltage, before it was fed into the power pack. This pack supplied 150 volts A.C. to the circuit and had a separate tap which served the heater circuits of the two 6J6 valves by supplying them with a 6.3 A.C. voltage.

As the balance beam was displaced from its zero position, due to film pressure, the loop attached to it, would move in a vertical plane and thus changed the Q value of the coil. This small displacement was indicated as a corresponding rise or drop in the voltage on the meter.

This novel method of detecting the null-point of the balance beam, was found to be far more sensitive than the optical system which had been employed previously. Small deflections were very readily perceived and could instantly be corrected by adjustment of the control knob. Another important aspect of this detector was the fact that the circuit could be contained in a small case not necessarily near the balance itself. Thus the heat generated by the power pack and valves in the circuit, could not adversly affect the temperature stability of the atmosphere inside the dust cover. Also, this method eliminated the eye-strain associated with all optical systems which have to be operated in semi-darkness in order to be really effective.

(9) The Substrate-Level Indicator.

As a result of the contact angle of water and aqueous solutions with "Teflon" being greater than 90°, the substrate level in the trough could readily exceed the level of the edges of the trough and bulge out above the rim. For this reason it was considered imperative to have a level-indicator situated somewhere along the trough in order to retain the level of the substrate liquid always at a predetermined height above the trough. It was decided to house this indicator behind the float assembly near the rear corner of the trough.

The indicator consisted essentially of three sections: (a) a vertical chrome-plated steel rod which was screwed into the metal base-plate and served as a rigid support for the indicator; (b) a brass slider which slid up and down the rod and could be clamped at any required height. It could move freely in a horizontal plane; (c) a "Perspex" indicator rod with a "Teflon" pointer attached to the brass slider. A positive stop was screwed firmly to the steel support. This was permanently fixed in position. The brass slider rested on this stop and could thus be locked into position.

After the trough had been levelled on the three leveling screws and the desired substrate level attained, the "Perspex" indicator was adjusted so that the "Teflon" point just appeared to touch its image in the substrate surface.

All subsequent experiments were then carried out with this setting of the indicator rod.

The level of the substrate was generally arranged to be 0.2 cm above the edges of the trough. Thus a small correction had to be applied to obtain the effective width of the trough. The actual width was 15.2 cm and having the level 0.2 cm above the edges, necessitated the calculation, by means of geometry, of a small correction factor. This correction increased the width to an effective width of 15.4 cms. With the aid of this level-indicator the substrate level could always be reproduced and added to the sensitivity of the balance and hence the accuracy of the molecular area determinations.

(10) The Dust Cover.

The entire film balance was enclosed in a dust cover made of thin, transparent polythene sheeting which was stretched over a robust wooden framework. This measure was adopted to preclude the ingress of dust particles.

The framework had the following dimensions: 60 cm in height, 60 cm in width and 105 cm long. It was hinged to the wall at the rear and rested on the table along the front and side edges. The framework was equipped with a handle to facilitate lifting the cover during cleaning. It could be kept open by hooking the frame to two eyelets on the wall.

The polythene film used was of a very clear, transparent variety and it was thus possible for the operator to view operations being conducted inside the cover.

In the lower right-hand corner, facing the operator, a small polythene trap-door was made in the cover. This allowed access to be made to the control knobs and the calibrating slider of the beam.

The brass undercarriage was moved about by means of two lengths of dial-cord. These were attached to the front and rear of the carriage. The cords were passed through small holes, one at either end of the table, inside the cover. Thus by pulling the cords from outside the cover framework and beneath the table-top, the carriage and hence the mobile barrier could be manipulated along the centimeter scale running parallel

to the trough.

(11) The Mounting of the Glass Attachment to the Beam.

In order to facilitate the mounting of the "Pyrex" glass attachment to the brass beam of the balance, a specially constructed jig was used. The jig held the beam and glass T-piece rigidly in position during the operation.

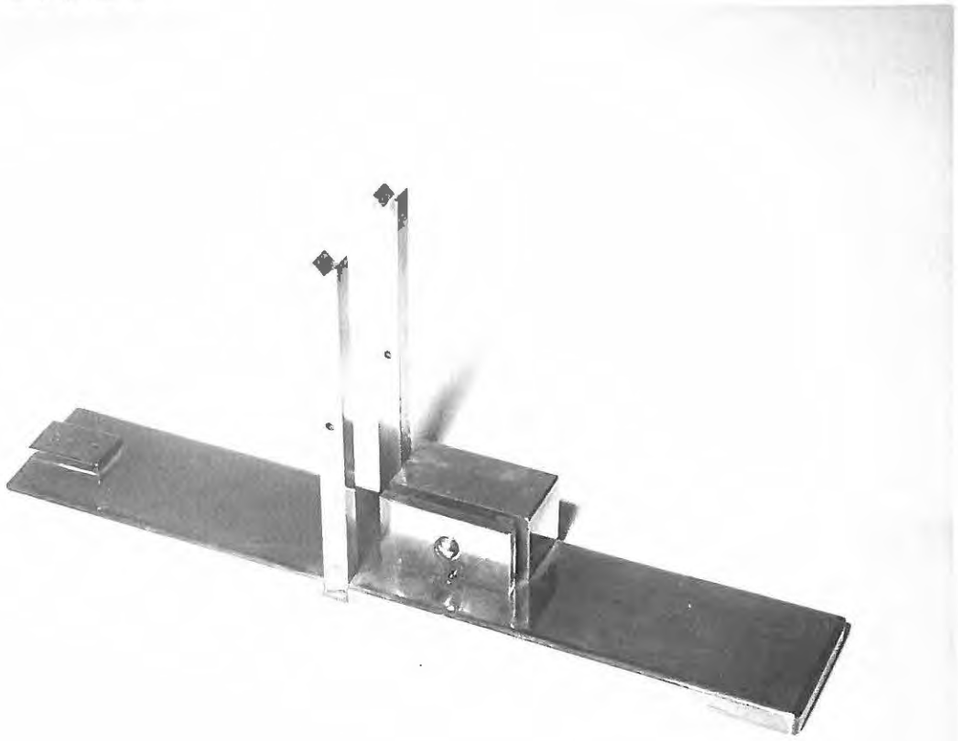
The jig (see Fig. 10a.) was of brass construction and consisted of a flat rectangular base 20.8 x 3.9 x 0.6 cm in dimensions with two upright pillars in the centre, one on either side. These pillars were 8.9 cm in height by 0.6 cm square and had V-shaped grooves cut in the upper ends. The two pillars were screwed down on the base by means of brass screws, as was a rectangular block of brass 3.6 x 1.9 x 1.9 which was attached near the one pillar. A flat clamping plate of the same dimensions was screwed into the brass block with the aid of a small screw. At the one end of the base-plate a rectangular stop was bolted to act as a positioner for the brass beam. The beam was inverted and clamped down on the jig by means of the "vice". The glass attachment was suspended from the two V-shaped notches in the upright pillars so that the tips of the three glass rods just rested on the beam. The glass T-piece was further located and held securely by a rubber band which was passed through two holes in the upright posts and round the central arm of the glass beam. A drop of "Samsonite" cement was applied at the three contact points of the glass tee and the beam and the assembly was allowed to set hard.

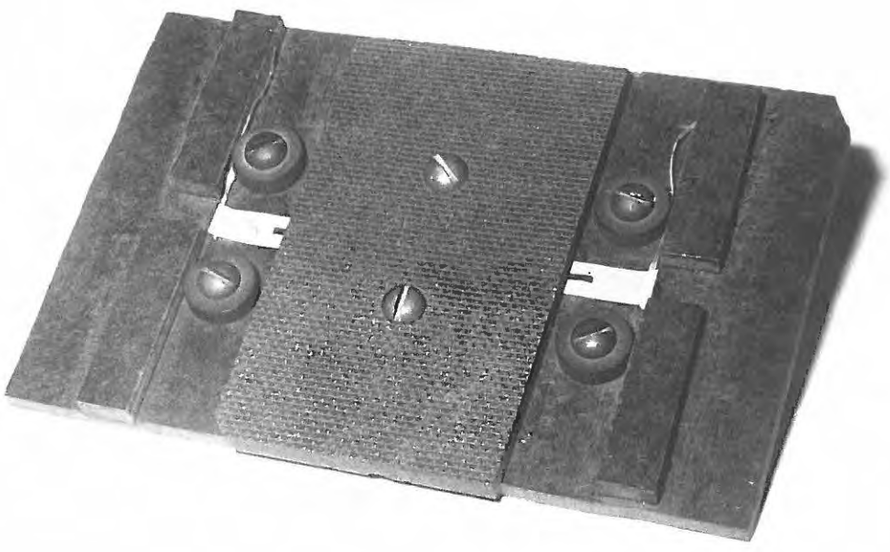
This method ensured that the brass beam and glass attachment were in perfect alignment and also that the T-piece was exactly at right angles to the balance beam.

The jig was also used to clamp the saddle-shaped fitting (Fig. 7.) through which the torsion wire passed, securely during the process of cementing the torsion wire into position. The fitting was carefully aligned in a vertical and horizontal plane and the torsion wire was stretched across it so that the wire fitted into the recess of the fitting. It was then cemented with a drop of "Samsonite" cement and left to harden while held in this position.

- In this way -

3. JIGS.





In this way a very firm bond between the torsion wire and the fitting was achieved. The fitting in turn, was firmly screwed into position on the balance beam and hence a very rigid connection between the torsion wire and the beam assembly was obtained.

During the whole period of the research, this type of connection gave excellent service. Tungsten wire was used as the torsion wire because of its very high tensile strength, which is approximately twice that of high-grade steel.

(12) The Attachment of the "Teflon" Ribbons to the Float.

In this case use was also made of a specially constructed jig, made of hardboard, to facilitate the joining of the ribbons to the float (see Fig. 10.). The jig consisted of a rectangular piece of hardboard, 19.5 x 12.7 cm in dimensions. At a distance of approximately 4 cm from each end, in the centre of the board, two holes were drilled 0.6 cm in diameter. Flanking these holes, were four small hardboard blocks (5.5 x 1.5 x 0.7 cm) which were cemented to the board; two at each side. This was done in such a way that their inner surfaces were in direct alignment with the centres of the holes. Adjacent to each set of blocks, two oblong holes, at right angles to the blocks, were made into which fitted nuts and bolts with fibre washers, approximately 2.0 cm in diameter and 0.5 cm thick. These washers could thus be fitted into the nuts and bolts, and slide along the holes in such a way that at the closest point to the hardboard blocks, they actually came into contact with the blocks and could be clamped into position with the aid of the brass nuts and bolts.

In the centre of the hardboard base a rectangular piece of board, 7.5 x 12.5 cm, was fitted by means of brass screws so that it was easily detachable.

The method of attachment of the ribbons to the float was as follows: the ribbons were slipped over the ends of the float so that the small holes in the ribbons were carefully aligned with those in the float. The float was placed in the hardboard base and clamped into position by the detachable piece. The washers were loosened and the ribbons so arranged that they were located at right angles to the float along the

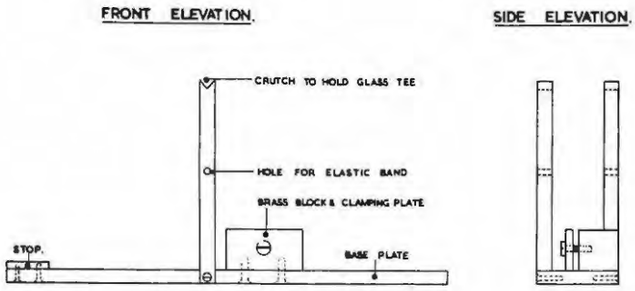


FIG.10[a]. JIG FOR MOUNTING GLASS TEE ON BEAM.

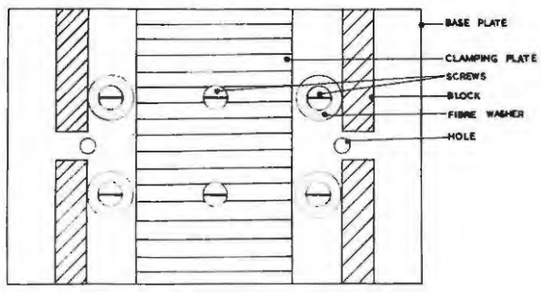


FIG.10[b]. JIG FOR MOUNTING RIBBONS ON FLOAT.

blocks fixed to the base. The ribbons were then clipped into position by the fibre washers. This resulted in the float lying flat along the base, the ribbons clamped vertically to float and the holes in the "Teflon" sheeting superimposed on the apertures in the base.

After this, the epoxy-resin was applied to form the so-called "rivets" (Fig. 9.) which held the pieces together. The "Epon 823" epoxy-resin was used in conjunction with a special hardener, D.E.T., in the ratio of 16 measures of resin to 1 of the hardener. The two were premixed on a watch-glass until the resin turned a milky colour and then applied to the selected spots. The resin usually set within two hours, or alternately, in about half an hour in an oven which was kept at about 60°C.

"Epon" epoxy resin was chosen because of its excellent non-wetting properties as well as its resistance to both inorganic and organic materials . Virtually the only chemical known to attack it, is boiling phenol.

After the cement had set and thus effectively "rivetted" the float assembly together, the ribbons were trimmed to a more suitable size. This was done by cutting off the one end of each ribbon and paring the ribbons down to a final width of 0.2 mm. This was carried out on the upper surface of each ribbon, leaving the lower edges intact.

By this means a very light but rigid float was obtained which, when lying on the surface of the substrate, and connected to the glass beam, formed an effective barrier to films at the surface.

Leakage past the ends of the float was completely eliminated with the aid of the semi-circular "Teflon" end-loops. These loops dipped slightly below the surface and were held in position by the composite clips over the edges of the trough.

Due to the extreme flexibility of the thin ribbons, there was no resistance to lateral movement of the float which could affect the sensitivity of the balance.

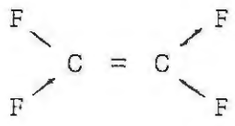
During the process of force-area measurements, account had to be taken of the areas enclosed by these semi-circular loops and this "end" - or "dead area" - had to be added to the total area occupied by the film at any one time.

It was found quite an easy operation to measure up these end-areas after completion of a series of runs on the same substrate. Later, however, a technique was developed whereby the float assembly and clips could be cleaned without detaching the ribbons from the clips, and hence these areas were kept constant to a marked degree. Hence it was only required of the operator to measure up these end-areas very carefully. By means of geometry, the total dead-area was calculated. This small area, of approximately 8 cm^2, was then added to all subsequent areas to obtain the total area covered by the film.

(13) The Structure, Properties and Uses of Polytetraflucroethylene ("Teflon") [78, 34].

(a) Structure.

Polytetraflucroethylene ("Teflon") consists essentially of ethylene molecules with the hydrogen atoms replaced by fluorine atoms:



Large numbers of molecules, such as the one illustrated above, combine to form a chain polymer of high molecular weight. This process involves the initial formation of an activated molecule which reacts with another molecule to produce a dimer which in turn retains the activity. This procedure is repeated until some external factor terminates the chain and so removes the activity.

$$R^{\bullet} + CF_2 = CF_2 \longrightarrow R - CF_2 - CF^{\bullet} \longrightarrow R - CF_2 - (CF_2 - CF_2)_n - R^1$$

($R^{\bullet}$ represents the catalyst which activates the molecule while R^1 acts as a chain-breaker.)

The final product of polymerisation is a highly crystalline, linear polymer possessing unique properties.

(b) Properties.

The polytetrafluoroethylene polymer stands alone among organic compounds as far as its chemical inertness and resistance to change of phase, at high temperatures, is concerned. "Teflon" is completely

inert to all chemicals and solutions of chemicals up to their boiling points, with the exception of molten alkali metals, and fluorine and chlorine trifluoride under certain conditions. It is not affected by such potent reagents as aqua-regia and as yet no substance has been found that will dissolve or even swell the polymer.

An outstanding property of "Teflon" is its stability at high temperatures. Although the tensile strength of the material is appreciably lower at 300°C than at room temperatures, there is very little change to "Teflon" at this temperature. It does not possess a melting point in the usual sense, in that it undergoes a solid-phase transition at about 327°C and vapourises without the formation of carbon. Unusual too, is its low-temperature behaviour when it will not become brittle. A film of this polymer may be flexed without fear of breaking at temperatures as low as -100°C.

"Teflon" has a very low coefficient of friction and is thus admirably suited for use as a dry lubricant.

Film sections of the polymer, thinner than 0.005" are transparent. However, in thicker sections it is opaque with a waxy appearance. "Teflon" is not hard by normal standards and the surface may easily be scratched or dented. However, because of its waxy nature, it is not easily abraded because the surface tends to be self-lubricating.

The material is subject to cold-flow under stress, and this property increases with an increase in the temperature. Moulded articles of "Teflon" can easily be machined by standard tools such as drills, lathes or mills; although some difficulty may be experienced in gripping the surface, due to its slippery nature. Although special methods have been developed for bonding the polymer[79, 80], in certain cases, no adhesives have been found which are generally useful for cementing polytetraflucroethylene.

(c) Uses of "Teflon".

Due to its rather unique properties, polytetrafluoroethylene finds numerous applications in industry. As a result of its slippery character it may be used as a dry lubricant for such

diverse items as oxygen regulators, weapons, pumps, bearings and surgical instruments. It may also be utilised, because of its resistance to chemical corrosion, for articles such as gaskets for pumps, flanges, etc. In addition, due to its excellent thermal stability, the polymer is well suited to high-temperature work.

"Teflon" is absolutely "anti-stick" and spray-coatings have been applied to rubber moulds, baking utensils, agitater paddles, etc., with such success that a great future awaits the material.

Spray coatings of the polymer may be used as absolute seals in hydraulic systems.

(14) The Process of applying "Teflon" Coatings to Steel Surfaces.

Coats of "Teflon" are applied as dry lubricants and corrosion deterents on steel surfaces. The procedure for spray-coating "Teflon" is highly specialised and certain precautionary measures have to be observed to facilitate satisfactory results.

Fitzsimmons and Zisman[81] investigated the process. Articles to be coated with the polymer should initially have a high quality surface finish, prior to the sandblasting operation. In order to obtain a so-called "satin" finish, all objects have to be sand-blasted with clean, dry silica sand no coarser than grade 80. The sandblast-pressure must be regulated to suit the equipment and jet size of the blower.

To achieve optimum results, there should be no delay between the sandblasting procedure and the ensueing oxidising process. However, if the oxidising cannot be done immediately, the sand-blasted articles may be stored, submerged in dry, unleaded petroleum-based solvents. When the desired finish has been obtained, the article is washed very thoroughly with a solvent to remove all traces of sand particles and then dried by means of an air blast which should be free from moisture, oil and dust particles.

Next the oxidising procedure is carried out in an oven which is maintained between 370 and 380^{o}C. The object of this process is to drive off gas occluded on the surface of the metal and to oxidise

the surface sufficiently in order to increase the adhesion of the "Teflon" coat on the metal. Oxidation is complete when a slight change in colour of the surface is observed. Interference colours may sometimes be seen giving various hues ranging from brown to blue and purple.

After completion of the oxidation process, the object is allowed to cool to room temperature in the oven and then the first spray coating is applied as soon as possible. Clean rubber gloves are usually used to handle objects so as to avoid contaminating the surface with fingerprints or other foreign matter which would later prevent satisfactory adhesion of the polymer on the metal surface. Fitzsimmons and Zisman recommended the use of a "De Vilbiss E.G.A." spray gun with a number 390 nozzle for coating with "du Pont" polytetrafluoroethylene. To prevent contamination of the metal surface, the spray gun should incorporate traps for removing oil, moisture and dust particles.

The "Teflon" is strained through either unused cheesecloth or a 150-mesh stainless steel sieve to remove larger particles which may affect the quality of the coating. The gun should be operated without the blower, with an atomising pressure in the region of 20 - 25 pounds per square inch. The "Teflon" in the gun should at no stage exceed the 16^{o}C mark. The nozzle should also be regulated to deliver the smallest quantity possible, giving a spray just visible. Such a spray will deposit a coating 0.0002 - 0.0003" thick on steel. Usually two coats are applied. The amount of "Teflon" per coating should just fully cover the surface of the object being sprayed. Attention should be paid during spraying to prevent dust and foreign matter from settling on the wet coat.

During the first application, all the internal surfaces should be coated first and any excess build-up should be avoided on the edges and in the holes. Judging the coat for the required thickness is fairly difficult, but one which causes the surface of the object being sprayed to become just visible will give satisfactory results. The coat should possess a dry dull (matt) finish unlike the smooth

shiny deposit which is normally associated with spray painting. The spray gun is held approximately 6 - 10" from the object during spraying. It is of paramount importance that each coat is dried thoroughly before fusing it in a furnace. The drying operation must be carried out slowly, since the expulsion of water vapour from the coating will result in porosity of the final, fused article. The objects are therefore air-dried for about 16 hours under dust-free conditions. After air-drying, each coat of "Teflon" must be fused by baking at about 400°C in a furnace. This is done to achieve satisfactory adhesion of the "Teflon" on the metallic surface. The fusion time is determined by the conduction, mass and type of metal in use. Due to the low thermal conductivity of "Teflon", articles which are fully covered by the polymer, will have an appreciably larger fusion time for the second coating. For instance, a piece of metal 1/4" in thickness will take about 10 minutes for fusion, while a metal surface 1" thick will take as much as 30 minutes at 380°C for complete fusion.

For the best results a recirculatory type of hot-air furnace should be used. Precautions must be taken to ensure adequate ventilation whenever "Teflon" is heated to about 200°C due to the fact that small amounts of toxic substances are driven off.

In order to produce a tougher "Teflon" coating the object should be rapidly cooled from 400°C to 200°C after fusion. This method yields an amorphous type of coating which has proved to be tougher than the crystalline type. Further cooling of the article is effected by immersion in water.

The second coat is applied, after drying the first coat, in the same way as the first case except that the baking time has to be extended by about 10 minutes. After the second coat the combined thickness of the "Teflon" should be between 0.0004" and 0.0006".

Finally the object may be buffed manually by using a coarse piece of canvas or a buffing wheel.

The quality of the "Teflon"-coated surface may be judged

visually and should show no high-spots, cracks or wrinkles and the coating should not peel off when scratched with a fingernail.

(15) Cleaning the Various Parts of the Film Balance.

The method used for cleaning the float-assembly varied according to the degree of contamination of this section.

Between each series of experiments on the same material on the surface, the float and its accessories were cleaned by scrubbing the parts with redistilled benzene, with the aid of a small soft brush or a piece of surgical cotton-wool, in a beaker. After this, the parts were rinsed twice with fresh quantities of the benzene and allowed to dry. However, between series of runs on different materials, the float assembly was cleaned in a bath of chromic acid solution in such a way that the stainless steel sections of the clips were prevented from coming into contact with the acid. After an overnight soaking in the acid solution, the parts were thoroughly rinsed, first in distilled water and then in conductivity water and dried with the aid of filter paper.

The glass T-shaped beam of the balance was also cleaned in a similar fashion, by sponging down with redistilled "Analar" benzene, but before a new material was spread on the substrate, the glass beam was dipped for a while in a chromic acid solution in a flat dish and then thoroughly rinsed with pure water and dried with the aid of filter paper. The paper was just held touching the beam to absorb most of the excess water adhering to the beam. This procedure was essential for the satisfactory adhesion of the water film to the beam, due to the fact that water would not adhere to and wet the beam completely if particles of grease or foreign matter were left on the surface of the glass.

The method adopted for cleaning the "Teflon" trough was essentially the same. Between series of runs on the same compound, the trough and barriers were left to soak overnight in a solution of detergent. The following morning the "Surf" solution was rinsed out with tap water and the parts were gently scrubbed with surgical cotton-wool. Copious amounts of distilled water and finally about 250 ml of conductivity water were used to rinse the trough. Filter paper was used to draw off any

drops of water remaining on the surface.

The metallic parts of the film balance were cleaned when it was deemed necessary by means of a slightly moist cloth which effectively removed most of the dust particles. The constant temperature room was also kept as clean as possible to avoid errors in surface measurements due to contamination.

B. THE PURIFICATION OF WATER USED AS SUBSTRATE IN SURFACE CHEMISTRY.

From the earliest days, most investigators in the field of surface chemistry have realised that the water used should be as pure as possible in order to obtain satisfactory results in experiments which involved the spreading of surface films on aqueous substrates. For this reason they have usually made use of the purest form of water available, normally distilled water. Later, with the advent of ion-exchange resins, many workers have prefered to use water deionised by resins, as this was easily obtainable, apparently of excellent quality and relatively inexpensive to produce. However, to rid themselves of anomalies in surface measurements due to contamination by the water, certain investigators have made use of the highly pure conductivity water used in the measurement of the conductance of aqueous solutions.

During 1958 Schenkel and Kitchener[82] reported that conductivity water, prepared by ion-exchange methods, produced anomalous surface effects. They attributed these effects to traces of weakly basic particles, probably polymer fragments which were dissolved from the resin. A short while later Klein and Gordon[83], while engaged in research work at the Millipore Filter Corporation, Watertown, Massechussets, also observed evidence of contamination of water deionised by resins. They were in complete agreement with Schenkel and Kitchener that the conductivity was an unreliable index of the absolute purity of the water obtained by ion-exchange methods. They found that the contamination could be removed by passing the ion-exchange purified water through "Millipore" filters.

At approximately the same time Gaines[84] found that variations in

the force-area isotherms of stearic acid, originally thought to be due to the effect of the spreading solvent were also related to the purity of the aqueous substrate liquid. He tested water from three sources:

(a) Ordinary laboratory distilled water.

(b) Deionised water, prepared by passing distilled water through a column of fresh commercial mixed-bed resin.

(c) Water redistilled from a two-stage fused quartz still, using ordinary distilled water as starting material.

With the aid of a "Cenco Hydrophil" balance and a careful technique, Gaines was able to obtain force-area isotherms on "fresh" and "used" surfaces for stearic acid films. He found that the molecular areas were smaller on quartz-redistilled water than with that from the resin column. For example, stearic acid gave an area per molecule of 20.4Å^2 on resin deionised water, while the value was reduced to 20.02Å^2 on water obtained by distillation from quartz. (No specific indication of the precision was given.)

Fowkes, Ronay and Schick[85] during their researches on "Monolayers in equilibrium with lenses of oil on water", made use of water which had been redistilled twice. The second distillation was from a dilute solution of alkaline permanganate using a stream of water-pumped nitrogen to sweep out any carbon dioxide. The water was finally collected in a block tin condenser.

Franks[86] observed that the introduction of ion-exchange resins had opened new fields for obtaining good quality water which was suitable for most types of laboratory operations. Most workers have used the specific conductivity of the water as a criterion for its purity. Whilst this method provided an excellent indication of the absence of electrolytes, it could give no assurrance of freedom from contamination in the water of an organic, colloidal or non-electrolytic nature. Such impurities, due to the fact that they would very readily be concentrated at liquid interfaces, could exert quite a powerful influence on the surface behaviour of films spread on aqueous substrates. As already mentioned, Schenkel and Kitchener cast doubts on the suitability of ion-exchange purified water for use in surface work. Franks maintained that in addition to the specific conductance, the surface

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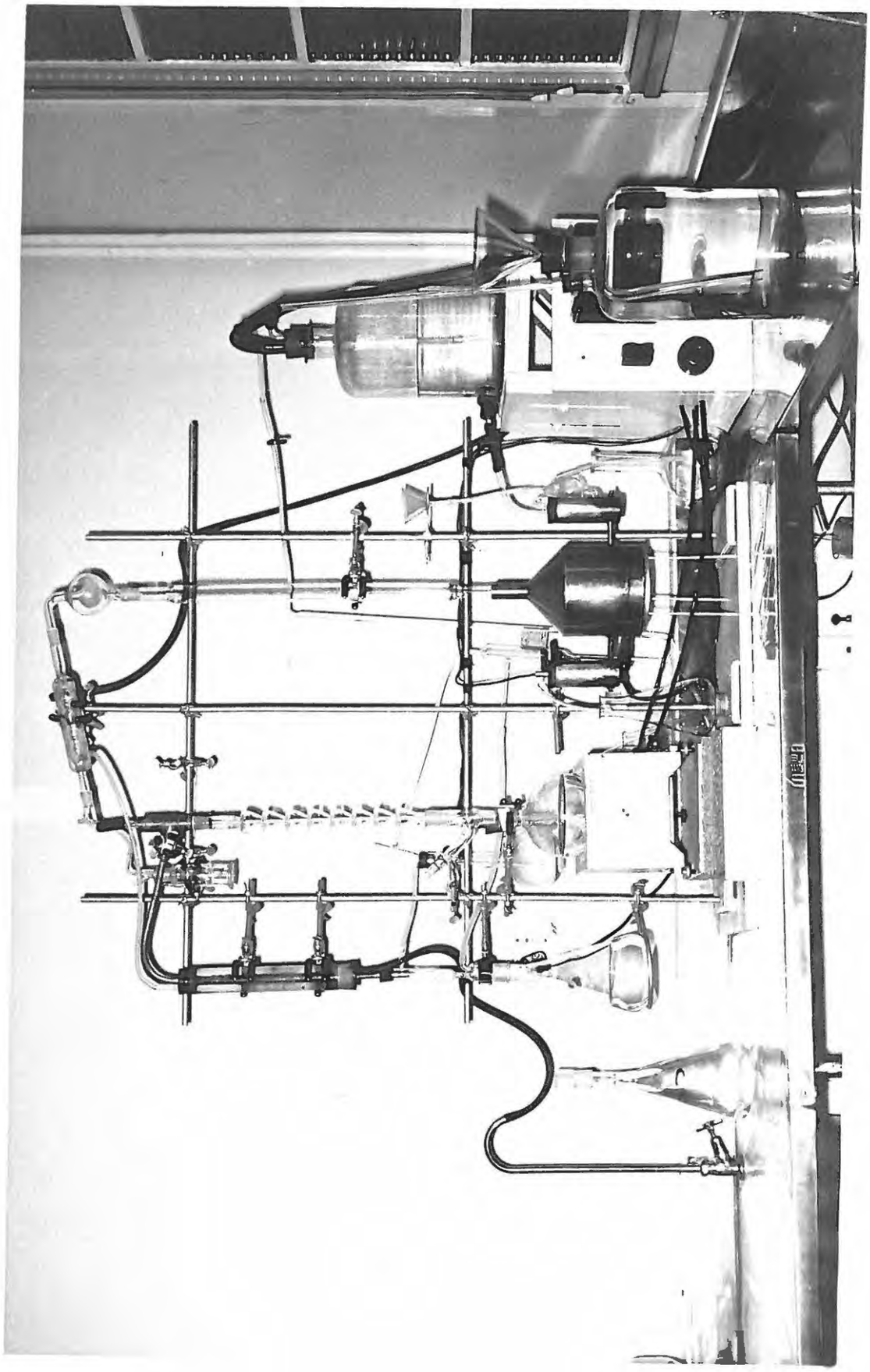
tension of the water should be used as a criterion of its purity. He designed a laboratory still for the production of ultra-pure water. It consisted essentially of a distillation of the water from an alkaline permanganate solution, after which the steam was bubbled through boiling phosphoric acid to remove volatile impurities. This procedure had been developed in these laboratories many years ago and was published in 1951[87].

(1) The Conductance Water Still.

During the early stages of the present research, use was made of pure water from a "Dowex" mixed-bed resin. The water obtained in this way was found to be free from interfering electrolyte ions, yet gave erratic results when films were spread upon substrates consisting of this water. It was also observed that, after having been in contact with the resin for some time, the water attained a slightly brownish colour and subsequent tests confirmed the suspicion that colloidal organic impurities were leached out of the resin bed and appeared in the effluent. A great deal of trouble was experienced in the earlier stages by using such resin-deionised water on the substrate for surface studies. At certain times, when the resin was nearing exhaustion, the situation became so critical that it was virtually impossible to obtain a clean surface by sweeping and sucking off the impurities. The contamination rose to the surface from the body of the liquid after each sweeping.

When it was realised that these difficulties might arise from the use of resin-deionised water, it was deemed advisable to use a conductance water still for preparing the water used for surface experiments. The one used had been constructed for producing the highest possible quality water for precision measurement of conductances of dilute aqueous solutions. It was designed and built by Faure, Faure and Gledhill[87]. It was designed with an eye on compactness and capacity for the routine production of high quality water within a reasonably short period. It was found that the quality of the water improved with the length of time the still had been in operation, only reaching a minimum conductance after many hours. This was probably due to the fact that certain parts of the still, not in continuous contact with the water, were progressively leached out and the impurities removed. Hence the still was designed so

4. CONDUCTANCE WATER STILL.



that it would operate automatically for long periods without attention. After the collecting flask had been filled, the water was automatically syphoned back into the reservoir. By this arrangement water of an extremely high purity was continuously available with the minimum of attention.

(a) Description of the Still. (See Fig. 11.)

Two 10 litre "Pyrex" aspirators were used as reservoirs for laboratory distilled water. The first aspirator was fitted with a short-stemmed funnel for pouring the water in, and a glass tube which connected it to the second aspirator. The second one was situated above the first on a wooden stand which served to house the electrical control apparatus.

The second reservoir was equipped with a rubber stopper through which was passed three glass tubes; one from the first aspirator, the second from a vacuum pump, while the third formed part of the recycling device. This stopper was rendered air-tight by putting a layer of stop-cock grease round the holes through which the tubes passed.

From the upper reservoir, the water flowed along a glass tube with a short rubber insert into the metal boiler via a side-arm which was also provided with a constant-level device. A stop-cock fitted over the rubber tube, enabled the water supply to be turned off when the still was inoperative, while the rubber tube served as a flexible joint to facilitate the alignment of the still and the aspirator.

The metal boiler was provided with two small reservoirs, one on each side, connected to the main boiler via capillary tubes. The reservoir, connected to the upper aspirator, contained the inlet tube which determined the level of the liquid in the boiler, also a level indicator and an airbleed which consisted of a thin glass capillary tube of about 0.3 mm internal diameter.

The inlet tube was flared open at its lower end and had a spout along the periphery. This was to enable air bubbles to rise into the aspirator when the level of the liquid fell below the orifice

1&2 RESERVOIRS
3 OUTLET
4,5 &6 SCREW CLAMPS
7 VACUUM LINE
8 AIR BLEED
9 LEVEL INDICATOR
10 INLET TUBE
11 ELECTRODE VESSEL
12 OVERFLOW
13 RESERVOIR
14 BOILER
16&15 CAPILLARY TUBES
17 AIR BLEED
18 ELECTRODE
19 SOCKET
20 REFLUX COLUMN
21 SPRAY TRAP
22 CONDENSER
23 VENT
24 RUBBER CONNECTOR
25 TIN STILLHEAD
26 INLET TUBE
27 FRACTIONATING COLUMN
28 SIDE ARM
29 BOILER
30 CAPILLARY TUBE
31,32&33 ELECTRODES
34 ELECTRODE VESSEL
35 CONDENSER
36 FILTER
37 COTTONWOOL PLUG
38 CONNECTOR
39 FLASK
40 RECYCLING TUBE
41 BULB

WATER FLOWS THOUGH A,B,C & D IN CONDENSERS.

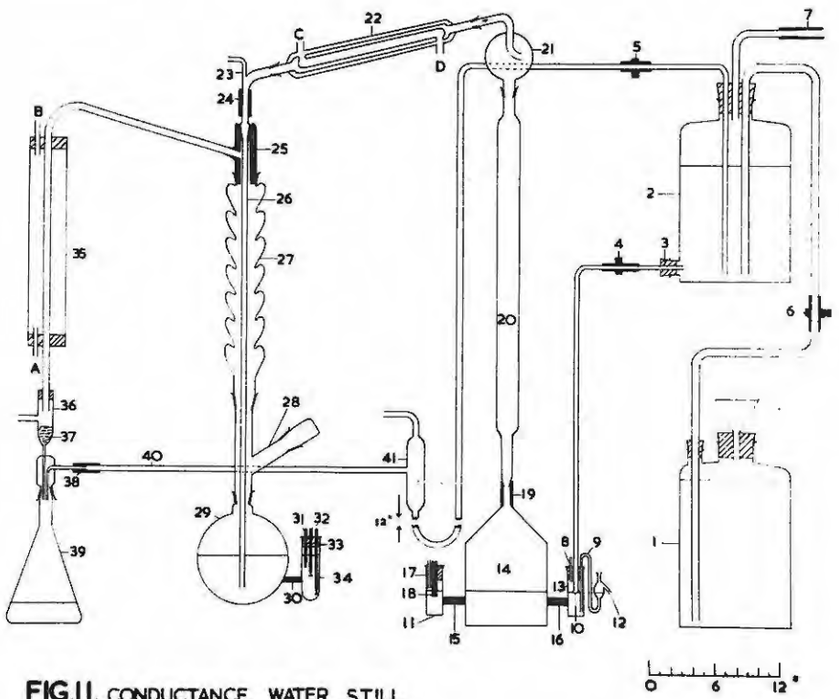


FIG.11. CONDUCTANCE WATER STILL.

of the inlet tube. The increase in air pressure then forced more distilled water down the inlet tube into the reservoir, and in so doing kept the liquid level constant in the boiler.

Air was sucked into the reservoir by way of the air-bleed and hence via the glass tube into the aspirator. The level indicator device consisted of a S-shaped glass tube connected to a small reservoir with side and top outlets. The glass bulb-reservoir was constructed to aid the bubbling process in such a way that it limited the volume of water, entering the side-arm, to a quantity that could easily be handled by the side-arm reservoir. The overflow from the bulb discharged into a receptacle and thus served as an outlet for the water in the event of an air-leak occurring in the main reservoir , causing more water to flow down the inlet tube than could be safely dealt with by the levelling device.

Two litres of a solution, which was approximately 1 N with respect to caustic soda, was contained in the metal boiler which also held enough $KMnO_4$ to give an approximately 0.1 N solution. This mixture was intended to oxidise organic impurities and to retain contamination introduced via slight traces of acid in the distilled water.

The boiler was made from stainless steel to resist rapid corrosion by the caustic solution, which rapidly attacks ordinary glass under the conditions of operation. To heat the boiler use was made of a 900 watt element similar to those used for heating electric kettles. A standard-taper B16 socket, turned from stainless steel tubing and welded to the top of the boiler, fitted into the lower end of an air-cooled reflux condenser. This column was connected to a double-walled water condenser via a spray-trap. All these sections were fitted together by means of "Quickfit"-type joints.

The condenser was joined to the inlet-tube of the glass boiler by means of an adapter with the aid of a glass-to-glass join. A sleeve of specially purified rubber pressure-tubing was used for the purpose of holding the two glass tubes in alignment. This measure

- had to be -

had to be adopted in order to achieve some measure of flexibility during the assembly of the still. The inlet tube to the glass boiler was slightly narrowed at its lower end to avoid any solution, from this boiler, blowing back under conditions of severe bumping.

A pressure-equalizing tube, communicating with the atmosphere through the flask, prevented pressure build-up between the two boilers and so obviated the danger of the apparatus breathing contaminated fumes from the laboratory.

The second boiler consisted of a 2 litre round-bottom flask having a side-arm which was made from a length of capillary tubing 0.7 mm in diameter. A cup, attached to the side-arm, housed the three electrodes which formed part of the control apparatus. The glass boiler normally held about 1 litre of 0.1 M phosphoric acid solution to absorb any volatile basic impurities. It was connected to a fractionating column which acted both as a spray trap and a reflux device. Inside the boiler a boiling-rod was placed to counteract bumping during boiling of the solution.

The fractionating column was surmounted by a block tin condenser having a standard-taper joint to fit the glass column. The tin pipe was inclined slightly at an angle to ensure that the first portion of the distillate, which was usually slightly contaminated by ions, returned to the boiler. The steam was condensed in the tin tube which was surrounded by a water jacket and the pure water was finally collected in 2 litre conical flasks, after passing through a porous plug made of well-leached, high quality surgical cotton-wool. This method had to be adopted to eliminate slight traces of dust particles or greasy impurities.

After the collecting flask had been filled, the water was forced to pass up a tube which caused it to be recycled via the U-tube and reservoir.

The entire still was mounted on a frame-work made from retort stands which was cross-braced and attached to a wooden base. This whole assembly, in turn, was firmly screwed to a stainless steel table and the wall by means of "Jiffy Joint" rods and clamps.

The heating elements of the glass boiler were housed in an asbestos case, and consisted of a 750 watt permanent heater and a 600 watt intermittent or "booster" heater. These elements were hand-wound on a spiral porcelain insulator and the case lagged with glass-wool to prevent, as far as possible, heat losses through conduction.

The asbestos box was equipped with three levelling screws, attached to its base, to facilitate the alignment of the heating mantle with the glass-boiler.

(b) The Electric Circuit Controlling the Still.

In order to allow the still to operate for long periods of time without attention, it was deemed necessary to protect the apparatus against various types of malfunction which could arise.

Another aspect which received consideration, was the ensuring that the two boilers distilled at approximately equal rates, otherwise the second boiler could overflow, or boil dry and crack. The electrical circuit designed for this purpose, guarded against such faults.

The circuit, given in Fig. 12, was so arranged that the 750 watt element of the glass boiler was permanently on, while the 600 watt element, and the 900 watt element of the metal boiler, were regulated by a "Sunvic" type F 102-4 hot-wire relay. The relay circuit was so arranged that the line was connected to electrode 33 in the control device. The electrodes 32 and 18 were also connected, while the metal boiler was earthed. Thus the permanent heaters would only function if the liquid level in the two electrode vessels was sufficiently high to cover the electrodes.

The 600 watt "booster" heater was also controlled by a "Sunvic" relay which was operated by the electrodes 31, 32 and 18. When the liquid level in 29 rose to the level of electrode 31, the "booster" element came into operation and thus a total wattage of 1350 was available in the glass boiler. Hence the liquid in this boiler was boiled more than that in the metal boiler and the level tended to drop in the first boiler.

- The electrodes -

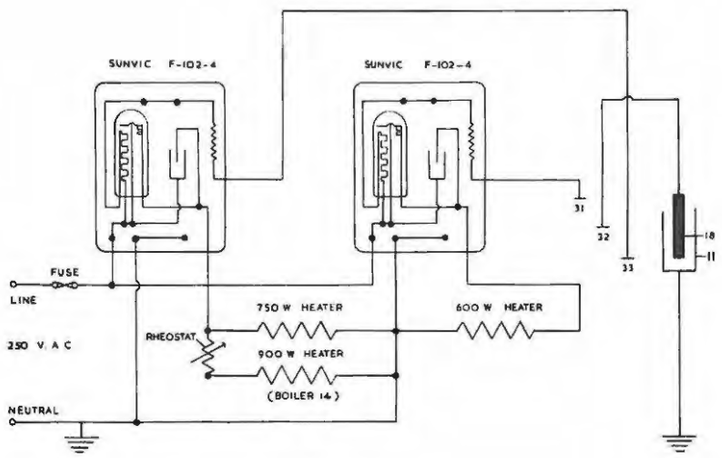


FIG .12. CONTROL CIRCUIT FOR STILL.

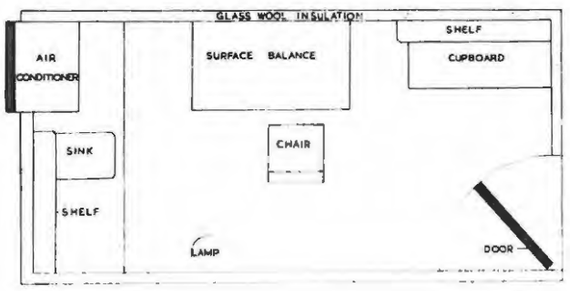


FIG.13. CONSTANT TEMPERATURE ROOM.

The electrodes were made from 0.5 cm^2 platinum foil which were sealed into glass tubes. The electrode vessel was fitted with a rubber stopper through which the three electrodes protruded. Mercury was used to connect the electrodes to the leads of the circuit.

To prevent the still from becoming overheated, in the event of a failure of the water supply to the two condensers, an ingenious device has been developed. This consisted of a small plastic bucket, with holes pierced in its bottom, attached by a lever to a mercury trip-switch. The outflow from the two condensers was allowed to run into this bucket and caused the mercury switch to tilt and complete the circuit to the heaters . However, if the water supply should fail, the bucket would run dry and, thus lightened, would rise and cause the mercury switch to break the circuit. In this way the heaters were cut off and any damage to the boilers avoided.

The boiling rate in the two boilers could also be adjusted to a fine degree with the aid of a rheostat which was connected in the circuit.

Pure water from the still was delivered at the rate of approximately 500 ml per hour. By having the still recycling overnight, pure water was in plentiful supply whenever required. Several conical flasks which had been thoroughly cleaned and leached out, were used as receptacles for collecting the pure water. The pH of the water was found to be moderately constant and a periodic check showed that it very seldom varied beyond the limits 6.5 to 7.5 pH units. Usually the pH was found to be more acidic i.e. in the range 6.5 - 7.0.

The minimum conductance obtained by previous workers for water from this still was of the order of 0.071 micromho/cm. The water obtained from the still was undoubtedly of a very high quality and, because of the absence of organic contamination, admirably suited for use in surface work.

No difficulty was experienced in obtaining clean surfaces

in the trough with this water as substrate liquid. A couple of sweeps served to remove any dust particles. At certain times, only one sweep sufficed to give a clean surface with a negligble surface pressure.

C. THE MICROMETER SYRINGE.

The "Agla" micrometer syringe was developed by the Wellcome Research Laboratories[88] for use in experiments involving the accurate measurement of exceedingly small volumes of liquid. Basically this syringe consisted of a precision-made, all-glass hypodermic syringe which was attached to a micrometer screw-gauge by means of a rigid metal support (see Plate 5.). The screw-gauge actuated the plunger of the syringe.

The glass syringe consisted of three parts - a precision made glass barrel which was accurately calibrated, a glass plunger which was carefully fitted to the barrel and an end-fitting which accepted the steel needles. Number 20 stainless steel needles were almost invariably used. This size being chosen because it formed fairly small droplets which were essential for the satisfactory spreading of films.

The micrometer screw-gauge was attached to the syringe by means of a metal support with a V-shaped groove cut along its length. The glass barrel fitted into the groove and was clamped into position by means of two screws.

One revolution of the micrometer head advanced the plunger of the syringe by 0.5 mm and in so doing delivered a volume of 0.01 ml. The total travel, graduated on the body of the micrometer, was 25 mm i.e. 50 revolutions which corresponded to a delivered volume of 0.5 ml.

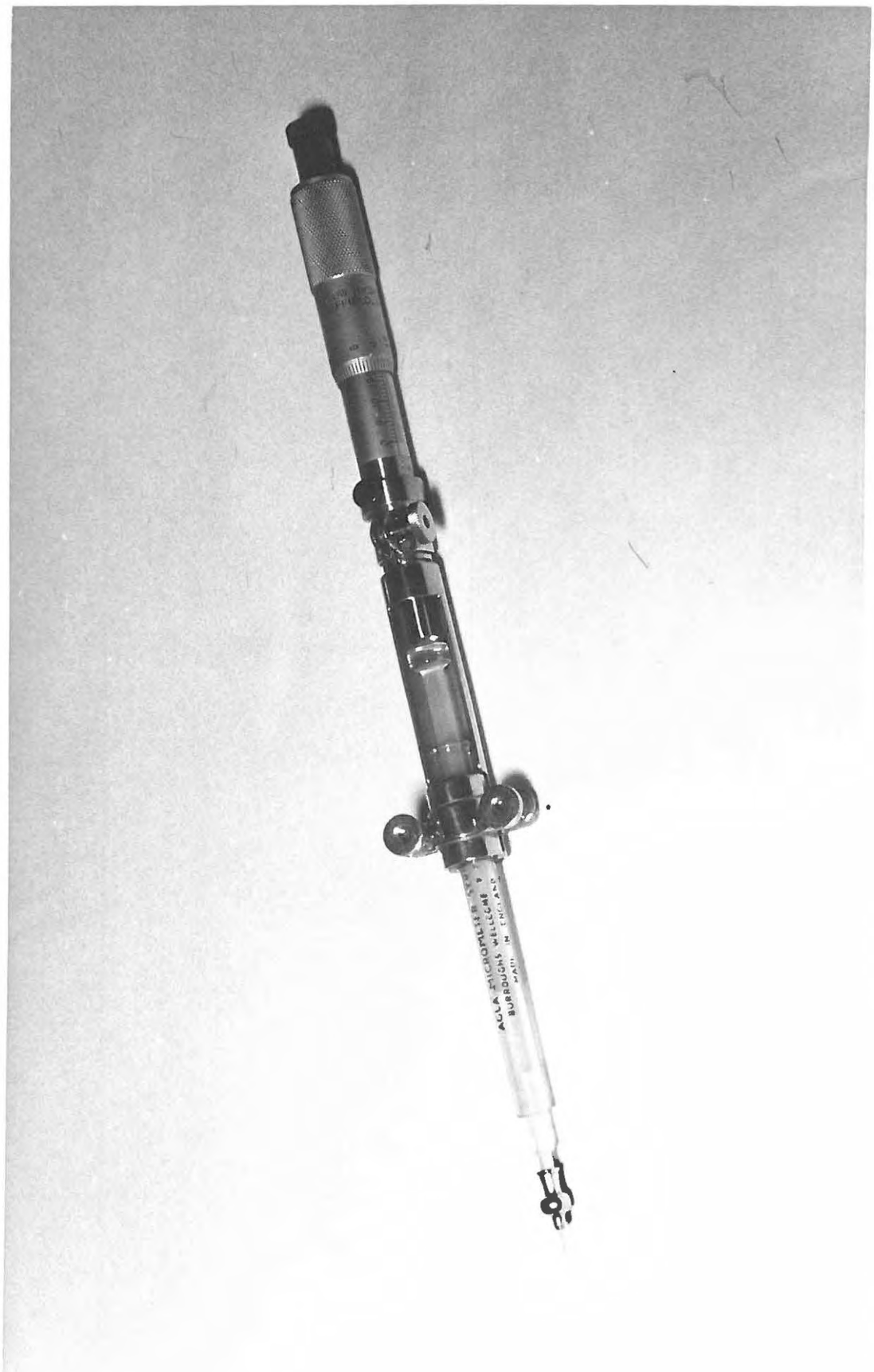
The scale around the periphery of the head was subdivided into fiftieths of a revolution, each graduation thus corresponding to a volume of 0.0002 ml.

(1) The Operation of the Syringe.

In order to fill the syringe it was found easier to detach it from the micrometer section. The needle was dipped into the solution which was to be spread, and the plunger slowly withdrawn until an

- appropriate volume -

5. MICROMETER SYRINGE.



appropriate volume of the solution had been drawn up. The syringe was then inverted so that the needle pointed upwards at an angle, a small bit of cotton-wool was held against the tip and the plunger carefully pushed back so that any air bubbles were expelled. The cotton-wool served to absorb the excess of solution and so kept the needle free from additional droplets.

The syringe was placed in its holder and screwed down into position. The process of tilting the needle upwards and hold a piece of cotton-wool in position at the tip of the needle, was repeated while the plunger was moved along by the screw-gauge until the scale was set at a convenient figure.

For the best results, the solutions were spread on the substrate surface in a regular pattern of droplet, with the needle tip held about 0.5 cm from the surface. After delivery of the required volume of solution, the tip of the needle was caused to just touch the surface momentarily in order to remove residual droplets at the needle orifice.

(2) Cleaning the Syringe.

The glass syringe was cleaned after every series of experiments with different solution by immersion and soaking in a chromic acid solution. The acid was then washed off under a running tap for serveral minutes, rinsed about half a dozen times with ordinary distilled water and finally three times with conductivity water. The various parts were allowed to dry overnight in a dust-free atmosphere and then assembled, ready for use.

Between successive spreadings of the same solution, the syringe was rinsed thrice with redistilled "Analar" benzene and allowed to dry before sucking up further volumes of the solution.

(3) Precision.

The precision claimed for the "Agla" micrometer syringe is such that volumes as small as 0.01 ml could be measured to within $\pm$ 0.00005 ml i.e. a precision of 0.5%.

The volume of solution which was most commonly used during spreading operations was 0.10 ml.

D. THE CONSTANT TEMPERATURE ROOM.

The constant temperature room was situated in the south wing of the physical chemistry block and received about the same amount of sunshine in the morning as in the afternoon. As the building was of prefabricated asbestos construction, the above factor contributed a great deal to the ease of keeping the temperature moderately constant throughout the day.

The dimensions of the room were 12. x 10.0 x 6.2'. In order to insulate the interior from the extreme variation of temperature prevalent throughout most of the year in Grahamstown, it was decided to place a 3" layer of glass-wool insulation between the outer and inner walls of the room. The outer walls consisted of a compressed asbestos compound, while the inner wall was of fibre-board construction.

The wooden door was slightly recessed in its framework and no windows were fitted. The floor, of wooden boards, was also lagged with glass wool.

All these precautions served to give a reasonably well insulated room with an unregulated temperature variation of 15°C overall during the year. It varied from a minimum of about 10°C to a maximum of about 25°C in extreme conditions.

As nearly all the experiments were carried out at 20°C, use had to be made of a temperature regulating device. For this purpose a specially adapted "Frigidaire" air-conditioning unit was used. It worked on the reversible-cycle principle and could thus either heat up or cool down the interior of the constant temperature room. In this way the temperature could readily be kept to 20°C.

For cooling the room, the compressor precooled the refrigerant and sent the cold liquid through a radiator. The hot, humid air was sucked in by means of a fan and was dehumidified and cooled. The resultant air had a relative humidity of 50-60%.

On the other hand, for heating, the conditioner could reverse its cycle and heat up the cold air from outside. In this case it was necessary to switch the cooler on first, and after about 5 minutes move the control knob to the heating position.

- The room -

The room conditioner offered the following funtions:

1. Circulation of the air in the room by means of three deflector gratings.
2. Filtering of the air in the room and from outside.
3. Ventilation of the air conditioned area.
4. Exhaustion of the stale air inside the room.
5. Cooling or heating of the interior of the room.
6. Dehumidification of both the air inside and the incoming air from the outside.

The temperature control switch had a set differential of about $1^{o}C$ i.e. although the temperature of the room could vary by about $1^{o}C$, the apparatus inside, would remain at a temperature which varied between smaller limits. In practice it was found that the temperature could be controlled to within $0.5^{o}C$ of the required $20^{o}C$.

The conditioner had built-in thermostatic control switches for full temperature control. In addition, selector switches were provided to give fresh air or circulation of air already inside the room by means of adjustable air control louvres. Fresh air could be introduced up to a maximum of 150 cubic feet per minute, while the exhauster allowed the room to be exhausted of stale air at a rate of 100 cubic feet per minute.

The air filter was made from an oil-treated type of fibre-glass network and effectively removed air-borne impurities inside the room and also from fresh air entering from the outside atmosphere.

The conditioner was housed in the south wall of the room about six feet from the floor. By means of louvres the air could be circulated throughout the entire room.

From Fig. 13, it may be seen that the south wall also housed a sink of stainless steel.

The table supporting the balance was attached to the west wall, while the north wall, beside the door, housed a cupboard for storing various accessories for the balance.

Two shelves were fitted to the walls of the room in order to store the chemicals used during the experiments. It was found convenient to store all materials, especially solvents and the pure water in the

constant temperature room where they could equilibrate under operating conditions.

On the whole, the constant temperature room was well suited to research on monomolecular surface layers, for it provided not only constant temperature, but also gave a controlled humidity and a relatively dust-free atmosphere.

E. THE pH METER.

A periodic check was kept on the pH of the substrate liquid in order to ascertain the variation in the pH of the liquid from one batch of water to the next. To carry out this procedure, use was made of a "Beckman model G" battery operated pH meter.

(1) Operation of the Meter.

The pH meter had to be standardised frequently to ensure precision in measurements of the pH of the solutions which were being used. For this purpose pH buffers were used, usually of pH = 7 and pH = 4. After standardising the meter, the pH of samples were measured merely by introducing these into the small vessel and noting the pH on the dial. The precision of the instrument, claimed by the manufacturers, was a reproducibility of 0.02 pH units.

During the periodic checks which were kept on the conductivity water, it was found that the pH varied within certain limits, probably due to minute traces of phosphoric acid distilling over from the glass boiler. Slight traces of $KMnO_4$ from the first distillation might also have accounted for these variations. However, certain workers [17, 21] have proved that concentrations of PO_4^{2} and MnO_4^{-} ions, of the order of a few parts per million, could not seriously affect the orientation and spreading of monolayers

The pH variation was usually in the range 6.5 - 7.5 pH units, with a tendency toward the acidic side.

IV. THE PREPARATION AND PURIFICATION OF MATERIALS.

The chemicals which were used were usually of the highest quality available from the various chemical suppliers. The following list will serve as an indication of the grades of chemicals which were used during the research for spreading on substrate liquids:

Chemical.	Supplier.	Grade.
Myristic Acid.	Eastman Kodak Co.	White Label.
Palmitic Acid.	"	"
Stearic Acid.	"	"
Marganic Acid.	"	"
Tridecanoic Acid.	"	"
Arachidic Acid.	"	"
Tristearin.	"	"
n-Octadecyl Acetate.	"	"
1-Tetradecanol.	"	"
Behenic Acid.	"	Practical
Margaric Acid	Light & Co.	95 - 98% Purity.
Lignoceric Acid.	"	"
1-Pentadecanoic Acid.	"	"
Nonadecanoic Acid.	"	"

Before use, all chemicals were recrystallised twice from suitable solvents, usually benzene, alcohol or petroleum ether. The method used was to reflux the material for a few minutes with the solvent and some activated charcoal. The mixture was then filtered and the excess solvent evaporated on a water-bath or under radiant heat from a battery of infrared lamps. Finally the materials were dried in a desiccator.

A. THE PURIFICATION OF MATERIALS BY ZONE MELTING.

The origin of the process of zone purification might be traced back to 1952 when the first paper on the subject was published by Pfann[89].

Zone refining is a process whereby a rod of impure material is purified by means of heating a small zone at a time and moving this molten zone along the length of the rod. (See Fig. 14.)

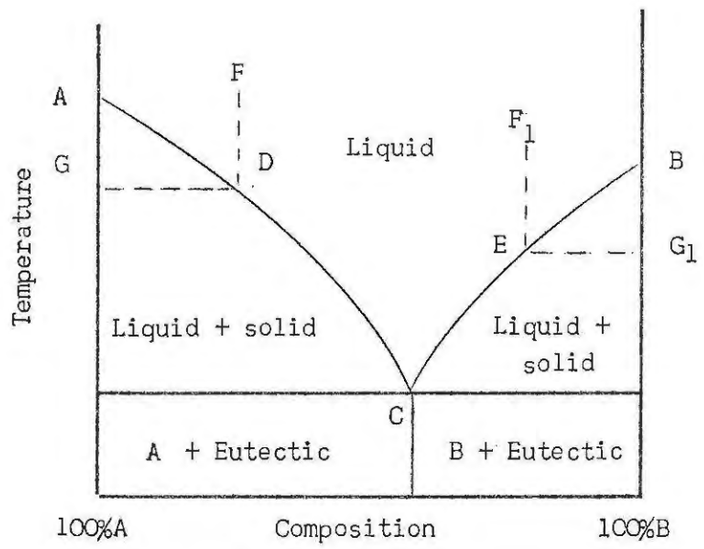
- Pfann[90] -

Pfann[90] found that impurities in the material tended to be transported in the molten zone, and by repetition of this process, a high degree of purity could be obtained. One of the first applications of the process of zone melting was in the preparation of ultra-pure Germanium for the use in transistors for radios. The technique has subsequently found wide applications in the purification of certain organic and inorganic compounds.

The theory of zone refining has been dealt with in great detail by such investigators as Pfann, Herrington[91] and Braun[92]. Pfann and Braun treated the process in a mathematical way, while Herrington explained it with the aid of phase diagrams for systems which either exhibit a simple eutectic or a series of solid solutions.

Principles of Zone Refining.

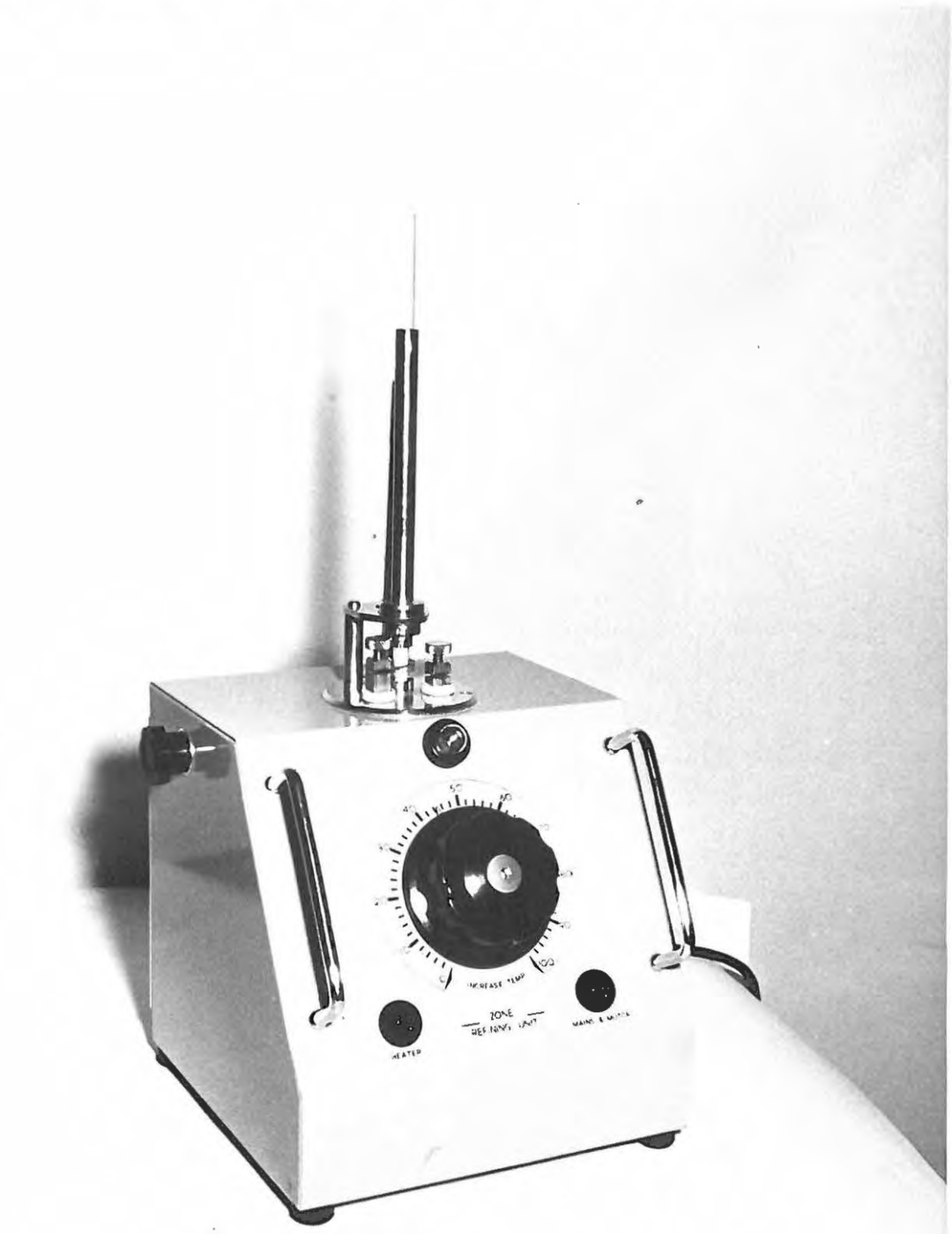
When a liquid mixture is cooled, the solid that crystallizes out has a slightly different composition from that of the liquid: the purification of materials by zone refining depends on this difference. In a system where the phase diagram is of the type given below:



The cooling of liquid of composition F causes crystallization of pure component A when the temperature D is reached; if the original composition, however, corresponds to F_1, the first solid to separate will be pure component B. The pressure throughout the process is kept constant.

In theory, a material may be purified by a single passage of the

6. ZONE MELTING APPARATUS.



zone along the length of the rod. In practice, however, small volumes of liquid containing some of the impurity, is trapped in the growing crystals during the process of solidification and the material remains impure to a certain extent.

Repetition of this zone purification process results in the formation of larger crystals, and consequently less impurity is trapped by the liquid which forms the crystals. Hence the purification continues at a more rapid pace. Many organic chemicals have been zone refined, notably benzoic acid, which after eight passes was found sufficiently pure to be used as a volumetric standard.

(1) Apparatus.

In order to purify samples of the materials, which were used for spreading as monomolecular layers on aqueous substrates, use was made of a "Baird and Tatlock" semi-micro zone-melting apparatus. This instrument was constructed to "National Chemical Laboratories" pattern.

The apparatus consisted essentially of an electrically driven reduction gear which was coupled to a vertical leading screw and a heating element which was controlled by a Variac. The motor drove the screw at a rate of about 2 cm per hour. At the lower extremity of the screw, a small metal platform was attached to serve as a support for the glass tubes containing the samples of the material.

These melting tubes were manufactured from "Pyrex" glass and had the following dimensions: 280 mm in lenght, 12 mm external diameter for the widest bore tube, while the two other sizes had diameters of 8 mm or 5 mm. The tubes were open at the top, but closed about 40 mm from their lower ends.

Three interchangeable metal guide-sleeves and nichrome heating elements, to suit these three sizes of melting tubes, were supplied with the apparatus.

The maximum temperatures that could be obtained by the three sizes of melting tube were 210°C, 256°C and 310°C, with the widest bore tube giving the lowest temperature.

Current was supplied to the heating element through a step-down

transformer and potentiometer, giving a means of adjusting the current flowing through the heating element.

(2) Operation of the Instrument.

A melting tube of the desired size was selected by taking account of the temperature required for the sample to melt, and the amount of substance to be used. Normally the small bore tubes were used since the amounts of material necessary for spreading were very small.

The tubes were cleaned with chromic acid and washed with copious amounts of distilled water, and finally three times with conductivity water. They were dried in an oven at about 60°C for about an hour and then allowed to cool.

The tube was filled with the substance to the top. The material was then melted and allowed to resolidify so that the tube was filled to about 75 mm from the opening.

A heating element, of the size to suit the tube, was fitted to the terminals of the the instrument and the control sleeve was placed into position above the coil of the heating element.

Next the melting tube was inserted through the guide sleeve so that it passed through the coil of the heating element and was supported on the platform of the vertical screw inside the apparatus.

The heating element was so arranged that the glass tube could pass freely up and down through the element, giving it an even clearance from top to bottom.

On the left hand side of the instrument a control knob was situated, by means of which the tube could be wound up or down as required. With the aid of this knob the position of the tube was adjusted manually until the upper surface of the substance in the tube was just below the heating element.

The "Mains and Motor" switch was brought into action. Next the "Heater" was switched on and the potentiometer control knob adjusted until the solid material in the tube started to melt. The length of the molten zone could then be adjusted to a 10 or 15 mm section of the rod of material. After this adjustment , the melting tube was raised

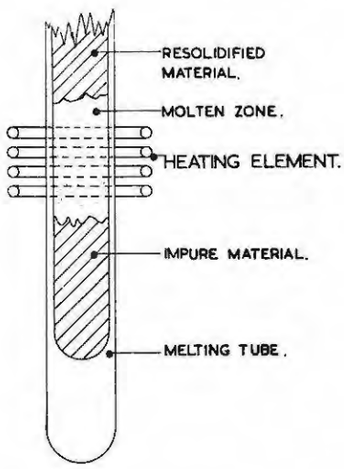


FIG.14. ZONE MELTING APPARATUS.

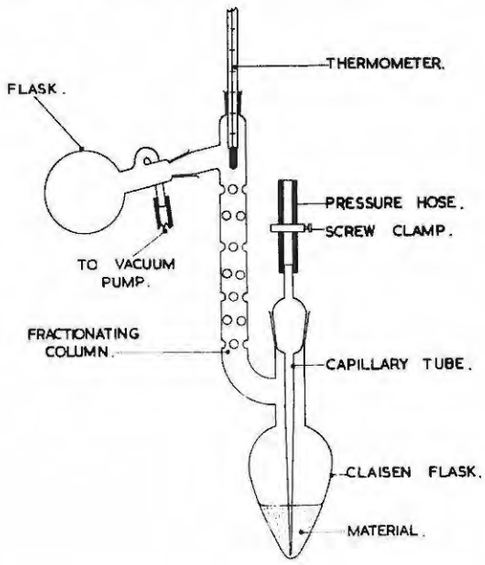


FIG.15. VACUUM DISTILLATION APPARATUS.

automatically at a rate of ahout 2 cm per hour until it reached the end of its travel. At this point a freewheel device was brought into action. As the total travel was approximately 12 cm, each melting run last about 6 hours. If further runs were necessary, the tube had to be would down manually, by means of a knob, to its original position. A new run would the start automatically. After a few runs, all the impurities were concentrated at the lower end of the column and the purified substance could be obtained by melting out only the upper section of the material in the tube.

All the fatty acids, which were purified by this zone melting procedure, were given 10 passings and were obtained in an excellent state of purity. The melting points of palmitic, stearic, arachidic and behenic acids were found to be 62.9, 69.4, 75.0 and 79.5°C respectively. These values compare very favourably with the values obtained by other investigators for the purified acids.

In order to obtain accurate melting points of these materials, use was made of a special melting point apparatus which incorporated an insulated air-jacket surrounding the melting point tube and bulb of a finely graduated thermometer.

B. THE PURIFICATION OF MATERIALS BY VACUUM DISTILLATION.

Fig. 15 illustrates the vacuum still which was used for purifying certain long-chain fatty acids.

A "Claisen" flask with a pear-shaped bulb was used, due to the fact that this type was found to be most suitable for the small amounts of substance used. The side-arm of the flask was fused to a fractionating column about 10 cm in length. This column was of the type consisting of a glass tube with indentations at regular intervals. Surmounting the column was an outlet to the collection flask and a socket which held a 0 - 250°C thermometer which was equipped with a "Quickfit" taper B10. A capillary tube was fused to a standard B14 taper which, in turn fitted the "Claisen" flask. The capillary tube reached to within 2 or 3 mm of the bottom of the flask. A short length of rubber pressure-hose which could be closed with the aid of a screw clamp, was attached to the

capillary tube on the outside. This device regulated the amount of air entering the apparatus.

The collecting flasks had standard B14 taper sockets to fit the outlet of the fractionating column. In addition, a side outlet was provided on these flasks in order to connect the apparatus with the vacuum pump. The connection was achieved with the aid of a short length of rubber pressure-hose. Incorporated in the vacuum line was a U-shaped direct-reading manometer which was graduated in mm of mercury.

A "Speedivac" vacuum pump with trap was used. This pump gave pressures of 3 mm Hg which were low enough for the purpose in hand.

As a result of the high boiling points of these acids, even under reduced pressure, a heating mantle had to be provided for the column and side outlet. This was done to prevent the materials from condensing on the walls of the column and the outlet. After some experimenting with various types of lagging, the following method was adopted:

A single layer of asbestos paper was wrapped round the column and outlet. Over this was wound a length of resistance wire of the type used in electric radiators. It formed a closely-wound spiral heating element which was connected to the mains supply via a Variac. This Variac served to adjust the current passing through the wire and consequently the resultant temperature. Over the wire a layer of closely-spaced asbestos string was wound to insulate the column even better.

This heating mantle worked very well indeed and by fine adjustment of the temperature by means of the Variac, choking of the column, through condensation of the material, was totally eliminated.

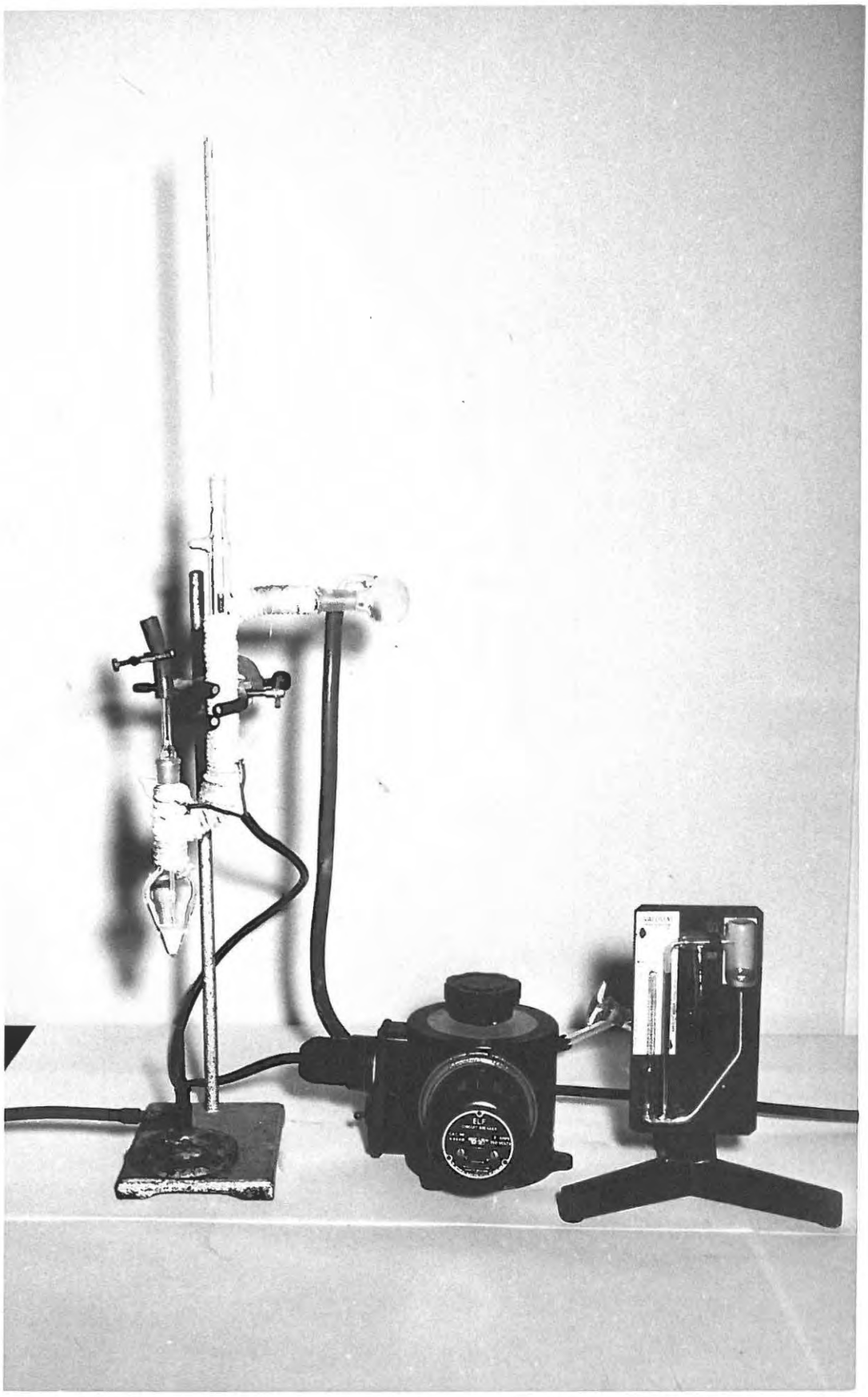
The Variac incorporated a trip-switch type of fuse which effectively prevented the operator from putting too high a load on the resistance wire.

The materials which were to be vacuum distilled, had already been recrystallized as mentioned earlier.

(1) Procedure for Vacuum Distillation.

The glass sections of the apparatus were cleaned by means of soaking in a chromic acid solution, washing with copious amounts of tap

7. VACUUM DISTILLATION APPARATUS.



water and finally rinsed with conductivity water. Care was taken to prevent any acid from coming into contact with the mantle which jacketted the column. Within about 2 minutes of switching on the Variac, the mantle reached the required temperature. Then the vacuum pump was brought into action while the material in the flask was gently heated. The volume of air entering the apparatus could be adjusted with the screw clamp.

The initial distillate was discarded, as was the last fraction.

(2) The Boiling Points of the Fatty Acids.

Name of Acid.	Number of Carbon Atoms.	Boiling Point in °C. (according to Markley[93].)
Palmitic	16	351.5 at 760 mm Hg
Margaric	17	363.8 "
Stearic	18	376.1 "
Nonadecanoic	19	299 at 100 mm Hg
Arachidic	20	204 at 10 mm Hg
Behenic	22	306 at 60 mm Hg
Lignoceric	24	-

As may be seen from the above table, the boiling points of the fatty acids are fairly high. Hence it was necessary to distil the higher members under partial vacuum. The following 3 acids were selected by the author for purification by this means and gave the following boiling points:

Name of Acid.	Boiling Point in °C.
Palmitic	185 at 4 mm Hg
Stearic	195 "
Behenic	195 at 3 mm Hg

C. THE PURIFICATION OF THE SOLVENTS WHICH WERE USED FOR SPREADING THE MATERIALS.

The solvent which was most commonly used in spreading the materials, was benzene. In certain cases, however, light petroleum ether of b.p. 60 - 80°C was used. The benzene was "Analar" reagent quality, obtained from B.D.H. The maximum limits of non-volatile matter were stated to be 0.002%, organic impurities

- were stated -

were stated to be absent, while the water content was 0.1%.

In order to purify the benzene further, sodium wire was added to the benzene which was the left standing for 24 hours to remove all the moisture. Then the benzene was redistilled in al all-glass still. Only the fraction boiling between 78 and 79°C was collected. The benzene residues, obtained from the solutions which were left over after spreading, were collected and reclaimed. The residues were shaken up with NaOH solution to remove the acid impurities in a 2 litre separating funnel and then allowed to settle out. The lower contaminated layer was run off and discarded. The process was repeated until the extract was quite colourless. The benzene was then washed three times with pure water to remove traces of NaOH in the solution. Concentrated H_2SO_4 was next added to remove the last traces of alkali present. This was also shaken up and extracted until the layer was colourless. Again the benzene was washed several times with distilled water; then dried with anhydrous P_2O_5 and finally filtered. After this preliminary purification the benzene was distilled.

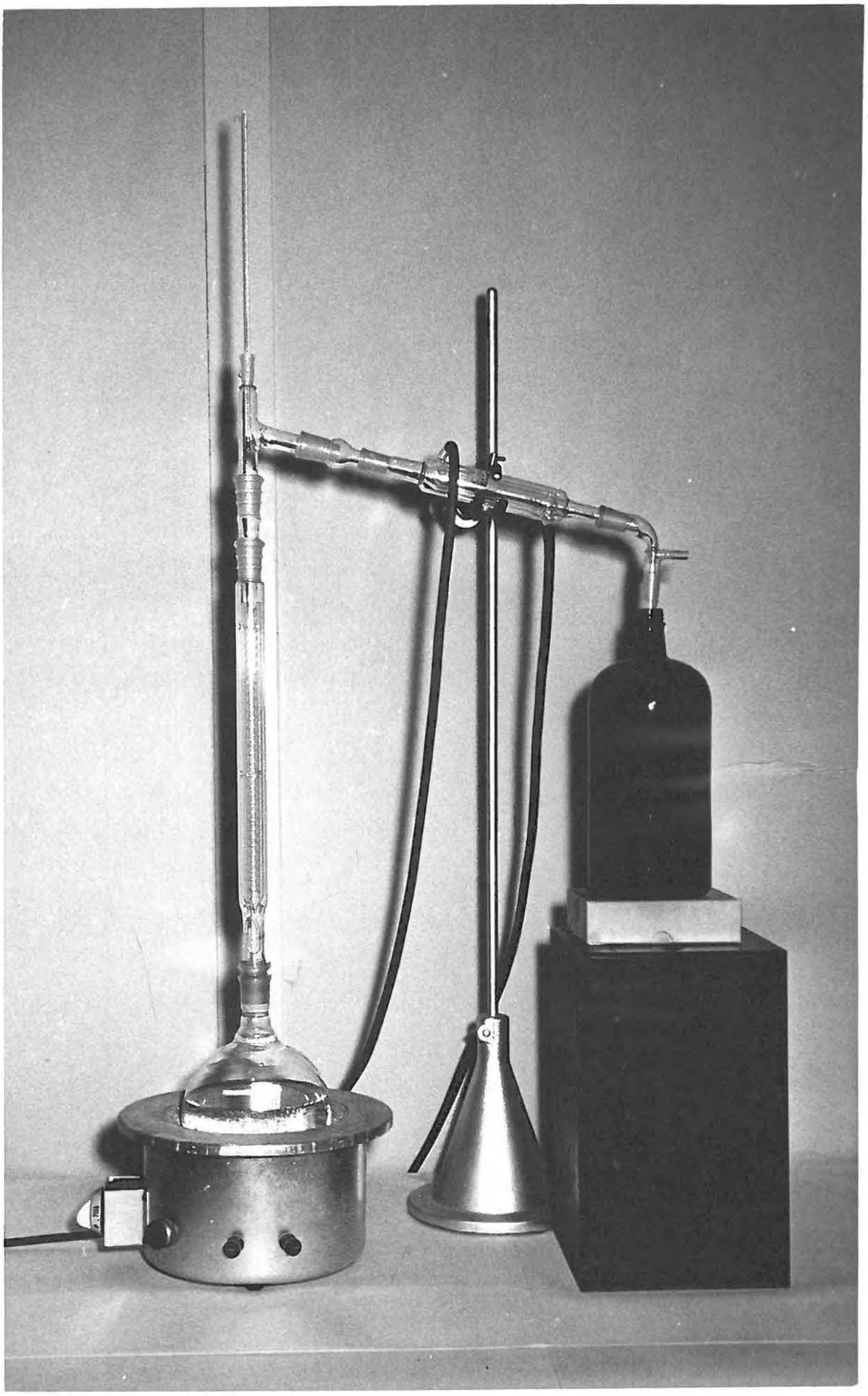
(1) The Benzene Still. (See Plate 8.)

The still consisted of a 2 litre "Pyrex" round-bottom flask surmounted by a fractionating column made entirely from "Pyrex" glass. This column consisted of 3 concentric tubes, the innermost of which had a closefitting glass spiral. The benzene vapour rose inside the outer jacketing space, was diverted downwards through the annular space between the tubes and finally spiralled upwards along the glass spiral. A spray-trap was mounted on top of the column and was connected to a double-surface water-cooled condenser.

The flask rested in an electrically heated mantle with a built-in rheostat device to regulate the rate of boiling which had to be critically adjusted to avoid choking the column.

The entire still was set up in a framework made from retort stands and clamps. The bottle which was used for collecting the purified benzene was cleaned with chromic acid to remove all organic impurities, rinsed with copious amounts of distilled water and finally several times

8. BENZENE STILL.



with conductivity water and allowed to drain and dry in a dust free atmosphere. This bottle was placed below the outlet of the condenser in such a way that very little of the benzene could be lost through evaporation.

A boiling tube or boiling beads facilitated the boiling of the benzene and prevented serious "bumping".

To avoid choking the column in the initial stages of the distillation, the temperature of the heating mantle had to be regulated very carefully, but as soon as the lower boiling point fraction had been discarded, the still functioned perfectly and distilled at the rate of 1 litre every 2 hours. By this means benzene of very high purity was obtained which was found eminently suitable for spreading procedures.

V. THE CALIBRATION OF THE APPARATUS.

A. THE CALIBRATION AND OPERATION OF THE FILM BALANCE.

After the torsion wire had been securely clamped between the hemispheres on both sides and the correct tension applied to the wire (this was done by the note it gave when touched), the magnets were adjusted to give a suitable damping action and the coil of the electronic null-indicator was so arranged that it was centrally positioned in relation to the loop which was attached to the balance beam. The height of the movable coil was then adjusted so that the coil and the loop were in the same horizontal plane when the balance beam was in its zero position.

The three screws, on the metal base, were adjusted to level the trough. The latter, which had been thoroughly cleaned, was placed in position on the three-point suspension and the float was clipped into position over the edges so that the glass beam of the balance fitted snugly into the slit which was cut in the float.

This position was noted on the longitudinal scale by moving the mobile barrier along until it touched the clips attaching the float to the edges of the trough. This reading proved to be 41.5 cm on the scale and remained at this value throughout the research. The mobile barrier fitted over the two pins of the under-carriage and slipped neatly into position over the edges of the trough.

Next the substrate level indicator was lowered to give a water level of 2 mm above the rim of the trough. The magnifier and illuminating lamp were so arranged that the dial readings could be made without difficulty. Water was added to the trough to bring the level up to the required mark. This was easily done by adding water until the point of the level indicator just appeared to touch its image in the water.

The float was correctly positioned and the ribbons depressed slightly into the substrate. This prevented leakage in the float during spreading.

The dust cover was lowered and the mobile barrier moved towards the float by means of the cords protruding through the holes in the table. When the mobile barrier was about 1 cm away from the float, the contamination was sucked off the surface with the aid of a small glass jet which

was connected to a vacuum pump. The area behind the float was also cleaned in this way. To compensate for the water removed in this cleaning operation, a little was added until the level once again reached the predetermined height.

Everything was now in readiness for the calibration. The control knob was adjusted so that the coil was correctly positioned in the centre of the loop with the measuring dial set on zero. The electronic null-indicator was connected to the 20 volt range of the voltmeter, and set on the 10 volt mark i.e. the middle of its range. This position represented the zero point of the balance beam. A small platinum rider was placed on the beam by means of the remote control lever. The position of the rider could be read from the scale below the lever with the rider placed on position 1 on the beam. The dial knob was turned until the needle of the voltmeter was brought back to its zero position on the scale.

The reading was noted on the dial, and the procedure repeated for successive positions of the rider on the beam. A graph of these beam scale readings against the dial readings was plotted. This gave a calibration graph for the balance beam. It was linear as expected and is shown in Graph 1.

From this graph a relation between the angle of torque and the force in dynes per cm. necessary to restore the float to its zero position, was obtained.

After spreading, about 10 minutes was allowed for evaporation of the solvent. The films were then compressed between the mobile barrier and the float. For each position of the barrier, the scale reading and the reading on the circular dial were noted.

A graph of the film area against the force in dynes per cm was plotted and from this curve cross-sectional areas for materials could be calculated. This involved extrapolation of the curves.

B. THE CALIBRATION OF THE FLASKS.

A set of three 100 ml "Pyrex", grade B, volumetric flasks was used to make up solution of the fatty acids. These flasks were fitted with ground glass stoppers which effectively prevented leakage of the

volatile solvents used. They were calibrated at 20°C by weighing, by difference, the volume of water in each flask at this temperature. Hence the corrected volumes were calculated by the use of density tables.

C. WEIGHING OUT SAMPLES OF THE MATERIALS.

During the early stages of the investigation a double-pan, air damped "Sartorius" balance was ued for weighing out small samples of the materials. The balance weighed to 4 decimal places. Approximately 0.5 g of the material was weighed out and made up (with "Analar" benzene), to 100 ml in the flask. 10 ml of this solution was then pipetted out into another 100 ml flask by means of a "Caulfield" automatic pipettor. This flask was also filled to the mark with pure benzene. Hence a solution, containing about 0.05 g of the substance per 100 ml was obtained.

However, the process of tenfold dilution by means of the pipette could introduce a small but significant error in the correct measurement of the small quantities added. Hence it was decided to discard this method with its inherent sources of error and when a semi-micro balance became available this was used to weigh out approximately 0.05 g of the material directly into a 100 ml flask. The flask was filled with benzene to the mark and aliquots of about 0.10 ml of this solution were extracted by means of the "Agla" syringe and used directly.

The balance employed for this latter procedure was a "Sartorius" selecta semi-micro model, single-pan balance, weighing to 5 decimal places. It had a direct-reading scale for the last 3 figures. This method removed dilution errors.

Due to the fact that all experiments were carried out at 20°C, the solutions were made up at this temperature in the constant temperature room. After weighing out the sample in the balance room, the benzene, which had been allowed to equilibrate for a few hours, was added to the flask in the constant temperature room.

By taking due precautions, the errors involved in the process of making up solutions of the materials, were reduced to a minimum.

VI. A THEORETICAL CONSIDERATION OF THE HORIZONTAL TYPE OF FILM BALANCE.

The horizontal type of surface balance offers a differential method of measuring surface pressures, caused by the compression of monomolecular films on the substrate. In other words, the balance measures directly the difference between the surface tension of a clean water surface and that of a film-covered surface.

Harkins and Anderson[94] made a theoretical and experimental comparison between the Wilhelmy vertical pull type of film balance and the Langmuir horizontal pull type of balance. The following derivation of the total horizontal force per cm which acts on the float of the balance, is condensed from their discussion.

The film balance is employed for the determination, by means of a torsion balance, of the total horizontal force per cm (F_h) which acts on a float, resting on the substrate surface. The horizontal force per cm due to the clean water surface on the one side of the float is:

$$\gamma_w \cdot \cos A_w$$

where γ_w is the surface tension of pure water, and A_w is the angle of inclination of the surface to the horizontal at the point of contact. Similarly, the force per cm, in the opposite direction, due to the film covered water surface is:

$$-\gamma_f \cdot \cos A_f$$

where γ_f is the surface tension of the contaminated surface and A_f is the angle of inclination of the film covered surface to the horizontal at the point of contact.

If Z_w is the depth of the line of contact of the pure water surface with the float below the horizontal surface and Z_f is the depth of the line of contact of the film covered surface with the float, then the horizontal force per cm due to the pressure of the water on the float is:

$$\tfrac{1}{2}\, g \rho_w \cdot (Z_w + Z_f)(Z_w - Z_f)$$

where ρ_w is the density of the water and g is the acceleration due to gravity.

The total horizontal force on the float is then given by the equation:

$$F_h = L[\gamma_w \cdot \cos A_w - \gamma_f \cdot \cos A_f + \tfrac{1}{2} g \rho_w (Z_w + Z_f)(Z_w - Z_f)] \qquad (1)$$

where L is the total length of the float.

Now the equation of the cross-section of the water surface taken perpendicularly to the float is:

$$z_w^2 = \frac{2\gamma_w (1 - \cos \alpha_w)}{g \rho_w} \qquad (2)$$

where α_w is the angle of inclination to the surface at point z_w. A similar equation holds for the film covered surface:

$$z_f^2 = \frac{2\gamma_f (1 - \cos \alpha_f)}{g \rho_w} \qquad (3)$$

At the line of contact between the float and the liquid surface:

$$z_w = Z_w, \alpha_w = A_w, z_f = Z_f \ \& \ \alpha_f = A_f$$

in equations (2) and (3). Hence the following relations are obtained:

$$\text{Cos } A_w = 1 - \frac{\rho_w \cdot g}{2\gamma_w} Z_w^2$$

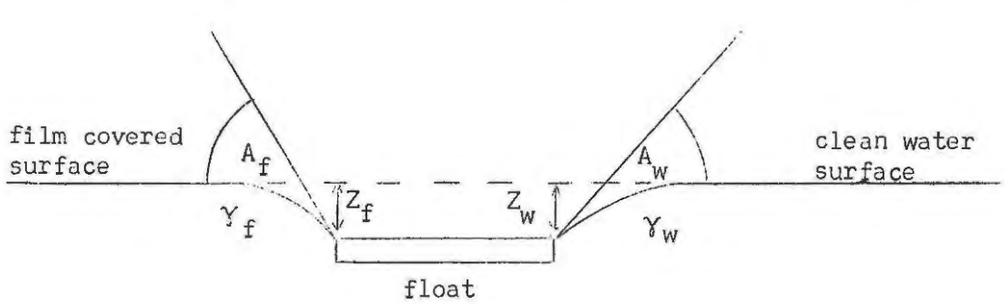
$$\text{Cos } A_f = 1 - \frac{\rho_w \cdot g}{2\gamma_f} Z_f^2$$

Inserting these values for Cos A_w and Cos A_f in equation (1), we obtain:

$$F_h = L[\gamma_w (1 - \frac{\rho_w \cdot g}{2\gamma_w} Z_w^2) - \gamma_f (1 - \frac{\rho_w \cdot g}{2\gamma_f} Z_f^2) + \tfrac{1}{2} g \rho_w (Z_w^2 - Z_f^2)] = \qquad (4)$$

$$L (\gamma_w - \gamma_f) \qquad (5)$$

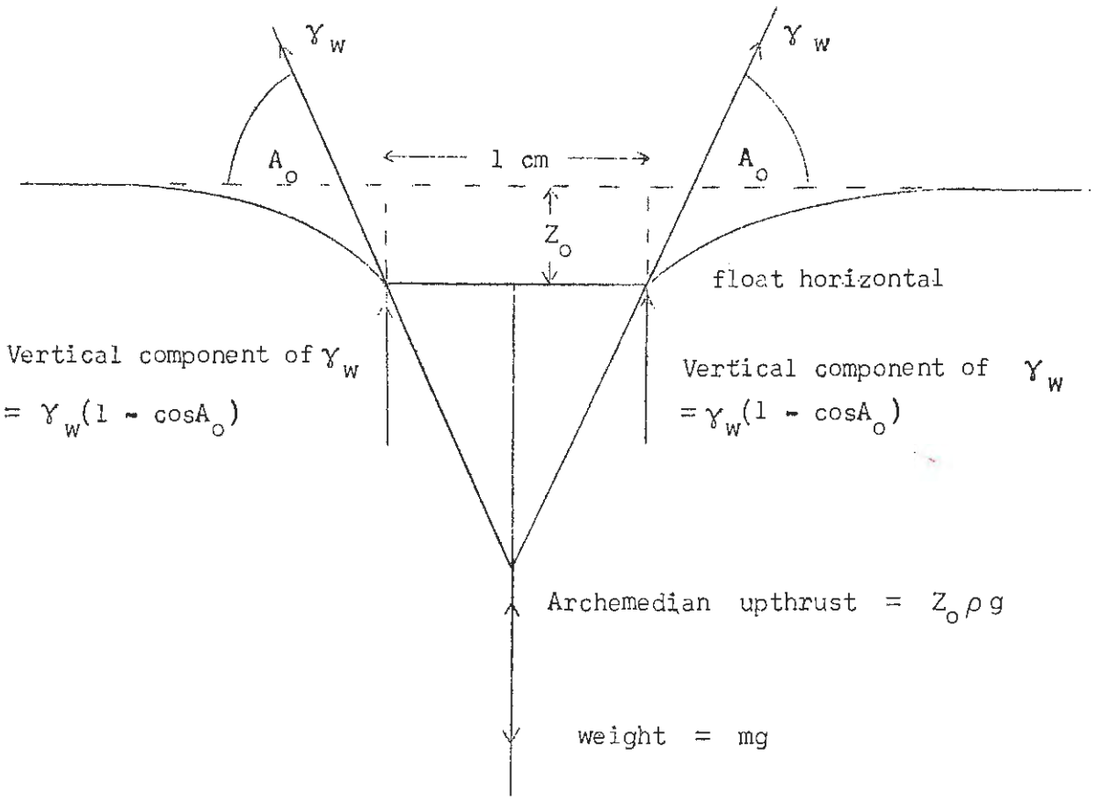
Thus the total horizontal force on the float is equal to its length times the difference in surface tensions of the pure water and the film covered surface. The force is independent of the tilt of the float or the way in which the substrate liquid wets the float.



- The following -

The following derivation, by Barker and the author, is an attempt at obtaining a relation between the mass of the float and the depth to which the float is depressed in the substrate. The first case deals with a clean water surface on both sides of the float, while the second case considers the effect of spreading a film on the one side of the float with the other side remaining free from contamination. In the second case, the float is tilted through an angle (α), due to its low mass. Floats used by earlier investigators were heavy enough to remain horizontal on the surface under the above conditions.

1. Clean water on both sides of Float.



If m = mass of the float, ρ = density of substrate and g = acceleration due to gravity.

Then $mg = Z_o \rho g + 2\gamma_w(1 - \cos A_o)$

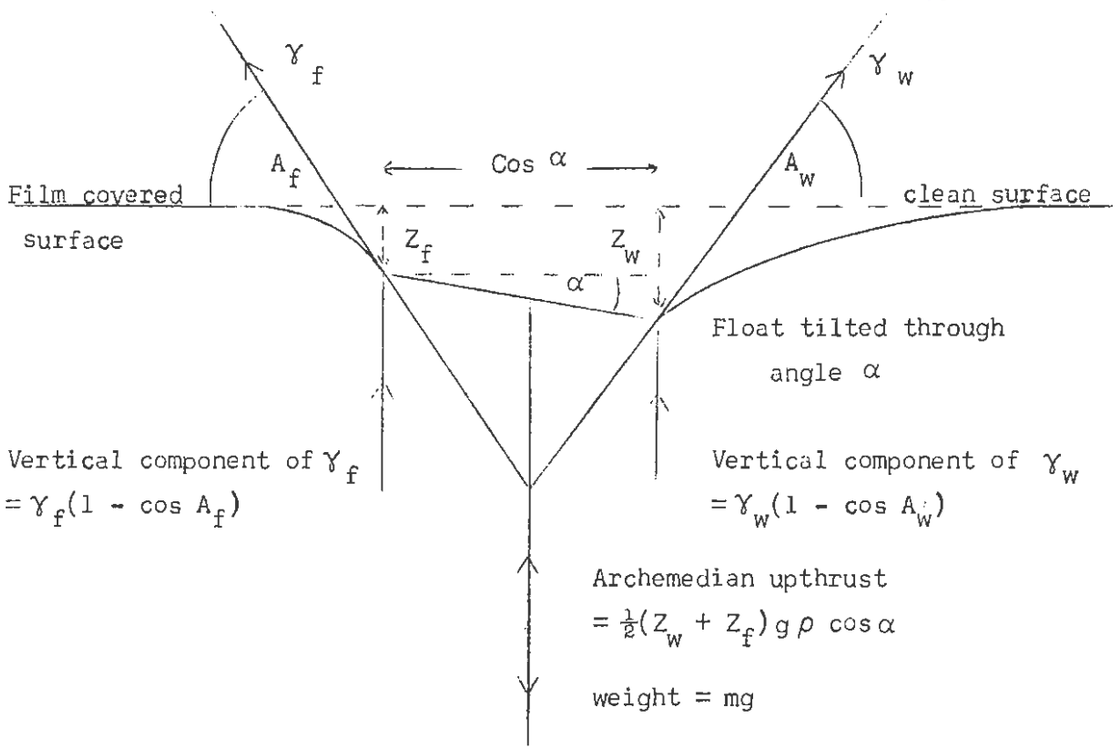
$$\text{But } 1 - \cos A_o = \frac{Z_o^2 g \rho}{2\gamma_w} \qquad \text{Hence } \cos A_o = 1 - \frac{Z_o^2 g \rho}{2\gamma_w}$$

$$= Z_o \rho g + 2\gamma_w \frac{Z_o^2 g \rho}{2\gamma_w}$$

$$= (Z_o + Z_o^2)\, g \rho$$

$$\therefore m = Z_o(1 + Z_o)\rho \longrightarrow$$

2. Film on one side of Float, clean water on the other side.



If m = mass of the float, ρ = density of substrate and g = acceleration due to gravity.

Then $mg = \frac{1}{2}(Z_w + Z_f)\rho g \cos\alpha + \gamma_f(1 - \cos A_f) + \gamma_w(1 - \cos A_w)$

$$= \tfrac{1}{2}(Z_w + Z_f)\rho g \cos\alpha + \gamma_f \frac{Z_f^2 g\rho}{2\gamma_f} + \gamma_w \frac{Z_w^2 g\rho}{2\gamma_w}$$

because $\cos A_f = 1 - \dfrac{Z_f^2 g\rho}{2\gamma_f}$ and $\cos A_w = 1 - \dfrac{Z_w^2 g\rho}{2\gamma_w}$

$$= \frac{g\rho}{2}\left[(Z_w + Z_f)\cos\alpha + Z_f^2 + Z_w^2 \right]$$

$$= \frac{g\rho}{2}\left[(Z_w + Z_f)\sqrt{(1 - \mathrm{Sin}^2\alpha)} + Z_f^2 + Z_w^2 \right]$$

$$\therefore\ m = \frac{\rho}{2}\left[(Z_w + Z_f)\sqrt{1 - (Z_w - Z_f)^2} + Z_f^2 + Z_w^2 \right] \longrightarrow$$

VII. RESULTS OBTAINED BY EARLIER INVESTIGATORS FOR THE CROSS SECTIONAL AREAS PER MOLECULE OF LONG-CHAIN FATTY ACIDS AND OTHER RELATED COMPOUNDS. (Data represented in approximately chronological order.)

Investigator.	Compound.	Area/molecule in A^2.	Temperature.	Remarks.	Reference.
Rayleigh	Stearic acid	22.1	15°C	-	3
Langmuir	Palmitic acid	21	±20°C	Spread on clean water surfaces which were heated with Bunsen burners.	4
	Stearic acid	22	"	-ditto-	
	Cerotic acid	25	"	-ditto-	
	Oleic acid	46	"	-ditto-	
	Tristearin	66	"	-ditto-	
Adam	Myristic acid	21	±20°C	Spread on solutions of salts.	5,6,7
	Tetradecanol	21.6	"	-ditto-	
Woog	Stearic acid	22.3	"	-ditto-	8,9
	Palmitic acid	20.8	"	-ditto-	
	Oleic acid	42.7	"	-ditto-	
	Tristearin	66.9	"	-ditto-	
Harkins & Co-workers	Myristic acid	25-27	6-12°C		10,11
	Pentadecanoic acid	24-26	18-27°C	Spread on 0.01n H_2SO_4.	
	Palmitic acid	24	19-29°C		

- continued -

Investigator.	Compound.	Area/molecule in $Å^2$.	Temperature.	Remarks.	Reference.
Harkins & Co-workers	Stearic acid	24.3	25°C		
	Nonadecanoic acid	24.0	25°C	pH = 2	
	Arachidic acid	23.7	25°C		
Müller	Stearic acid	20.5	-	Obtained from X-ray analysis.	12
	Bromo-stearic acid	27.6	-	-ditto-	
Guastalla	Oleic acid	45	19°C	On 0.01N HCl	36
Emir	Myristic acid	26	19-21°C	On 0.05N HCl	95
Tamamishi	Lauric acid	20	15°C	On neutral water	13
	Palmitic acid	21	"	" " "	
	Cetyl alcohol	22	"	" " "	
Sameshima & Sasaki	Palmitic acid	25.6	14°C	On pH = 8 substrate	14
	Myristic acid	34.6	5°C	-ditto-	
	Oleic acid	43.7	14°C	-ditto-	
	Tetradecanol	25.1	17°C	-ditto-	
Havinga & de Waal	Pentadecylic acid	26	±20°C	-	15
	Myristic acid	26	"		
	Ba-stearate	19.9	"		

- continued -

Investigator.	Compound.	Area/molecule in A^2	Temperature.	Remarks	Reference.
Achmatov	Oleic acid	±38	17°C	On HCl solution.	16
Pankratov	Ethyl Palmitate	24-42	20°C	On various electrolytes.	18
	Cetyl alcohol	22	"	On distilled H_2O .	
	" "	25	"	On 3.3 N KI solution.	
Trapeznikov & Rehbinder	Palmitic acid	20.1	-	On solutions of pH = 3.6.	17, 19
	Cerotic acid	25	-	-ditto-	
	Tripalmitin	65	-	-ditto-	
Harkins & Nutting	Stearic acid	21.9	20°C	On dilute HCl solutions of pH = 2.	24
	Myristic acid	23.6	9-5°C	-ditto-	
	" "	28.9	21.7°C	-ditto-	
	Pentadecylic acid	20.9	21.7°C	-ditto-	
Adam, Askew & Pankhurst	Myristic acid	20-24	22°C	On phenolic solutions	26
	Palmitic acid	20.2-24	20-22°C	-ditto-	
Mibashan-Saraga	Lauric acid	±30	20°C	On O.01N HCl	35
Alexander	Myristic acid	±24	16°C	On O.01N HCl at the benzene/water interface	37
	Octadecyl sulphate	±80	20°C	-ditto-	
Seelich & Hendler	Stearic acid	20	20-25°C	On Decalm-phosphate buffers	39
	Arachidic acid	20	"	-ditto-	

- continued -

Investigator.	Compound.	Area/molecule in A^2	Temperature.	R e m a r k s	Reference.
Anderson & Evrett	Stearic acid	20.3	-	Using an automatic recording balance.	42
Few & Pethica	Myristic acid	±30	18°C	On 0.01M HCl by electrode-potential measurements.	43
	" "	±50	"	-ditto-	
Allan & Haigh	Stearic acid	28-30.5	±20°C	pH of substrate = 1.5-6.6.	46
	" "	29-30	"	pH = 1.32-6.74 + $CoCl_2$	
	" "	30-33	"	pH = 2.85-4.65 + $CuCl_2$	
Inokuchi	Myristic acid	±30	18°C	On 0.01N HCl	47
Daguerre	Behenic acid	19.5	22°C	On substrates of pH = 2	52
	Arachidic acid	21.6	"	-ditto-	
Bruun	Myristic acid	40	20°C	pH of substrate = 3 with dilute HCl.	53, 54
	Palmitic acid	30-45	"	On admixture of isodextro-pimaric acid	
	Stearic acid	23	"		
	Arachidic acid	23			
	Behenic acid	23			
	Lignoceric acid	23			
Durham	Lauric acid	27	±20°C	pH = 3.5	55
	Myristic acid	25	"	-ditto-	
	Palmitic acid	20.5	"	pH = 7.5	
	Stearic acid	21.0	"	pH = 3.5	
	Arachidic acid	21.0	"	-ditto-	

- continued -

Investigator.	Compound.	Area/molecule in $Å^2$.	Temperature.	Remarks.	Reference.
Ellison & Zisman	Stearic acid	20	22.5°C	Solid film.	56
	" "	21-24	25°C	Liquid condensed film.	
	Pentadecylic acid	21-23.2	27.5°C	-ditto-	
Robertson, Winkler & Mason.	α-Iodostearic acid	30	9°C	On 0.01N HCl solution	59
	-ditto-	±40	27.4°C	-ditto-	
Semeluk, Hahn & Morrison	Myristic acid	±3000	20±0.1°C	On 0.01N HCl, at surface pressures of 0.24 dynes/cm.	60
Guastalla	Oleic acid	45	22-25°C	On neutral water surfaces.	63
	Myristic acid	25	"	-ditto-	
	Stearic acid	19	"	-ditto-	
La Mer & Robbins	Stearic acid	24.19-25.17	25°C	On 0.01M HCl solution.	67
Merker & Daubert	1-Monopalmitin	21.4	20°C		68
	1-Monostearin	21.5	"		
	2-Monopalmitin	20.2	"		
	2-Monostearin	20.2	"		
Boyd	Tridecylic acid	20.6	0°C	All on 0.01N HCl solutions.	69
	" "	26.3	20°C	-ditto-	
	" "	27.2	41.5°C	-ditto-	
	Myristic acid	24.2	5°C	-ditto-	
	" "	30.1	20°C	-ditto-	
	" "	30.6	54.4°C	-ditto-	

- continued -

Investigator.	Compound.	Area/molecule in $Å^2$.	Temperature.	R e m a r k s.	Reference.
Boyd	Pentadecylic acid	20.5	10°C	All on 0.01N HCl solutions.	69
	" "	21.1	20°C	-ditto-	
	" "	30.0	52.3°C	-ditto-	
	Palmitic acid	21.7	15°C	-ditto-	
	" "	21.8	20°C	-ditto-	
	" "	32.5	62.9°C	-ditto-	
Durham	Arachidic acid	±25	20±0.5°C	On pure H_2O.	70
	" "	21-22	"	On 0.00025M $CaCl_2$ solution of pH = 7.5.	
Cook & Ries	Stearic acid	20.2	-	-	71
Rabinovitch, Robertson & Mason	Stearic acid	19-21	20°C	On 0.001N HCl solution.	72
Gaines	Stearic acid	20	-	-	73

As may be observed from the tabulated values, of the cross-sectional areas of molecules, above, the magnitude of the area per molecule as given by various investigators of these materials, varies greatly.

These discrepancies may be attributed to a number of causes - amongst them personal errors, errors due to impurities in the substrate, contamination of the surface by dust and other extraneous matter, insufficient purity of the chemicals which were used for spreading, variations in temperature of the substrate and surroundings, lack of consistency in the method of measurement of surface pressures, insufficient sensitivity of the film balance employed and last, but not least, the procedures employed for the spreading of materials from volatile solvents.

All the above errors were considered and methods were devised for eliminiating as far as possible the more serious ones from the present research. An attempt was made to obtain reliable, consistent and reproducible results for the molecular cross-sectional areas of the selected materials which were used in this investigation.

VIII. DISCUSSION OF THE ORIENTATION OF SURFACE ACTIVE MATERIALS AT THE AIR-WATER INTERFACE.

Although the origin of the surface balance technique, for studying materials at the air-water interface, is to be ascribed to Pockels[1], the development of this method must be attributed Rayleigh[3], Langmuir[4], Adam[5] and Harkins[10, 11].

Rayleigh was the first to postulate that oil molecules spread over the substrate surface until at a certain critical pressure, they form a single layer of molecules touching one another over the entire available surface.

Langmuir measured the force exerted by a film on a barrier and regarded it as the difference between the surface tension of a clean surface and of a surface covered by a monomolecular layer. He put forward the theory that the polar hydrophilic group of the surface active molecule located itself in the surface of the substrate, while the hydrophobic hydrocarbon chain arranged itself in the air at right angles to the substrate. After completing work on a series of long-chain fatty acids, Langmuir concluded from his results that the chains of these materials must be regarded as extremely flexible. After compression of the film, a closely packed layer resulted and he found that the area occupied by a single molecule at closest packing of the film therefore gave the area of cross section of a single molecule. From the weight of the sample of the material and the observed total area occupied by the film at the critical point of closest packing, he was able to deduce the area per molecule and length of the hydrocarbon chain. However, it was left to Adam[6] to improve the surface balance technique of measuring film pressures. He studied homologous series of a large variety of aliphatic materials, and conceived the idea of the orientation of heteropolar (amphiphilic) molecules at surfaces and interfaces.

In every case of the several substances that Adam studied, he found that when the temperature of the experiment was sufficiently

high, a definite change took place in the properties of the film. This usually resulted in a considerable increase in the area occupied per molecule. This observation applied particularly to molecules containing hydrocarbon chains of 12 - 22 carbon atoms. The change appeared to be due to the separation of the molecules from one another in the surface, brought about by thermal agitation, this becoming so violent above a cer- temperature that the lateral attraction of the molecules for one another was overcome. Such films were called "expanded films", and they appeared to have properties analogous to those which might be attributed to a "two-dimensional gas". On the other hand, those films in which the molecules appear to be in contact over the whole area covered by the film were designated "condensed films".

In their investigation on the "Angles of contact and Polarity of Surfaces", Adam and Jessop[96] found that the "contact angles" between the axis of the molecular chain and the surface of the substrate, for palmitic, stearic and eicosanoic acids varied between 100 and 105°C. This meant that the chains were very nearly perpendicular to the substrate surface.

Investigators found that the limiting area per molecule of palmitic acid was dependent on the pH of the substrate solution, increasing with a rise in the acidity of the solution. Langmuir ascribed this increase in the area of the film to an increase in the size of the polar groups due to adsorption of H^+ ions. According to Lyons and Rideal[97], the rise in molecular area on acidifying the solutions was connected with the tilt of the molecules making up the film.

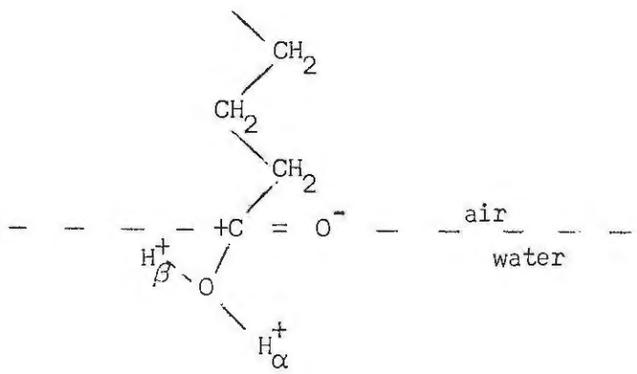
Havinga and de Waal[15] interpreted the results of their investigations on pentadecylic acid and myristic acid in the following way: in compressed unimolecular films the carbon chains were tightly packed and vertical to the surface with the hydrophilic groups protruding into the water. Or. the less compressed state the CH_2 groups were not oriented vertically but were tilted at an angle to the substrate surface. At very low surface concentrations, the long chains lay flat on the water surface with the polar groups in the surface of the liquid. On com-

- pression, the chains -

pression, the chains associated and began to erect themselves. Thus a "duplex" film was formed, consisting of a hydrophobic CH_2 chain and a hydrophilic part protruding into the substrate. In the final stages of compression, the film formed a type of two-dimensional crystal, while the water molecules were forced out between the chains. Completely "condensed" films could be compared with a three-dimensional solid and they were characterized by a small compressibility.

During 1939 the Russians, Pankratov and Frumkin[20], studied the properties of monofilms on solutions of salts. The investigation entailed a study of the adsorption of ions on films of organic compounds and also the influence of this adsorption on the forces acting between the molecules of the compound. They also verified to what extent the change in the concentration of the electrolyte in the substrate was connected with a change in the hydration of the polar groups.

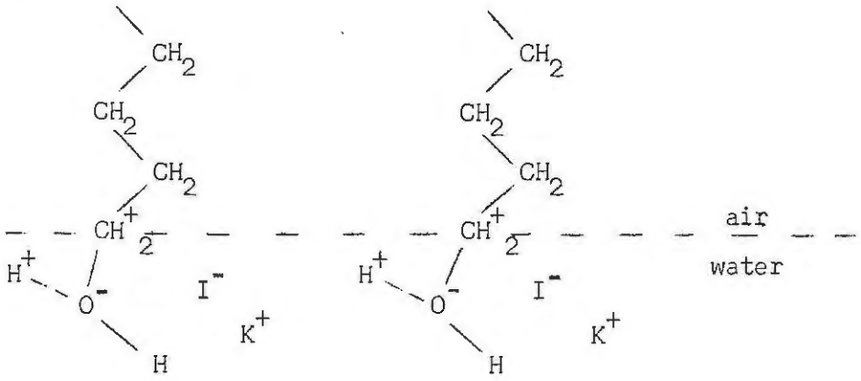
From surface potential measurements and calculations of the dipole moments of long-chain acids, these investigators were able to deduce the following orientation for the acids at the air-water interface:



The hydrocarbon part of the molecule of the fatty acid was located vertically to the surface of the substrate and the double band (C = O) lay in the interface. The position of the atoms of the -COOH group in relation to the surface were fixed with the exception of the of the hydrogen atom of the OH group. This atom was able to rotate about the line of the valency bond which connected the carbonation with the oxygen atom of the molecule. The possibilities of the location of the H atom are represented in the above diagram by the H^+_α and H^+_β positions.

On HCl solutions, according to Frumkin, an electrical double layer appeared at the solution-air interface, with the chloride ions turned towards the air phase, due to which the surface of the solution acquired a negative charge. Therefore the H^+ part of the polar group, immersed in the HCl solution, will be attracted nearer the β position. Hence the conclusion was reached that the larger the adsorption of anions at the solution-air interface, the more negative the surface charge would become. Therefore the H^+ part of the polar groups will be more powerfully attracted to the β position thus increasing the vertical component of the dipole moment.

These investigators proposed a scheme of interaction of the polar groups of cetyl alcohol with a double ionic layer from KI solution as follows:



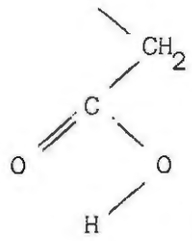
The increase of the vertical component of the dipole moment of the polar groups was ascribed to the rotation of the H^+ part to a position nearer the surface. This rotation was thought to be caused by an electrostatic interaction with anions absorbed from the solution.

While studying the "Evaporation of Polar Hydrocarbon Monolayers" in 1949, Karle[98] formed monolayers of cerotic acid containing 25 carbon atoms in its chain, and n-octadecylamine, on soda-glass slides, from melts of the pure materials. Analysis of the diffraction patterns from cerotic acid showed that the angle of tilt remained at $25 \pm 3^{\circ}$ throughout the course of the evaporation.

Kipling and Norris[99] made a thorough study of molecular cross sections in fatty acid films on water surfaces. They discussed the fact that the paraffin hydrocarbon chain lacked cylindrical symmetry, and that this

- should be -

should be considered in the packing of the long-chain fatty acids on aqueous substrates. This matter had been pointed out by Vold[100], who suggested in her drawings that the stearic acid molecule, occupying an area of 20.5Å^2 per molecule, had the OH groups directed into the substrate where they probably formed hydrogen bonds with the water:



"closed" configuration.

The above configuration was preferred to Alexander's[101] suggestion of hydrogen bonding to adjacent molecules, which would involve very long and therefore fairly weak bonds. Kipling and Norris put forward two points relevant to the discussion:

(1) Earlier workers were mystified by the discrepancy between the molecular areas of 20.5Å^2 of fatty acids and 18.5A^{o2} in crystals of the same materials. From models Norris and Kipling were able to show that if the hydrocarbon chain was vertical to the substrate, the carboxyl group had the axis, joining the centres of the two oxygen atoms, inclined at an angle of $\pm$ 26.5^o to the horizontal. This configuration was also found in the crystal, where hydrogen bonding occurred between carboxyl groups of adjacent layers. In the crystal the cross sectional areas were found to be 18.5Å^2.

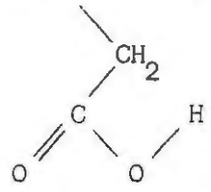
On the water surface, however, a wider spacing was adopted by the molecules, in which the hydrocarbon chains were not in contact, thus leading to a molecular area of 20.5Å^2. They showed that the molecular area, if measured along the surface instead of perpendicular to the chain, became:

$$\frac{18.5}{\text{Cos } 26.5^o} = 20.5\text{Å}^2$$

(2) According to Alexander[101] "intra-layer" hydrogen bonding occurred in monolayers, of fatty acids on acidic substrates, at molecular areas of the order of 25Å^2. This implied the open

- configuration of -

configuration of the carboxyl group:



"open" configuration.

and inclined chains.

However, according to Norris and Kipling, it meant a vertical arrangement of the chains with "open" carboxyl groups lying along the horizontal axis of the chain giving a molecular area of 25.2$\AA^2$. This spacing required that the height of the the monomolecular film should be the full height of the molecule.

In 1955 Bruun[54] made a study of mixed monolayers of Isodextropimaric acid and normal long-chain fatty acids. Owing to the difference in dimensions of the component molecules of these mixtures, the hydrocarbon part of the monolayer was considered to be composed of two layers, an upper formed by the top sections of the flexible fatty acid chains that project above the isodextropimaric acid molecules, and a lower densely packed layer comprising the bulky inflexible isodextropimaric molecules and the lower sections of the fatty acid molecules.

The average area per molecule was found to be primarily dependent on the densely packed lower layer, but was also influenced by thermal agitation of the free fatty acid chains in the upper layer. This caused an expansion in the film and consequently the cross sectional areas were found to increase.

Bigelow and Brockway[102] showed, from a study of the "Variation in Contact Angle and Structure with Molecular Length and Surface Density in adsorbed films of Fatty Acids", that the average angle of tilt of several fatty acids were as follows:

Acid.	Angle of Tilt (in the condensed film).
Behenic	2°
Arachidic	2°
Stearic	4°
Palmitic	6°

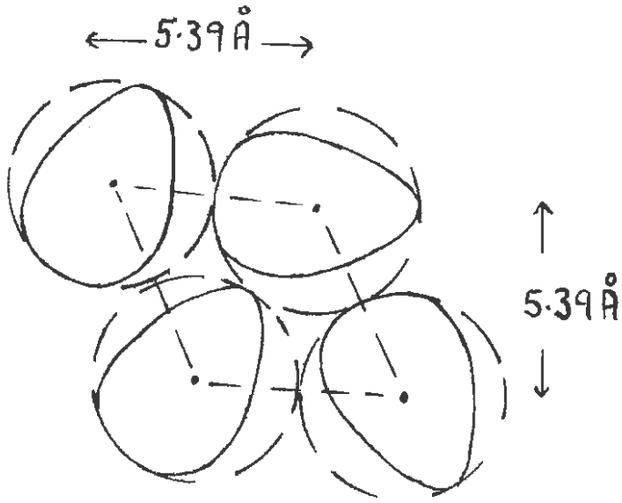
- These angles -

These angles indicated the deflection of the long-chain molecules from the normal to the surface. From their results they obtained the relationship between the angle of tilt and the length of the hydrocarbon chain of the series of fatty acids. It was found that the angle of tilt increased with a decrease in the chain length.

While investigating energy relations during the formation of monolayers, Boyd[69] came to the conclusion that it was impossible to obtain reliable isotherms for tridecylic, myristic, pentadecylic and palmitic acids at temperatures higher than $0^{\circ}C$, $5^{\circ}C$, $10^{\circ}C$ and $15^{\circ}C$ respectively due to the solubility of the monolayers in the aqueous sub-phase. At temperatures higher than the above, the molecular cross sectional areas increased considerably.

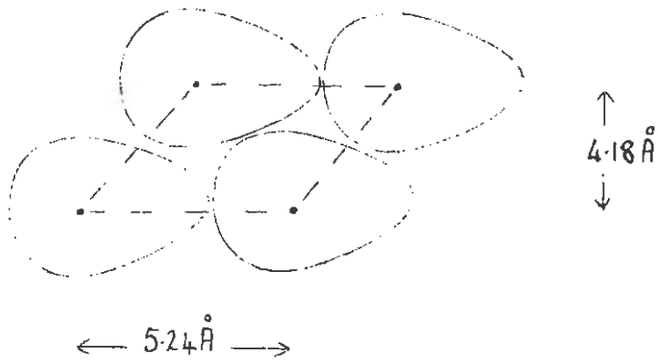
The author feels that this phenomena was not due to the solubility of these materials alone, but also due to thermal agitation of the molecules, and possibly an increase in the angle of tilt of the hydrocarbon chains with decreasing chain length.

According to Rabinovitch, Robertson and Mason[72], a molecular cross sectional area of 25.2Å^2 for the stearic acid could be calculated for the molecule from the volume swept out during the rotation of the vertically oriented fatty acid with the head groups close-packed and planar to the water surface:



However, when the stearic acid molecules were identically oriented on the surface, but no longer free to rotate, the cross sectional areas, which were now ovoid in shape were calculated to be 20.5Å^2 for the most efficient packing in the monolayer.

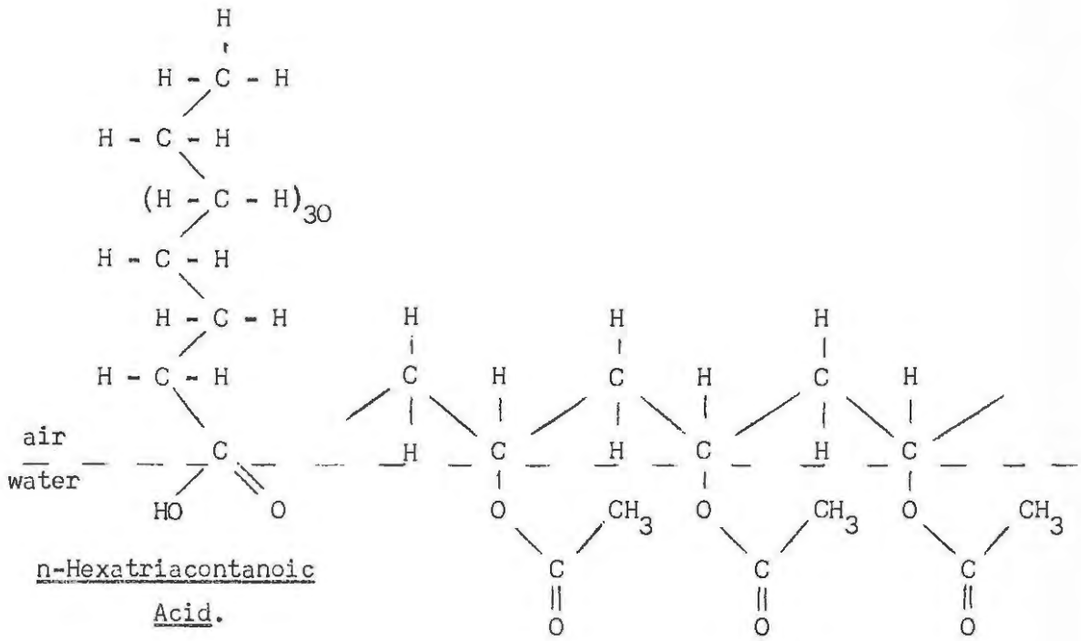
- (Diagram) -



The force-area isotherm of stearic acid on compression from 25Å^2 to 21Å^2 per molecule was assumed to reflect the progressive inhibition of free rotation until at the lower area, rotation was completely restricted. As the lateral compression was continued, the film approached collapse, and the planar configuration of the head groups gave way to a multiplanar one as the head groups were forced into new position above or below the original plane. Finally, certain of the acid molecules could invert under lateral compression to form a duplex layer with ensueing collapse.

Towards the close of 1960 Ries, Walker and Gabor[103] published an article on the investigation of thin film mixtures with the aid of a film balance used in conjunction with an electron microscope. The latter was ued to obtain details of the film's size, shape and thickness. They used n-hexatriacontanoic acid, which has 36 carbon atoms and a polar group at the one end, and polyvinyl acetate. From isotherms of each component of the mixture spread separately they were able to ascertain that a stearic film was 25Å in thickness, thus indicating a vertical orientation at the air-water interface. In contrast to n-hexatriacontanoic acid, polyvinyl acetate gave a thickness of 5Å, indicating that the polymer oriented itself horizontally. The following diagram suffices to show how an equiweight mixture of n-hexatriacontanoic acid and polyvinyl acetate orients itself molecularly:

- (Diagram)



n-Hexatriacontanoic Acid.

Polyvinyl Acetate.

From photographs, taken with the aid of the electron microscope, they were able to trace the stretch and collapse of a thin film of the above mixture under pressure. At a surface pressure of 10 dynes per cm worm-shaped islands of the acid were visible while at 25 dynes/cm these islands formed a cross shaped structure. Amorphous masses, probably of polymer, started to show up as the pressure was increased. At 40 dynes per cm these masses were very closely packed. Above 50 dynes per cm the film collapsed and left platelets of acid and large polymer masses.

IX. SCOPE OF THE WORK UNDERTAKEN.

This was not defined until preliminary measurements with the modified surface balance had been undertaken and until the survey of the literature had reached an advanced stage. It has already been shown that the literature on surface chemistry abounds with descriptions of methods for obtaining molecular areas of surface active compounds. The fatty acids, of general formula $C_nH_{2n+1}COOH$, have, in particular, been used for spreading procedures at the the air-water interface since the inception of the surface balance technique by pioneer investigators such as Langmuir, Rideal, Adam and Harkins. Subsequently, many workers in this particular field of surface chemistry, whether using the Langmuir technique or not, have initiated their research programmes by spreading one or more of these fatty acids at the interface between air and aqueous substrates. In this way molecular areas have been determined for individual acids under a variety of conditions. We have thus been left with a considerable store of data on molecular dimensions and orientation of the fatty acids in condensed monolayers.

In chapter VII the author has collected the results of earlier workers. A glance at these immediately reveals the great diversity in the values obtained for the molecular cross-sectional areas of such compounds as palmitic, stearic, arachidic and behenic acids.

Some of these investigators did not feel the need to specify their results with any greater precision than, say, 20Å^2 or 21Å^2. Such values do not convey any real idea of the limits of variation of the molecular areas to modern workers in the field.

Lately, it has to be admitted, a few authors have expressed their results, for the molecular areas, to the first decimal place, thus indicating an increase in the implied precision form $\pm 1\text{Å}^2$ to $\pm 0.1\text{Å}^2$, i.e. a tenfold increase. No statistical basis for this is given either explicityly or implicity in any of the many paper read by the writer.

- Due to the -

Due to the diverse results for the molecular areas of the fatty acid molecules obtained by earlier workers and to the general lack of information regarding the precision and accuracy of these values, the need was felt for investigating this and for attempting to improve upon the precision of measurement. For that reason, and also to assess the performance of the modified surface balance which has been described, it was decided to perform a statistical survey of the results using a series of long-chain fatty acids of general formula $C_nH_{2n+1}COOH$.

Such an investigation was thought to be necessary in order to give a sounder foundation to surface studies and to indicate the basis for realistic deductions about the details of molecular orientation particularly in close-packed "condensed" monolayers.

X. RESULTS.

A. CALIBRATION OF BALANCE BEAM.

POSITION OF RIDER ON SCALE.	ANGLE OF TORQUE.
1	1.75°
2	3.4°
3	5.1°
4	6.9°
5	8.5°
6	10.3°
7	12.0°
8	13.7°
9	15.6°
10	17.2°

Mass of Rider = 0.05719 g.

Length of arm of Beam = 6.35 cm.

Length of beam from torsion wire to float = 7.90 cm.

Rider on position 10 on scale corresponds to 17.2° of Torque.

$\therefore$ Total force per cm length of Float

$$= \frac{\text{Length of horizontal arm x Mass of Rider x g}}{\text{Length of vertical arm x 13.4}}$$

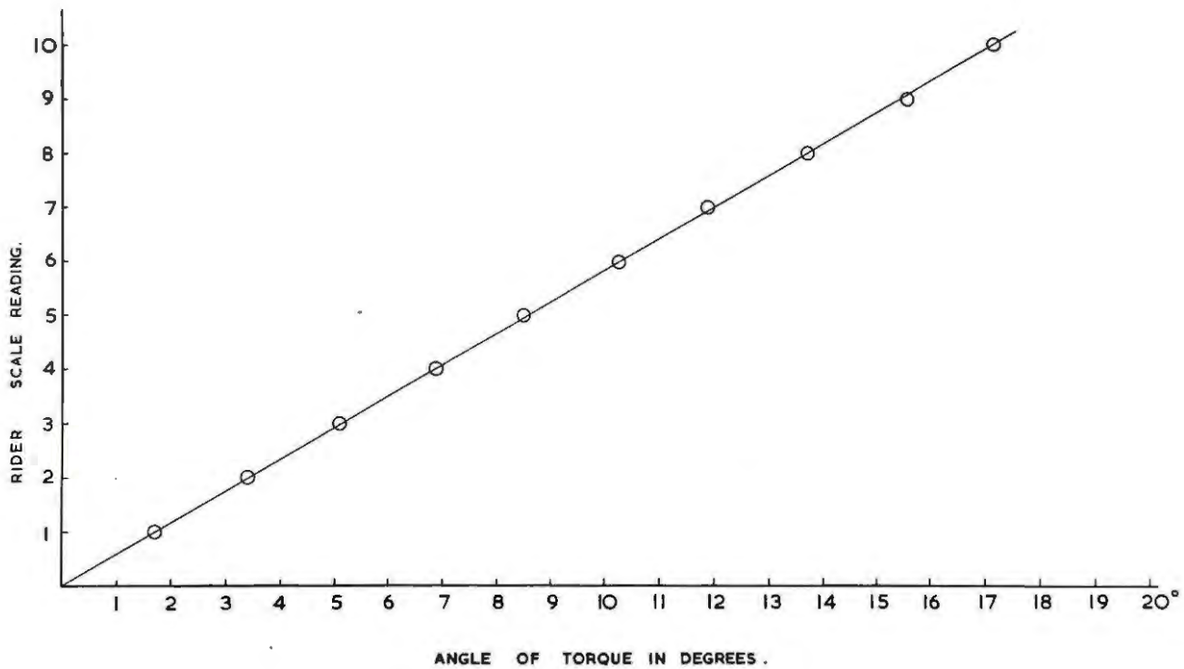
(g = acceleration due to gravity.)

$$= \frac{6.35 \times 0.05719 \times 981}{7.90 \times 13.4} \text{ dynes/cm}$$

$$= 3.366 \text{ dynes/cm}$$

$$\text{Surface Pressure per degree of Torque} = \frac{3.366}{17.2}$$

$$= 0.1957 \text{ dynes/cm/degree.}$$



1. CALIBRATION CURVE.

B. EXAMPLE OF CALCULATION OF MOLECULAR AREA.

Horizontal Scale Reading.	Corrected Scale Reading	Dial Reading	Force in Dynes/cm.
25.5	16.0	0.60	0.12
26.0	15.5	2.62	0.52
26.5	15.0	12.75	2.55
27.0	14.5	28.20	5.64
27.2	14.3	33.45	6.68
27.4	14.1	40.61	8.12
27.6	13.9	46.83	9.36
27.8	13.7	54.25	10.84
28.0	13.5	61.90	12.38
28.2	13.3	72.25	14.45
28.4	13.1	90.50	18.10
28.6	12.9	114.31	22.86
28.8	12.7	139.52	27.90
29.0	12.5	170.83	34.16
29.1	12.4	190.25	38.04

0.04385 g Palmitic Acid/100 ml Benzene. Volume of solution used = 0.10 ml.

A graph of the corrected scale readings against the force in dynes per cm was plotted. From this graph an area of 31.52 cm was obtained by extrapolation.

The effective width of the trough = 15.40 cm.

Hence the area covered by the film at a force of 38.04 dynes/cm

$$= 15.40 \times 31.52 \text{ cm}^2$$

$$= 543.56 \text{ cm}^2.$$

The "end-area" of float $= 13.72 \text{ cm}^2$

$\therefore$ Total area $= 557.28 \text{ cm}^2$

Hence the area per molecule $= \dfrac{\text{Total area x Molecular mass}}{6.023 \times 10^{23} \times \text{Mass of acid}}$

$$= \frac{557.3 \times 256.4}{6.023 \times 10^{23} \times 4.385 \times 10^{-5}}$$

$$= \underline{21.61 \text{ Å}^2} \longrightarrow$$

C. USE OF THE OLIVETTI TETRACTYS IN DETERMINING THE STANDARD DEVIATIONS.

For a series of n terms with a standard deviation S :

$$S^2 = \frac{\Sigma(x - \bar{x})^2}{n} = \frac{\Sigma x^2}{n} - \frac{2\bar{x}\,\Sigma x}{n} + \frac{\Sigma \bar{x}^2}{n}$$

But $\frac{\Sigma x}{n} = \bar{x} = \text{constant}$

Hence $S^2 = \frac{\Sigma x^2}{n} - 2\bar{x}^2 + \bar{x}^2$

$$\therefore \quad S = \sqrt{\frac{1}{n}\left[\Sigma_1^n x^2 - \frac{(\Sigma_1^n x)^2}{n}\right]}$$

The black register of the calculator was used to add the x terms, while the green added the x^2 terms. The sum of the x terms was squared and divided by the number of terms (n). This value was then subtracted from the sum of the x^2 terms and the resultant value divided by n and its square root obtained. This method yielded the standard deviation of a series of n terms.

D. STATISTICAL SURVEY OF THE MOLECULAR CROSS-SECTIONAL AREAS OF A SERIES OF LONG-CHAIN FATTY ACIDS OF GENERAL FORMULA $C_nH_{2n+1}COOH$.

n	Name.
15	Palmitic Acid
16	Margaric Acid
17	Stearic Acid
18	Nonadecanoic Acid
19	Arachidic Acid
21	Behenic Acid
23	Lignocernic Acid

Miscellaneous Compounds (also investigated).

Cetyl Alcohol
n-Octadecyl Acetate
Tetradecanol
Tristearin
9 - 10 Dibromo-anthracene

1. Recrystallised Materials.

Results obtained for 20 successive determinations of the molecular cross-sectional areas (in $\mathring{A}^2$) for the following:

(i) PALMITIC ACID.

21.61; 20.94; 21.04; 21.19; 20.91; 21.16; 21.44; 20.88;
20.98; 21.59; 21.15; 21.03; 21.19; 20.93; 21.38; 21.09
21.60; 21.37; 21.29; 21.37

Mean Value = 21.21 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.23

Variation = 20.98 - 21.44 $\mathring{A}^2$

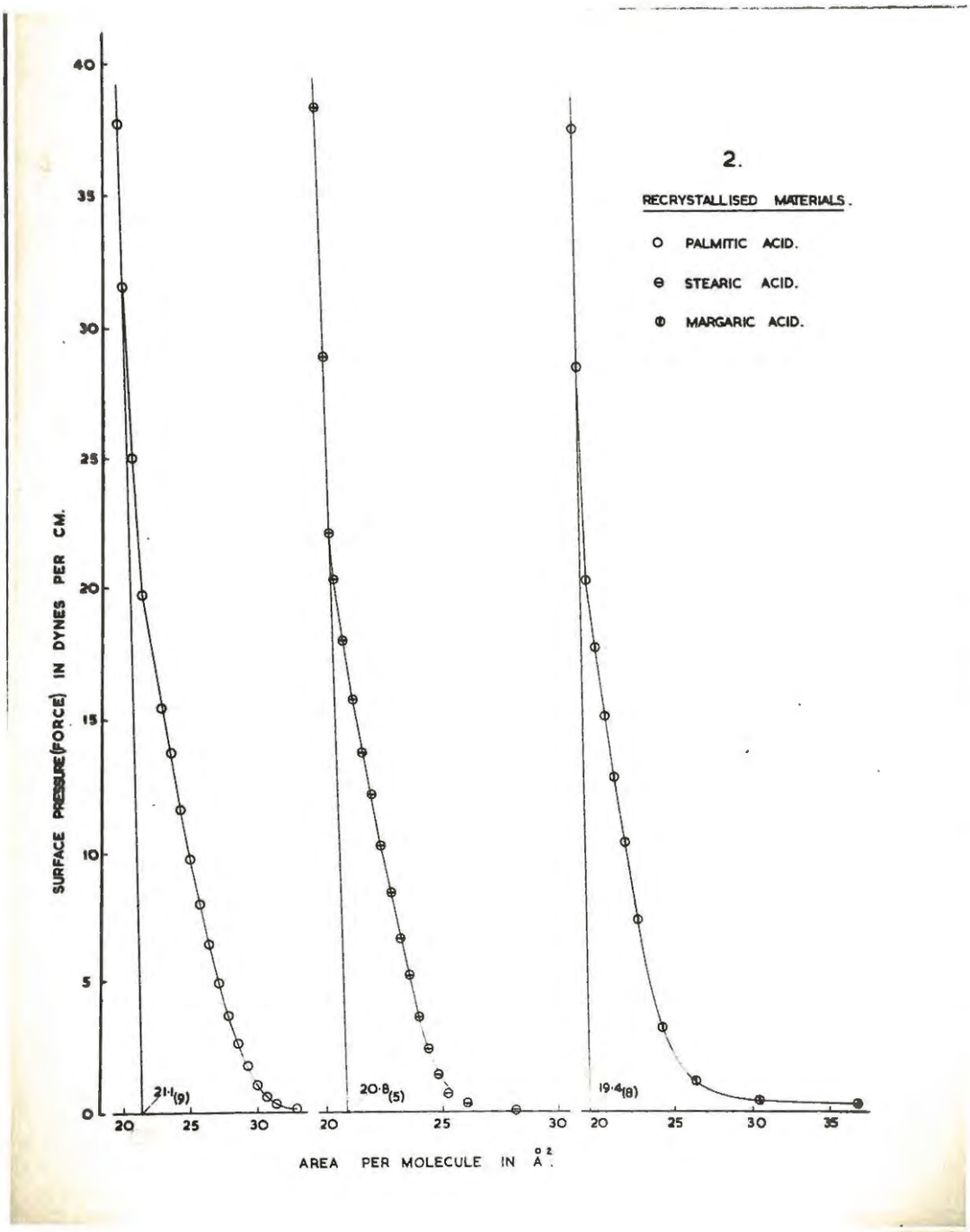
(ii) MARGARIC ACID.

19.18; 19.48; 19.18; 19.18; 19.48; 19.48; 19.18; 19.18;
19.66; 19.60; 19.43; 19.66; 19.48; 19.48; 19.66; 19.48;
19.48; 19.18; 19.66; 19.66.

Mean Value = 19.46 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.19

Variation = 19.27 - 19.65 $\mathring{A}^2$


2.
RECRYSTALLISED MATERIALS.
PALMITIC ACID.
STEARIC ACID.
MARGARIC ACID.
SURFACE PRESSURE(FORCE) IN DYNES PER CM.
AREA PER MOLECULE IN Å².
21·1(9)
20·8(5)
19·4(8)
0
5
10
15
20
25
30
35
40
20
25
30
35

(iii) STEARIC ACID.

20.50; 20.71; 20.50; 20.60; 20.94; 20.71; 20.71; 20.75;
20.71; 20.74; 20.85; 21.10; 20.66; 21.12; 21.07; 21.08;
21.08; 21.07; 20.95; 20.83.

Mean Value = 20.83 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.20

Variation = 20.63 - 21.03 $\mathring{A}^2$

(iv) NONADECANOIC ACID.

20.40; 20.30; 20.21; 20.41; 20.41; 20.21; 20.60; 20.34;
20.41; 20.37; 20.56; 20.41; 20.37; 20.60; 20.40; 20.41;
20.60; 20.41; 20.34; 20.49;

Mean Value = 20.41 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.11

Variation = 20.30 - 20.52 $\mathring{A}^2$

(v) ARACHIDIC ACID.

20.06; 20.44; 20.06; 20.23; 19.96; 20.34; 20.15; 20.34;
19.96; 19.97; 20.44; 20.15; 20.48. 20.01; 20.04; 20.15;
20.04; 20.15; 20.35; 20.10.

Mean Value = 20.17 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.17

Variation = 20.00 - 20.34 $\mathring{A}^2$

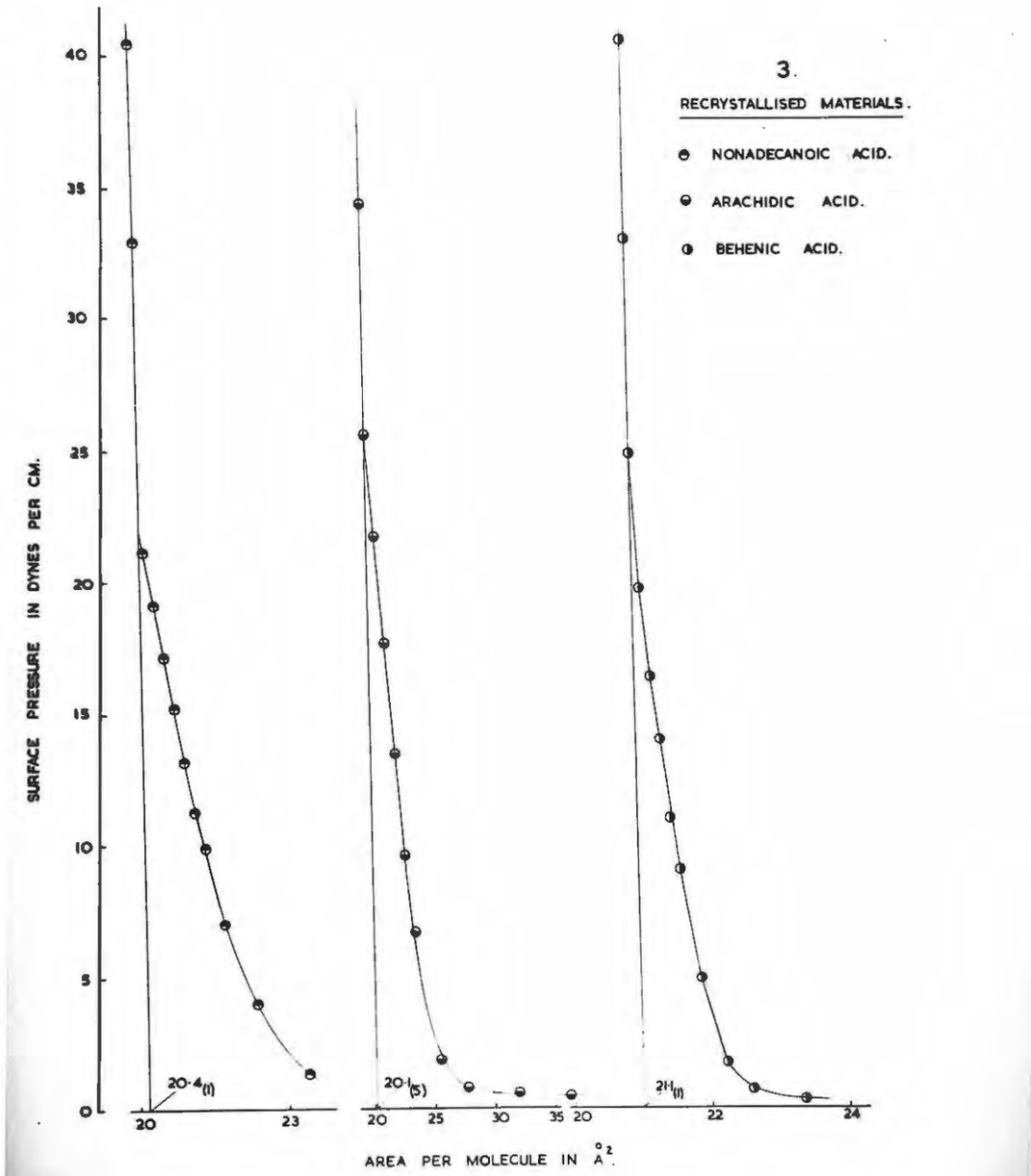
(vi) BEHENIC ACID.

21.29; 21.47; 21.12; 21.44; 21.46; 20.75; 20.95; 21.11;
20.75; 21.11; 21.28; 21.46; 21.11; 21.11; 20.93; 21.11;
21.11; 21.10; 21.28; 21.10.

Mean Value = 21.15 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.21

Variation = 20.94 - 21.36 $\mathring{A}^2$


3.
RECRYSTALLISED MATERIALS.
NONADECANOIC ACID.
ARACHIDIC ACID.
BEHENIC ACID.
SURFACE PRESSURE IN DYNES PER CM.
0
5
10
15
20
25
30
35
40
20·4(1)
20·1(5)
21·1(1)
20
23
20
25
30
35
20
22
24
AREA PER MOLECULE IN Å²

(vii) LIGNOCERIC ACID.

22.13; 22.02; 22.02; 22.08; 22.51; 22.02; 22.35; 21.97;
22.08; 22.02; 22.29; 22.29; 22.08; 22.02; 22.02; 21.91;
22.02; 21.91; 22.08; 22.13.

Mean Value = 22.10 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.15

Variation = 20.95 - 22.25 $\mathring{A}^2$

2. Zone Purified Materials.

Results obtained for 20 successive determinations of the molecular cross-sectional areas (in $\mathring{A}^2$) for the following:

(i) PALMITIC ACID.

21.03; 21.03; 21.01; 21.09; 21.13; 21.22; 21.22; 21.44;
21.40; 21.41; 21.03; 21.05; 21.22; 21.13; 21.20; 21.24;
21.22; 21.20; 21.22; 21.34.

Mean Value = 21.19 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.13

Variation = 21.06 - 21.32 $\mathring{A}^2$

(ii) MARGARIC ACID.

19.23; 19.23; 19.32; 19.27; 19.32; 19.20; 19.42; 19.42;
19.43; 19.42; 19.38; 19.36; 19.42; 19.27; 19.38; 19.32;
19.38; 19.42; 19.43; 19.42.

Mean Value = 19.35 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.07

Variation = 19.28 - 19.42 $\mathring{A}^2$

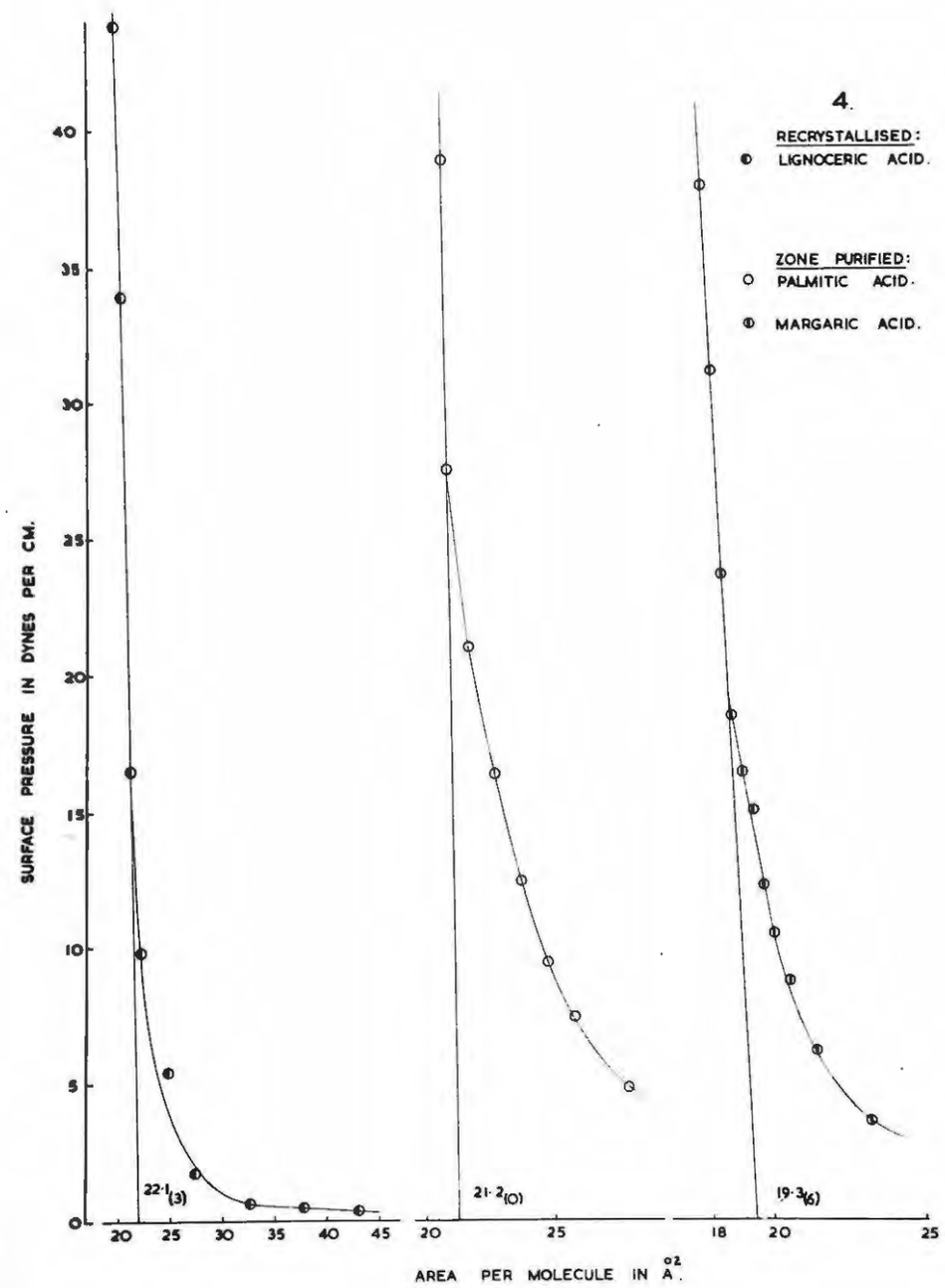
(iii) STEARIC ACID.

20.59; 20.65; 20.79; 20.52; 20.52; 20.79; 20.86; 21.04;
20.93; 21.04; 20.65; 20.79; 20.88; 20.79; 20.65; 20.65;
20.82; 20.88; 20.82; 20.84.

Mean Value = 20.78 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.15

Variation = 20.63 - 20. 93 $\mathring{A}^2$


RECRYSTALLISED:
LIGNOCERIC ACID.
ZONE PURIFIED:
PALMITIC ACID.
MARGARIC ACID.
SURFACE PRESSURE IN DYNES PER CM.
AREA PER MOLECULE IN A°2
22·1(3)
21·2(0)
19·3(6)

(iv) NONADECANOIC ACID.

20.46; 20.55; 20.24; 20.24; 20.32; 20.35; 20.44; 20.46;
20.44; 20.44; 20.09; 20.10; 20.10; 20.20; 20.24; 20.24;
20.32; 20.29; 20.32; 20.43

Mean Value = 20.31 $Å^2$ ⟶

Standard Deviation = ± 0.13

Variation = 20.18 - 20.44 $Å^2$

(v) ARACHIDIC ACID.

19.94; 20.22; 20.07; 20.05; 20.45; 20.07; 20.20; 20.20;
20.07; 19.94; 20.02; 20.07; 20.07; 20.20; 20.15; 20.16;
20.33; 20.45; 20.44; 20.00.

Mean Value = 20.16 $Å^2$ ⟶

Standard Deviation = ± 0.16

Variation = 20.00 - 20.32 $Å^2$

(vi) BEHENIC ACID.

21.22; 20.90; 21.55; 21.04; 21.06; 20.90; 21.06; 20.90;
21.55; 21.06; 21.22; 21.00; 21.22; 20.90; 21.04; 20.90;
20.97; 20.90; 20.90; 21.39.

Mean Value = 21.08 $Å^2$ ⟶

Standard Deviation = ± 0.20

Variation = 20.88 - 21.28 $Å^2$

3. Materials Purified by Vacuum Distillation.

Results obtained for 20 successive determinations of the molecular cross-sectional areas (in $Å^2$) of the following:

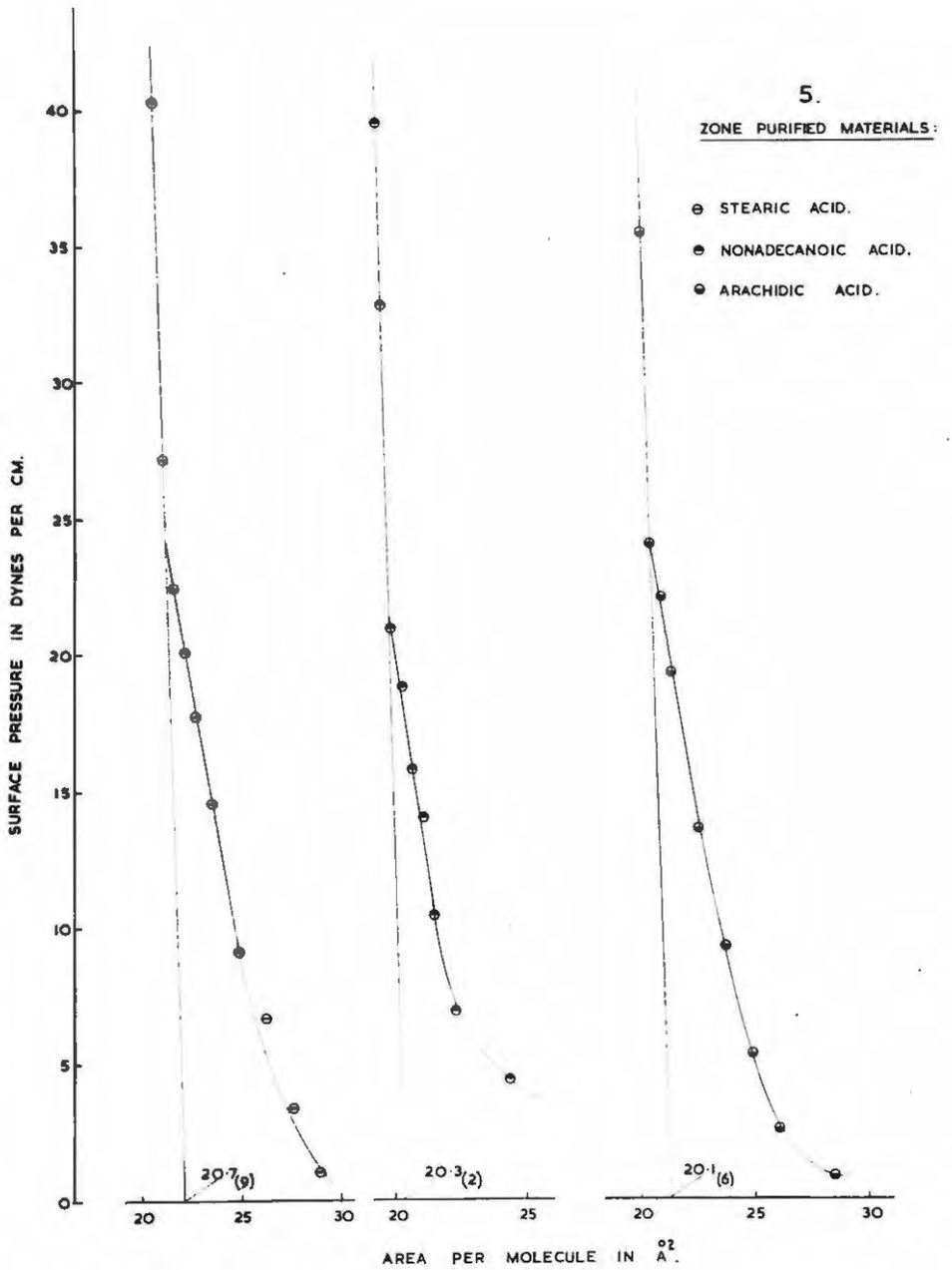
(i) PALMITIC ACID.

21.35; 21.43; 21.13; 21.10; 21.13; 21.29; 21.19; 21.31;
21.48; 21.53; 21.13; 21.12; 21.13; 21.16; 21.10; 21.31;
21.31; 21.35; 21.48; 21.53.

Mean Value = 21.28 $Å^2$ ⟶

Standard Deviation = ± 0.15

Variation = 21.13 - 21.43 $Å^2$


5.
ZONE PURIFIED MATERIALS:
STEARIC ACID.
NONADECANOIC ACID.
ARACHIDIC ACID.
SURFACE PRESSURE IN DYNES PER CM.
AREA PER MOLECULE IN Å².
20·7 (9)
20·3 (2)
20·1 (6)

(ii) STEARIC ACID.

20.86; 20.60; 20.79; 20.81; 20.79; 20.60; 20.97; 20.97;
21.38; 21.38; 20.53; 20.60; 20.81; 20.79; 20.68; 20.86;
21.10; 21.10; 21.28; 21.10.

Mean Value = 20.90 $\AA^2$ ⟶

Standard Deviation = ± 0.25

Variation = 20.65 - 21.15 $\AA^2$

(iii) BEHENIC ACID.

21.02; 21.14; 21.02; 20.69; 20.98; 20.98; 21.18; 21.32;
21.02; 20.94; 21.14; 21.24; 21.29; 21.18; 21.14; 21.24;
21.16; 21.34; 21.18; 21.14.

Mean Value = 21.12 $\AA^2$ ⟶

Standard Deviation = ± 0.15

Variation = 20.97 - 21.27 $\AA^2$

4. Miscellaneous Compounds.

Results obtained for 20 successive determinations of the molecular cross-sectional areas (in $\AA^2$) of the following:

(i) CETYL ALCOHOL.

21.13; 21.20; 21.26; 21.26; 21.26; 21.31; 21.23; 21.37
21.04; 21.11; 21.26; 21.28; 21.26; 21.28; 21.13; 21.26;
21.20; 21.07; 21.26; 21.28.

Mean Value = 21.22 $\AA^2$ ⟶

Standard Deviation = ± 0.26

Variation = 20.96 - 21.48 $\AA^2$

(ii) n-OCTADECYL ACETATE.

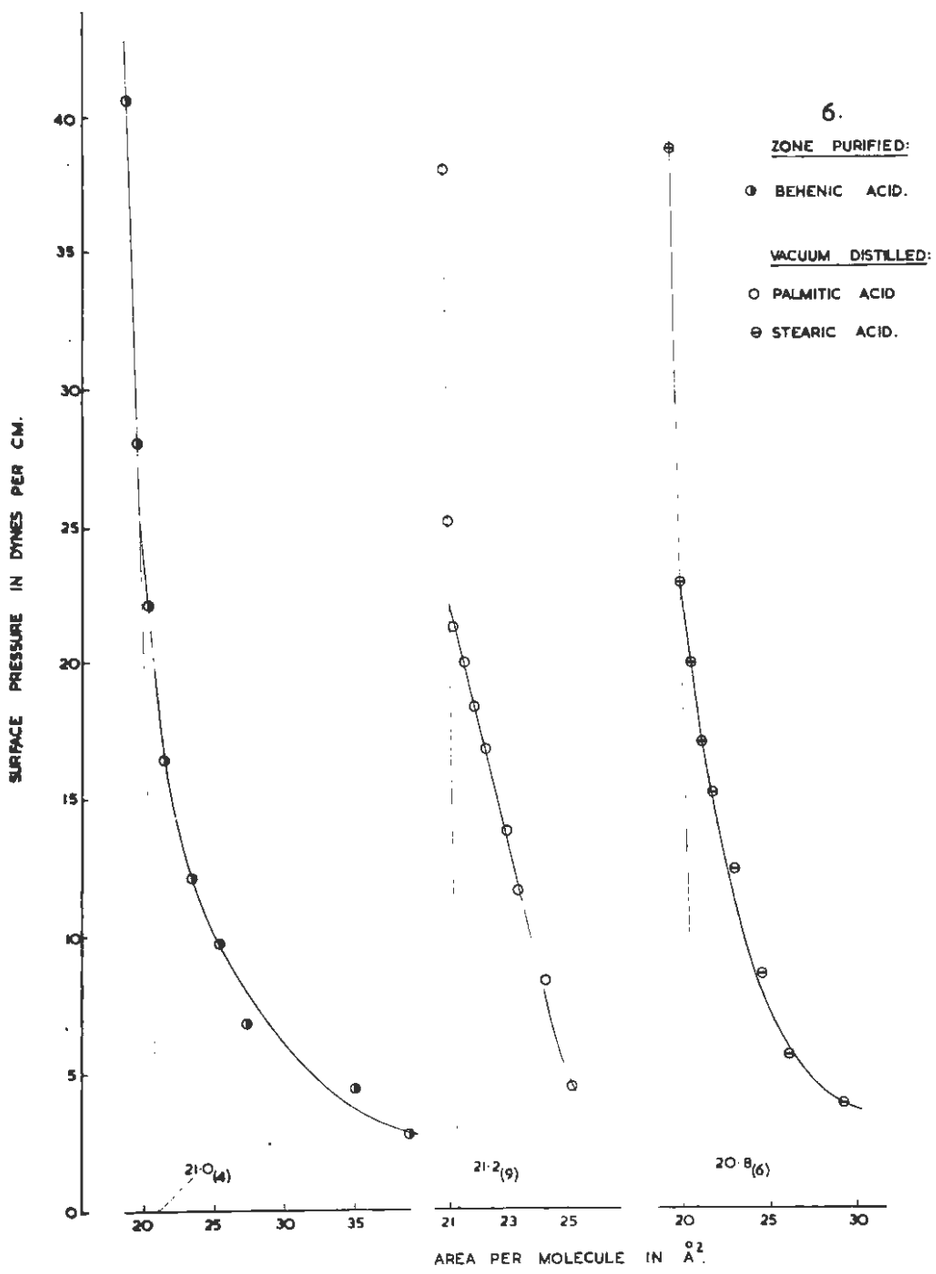
20.42; 20.65; 20.36; 20.42; 20.70; 20.70; 20.50; 20.42;
20.65; 20.42; 20.42; 20.65; 20.65; 20.70; 20.46; 20.42;
20.65; 20.70; 20.46; 20.42.

Mean Value = 20.54 $\AA^2$ ⟶

Standard Deviation = ± 0.13

Variation = 20.41 - 20.67 $\AA^2$

(iii)


ZONE PURIFIED:
BEHENIC ACID.
VACUUM DISTILLED:
PALMITIC ACID
STEARIC ACID.
SURFACE PRESSURE IN DYNES PER CM.
0
5
10
15
20
25
30
35
40
21·0(4)
21·2(9)
20·8(6)
20
25
30
35
21
23
25
20
25
30
AREA PER MOLECULE IN Å²

(iii) TETRADECANOL.

20.89; 20.73; 21.05; 20.73; 20.73; 20.89; 21.05; 21.05;
20.89; 21.05; 21.05; 21.05; 20.89; 20.89; 20.89; 20.73;
20.89; 21.05; 20.89; 20.89.

Mean Value = 20.91 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.12

Variation = 20.79 - 21.03 $\mathring{A}^2$

(iv) TRISTEARIN.

70.79; 71.48; 71.48; 72.64; 70.08; 73.11; 71.48; 72.64;
73.82; 72.64; 71.48; 71.48; 73.82; 72.64; 73.35; 73.35;
71.48; 73.58; 72.88; 71.48.

Mean Value = 72.3 $\mathring{A}^2$ ⟶

Standard Deviation = ± 1.05

Variation = 71.3 - 73.4 $\mathring{A}^2$

(v) 9-10 DIBROMO ANTHRACENE.

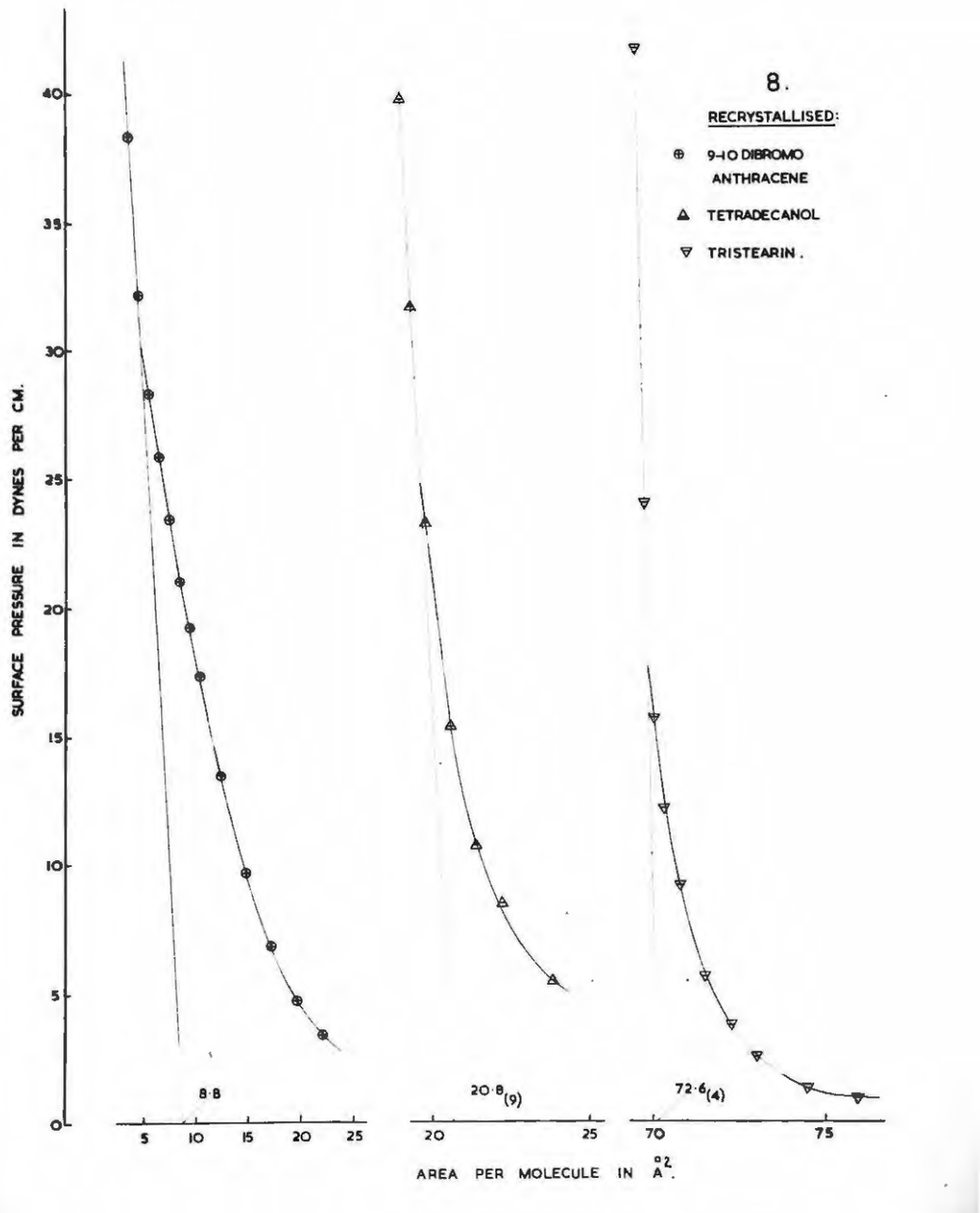
Results obtained for 10 successive determinations.

8.68; 8.28; 6.66; 9.56; 9.64; 8.88; 9.26; 9.07; 9.64;
8.88.

Mean Value = 8.86 $\mathring{A}^2$ ⟶

Standard Deviation = ± 0.84

Variation = 8.02 - 9.70 $\mathring{A}^2$


8.
RECRYSTALLISED:
⊕ 9-10 DIBROMO ANTHRACENE
△ TETRADECANOL
▽ TRISTEARIN.
SURFACE PRESSURE IN DYNES PER CM.
0
5
10
15
20
25
30
35
40
8·8
20·8(9)
72·6(4)
5
10
15
20
25
20
25
70
75
AREA PER MOLECULE IN Å².

5. SUMMARY OF RESULTS.

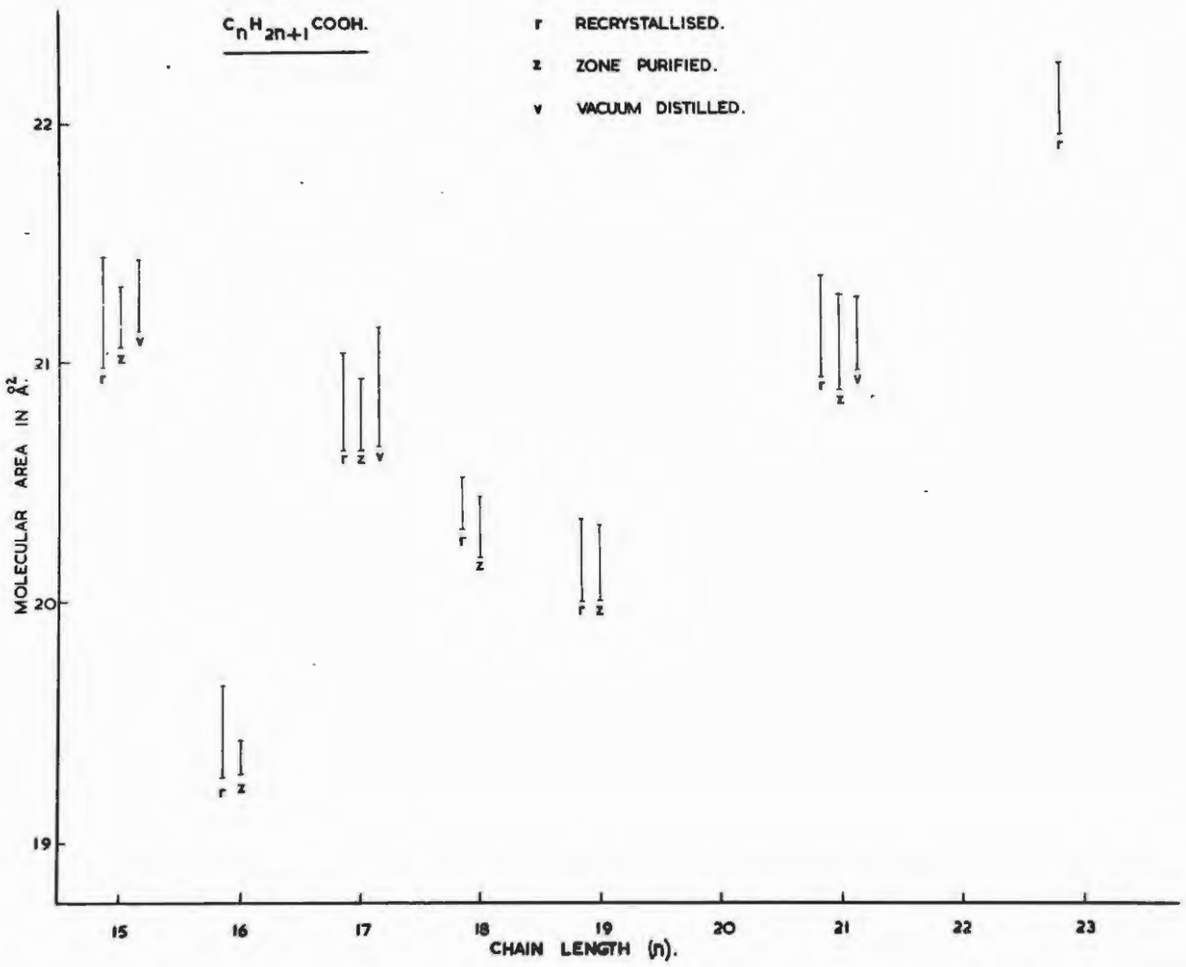
(i) FATTY ACIDS. $C_nH_{2n+1}COOH$

TEMPERATURE = 20 ± 0.5°C

(S = Standard Deviation).

n.	NAME	RECRYSTALLISED		ZONE PURIFIED		VACUUM DISTILLED	
		Mean Area	S	Mean Area	S	Mean Area	S
		$\AA^2$	±		±		±
15	Palmitic	21.21	0.23	21.19	0.13	21.28	0.15
16	Margaric	19.46	0.19	19.35	0.07	-	-
17	Stearic	20.83	0.20	20.78	0.15	20.90	0.25
18	Nonadecanoic	20.41	0.11	20.31	0.13	-	-
19	Arachidic	20.17	0.17	20.16	0.16	-	-
20	Heneicosanoic	-	-	-	-	-	-
21	Behenic	21.15	0.21	21.08	0.20	21.12	0.15
22	Tricosanoic	-	-	-	-	-	-
23	Lignoceric	22.10	0.15	-	-	-	-

- (ii) MISCELLANEOUS COMPOUNDS -


$C_nH_{2n+1}COOH.$
r RECRYSTALLISED.
z ZONE PURIFIED.
v VACUUM DISTILLED.
MOLECULAR AREA IN Å.²
22
21
20
19
15
16
17
18
19
20
21
22
23
CHAIN LENGTH (n).

(ii) MISCELLANEOUS COMPOUNDS (also investigated).

Name	Mean Area	S
Cetyl Alcohol	21.22	± 0.26
n-Octadecyl Acetate	20.54	0.13
Tetradecanol	20.91	0.12
Tristearin	72.29	1.05
9-10 Dibromo Anthracene	8.86	0.84

XI. DISCUSSION OF RESULTS.

From the summary of the results in table 5.(i) it may be observed that the precision which the surface balance is capable of giving is of a high order. The sensitivity is such that it will indicate differences in pressures of less than 0.002 dyne per cm. The overall precision of the measurements, made with the balance, is estimated at 1%.

Three main method of purification have been used for the series of fatty acids. Of these, the zone purified samples appear to give the most reliable results as evidenced by their smaller standard deviations. The vacuum distilled materials are next in order of preference, while the recrystallized samples yield rather larger standard deviations and thus give less precise results for the molecular areas.

A closer look at the values, obtained for the molecular cross-sectional areas of the fatty acids, will reveal certain variations. These anamalous results show a general decrease in the molecular areas from palmitic acid (n = 15) to arachidic acid (n = 19), while from arachidic acid to lignoceric (n = 23) the areas start increasing again. In addition to this general trend, we see that margaric acid (n = 16) and nonadecanoic acid (n = 18) (the only acids available with n even in the chain attached to the carboxyl group) exhibit slightly lower values than expected. This is a new observation made possible by the sensitivity of the balance.

In order to explain these phenomena, it is necessary at this point to bear in mind that the fatty acids in the homologous series are similar in every respect apart from the length of their hydrocarbon chains. The general formula $C_nH_{2n+1}COOH$ applies to all these acids, n being the only variable.

Under compression as "condensed" films, at the air-water interface, the acids assume a more or less vertical orientation with respect to the water surface. It has earlier been proved that these amphiphilic molecules arrange themselves in such a way that the polar, hydrophilic carboxyl groups lie in the water-phase, while the hydrophobic hydrocarbon chains project into the air-phase.

If we neglect, for the moment, the two anomalous values

- obtained for -

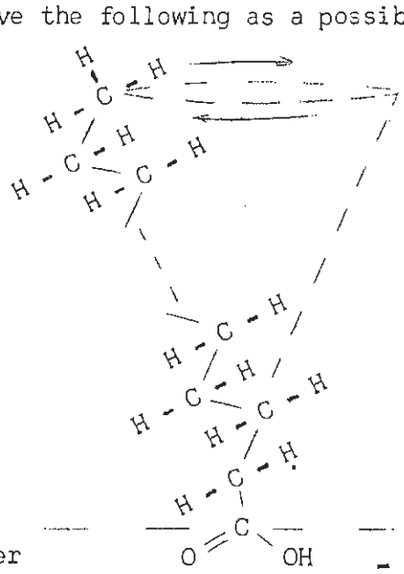
obtained for margaric and nonadecanoic acids, we see that, at the value of n = 19 i.e. arachidic acid, there is a reversal of the general trend constituting a turning point in the decrease of the molecular areas.

The cause of the decrease in molecular areas, up to arachidic acid, may be attributed to the fact that the acids lower than n = 19 in the series, having fairly short carbon chains and consequently lower molecular masses, are more prone to translational displacement in the suface layer than are the molecules of higher n-value with longer chains and proportionately greater molecular masses.

Another factor which might contribute to the general decrease in the values of the molecular areas up to arachidic acid, has been suggested by the work of Bigelow and Brockway[102], who studied the variation in the contact angle of a series of acids, in adsorbed films at the air-water interface, with their chain length. They found that the angle of tilt of the acids increased from 2° for arachidic acid (n = 19), to 6° for palmitic acid (n = 15). This means that the longer the hydrocarbon chain becomes, the smaller becomes the angle which the chain makes with the normal to the water surface.

It is also a well-known fact that the hydrophilic carboxyl (or "head") group of the fatty acid molecule is slightly larger in cross-section than the hydrophobic chain itself. Adam and Harkins postulated this in the 1920's and X-ray investigations have subsequently confirmed their views. Whereas the chain normally has an area of cross-section of between 20 and 22 $\mathring{A}^2$, the "head" group usually exhibits a slightly larger area of about 25 $\mathring{A}^2$.

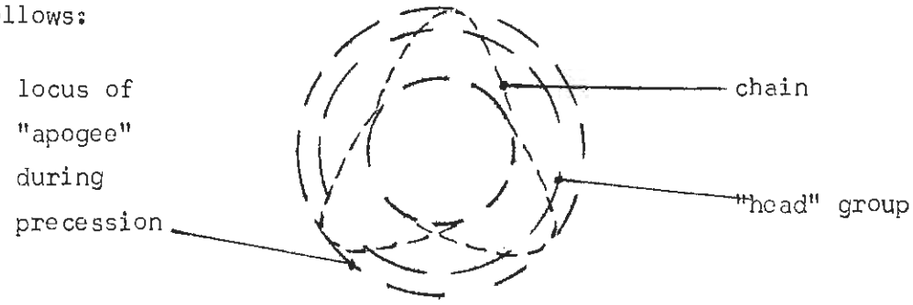
Hence we have the following as a possible situation at the air-water interface:



- where the -

where the hydrocarbon chain is able to precess about an approximately vertical axis, while the "head" group is anchored in the condensed film.

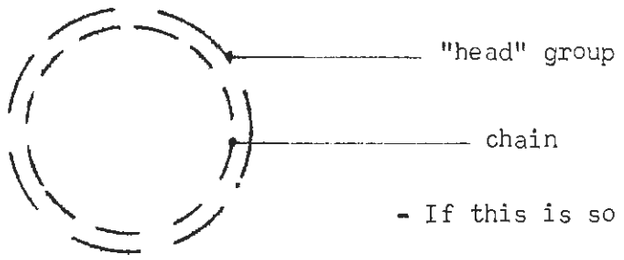
Thus the cross-sectional areas, as determined by the Langmuir trough technique are not strictly realistic, since the apparent cross-section of the chain is greater than the actual value. This is due partly to the ability of the molecules to suffer lateral translation, partly to changes in the angle of tilt of the molecules (which affects the actual area as projected on to the surface), and partly to the ability to precess, as illustrated diagramatically above. Due to these effects, the area of cross-section of the hydrocarbon chain may be visualized as follows:



If the molecules are not stationary and vertical, the projected area on to the surface is not circular but elliptical. This area will thus be slightly larger than would be expected for a hydrocarbon chain which is orientated exactly at right angles to the water surface.

However, the longer the hydrocarbon chain becomes, the higher the molecular mass becomes and consequently the effect of lateral translations due to kinetic energy is relatively less. This should yield a closer packing among neighbouring molecules, resulting in smaller areas.

At arachidic acid (n = 19) we observe a turning point. Up to this point the areas had been decreasing steadily from n = 15 to n = 19. After this we have a steady increase in the values. This may indicate that for arachidic acid, we have a relatively stable configuration with the molecules orientated virtually at right angles to the substrate surface. This situation may be visualized cross-sectionally as follows:



- If this is so -

If this is so, the area of cross-section of the chain should not be very different from the theoretically correct value.

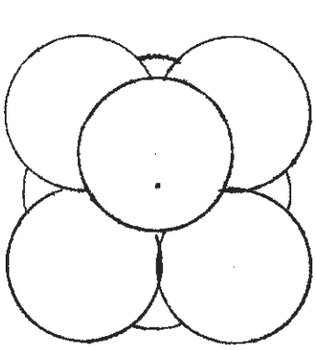
The increase in the molecular areas after arachidic acid may possibly be due to the fact that with increasing chain length and the attendant increase in molecular mass, the hydrocarbon chains may start to tilt, buckle or topple over in their upper regions, while the lower sections are relatively normally orientated to the substrate.

A point that supports this line of reasoning is the observation of Karle[98], who found during his work in which he produced monolayers of cerotic acid on soda-glass surfaces from melts of the pure compound, that molecules of cerotic acid (n = 25) exhibited an angle of tilt of 26° from the normal.

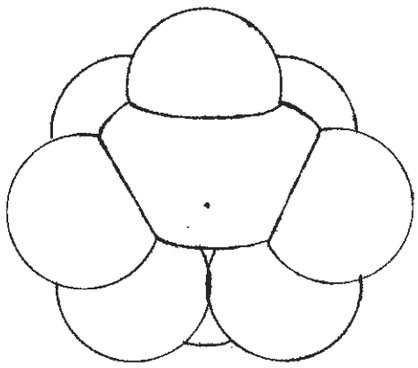
If the acids after arachidic acid in the series, show this phenomenon of tilting, the area of cross-section could conceivably increase due to the oblique section.

The above arguments hold for all the acids in the series with uneven n-values in the formula $C_nH_{2n+1}COOH$. However, as already mentioned, the acids of even n-value, namely margaric acid and noadecanoic acid, generally seem to exhibit anomalously lower areas of cross-section.

In order to attempt an explanation of these anomalies, use was made of scale models (1 cm = 1 Å) of the Fisher-Hirschfelder type. From a study of these models (see Plate 10) it was confirmed that the hydrocarbon chain generally lacked cylindrical symmetry, due to the $-CH_3$ group at the end of the chain being off the axis. The models were examined in a vertical position and projections for 90° incidence were made. From these projections it was observed that the acids with even n-values were more evenly balanced about the chain axis.



n = 16.



n = 17.

- For margaric acid -

9. MOLECULAR MODELS.

END VIEW OF CHAIN.

MARGARIC ACID.
N = 16

STEARIC ACID.
N = 17

For margaric acid (n = 16), in particular, we have 4 x 4 carbon atoms in the chain. Due to the tetrahedral nature of these carbon atoms we obtain a situation where the chain structure repeats itself in units of 4. Thus in the case of margaric acid we find greater symmetry about the chain axis than for example, in stearic acid with an n-value of 17. In margaric acid the end $-CH_3$ group is situated in such a way that is is impossible for it to rotate. The $-CH_3$ group of the stearic acid chain, on the other hand, is able to rotate about its bond with the penultimate carbon atom in the chain and thus will sweep out a greater area. This may well account for the difference in molecular areas, observed for margaric and nonadecanoic acids in comparison with the other acids in the series having uneven n-values.

XII. SUMMARY AND CONCLUSIONS.

The results obtained for the cross-sectional areas of the series of long-chain fatty acids may best be summarized with the aid of Graph 9. This graphical representation of the molecular areas, in $\AA^2$, against the chain length (n), of the fatty acid molecules, illustrates variation of the areas with chain length for the series in recrystallized form, and also for selected samples in the zone purified and vacuum distilled forms.

On the graph, the limits of variation of the molecular areas have been represented as lines of a length corresponding to twice the standard deviation (2S). This is to give representation that the standard deviation may be positive or negative in relation to the mean.

For molecules with n odd and lying between 15 and 19, the molecular area decreases. This may be due to the effect of 3 factors:

(1) A general decrease in lateral translation because of the increasing molecular mass (translational kinetic energy per molecule $= \frac{1}{2} mc^2$), resulting in closer spacing of molecules.

(2) A general, but steady decrease in the angle of tilt of the molecules which thus tend to be held more erect in the condensed film.

(3) A general decrease in the precessional motion of the hydrophobic chain groups.

For molecules with n odd and between 19 and 23, the molecular areas increase probably due to the steady increase in molecular mass causing the long chains to commence to buckle, tilt or topple in their upper regions. This tilting becomes greater because of the increasing gravitational effect on the heavier molecules which tends to make them assume a flatter posture in relation to the surface.

The lower values observed for margaric and nonadecanoic acids, may be due to increasing symmetry in the chain, with corresponding economy in packing in condensed monolayers. This effect may be connected with increasing cylindrical symmetry of the hydrocarbon chain for even values of n.

The results of this investigation, incomplete as it is,

serve to indicate what might reasonably be expected to happen in the orientation of these fatty acids in monolayers. Further work, especially on a greater range of acids with even n, is clearly necessary in order to establish the tentative ideas which have been suggested. However, in the present research, work was limited to those acids in the series which were obtainable without undue difficulty or delay, those which would spread readily under the conditions of experiments carried out at 20°C, and those which could be purified relatively easily.

The acids below n = 15 in the series were found to be too soluble in aqueous substrates, at operating temperatures of 20°C, to yield reliable evidence with the Langmuir trough technique. The acids above n = 23 were unobtainable commercially and the synthesis of these acids from the lower members in the series presented problems, of isolating the required specimens and difficulty in purifying these, which were considered to be beyond the scope of the present research.

XIII. # B I B L I O G R A P H Y.

Abbreviations of the titles of journals conform with the system used in "Chemical Abstracts".

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