

AN AUTOMATIC-RECORDING, WILHELMY SLIDE,
FILM BALANCE

by

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ABSTRACT

A stainless steel water trough with a movable aluminum undercarriage was designed and built to serve as the basic component of an automatic-recording film balance. The trough and undercarriage were enclosed in a lucite box to provide a controlled atmosphere. The trough was thermostated to a constant temperature by a series of water baths. An ordinary analytical balance was modified to contain a linear differential transformer at one end of the balance beam. A 1/16" aluminum rod was attached to the other end of the balance beam and extended through the bottom of the balance to the surface of the water trough. This rod held a glass slide which was used to determine changes in surface tension according to the Wilhelmy method. The linear differential transformer was calibrated against a recorder for definite ranges. A Vycor still was constructed to purify the water used in the film balance. Solutions of Cetyl alcohol in ligroin were applied to the film balance and the resulting $\pi - \sigma$ isotherms were compared to those found in the literature.

I - INTRODUCTION

Of all the world's natural resources water is one of the most basic to man's survival. In fact, one is hard pressed to think of anything that is more vital or more universally in demand. Over 250 billion gallons of water per day are used in the United States alone. Projected calculations show that by 1980 at least 250 million people are expected in this country. They will require approximately 600 billion gallons of water per day - an increase of over 100 per cent. The alarming fact about these estimations is that all of the water that is readily available is now being utilized. The basic supply of water is, on the whole, fixed by the inelastic factors of precipitation and runoff. Obviously then, a comprehensive program must be organized to use more effectively the water we already have. One aspect of this program would be to increase the capacity of the storage reservoirs. Thus the river flows that are now only partially used could be conserved before they discharge into the oceans. As expected, such an increase would greatly affect water losses by evaporation.

The idea that evaporation could be suppressed by applying a layer of some type of oily, viscous material to the surface of the water is a very old one. However, the

cost of applying a film thick enough to be effective on a large body of water precluded serious consideration for a long time. Then, the discovery that some substances spread spontaneously on water to produce films one molecule thick gave new impetus to the idea. This impetus was derived from the fact that the newer, thinner films could retard evaporation efficiently through a more effective mechanism than that exhibited by a thick layer of oil.¹ Since the amount of film-forming substance required to form a monolayer is quite small, the cost no longer becomes a problem. Clearly, the major factor now is the effectiveness of the monomolecular film in suppressing evaporation. The film balance evolved as a device for studying the properties of these monomolecular films, and hence their effectiveness in retarding evaporation. As such, its basic conception and design are due mainly to efforts of Fraulein A. Pockels, I. Langmuir, and N. K. Adam.

Experiments on the formation of thin films of oils on water date from the time of Benjamin Franklin who studied the thickness of these films in the field.² Nevertheless, the first significant innovation in this area came in 1891 when Fraulein Agnes Pockels developed an apparatus to measure the change in surface pressure with respect to the area covered by a film of oil.³ Her general design incorporated a feature of major importance to the study of these interfaces, i. e., the surface must be accessible for manipulation. This was accomplished by making it rise slightly above the brim of the

trough. The barriers for manipulation of the film can then rest upon the edges of the trough.

In 1917 Irving Langmuir formulated the experimental and theoretical concepts which led to our modern understanding of the behavior of molecules in insoluble monolayers. During the course of his studies he developed the prototype of the surface balance which now bears his name. This is a device in which a movable float separates a clean water surface from the film-covered area.⁴ The differential surface tension or surface pressure can then be measured directly by an analysis of the deflection of the float.

N. K. Adam examined a variety of monolayers in the decade between 1920 and 1930. In the course of this work he introduced many refinements in technique which made the Langmuir film balance a precise tool for the measurement of the properties of monomolecular films.⁵ For example, he eliminated the errors due to film leakage around the ends of the float by blocking the gaps with thin flexible ribbons of gold or platinum foil, waxed to prevent wetting.

Another type of film balance which was used by Rayleigh⁶ and other early workers is the Wilhelmy surface balance. In this method an absolute measurement of the surface tension is made by determining the force exerted on a plate partially immersed in the liquid. Comparison with a similar measurement on a clean water surface yields the

surface pressure. This type of film balance and subsequent refinements are the subjects of this thesis.

It must be emphasized that although the film balance plays a major role in studies of evaporation suppression, it is not restricted to that area alone. Indeed, it can be used to gain invaluable information about transport processes in general. In doing so, it would illuminate such vital areas as sensitizing reactions, agglutination behavior, immunization reactions, and many other biologically active systems.

II - THEORY

The boundary between two homogeneous phases cannot be regarded as a simple geometrical plane, upon either side of which the homogeneous phases extend. Instead it must be thought of as a layer of a characteristic thickness. The material in this lamina shows properties differing from those in the adjacent homogeneous phases. With regard to an interface between a gas and a liquid, i. e., air and water, it is a matter of common observation that the liquid behaves as if it were surrounded by an elastic skin with a tendency to contract. Young was the first to attempt an explanation of this surface tension in terms of the attractive and repulsive forces between the molecules of the liquid.⁷

The cohesion between the molecules of a liquid must surpass their tendency to separate due to thermal agitation. This net attraction between neighboring atoms is satisfied most completely in the interior of the phase. Those molecules in the surface region are subjected to a less symmetrical force field than those in the bulk. Consequently, the free energy of the surface molecules is greater. Since the free energy of any system tends toward a minimum, the surface of such a pure phase will contract spontaneously. Expressed mathematically using γ_0 to represent the force per

centimeter tending to contract such a surface, the first law for the system can be written as:

$$dE^S = TdS^S + \gamma_0 dA^S + \sum U_i dn_i^S$$

where $\sum U_i dn_i^S$ covers all physical and chemical changes not specifically defined and superscript s refers to the surface region. Defining dH^S as dE^S and dG^S as $dH^S - d(TS^S)$, leads to the following expression for dG^S :

$$dG^S = -S^S dT + \gamma_0 dA^S + \sum U_i dn_i^S$$

At constant T, P, and n_i^S this reduces to

$$\gamma_0 = \left(\frac{\partial G^S}{\partial A} \right)_{T, n_i}$$

Under these conditions a spontaneous contraction of the surface area, A, will decrease G^S provided γ_0 is positive.

When a monolayer of film-forming material is spread at the air-water interface, the tendency of the surface area to decrease spontaneously is altered. This effect is illustrated in the following example: if a little butanol is added to the water, it will dissolve because of the tendency of the polar hydroxyl group to be hydrated in spite of the partial dislocation of the hydrogen-bonded water structure due to the hydrophobic hydrocarbon chain. If, however, the butanol molecules reach the surface, they can keep their hydroxyl groups in the water while the hydrocarbon chains can escape into the vapor phase where they are energetically

more welcome. Thus the molecules of butanol tend to accumulate in the surface region, i. e., adsorb at the surface. This migration to the surface can be considered to oppose the contractile tendency of the pure water surface. The net result being that if the repulsive pressure of the butanol molecules adsorbing at the surface is called π , the surface tension is lowered by that amount, i. e., $\pi = \gamma_0 - \gamma$. A closer look at the nature of π would reveal that it is slightly incorrect to think of it as a simple repulsive pressure. To be entirely rigorous π must be considered as being analogous to an osmotic pressure with the water surface acting as the membrane. However, utilizing the simple concept of a repulsive pressure allows an elementary qualitative insight as to how π , the film or surface pressure, is related to the evaporation suppression ability of the monolayer. A large film pressure would mean that more molecules were adsorbing at the surface, or looking at it another way, that there were more molecules per unit area in the surface region. This in turn might mean that a water molecule trying to find a way through the monolayer would have a more difficult time, i. e., the evaporation resistance of a film is a function of the surface pressure which is a function of the surface tension which in turn is a function of the molecules of film-forming material per unit area. It is obvious that the temperature would have a profound effect upon the surface tension and hence the evaporation suppression ability of a film since it

affects the balance between the cohesive forces of the molecules in the liquid and their tendency to separate due to thermal agitation.

It follows directly from the preceding discussion that any device which hopes to study the properties of insoluble monomolecular films at air-water interfaces must incorporate three major features into its design:

1. A means of measuring the surface tension-either differential or absolute.
2. A method by which the surface pressure may be varied.
3. Adequate control of the temperature.

III - EXPERIMENTAL

A. Construction of the System

1. General Description

The system, pictured in Figure 1, rests on a large table. Three inches of concrete form the top of the table to give it stability. In order to insure a minimum amount of vibration in the system the table is set in a six inch sand bed on the ground floor of the Chemistry Building. A one inch plywood sheet lies on top of the table. To this the drive motors, lucite housing, and electrical outlets are fastened (Figure 2). A small table constructed to cover the left half of the lucite housing also fits on top of the board. The table holds the balance and the various electrical accouterments necessary for the operation of the system (Figure 2).

2. The Trough

The trough, shown in Figure 3, is constructed out of 1/8" stainless steel plate. It contains a shallow bed in which water is placed prior to a measurement. Films are spread upon the water and their surface properties are studied. The edges of the bed of the trough are one half inch high and one fourth inch wide. Both the bed and edges are sprayed with "Vydax" AR Telomer Dispersion obtained from I. E. Du Pont de Nemours and Company. The trough is then heat-treated in an oven to 300 °C for one minute. This provides

a coherent, uniform, teflon surface for the trough which is hydrophobic in nature. The bottom of the trough is baffled to provide adequate water circulation for the purpose of temperature control. Water flow is controlled by the inlet valve mounted on the front of the trough. The edges of the bed are surface ground to within 0.003 of an inch to allow the sweeping bars to ride uniformly along the length of the trough.

3. The Suspension System

The trough rests on a three point suspension system which consists of two adjustable legs in the front and a saddle at the rear containing a single contact point. The legs slide into "V" blocks that are welded onto the trough. They are held in place by a single set screw and can be completely removed if need be. The tapped barrel of the legs extends two and one half inches from the bottom of the trough and the threaded leg, itself, screws into the barrel for a minimum height of three and one half inches and a maximum height of five and one half inches. The saddle support at the rear consists of a steel frame welded out of 5/16" plate (Figure 4). The saddle is designed in the shape of a "goal post". The trough makes contact one half inch above the saddle on a 5/8" bolt one end of which is ground to the shape of a hemisphere and the other end of which fits into a hole in the center of the "crossbar". The arms of the saddle

extend vertically two inches from the crossbar and hold the sweep supports.

4. The Sweep Assembly

The supports are L-shaped and are machined from 1/16" aluminum sheet. The vertical part of the L rises above the saddle arm and the horizontal leg of the L is inverted so that it lies along the top of the trough. The sweeps, themselves, are 1/4" square stainless steel bars, sixteen inches long. Holes are drilled in the bars one and one fourth inches from each end. These allow the vertical lifts of the movable undercarriage assembly to pick the bars off the rests. Then the entire assemblage can move horizontally along the length of the trough.

5. The Drive Assembly

The undercarriage moves along a "track", (Figure 5a), consisting of 2-1/2" steel guide rods, 1-5/8" steel drive screw, and a 1/4" spline. The two end plates that anchor the "track" are bolted directly to the bottom of the lucite housing surrounding the trough. These end plates, (Figure 5b), are made from 3/4" aluminum. The guide rods fit into ball joint sockets and are secured by aluminum collars on either side of the end plates. The drive shaft also fits into ball joint sockets and has a pitch of eight threads to the inch. In the rear the drive shaft terminates outside the lucite housing as a manual clutch. This allows the drive motor to be disengaged at any time. The drive motor is an Insc

Multi-Speed Gear Motor. This is a Holtzer - Cabot synchronous motor combined with a multiple speed transmission. This particular model is Number 06700-1S. It is rated at 1 rpm for a 1:1 ratio with five other ratios available, i. e., 2:1, 5:1, 10:1, 20:1, and 50:1. In the front of the system the drive screw stops short of the plexiglass housing. However, there is access via a hole in the side of the cover for a hand crank. A "faster" return motor is also mounted here and can be used with the proper connection should the occasion warrant it.

6. The Undercarriage

The undercarriage, itself, (Figure 5c) corresponds to the "saddle" design mentioned earlier. It moves along the track according to the "captive" screw principle. It is machined out of 3/16" aluminum.

The spline passes through a small gear box at the top of the carriage. When the spline is rotated, it activates a small worm gear which turns the gear mounted on the carriage directly above the spline. This causes the lifts to move vertically along the arms of the carriage. When the aluminum collars are inserted in the lifts, they can be used to remove or replace bars on the sweep supports. Once a bar is removed from the support, it can be carried along the length of the trough for a sweeping operation or used to manipulate the film covering the water surface. The spline is operated by

a knurled knob extending outside the lucite housing at the rear of the system.

7. Temperature Control

The water circulated through the bottom of the trough is pumped via tygon tubing from a constant temperature bath to holes cut in the side of the lucite. Teflon connectors in the holes lead to more tygon tubing inside the housing which then carries the water to and from the trough, itself. By using two constant temperature baths in series, the temperature of the trough can be controlled to a tenth of a degree Centigrade. The first constant temperature bath is a Central - Scientific Thermostat Bath, Catalogue Number 97200-1, containing a "Blue M" cooling unit, Model Number PCC-2a. The water which is kept at $15^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ is pumped from this bath through a cooling coil that is immersed in the second bath. The second bath has an autonomous control unit and holds the temperature to better than a tenth of a degree. It is the water from this bath that is cycled through the trough.

8. The Measuring System

The balance, as mentioned before, sits upon the small table above the lucite housing which covers the trough. It is an ordinary Voland Analytical Balance, Number 200, that has been modified slightly. Both pans and pan rests are removed from the balance and a 1/2" hole is drilled through its base directly under the right end of the balance beam. Holes are

drilled through both the table and the lucite housing on a direct line with the one in the bottom of the balance. A 1/16" aluminum rod hangs from the balance beam down to the surface of the water. A glass slide is fastened to the rod by means of an aluminum holder (Figure 6). 1/8" holes are drilled in the glass slide so that it is, in effect, pinned in the holder. The Linear Variable Differential Transformer core is suspended from the left side of the balance beam by aluminum end pieces (Figure 7). One piece is needed at each end to keep the flux through the core as uniform as possible. The transformer is fastened to the balance beam support by means of a special lucite "clamp" (Figure 8).

When a six volt input is fed to the transducer, the core is pulled up against the inside of the transformer. To eliminate this source of friction, the input voltage is reduced to four volts and a brass nut was added to the end of the lowermost aluminum end piece. The added weight and reduced field inside the transformer allows the core to hang straight from the beam and move freely within the transformer. The Linear Differential Transformer used is a product of Schaevitz Engineering, Model Number 500-SS-L.

9. The Lucite Housing

The plexiglass housing which is used to protect the trough from dust and other contaminants is fashioned from 1/4" Lucite sheets. The sheets are first cut to size and then fastened together by 6-32 machine screws. The

plexiglass base is 1/2" thick and 8-32 machine screws are used on it. The entire front of the housing is attached to the top by a piano hinge which allows it to swing up like a trap door. This door is cut in half to allow access to the trough after the table and balance are set in place. An injection port is cut in the half of the door that cannot move. This facilitates the application of the monolayer once the system is ready to run.

B. Operation of the System

1. Purification of Water

Water that is used in the bed of the trough is taken from a Barnsted still and stored in a plastic container. It is then distilled through a vycor still while oxygen is bubbled into the distilling pot. It is stored until it is ready to be used in a glass container that has been steamed. Then the water is redistilled through the same vycor still with an oxygen bubbler and collected in steamed receiving flasks. It is then transferred directly to the trough.

2. Calibration of the LVDT

The linear differential transformer is calibrated against the recorder used in the system. The recorder is a Heath Kit 10" strip chart recorder with a maximum range of 250 mv. The transformer is attached by means of its lucite "clamp" to a steel grid. A 1" micrometer head graduated in thousandths of an inch is clamped directly above the

transformer. The magnetic core of the transducer with its aluminum end pieces is fastened to the micrometer head via a teflon connector. The transformer is connected to the Schaevitz LVDT Regulator Demodulator Unit, Type DMPS-1. This unit when connected to a 60 cps power source provides a low voltage excitation to the LVDT by means of a constant voltage step down transformer. The output from the LVDT is fed into a solid state doubler rectifier circuit contained in the same unit. This furnishes filtered DC voltage to a meter or recorder. In this system the unit is connected through a variac to a constant voltage supply. The variac allows a four volt input to the LVDT transformer to be picked off from the power source. The input is continually monitored by a Simpson Volt Meter hooked in parallel with the transformer. The output from the unit is fed simultaneously to the recorder and to a Keithley 151 null detector which is hooked in parallel to the recorder. Null is set by adjusting the core within the transformer via the micrometer head to within one to two per cent of zero as read on the Keithly 3mv scale. A final adjustment to zero is made by the zero adjust potentiometer on the Demodulator Regulator Unit, itself. The core's position in the transformer is then changed in regular steps as determined by the micrometer and the output is taken by the recorder (Tables 1 and 2). By this method the output of the LVDT is found to change 0.8 division of the recorder scale for every 0.001 inch deflection in the core's position.

3. Calibration of Lambda Pipet

A Lambda pipet is used to transfer the solution of film-forming material from the container to the water surface. The pipet is calibrated once with the purified ligroin used to make the solution (Table 3) and once with Research Grade Normal Pentane, 99.84 per cent pure, obtained from Phillips Petroleum Company (Table 4). The calibration is performed by weighing the pipet when it is full and once again after it is emptied. The difference gives the amount delivered. The pipet, rated to contain one milliliter at 20 °C, is connected by teflon tubing to a micrometer syringe with a two milliliter capacity. The solution is drawn into the pipet and discharged several times to "wet" the pipet. Finally, the solution is drawn into the pipet and allowed to drain until the meniscus just touches the calibration mark. The micrometer syringe is then backed off a little to draw the solution away from the tip of the pipet. A teflon cap is placed on the tip and the micrometer syringe is removed. A similar teflon cap is placed over that end and the pipet is weighed on an analytical balance. After weighing, the teflon caps are removed, the micrometer syringe replaced and the solution is discharged. The capping procedure is then repeated and the empty pipet reweighed. In this manner the pipet is found to deliver 0.9860 milliliter and it is felt that the correction factor is too slight to affect the results significantly.

4. Preparation of the Solution

Solutions are made by transferring a known amount of Cetyl alcohol, 99.8+ per cent pure, furnished by Applied Science Laboratories, Inc., to a one liter, grade A, volumetric flask. The same ligroin used in the calibration of the pipet is poured into the flask until the meniscus reaches the designated mark on its neck. The ligroin is purified by passing it through a chromatography column one inch in diameter and twenty-one inches long filled with alumina. The Cetyl alcohol is weighed by difference from a weighing bottle directly into the volumetric flask.

5. Preparation of Electrical System

The Linear Variable Differential Transformer and its accompanying electrical measuring devices are set up in the system exactly as described in the calibration procedure with one exception. The transformer and special lucite "clamp" are now attached to the beam support of the balance, and the core, with its aluminum end pieces, is hung from the left end of the balance beam. Thus any change in the depth of immersion of the glass slide, hung from the right end of the balance beam, is transmitted to the core and a corresponding signal is generated by the transformer. This forms the basis of the automatic-recording, Wilhelmy Slide, film balance because the electrical signal can then be transcribed by a suitable recording instrument.

6. Experimental Procedure

The procedure used in the measurement of an isotherm, i. e., the change in surface tension versus the area per molecule of film, is as follows:

The trough is filled with freshly distilled water from the vycor still until the water surface stands up over the edge of the trough. Then, time is allowed for temperature equilibrium to establish itself. The temperature is determined by a thermometer lying on the bottom of the bed of the trough. The thermometer has a range of -10°C to 50°C graduated in tenths of a degree. Its ice point is checked periodically and is found to be satisfactory. After allowing the water to remain in the trough for a period of six to eight hours, the current is turned on in the LVDT, and the sweeping is begun. A bar is picked up from the sweep supports by the undercarriage. It is laid on the edges of the trough so that enough of the lifts remain in the holes to propel the bar along the length of the trough. The bar is then hand-cranked to the front of the trough. In doing so, the surface of the water is literally swept free of floating or adsorbed contaminants. This procedure is repeated three times taking a total time of fifteen minutes. The third bar is deposited so that its edge overlaps a scale mounted on the side of the trough. The scale is a thirty centimeter steel rule graduated in five tenths of a millimeter. The point at which the trailing edge of the bar meets the scale is read through a

telescope. This bar serves as a permanent barrier for the film. A fourth bar is now picked up from the sweep supports and carried free of the water surface to the other end of the scale. It is laid on the edges of the trough so that the lifts still remain in the holes. The drive motor is connected and the point at which the leading edge of the bar intersects the scale is read through the telescope. This bar serves as the compression barrier for the film. At this point the glass slide is lowered into the water by releasing a pinch clamp applied to the rod at the base of the balance. The rod and slide are balanced against the core of the LVDT by adjusting several riders on top of the balance beam. Since the surface tension always decreases upon compression of the film, a balance point is chosen near one end of the limit of travel of the balance, i. e., the glass slide is immersed to its maximum depth as determined by the balance's movement.

The Keithley null detector is zeroed on its 0.1 millivolt scale and the LVDT is adjusted to within one to two per cent of null by moving the transformer in its lucite barrel in a vertical direction. The LVDT is then set at zero as read on the Keithley 3 millivolt scale, by the zero adjust potentiometer on the Demodulator-Regulator Unit. The recorder is turned on and the balance beam is raised and lowered several times to determine the reproducibility of the

null position. When the null position becomes reproducible, the monolayer is applied via the Lambda pipet through the injection port.

The ligroin solution of Cetyl alcohol is kept under a positive nitrogen pressure in a two-necked, 100 milliliter round bottom flask. The Lambda pipet is rinsed several times with the solution. It is then filled and allowed to drain until the meniscus reaches the calibration mark. The solution is now ejected on to the water surface. Fifteen minutes elapse while the ligroin evaporates. The drive motor is then started and that point marked on the chart paper of the recorder. The motor is set on the 5:1 ratio which means it turns one fifth of a revolution per minute. Since the drive screw has eight threads per inch, this corresponds to the carriage moving one fortieth of an inch per minute. When the recorder goes off scale at approximately 250 millivolts, the motor is stopped and that point also marked on the chart paper. The new intersection of the leading edge of the compression bar with the scale on the trough is read through the telescope.

C. Analysis of Experimental Data

1. Calculation of π

Points are chosen more or less randomly along the curve traced out on the chart paper. An attempt is made to choose the points so that they are representative of all

areas of the curve. Using the scale factor determined earlier in the calibration of the LVDT, the distance, in centimeters, the slide has moved is calculated at every point.

Since all forces acting on the slide except those due to surface tension and buoyancy remain the same, the change in surface tension can be calculated from the change in buoyancy by the equation:

$$2(t + w)\Delta\gamma = \rho g t w \Delta l$$

where t and w are the thickness and width of the glass slide respectively, $\Delta\gamma$ is the change in surface tension, ρ is the density of the liquid, g is the force due to gravity and Δl is the distance the slide has moved from the null position. The glass slide measures 2.512 centimeters by 0.297 centimeters. Thus $\pi = \Delta\gamma = 130.275 \Delta l$ where Δl is measured in centimeters (Table 5).

2. Calculation of σ

The distance in centimeters the compression bar has moved divided by the number of divisions between the initial and final marks on the chart paper gives a scale factor for the calculation of σ . This is always the same due to the constancy of the synchronous drive motors. It is 0.025 centimeters per division. This factor multiplied by the number of divisions from each point to the initial mark gives the distance the compression bar has moved. This distance subtracted from the difference between the initial scale reading

of the compression bar and the scale reading of the permanent barrier gives the distance between the bars at every point. The width of the trough remains the same as does the number of film-forming molecules so that the area per molecule is given by multiplying the distance between the bars by a constant for a particular solution (Table 6). For example the solution of Cetyl alcohol used in the experiments is found to be 2.780×10^{-4} molar. One milliliter or 2.780×10^{-7} moles of Cetyl alcohol is applied to the surface of the water. Therefore $2.780 \times 10^{-7} \times 6.023 \times 10^{23}$ molecules of Cetyl alcohol are present. The width of the trough is constant at 30.640 centimeters or 30.640×10^8 Angstroms. Dividing the width of the trough by the number of molecules gives 1.829×10^8 as the constant factor which gives the area per molecule in square Angstroms when multiplied by the distance, in Angstroms, between the restraining bars.

IV - RESULTS AND DISCUSSION

A. Experimental Data

1. $\pi - \sigma$ Isotherms and σ Intercepts

Three isotherms, taken the same day, of a Cetyl alcohol monolayer on a water surface are shown in Figure 9. Also shown in Figure 9 are three points from a $\pi - \sigma$ isotherm of Cetyl alcohol on water run by Harkins and Nutting at the same temperature.⁸

The σ intercepts correspond to the smallest area into which the film-forming molecule can be compressed and still remain a component of a monomolecular film. For the isotherms shown in Figure 9 they are 21.12, 21.25, and 21.40 $\text{A}^2/\text{molecules}$.

2. Reproducibility of Data

It is noticed that isotherm Number 1 differs considerably from the isotherms numbered 2 and 3. It appears as if the whole isotherm has shifted to the right. This is probably due in part to the difficulty of delivering a reproducible amount of film-forming material to the water surface. During the calibration of the Lambda pipet, the amounts delivered varied by as much as 0.008 grams. If it is assumed that in the application of the monolayer for isotherm Number 1 more was transferred to the surface this would cause the isotherm to shift in the observed direction.

The same null position is never found to occur in two successive isotherms. Furthermore the null position always changes in the same direction. It appears as if the surface tension of the clean water surface increases from experiment to experiment. Some increase in surface tension might be expected if the extra sweepings due to the additional isotherms are assumed to "clean up" the water surface. However, since the system has to be opened to the atmosphere after every isotherm to clean the glass slide and replace the sweeping bars on their supports, it is doubtful that the water surface is really getting "cleaner". In fact, from the magnitude of the change in the null position, it is more likely that the right side of the balance is picking up weight. This is possible through the handling of the glass slide, its holder, and the 1/16" aluminum connecting rod. This seems to be definitely more plausible and would produce the same effect as observed in the system. The fact that the null position does change from isotherm to isotherm undoubtedly affects the reproducibility of the data. Since the data represented by the isotherms depend on the deviation from a particular null position, it is too much to hope that the deviation from a different null position under exactly the same experimental conditions will be the same.

Thus the two major factors offered in explanation for the variations between isotherms are: 1) the uncertainty in the amount of monolayer delivered; and 2) the change in the

null position between experiments. It is not felt that the slight variations in temperature are enough to affect the results significantly.

3. Variations from the Literature

It is observed that the points taken from Harkins and Nutting's data disagree slightly from the isotherms given in Figure 9. The experimental procedure followed by Harkens and Nutting involved the use of the horizontal type of Langmuir balance. A detailed analysis of the method by Harkins and Anderson⁹ shows that the total systematic error due to the uncertainty in the effective length of the float and in the distance between the float and the torsion wire may be as great as ± 3 per cent of the pressure. This could not account for the observed differences since in the region of greatest disagreement, it would only amount to a few tenths of a dyne per centimeter.

The systematic error in the Wilhelmy type film balance described in this thesis is due almost entirely to the linearity or lack of linearity of the LVDT. In the area of disagreement the error can be shown to be approximately ± 3.0 per cent of the pressure. Of course, the possibility of an apparatus constant due to other factors cannot be overlooked. If the sides of the trough are not parallel, an error is introduced in the calculation of the area per molecule. If the barriers are not perpendicular to the sides of the trough, σ will again be in error. However, these are relatively

minor considerations. The total area is so large that the geometrical defects would have to be enormous to cause a significant deviation. There is some evidence that the glass slide may not have been exactly perpendicular to the water surface. This would generate an error in the calculation of the film pressure but it still could not be considered as a major error.

One possible explanation for the disparity lies in the purity of the samples used. The Cetyl alcohol used by Harkins and Nutting was prepared in the early 1930's. This was before the discovery of vapor phase chromatography as a preparative tool. The only means of purification they had was selective fractionation. If their sample is assumed to be contaminated with higher molecular weight compounds, the areas they calculated would be too small thereby shifting the isotherm to the left. At higher film pressures these impurities would be "squeezed out" of the monolayer. This would explain the coincidence of the third point with the isotherms given in Figure 9.

B. Limitations of the System

1. Range of Instruments

The instrument is not capable of recording the entire isotherm due to the limited range of the Heath Kit Recorder. A recording instrument with a range of approximately 300-400 millivolts would be needed if it is desired to monitor the isotherm until the collapse point occurs.

In the present system the extreme limit of travel on the balance is approximately 4 millimeters. This corresponds to a change in surface tension of 50 dynes or more. Therefore, at most, the isotherms are 9 dynes per centimeter short of being complete. This is insignificant since the portion of the isotherm that is cut off is merely the remainder of a more or less straight line segment. Enough of the isotherms still exists to give reasonable values for the limiting σ intercepts.

2. Contact Angle

A severe disadvantage of the Wilhelmy balance is the problem of the contact angle of the liquid on the plate. It is apparent that evaluation of the surface pressure requires that the contact angle be known or as in this case that it be zero. It is fairly easy to assure that the plate is completely wetted at the beginning of the isotherm¹⁰ but when the monolayer is applied, the problem becomes more difficult. In the method ascribed to here, the film is being continuously compressed so that the slide always tends to rise. In this case the wetting problem is not so serious but care must be taken to see that the slide does not vibrate during the experiment.

APPENDIX A

Table 1. LVDT calibration data for 0.001" steps

Micrometer in.	Voltmeter mv.	Voltmeter Scale mv.	Recorder mv.	Recorder Scale mv.
0.7410	0.0	3	0.0	250
0.7400	2.4	3	0.8	250
0.7390	5.0	10	1.8	250
0.7380	7.2	10	2.6	250
0.7370	9.4	10	3.4	250
0.7360	12.2	30	4.2	250
0.7350	14.5	30	5.0	250
0.7340	16.2	30	5.6	250
0.7330	18.0	30	6.2	250
0.7320	19.5	30	7.0	250
0.7310	20.0	30	7.2	250
0.7300	22.0	30	7.9	250
0.7290	23.2	30	8.3	250
0.7280	25.6	30	9.1	250
0.7270	27.1	30	9.9	250
0.7260	30.0	100	11.0	250
0.7250	32.0	100	11.8	250
0.7240	35.0	100	12.8	250
0.7230	38.0	100	13.9	250
0.7220	41.0	100	15.0	250
0.7210	44.0	100	16.0	250

Table 2. LVDT calibration data for 0.005" steps

Micrometer in.	Voltmeter mv.	Voltmeter Scale mv.	Recorder mv.	Recorder Scale mv.
0.7410	0.0	3	0.0	250
0.7350	14.0	30	4.8	250
0.7300	21.8	30	8.0	250
0.7250	32.0	100	11.8	250
0.7200	46.5	100	17.1	250
0.7150	59.0	100	22.2	250
0.7100	70.0	100	26.5	250
0.7050	78.0	100	29.4	250
0.7000	85.5	100	33.3	250
0.6950	108	300	38.8	250
0.6900	120	300	44.0	250
0.6850	132	300	48.2	250
0.6800	140	300	51.0	250
0.6750	150	300	54.8	250
0.6700	160	300	60.1	250
0.6650	174	300	65.3	250
0.6600	184	300	69.7	250
0.6550	191	300	73.0	250
0.6500	201	300	76.5	250
0.6450	215	300	81.8	250
0.6400	229	300	87.0	250

Table 3. Calibration of Lambda pipet with ligroin

Wt. Full Pipet (gms)	Wt. Empty Pipet (gms)	Difference (gms)
9.07610	8.44920	0.62690
9.07850	8.44710	0.63140
9.07740	8.44771	0.62969
9.07666	8.44760	0.62906
9.17850	8.44870	0.62980
9.07805	8.44910	0.62995
9.07800	8.44816	0.62984
9.07830	8.44782	0.63048
9.07842	8.44900	0.62942
9.07800	8.44806	0.62994
9.07905	8.44910	0.62995
9.07950	8.44965	0.62985
9.08010	8.44738	0.63272
9.08022	8.44768	0.63254
9.08000	8.44734	0.63266
9.07933	8.44741	0.63192
9.07958	8.44840	0.63158
9.08010	8.44869	0.63141
9.08090	8.44845	0.63245
9.07968	8.44837	0.63131

Table 4. Calibration of Lambda pipet with normal pentane

Wt. Full Pipet (gms)	Wt. Empty Pipet (gms)	Difference (gms)
9.07745	8.45900	0.61845
9.07741	8.45942	0.61799
9.07768	8.46100	0.61668
9.07868	8.46115	0.61753
9.07825	8.46036	0.61789
9.07863	8.46100	0.61763
9.07775	8.46620	0.61155
9.07781	8.46333	0.61448
9.07808	8.45937	0.61871
9.07793	8.46110	0.61683
9.07800	8.46085	0.61715
9.07865	8.46060	0.61805
9.07790	8.46050	0.61740
9.07787	8.46061	0.61726
9.07960	8.46245	0.61715
9.08035	8.46123	0.61912
9.08023	8.46328	0.61695
9.08272	8.46255	0.62017
9.08049	8.46149	0.61900
9.08136	8.46285	0.61851

Table 5. Data used to calculate π for isotherm #2

Point No.	Δl in cm	π in dynes/cm
1	0.0000	0.00
2	0.0000	0.00
3	0.0003	0.04
4	0.0020	0.26
5	0.0041	0.53
6	0.0074	0.96
7	0.0102	1.33
8	0.0152	1.98
9	0.0206	2.68
10	0.0282	3.67
11	0.0389	5.07
12	0.0508	6.62
13	0.0572	7.45
14	0.0638	8.31
15	0.0714	9.30
16	0.0787	10.25
17	0.0861	11.22
18	0.0955	12.44
19	0.1080	14.07
20	0.1217	15.85
21	0.1367	17.81
22	0.1534	19.98

TABLE 5--Continued

23	0.1730	22.54
24	0.1969	25.65
25	0.2205	28.73
26	0.2454	31.97
27	0.2718	35.41

Table 6. Data used to calculate σ for isotherm #2

Point No.	Δd - dist. comp. bar has moved (cm)	d - dist. between bars (cm)	Area per Molecule (\AA^2)
1	2.75	15.25	27.88
2	3.25	14.75	26.97
3	3.75	14.25	26.05
4	4.00	14.00	25.60
5	4.25	13.75	25.14
6	4.50	13.50	24.68
7	4.75	13.25	24.23
8	5.00	13.00	23.77
9	5.25	12.75	23.31
10	5.50	12.50	22.85
11	5.75	12.25	22.40
12	6.00	12.00	21.94
13	6.13	11.87	21.71
14	6.25	11.75	21.48
15	6.38	11.62	21.25
16	6.45	11.55	21.12
17	6.53	11.47	20.98
18	6.60	11.40	20.84
19	6.68	11.32	20.70
20	6.75	11.35	20.57
21	6.83	11.17	20.43
22	6.90	11.10	20.29

TABLE 6---Continued

23	6.98	11.02	20.16
24	7.05	10.95	20.02
25	7.13	10.87	19.88
26	7.20	10.80	19.74
27	7.28	10.72	19.61

APPENDIX B

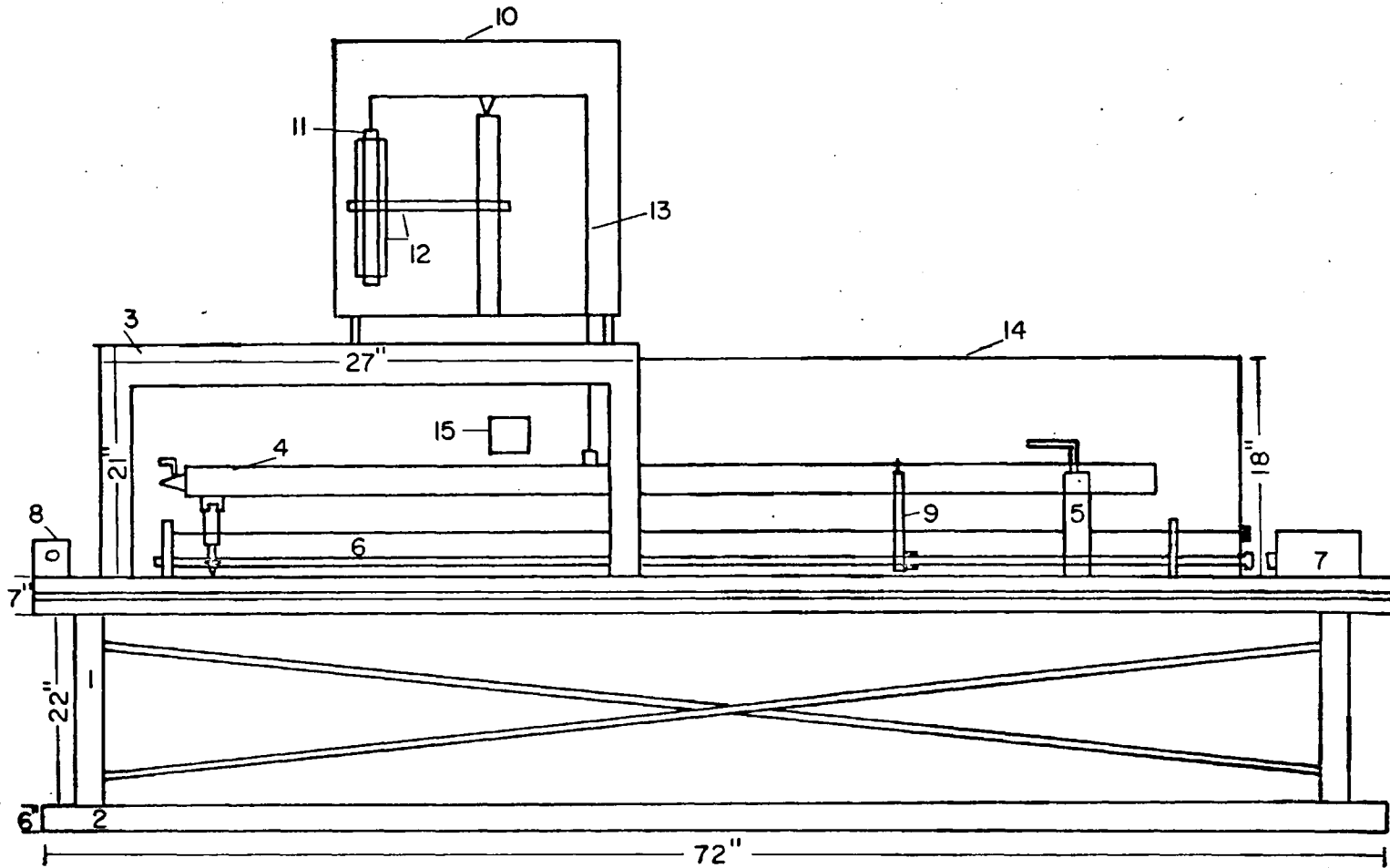


Figure 1. Side View of System

Figure 1

1. Concrete Table
2. Sand Bed
3. Overlying Table
4. Trough
5. Saddle
6. "Track"
7. Drive Motor
8. Return Motor
9. Undercarriage
10. Balance
11. LVDT (Linear Differential Transformer)
12. Lucite "Clamp"
13. Rod and Slide
14. Plexiglass Housing
15. Injection Port

Figure 2

1. Plywood Board
2. Lucite Housing
3. Pilot Box
4. Drive Motor
5. Switch and Outlets
6. Return Motor
7. Switch
8. Outlets
9. Balance
10. Demodulator
11. Null Meter
12. Variac
13. Constant Voltage Supply
14. Table

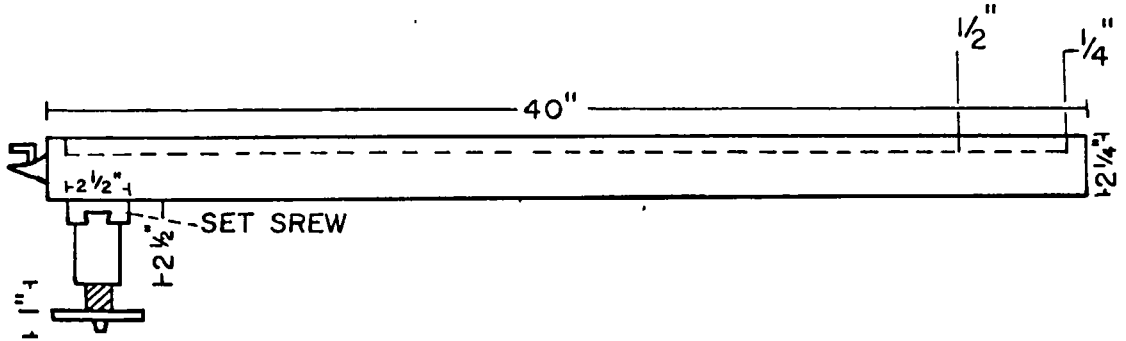


Figure 3a. The Trough

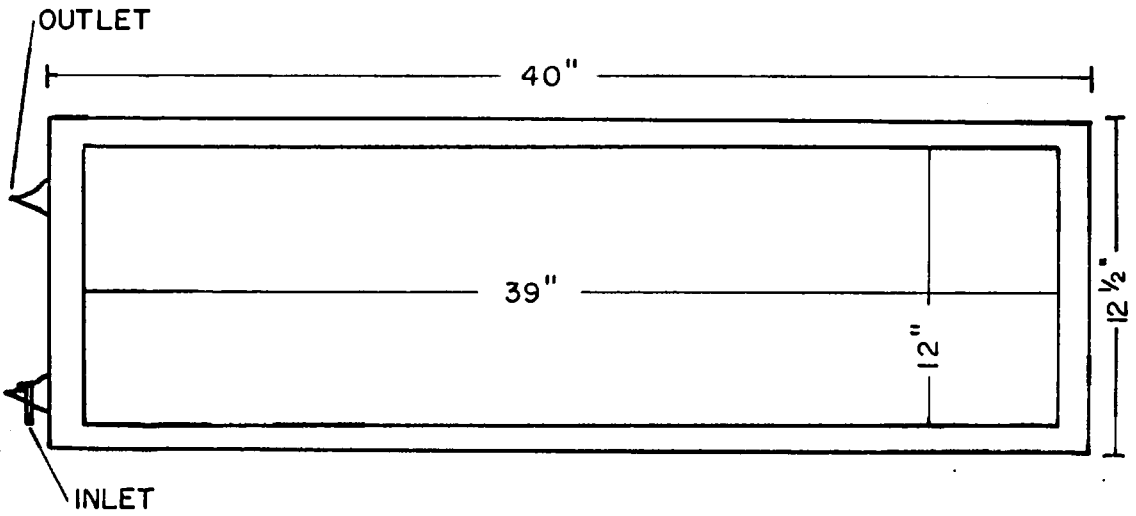


Figure 3b. The Trough

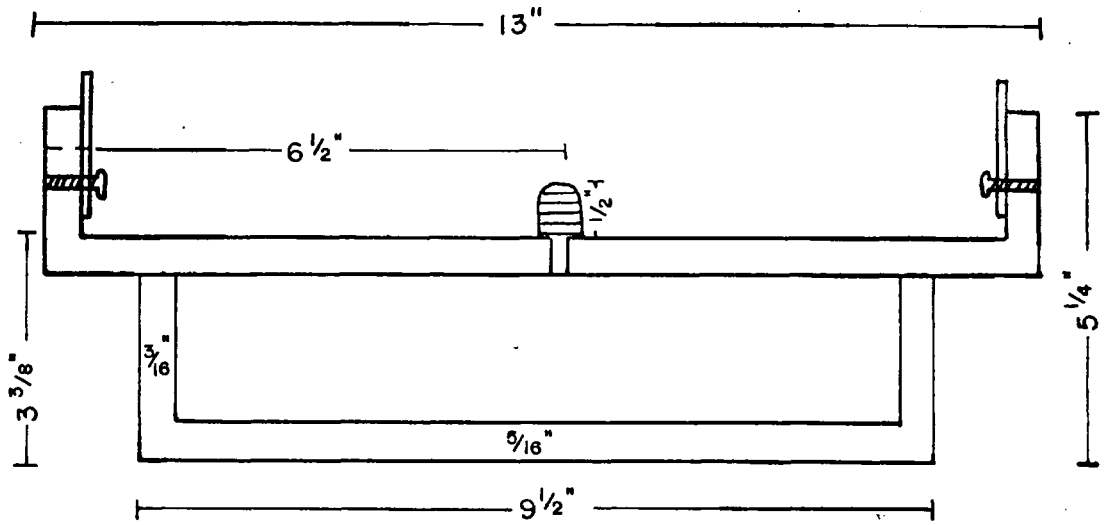


Figure 4a. The Saddle Support

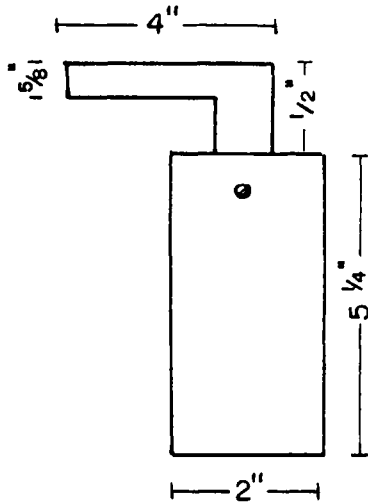


Figure 4b. The Saddle Support

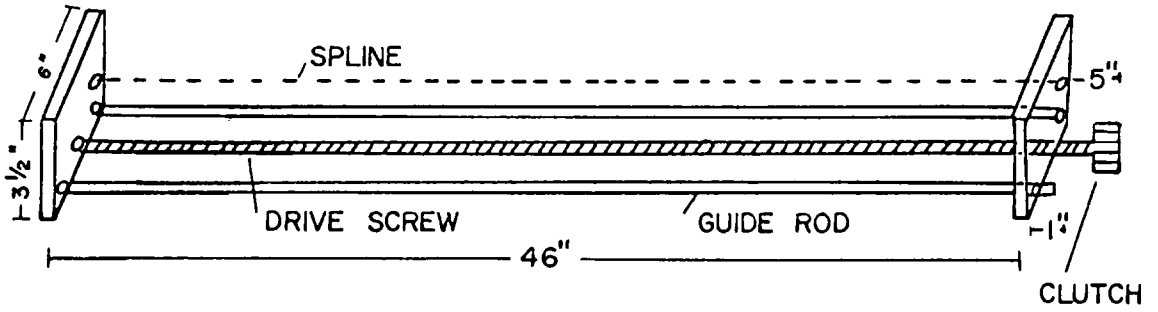


Figure 5a. The "Track"

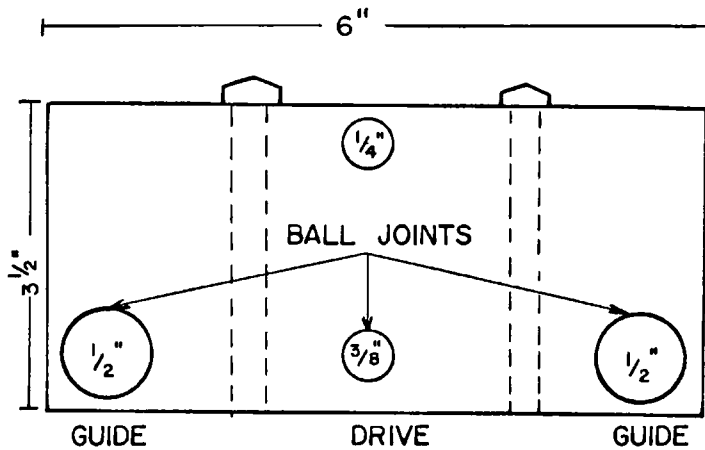


Figure 5b. The Endplate

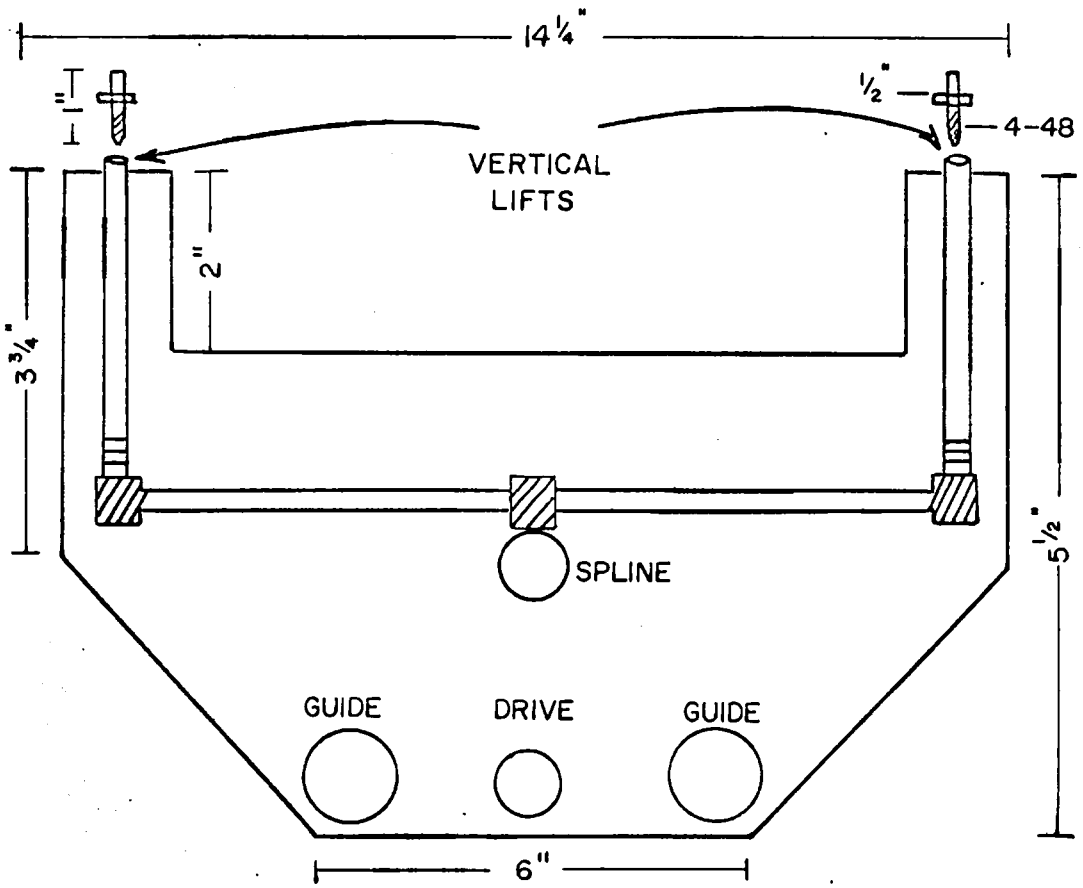


Figure 5c. The Undercarriage

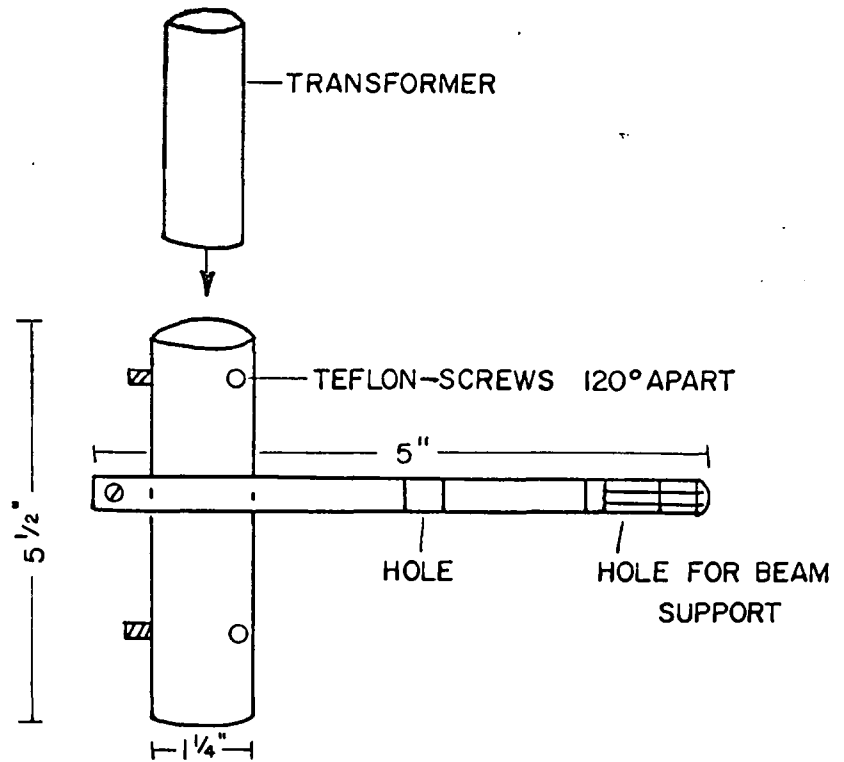


Figure 8a. The Lucite "Clamp"

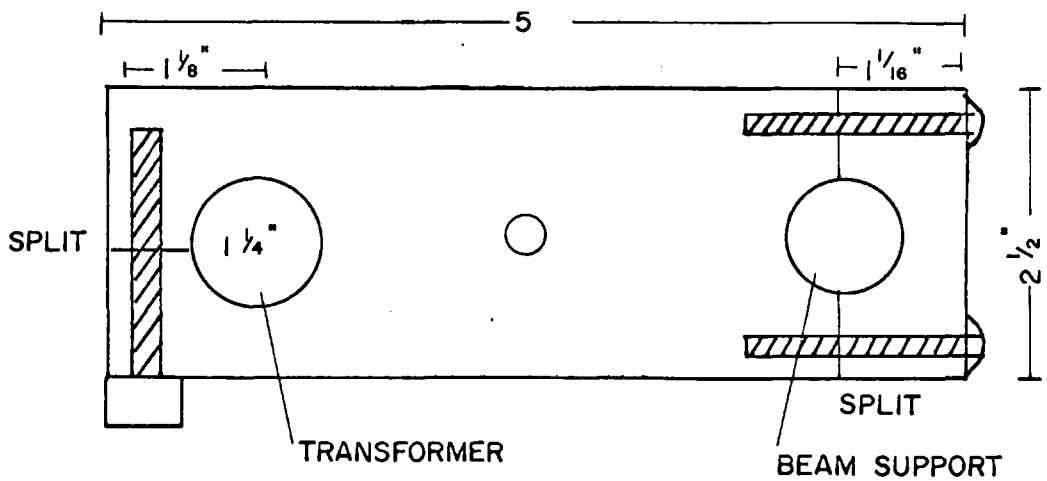


Figure 8b. The Lucite "Clamp"

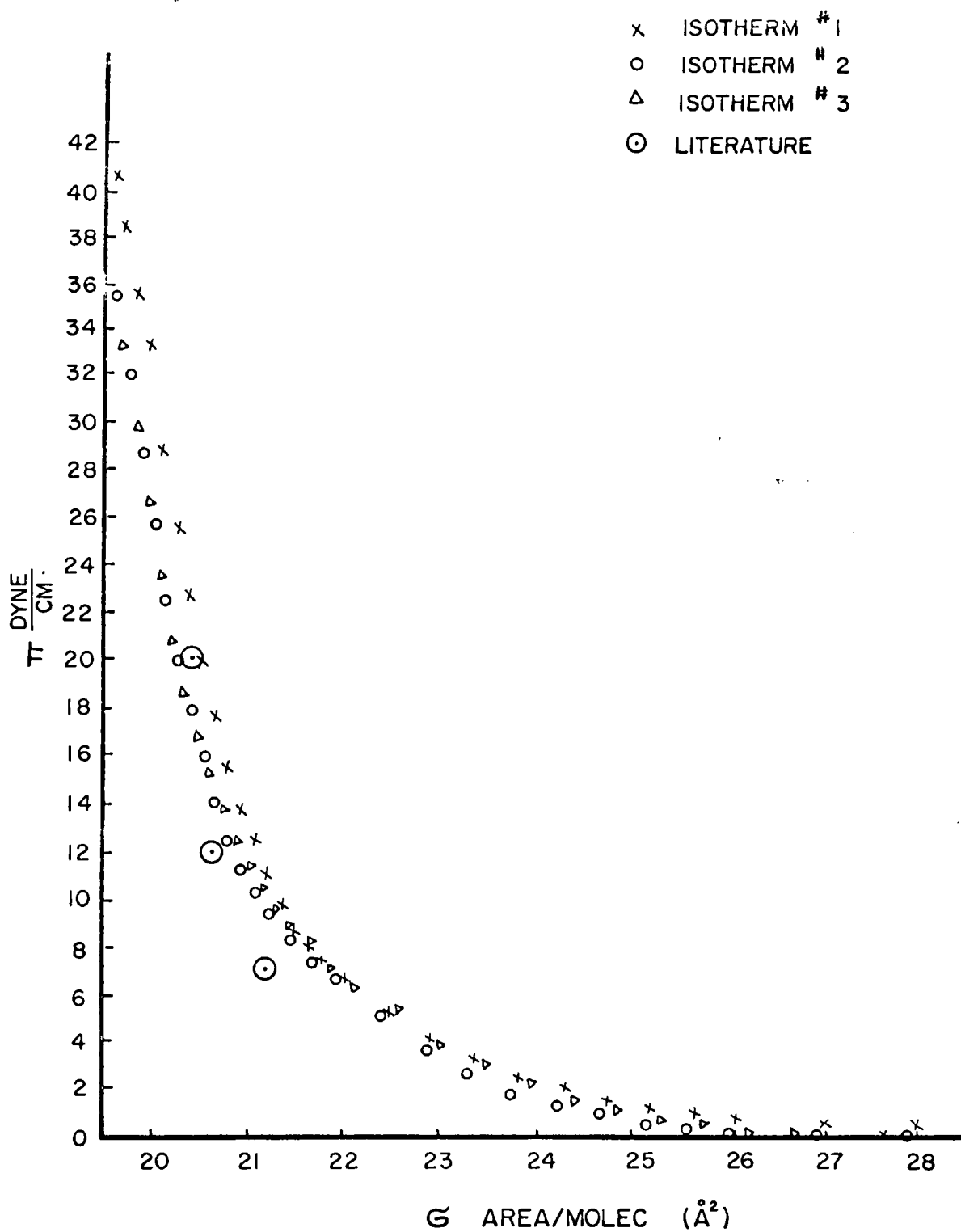


Figure 9. - Isotherms

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