# An Improved Accurate Film Balance*

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## Introduction

Measurement of low film pressure is a matter of increasing importance for the study of monomolecular layers. The apparatus for measuring film pressures generally falls into three types, i.e., dipping slide type, two-dimensional aneroid type, and float balance type. The dipping slide method, introduced by Dervichian[1], and Harkins and Anderson[2] is uniquely simple and yields reliable value when properly used. Bull[3], and Abribat et al.[4] recently used this type of apparatus for the monolayers of various macromolecules, such as proteins or long chain polymers, and obtained the molecular weight of the film molecules. The main drawback of this method, however, lies in the fact that the measurements become unreliable whenever the decreasing film pressures are involved. It requires, moreover, careful choice of materials for dipping slide, since a small change of contact angle of the slide owing to the deposition of monolayer may introduce large errors.

The aneroid type of balance, originated by Marcelin,[5] was recently modified by Puddington[6] and Kalousek.[7] The feature of this type is the fact that the movable float, indispensable for the float balance, is eliminated, and the construction is comparatively simple. The principal objection to this type, however, may be the difficulty of obtaining the absolute calibration for it, and the difficulty of removing the contamination which may, more or less, occur inside the enclosed area.

On the other hand, the float balance has an advantage over the above two methods, since it eliminates their objections and permits wide application. Although the disadvantage of this type lies in the comparatively laborious technique for preventing leakage at both ends of the float, it is a matter of technique which could be overcome in some way. Adam

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1) D. G. Dervichian, *J. Phys. Radium*, **6**, 221, 429 (1935).
2) W. D. Harkins and T. F. Anderson, *J. Am. Chem. Soc.*, **59**, 2189 (1937).
3) H. B. Bull, ibid., **67**, 4, 5 (1945).
4) M. Abribat and J. Pouradier, *Compt rend*, **227**, 1101 (1948).
5) A. Marcelin, *Ann. physique*, **4**, 505 (1925).
6) I. E. Puddington, *J. Colloid Sci.*, **1**, 505 (1946).
7) M. Kalousek, *J. Chem. Soc.*, **1949**, 894.

and Jessop's[8] apparatus, an adaptation of Langmuir's[9] balance for low pressure measurement, is too complicated in construction and laborious in operation. Sensitive float balances were presented by Marcelin,[10] Moss and Rideal,[11] and Guastalla,[12] and have proved their merits for measuring extremely low pressure. These apparatus, however, are not extensively used because of their unfavorable design for routine work. Thus, a generally accessible apparatus is now wanted, which enables film pressures of the order of millidynes per cm. to be accurately measured with ease of operation. The present paper deals with an improved apparatus and technique for use which meet all the requirements stated above.

## Construction

The apparatus to be described is of float balance type. The elevation views of the construction are illustrated in Fig. 1. The apparatus provides a vertical torsion wire (1), which suspends a torsion weight (2). Below the torsion weight, a cramp (3) for the wire is provided, which can be raised or lowered by turning the knob (4). This cramp fixes the weight at raised position and protects the torsion wire from accidental shock when the apparatus is out of measurement. Lowering the cramp makes the torsion weight free and sets the apparatus ready for use. At the top of the apparatus, a reading scale (5) is provided with a pointer (6), which is coaxial to the torsion head. The torsion head is connected to the knob (8) through the gear-wheel (7). Thus, the rotation of the torsion head is transmitted finely by the manual movement of this knob from the outside of the cabinet (32). The torsional angle of the torsion head can be read down to 0.1 degree by means of the vernier of the pointer.

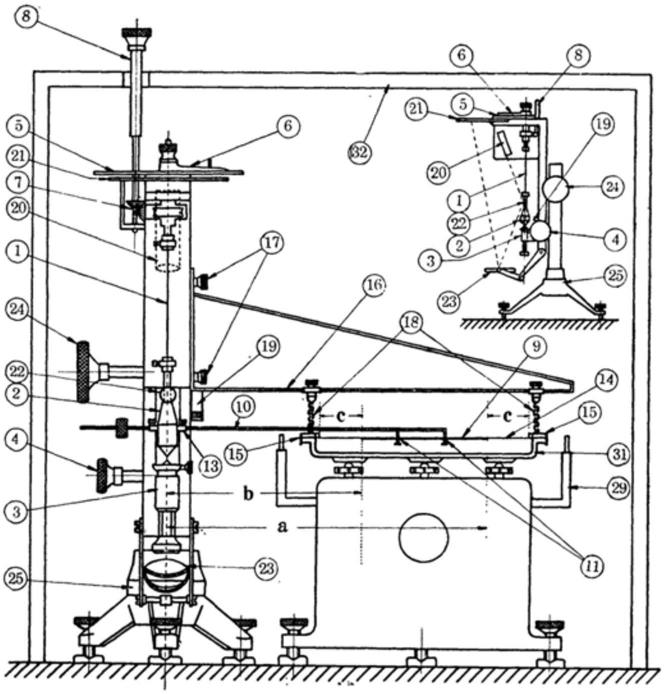


Fig. 1.—Elevation views of construction

On the surface of water, a paraffin-waxed mica strip (called a float (9) hereafter) is placed. The float is supported by the arm (10) which extends above the surface of water in parallel with the length of the float. The connection of the float with the supporting arm is as follows. The arm has two needles (11), which penetrate the float through two holes respectively. The holes are so loosely bored that the float can be moved freely according to the change of water level, but they are tight enough to follow the horizontal movement of

8) N.K. Adam and G. Jessop, *Proc. Roy. Soc.*, **110A**, 423 (1926).
9) I. Langmuir, *J. Am. Chem. Soc.*, **39**, 1848 (1917).
10) A. Marcelin, *Ann. physique*, **4**, 481 (1925).
11) S. A. Moss and E. K. Rideal, *J. Chem. Soc.*, **1933**, 1525.
12) M. J. Guastalla, *Cahier de physique* **10**, 36 (1942).

the float. The end of the supporting arm is fixed to the torsion weight (2) by the small stopper (13).

The leakage of the film past the ends of the float is prevented by thin silk threads (14) treated with paraffin or vaseline. The metal blocks (15) which ride on the rims of the trough (31) serve the purpose to fix the threads on the rims rapidly and surely with simple technique. At the side of the apparatus, a frame (16) of L-form is equipped being fixed by the screws (17). From the horizontal arm of this frame hang two short chains (18), which suspend the above metal blocks in such a way that the metal blocks just mount on the rims of the trough when the apparatus is just in condition for measurement. When it is necessary to wash the float, it is removed from the position (13) and attached to the clip (19) of the frame (16), which is removable from the system as a whole.

The apparatus also provides the optical system in order to visualize the fine dislocation of the float and to carry out the measurement rapidly in continuous work. A bulb and the convex lens with a slit, both assembled in a container (20), are attached behind the scale (5). Outside the scale, a frosted glass (21) with adjustable scale is attached on which the light image is projected. The torsion weight also provides a small mirror (22) which is movable with the rotation of the float. The other mirror (23), equipped at the lower part of the apparatus is about 4 cm. in diameter and the reflecting plane is adjustable to all direction by manuplation. The path of the light is arranged in such a way that the light image of the slit is reflected via both the moving mirror (22) and the fixed mirror (23) on the frosted glass (21).

By turning the knob (24), the apparatus can be raised until the float leaves the surface of the water. In such position, the apparatus can be turned around the vertical axis of the stand (25). By turning it to the right, the apparatus is made parallel to the length of the trough.

### Performance

**Operation of apparatus.**—The supporting arm of the float is fixed to the clip (19) of the frame, and thin silk threads, treated with paraffin or vaseline, are set across the gaps between both ends of the float and the metal blocks so as to make nearly semicircles. The frame (16) is then dismantled from the apparatus and the floating barrier is allowed to be washed under the tap water. After the washing is over, the frame is reassembled to the apparatus. The apparatus is so set that the length of the float becomes parallel to that of the trough. The supporting arm of the float is removed from the clip of the frame and fixed to the stopper of the torsion weight. After cleaning of water surface, the apparatus is so turned that the length of the float is at right angles to the trough. By turning the knob (4), the cramp (3) is lowered in order to let the weight be free; then, by turning the knob (24), the apparatus is lowered slowly down until the float, as well as threads, is allowed to swim on the surface of the water and the metal blocks come to ride on the rims of the trough (Fig. 2.).

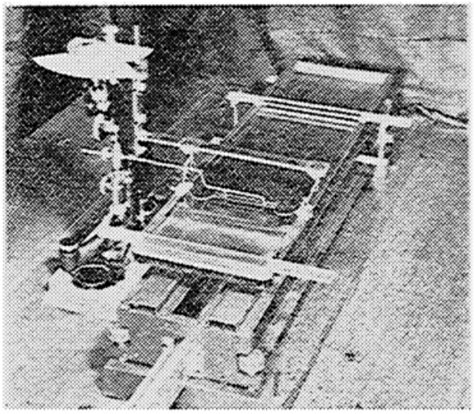

Fig. 2.—Apparatus ready for measurement.

The position of the pointer (6) is set to zero; the light image on the adjustable scale is brought to zero position by manuplating the mirror (23). The film-forming substance is now spread on the surface of water. Since the dislocation of the float due to the film pressures deflects the light image on the frosted glass, zero adjustment is conducted by turning the knob (8) so that the image returns to zero position of the scale. The film pressures exerted here, can be calculated from the readings of the angles thus distorted.

**Determination of Film Pressures.**—When the torsional angle of $\alpha$ radians is required to bring the dislocated float to zero position, the following equation will hold between the film pressures and the torsional angles

$$\int_{b-c/2}^{a+c/2} Fx\,dx = \frac{F}{2}(a^2-b^2+ac+bc)=\alpha k \quad \text{......[1]}$$

where $F$ represent the film pressures in dyne per cm., $k$, the torsion constant of the wire, $x$, the distance from the torsion wire, $a$, the distance from the torsion wire to the distant end of the float, $b$, that to its nearer end, and $c$, the distance of the gaps at both ends of the float, respectively (see Fig. 1). From the equation [1], follows

$$F=\frac{2\alpha k}{(a+b)(a-b+c)} \quad \text{..............[2]}$$

When the measuring of $a$, $b$, and $c$, are 20.0 cm., 12.0 cm. and 3.0 cm. respectively, using torsion wire of phosphor bronze of 0.273 mm. in diameter and 8.0 cm. in length gives the sensitivity of 0.273 dynes per cm. per scale degree and the measurable upper limit of about 40 dynes per cm. For lower pressures, the thinner wires are employed. The wire of 0.101 mm. in diameter and 8.0 cm. in length was found suitable for lower pressure measurement, giving the sensitivity of 0.004 dynes per cm. per scale degree and the measurable upper limit of about 0.7 dynes per cm. The torsion constant of the wire was obtained from the period of swing of a torsion weignt whose moment of inertia is possible to compute.

**Cleaning of Water Surface.**—Sweeping with a moving barrier, made of a paraffined glass rod, does not give perfectly clean surface of water, since the rubbing of the glass rod against the rims of the trough may more or less cause scratching of the paraffin surface. So, a rubbingless barrier is desired in which no scratching might occur. The suggestion is given by the method described by Guastalla.[12] The principle is that a band of talc powder which is sprinkled on the surface, is used as a barrier to arrest the contamination, and the driving of the talc powder thus formed is conducted by air-jet. The scheme of the sweeping is illustrated in Fig. 3. A long glass

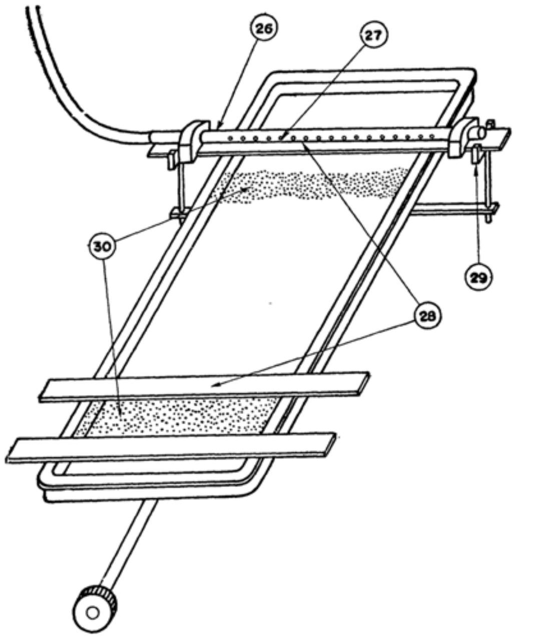


Fig. 3.—Schematic illustration of sweeping of water surface by talc blowing method.

tube (26), with fine orifices (27) along its length, is mounted on the movable glass rod which is held by a rod carrier (29) a short distance above the surface. Talc powder, purified by washing with water, alcohol, and benzene, and then heated properly, is spread on the surface at one side of the trough in the form of a band. Compressed air, filtered by cotton plug and purified by bubbling through the column of water, is sent out from the orifices of the glass tube. The movement of the glass rod with the above glass tube is conducted so that the air stream from the orifices blows off the talc barrier (30) to the opposite side of the trough. When the impurities are collected into the corner of the trough, the glass rod is lowered so as not to be in contact with water, in the order to prevent the talc powder from floating back. Such operation is repeated until the surface pressure attains a constant value.

**Prevention of Leakage past the Threads by Sprinkling Talc Powder.**—When the measurements are performed in a high pressure region, the operation which is recommended is that a small amount of purified talc powder is sprinkled around the solid-thread connections before the spreading of materials. This operation, though not always necessary, is useful for eliminating the possibility of leakage around the threads, and guarantees the measurement of high pressures up to 30 dynes per cm. or more.

## Example

Fig. 4 shows an example of the force-area curve of myristic acid at the air-water interface, measured with this apparatus. The

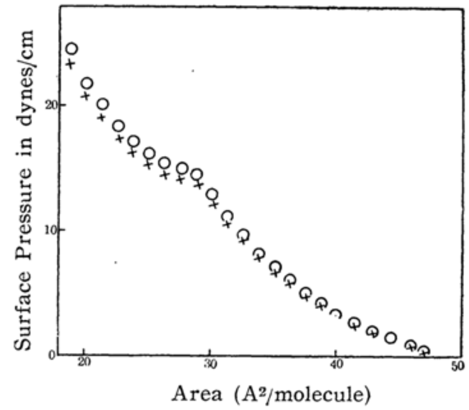


Fig. 4.—Force-area curve of myristic acid on 0.01 N hydrochloric acid at 18.0C°. Circles indicate the pressures determined by this apparatus, while crosses, the pressures by dipping slide method.

results obtained were in good accordance with that of Harkins.[13] The results, moreover, were referred to the one with simultaneous measurement using the dipping slide method. A fairly good agreement was obtained between the two methods. In details, however, it was found that the pressures obtained with the dipping slide method were

13) W. D. Harkins, "Physical Chemistry of Surface Films" p. 112, Reinhold Publ. Co. (1952).

** Purest sample (m.p. 54.5°C) given through the courtesy of Dr. H. Fukuba of the Nutritional Chemical Laboratory of this University, to whom the author's thanks are due.

consistently a little lower than those with this apparatus, and such a trend was emphasized in the higher pressure region, especially above the kink point of the curve. Harkins and Anderson[2] obtained just the same trend with pentadecylic acid and lecithin when they compared the values from both methods of dipping slide and of float balance, and they attributed this discrepancy partly to the errors made in the calibration of film balance. It is, however, noteworthy that the same tendency was obtained under the present experimental condition, where a different type of balance was used. This fact may suggest that this discrepancy may not be of accidental nature as they say, but of something essential associated with the instrumentation. It is rather reasonable to think that the discrepancy is due wholly to the increasing contact angle of the dipping slide owing to the deposition of the monolayer substance.

**Summary**

An improved apparatus and technique for measuring low film pressures, have been described. Although the apparatus bears resembalance to the Marcelin's balance, the following improvements were achieved in order to enable the low pressure measurement to be generally accessible.

(1) The main construction is laid beside the trough, unlike the usual apparatus whose construction is placed above the surface of water. This design is well suited for minimizing the chance of contamination which more or less occurs on the surface during assembling or operation of the instrument.

(2) Since one of the disadvantages of this type balance lies in the possibility of leakage at the solid-thread connections, especially at the connection between rims of the trough and thread, properly designed metal blocks are used to ensure the perfect connection with simple technique.

(3) An important point in the design of the apparatus is that it should be capable of easy dismantling and reassembling, so that the operation of cleaning can be easily conducted. This requirement is satisfied by the use of a carrier for the float and threads which is easily removable from the main construction of the apparatus.

(4) The float is so designed that the connection between the float and the supporter is an independent bearing, when the float is allowed to be in contact with the water surface. Owing to such construction, the change of water level during run does not matter.

(5) The optical system, which makes the deflection of the floating barrier visible, is equipped with the apparatus. Since the frosted glass, on which the light image is projected, lies just beside the reading scale, observations can be made with no unnecessary delay.

These designs meet well the requirements for measuring low film pressures. Continuous use for eighteen months has shown the apparatus to be very convenient and reliable.

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