

# Response of an Equilibrium Film to External Disturbances

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An equilibrium film situated in air saturated with water vapour is subjected to a disturbance consisting of a rapid change of the temperature of the surrounding atmosphere. The resulting large change in film thickness is found to be due to exchange of water between film and atmosphere, and not to expansion or contraction of the film. Pseudo-equilibrium films of widely varying thickness can be formed by means of this process. For a film with a sufficiently large area, the thickness of an element far from the border is determined by the water vapour pressure equilibrium rather than by the disjoining pressure equilibrium. The thickness profile of a large, vertical film in a state of apparent rest is explained on the basis of the different time scales associated with the various equilibrium processes.

It was noticed by Gibbs<sup>1</sup> that a thin liquid film in air need not necessarily be in complete thermodynamic equilibrium, even when it is in a state of apparent rest. In a small element of the film (i.e., having dimensions comparable to the film thickness), several of the equilibrium conditions will be rapidly satisfied. In particular, after a disturbance the uniformity of chemical potentials and of temperature will be re-established in a time which is very short compared to the usual observation time, and therefore these equilibrium conditions may be regarded as being permanently satisfied in a film element. The values of the chemical potentials in the film element may, however, differ from those in other parts of the system. Equilibration by transport along the film or through the adjoining bulk phases may then require a time comparable to the usual observations time, or even much longer.

The equilibrium thickness of the film element is determined by mechanical equilibrium of the forces acting in a direction perpendicular to the plane of the film.<sup>2</sup> The mere existence of thick films slowly draining to their equilibrium thickness shows that the time required for this equilibration process must be measured in minutes. Measurements of film thickness can be carried out before *this* mechanical equilibrium has been established, and such measurements can be used to obtain information about the rate and the nature of the other slow equilibration processes. For example, the experiment of Plateau, in which a soap bubble is thinned locally and reversibly by the warmth of a finger, indicates the effect of small temperature variations. Recent work<sup>3, 4</sup> has shown that films become thinner when exposed to an atmosphere with reduced water vapour pressure. Measurements of equilibrium film thickness<sup>2, 5</sup> require extreme caution to prevent evaporation, and even then they must be carried out in close proximity to the border, where complete equilibration with the contacting bulk solution may be expected to be fairly rapid.

The present investigation is concerned with a more detailed investigation of the effect of small changes in temperature on the thickness of a film which is in a state of apparent rest, in particular in regions well away from the film borders.

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## EXPERIMENTAL

In this work, it was necessary to take elaborate precautions to prevent uncontrolled temperature fluctuations in the system. The films were made and investigated in a completely closed glass bottle, placed in a large box of double-walled glass. Water of constant temperature was circulated between the bottom and side-walls of the box. The box was covered with sheets of foamed plastic, and placed into a constant temperature room. All the necessary manipulations with the film took place from outside the box, using magnetic coupling across the wall of the glass bottle. Under these conditions, the temperature in the glass bottle fluctuated over  $0.02^{\circ}\text{C}$  in a period of 10 h.

After the glass bottle had been provided with about  $400\text{ cm}^3$  of the solution, the system was left to equilibrate for at least 24 h. Then a film was produced by slowly raising a frame, originally submerged in the solution. The film of  $4 \times 4\text{ cm}$ , was suspended between nylon wires of about 10 microns thickness, weighted with a piece of glass tubing to ensure a perfectly flat film. The thinning process of the film was observed by following the downward motion of the interference fringes. Fast-draining films were used in most experiments. After a few minutes, a "black" region developed at the top of the film, and covered the whole area in about 30 min. Measurements of film thickness were started before the development of a black film, and continued for at least several days.

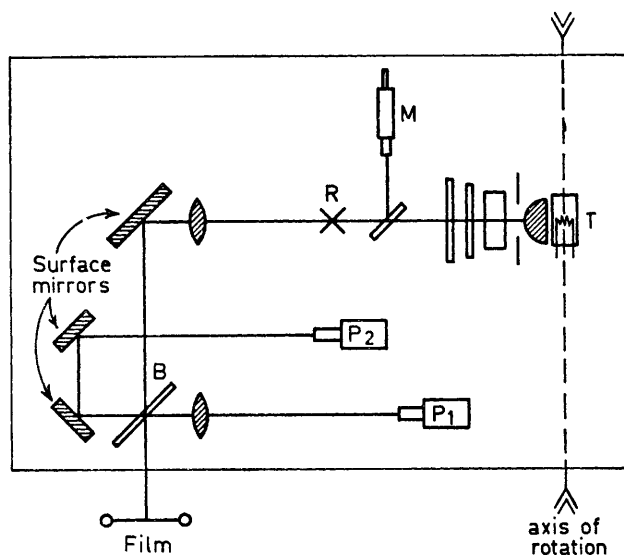


FIG. 1.—Schematic top view of the optical apparatus used for the scanning reflectometric film thickness measurements.

Film thickness was monitored by recording the intensity of reflected light. A light beam from a halogen lamp T (see fig. 1) passed through a layer of water, a heat filter, and an interference filter ( $5460 \pm 80\text{ Å}$ ). From the beam-splitter B, a part of the light moves on to the film and is reflected in the photomultiplier  $P_1$ . The remaining part of the original beam is reflected in the photomultiplier  $P_2$ , where it serves as a reference. The ratio of the output of the two photomultipliers was recorded. The maximum intensity of the light reflected by the film having the optical thickness of one-quarter wave-length was used for calibration. The equivalent water thickness of the film was calculated from the amount of reflected light by the usual procedure (e.g., ref. (2)). The optical apparatus was fitted on a rigid frame that was made to carry out small-amplitude oscillations around an axis perpendicular to the film. The distance between axis and film was about 1 m. In this

way the area of the film seen by the photomultiplier  $P_1$  ( $0.3 \times 0.02 \text{ cm}^2$ ) was made to oscillate over a nearly vertical line of about 2 cm length, in 19 s. Black surfaces were arranged in suitable locations to absorb stray light and to reduce background illumination.

Meaningful results can only be obtained if the film is perfectly flat and exactly perpendicular to the axis of rotation of the optical apparatus. Alignment was carried out before each measurement by means of cross-wire R and microscope M, using the autocollimation principle. It was verified that the presence of the light beam did not affect the film thickness. After several hours (see fig. 2), the film came to a state of apparent rest as indicated by a thickness profile remaining constant for at least many hours. Then the temperature of the circulating water was increased by  $1^\circ\text{C}$  in about 2 min, and the response of the film was observed.

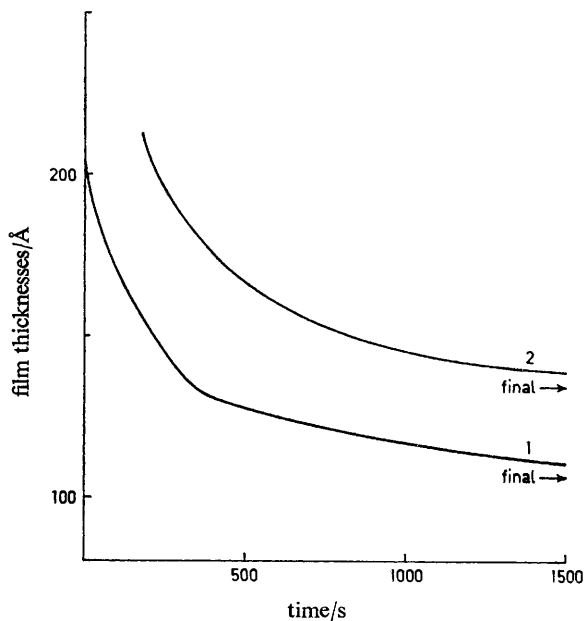


FIG. 2.—Film thickness as a function of the time, measured at the top (1) and the bottom (2) of the scanned area, for a black film stabilized with  $3 \times 10^{-5} \text{ mol cm}^{-3}$  sodium lauryl sulphate at  $25.0^\circ\text{C}$ .

The sodium dodecyl sulphate was a purified sample, containing an unknown but small amount of dodecanol. No attempt at further purification was made because hydrolysis cannot be avoided during the experiments lasting several days. Moreover, films of sufficient stability could only be obtained in the presence of some dodecanol and/or inorganic electrolyte; even then the concentration of the main surfactant had to be in excess of the c.m.c. The cetyl trimethyl ammonium bromide was the same sample used in an earlier investigation.<sup>6</sup> Water and other ingredients were of the highest purity available.

## RESULTS AND DISCUSSION

Results of film thickness profile measurements are shown in fig. 3 and 4. Even though elaborate precautions were taken to ensure that the system would be in complete thermodynamic equilibrium, the results show that this could not be achieved. For easy comparison, the "theoretical" profile has also been indicated in fig. 3 and 4. This profile was calculated on the assumption that the sum of the electrostatic repulsion between the charged film surfaces,

$$P_R = 64cRT\gamma^2 \exp(-\kappa\delta_w), \quad (1)$$

and the attraction due to Van der Waals' forces between the film molecules,

$$P_A = -A/6\pi\delta_A^3 \quad (2)$$

is just compensated by the hydrostatic head  $P_H = -\rho g H$  of the film liquid. Here, the electrolyte concentration  $c$  in the film liquid is expressed in  $\text{mol cm}^{-3}$  and was assumed to be the same as in the bulk liquid. The aqueous core of thickness  $\delta_w = (\delta_A - 20) \text{ \AA}$  is bounded on both sides by a layer of  $10 \text{ \AA}$  thick, consisting mainly of the hydrocarbon parts of the surface-active material. Using this model, the equivalent water thickness  $h = (\delta_A + 8) \text{ \AA}$ , which is the quantity plotted in the figures. The other quantities in the above equations have their usual meaning (see, e.g., ref. (2)), where  $\gamma \approx \tanh 1$  and  $A = 5 \times 10^{-13} \text{ erg}$ .

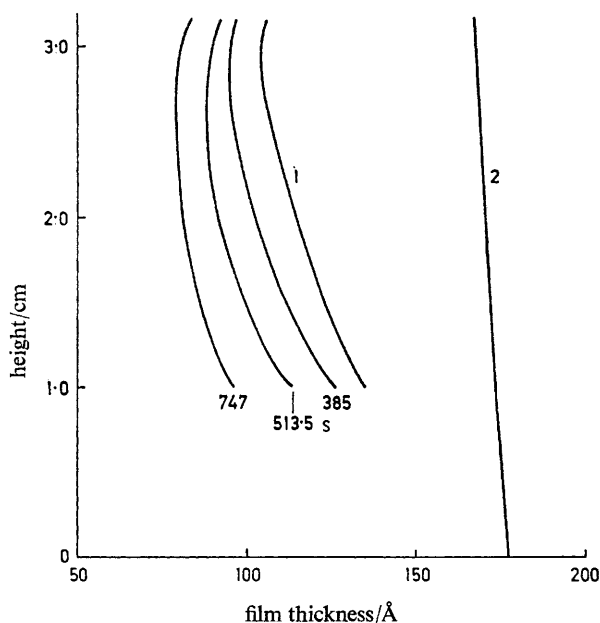


FIG. 3.—Thickness of a film stabilized with  $3 \times 10^{-5} \text{ mol cm}^{-3}$  sodium lauryl sulphate in apparent rest (1) and after heating for the time indicated. Curve 2 is the calculated "equilibrium" film thickness for an electrolyte concentration of  $3 \times 10^{-5} \text{ mol cm}^{-3}$ . Original temperature  $25.0^\circ\text{C}$ .

In all cases, the thickness profile of the "equilibrium" film differed appreciably from the profile expected on the basis of the usual criterion<sup>2, 5</sup> for determining equilibrium film thickness, i.e., the condition for mechanical equilibrium in a direction perpendicular to the plane of the film. This means that either this equilibrium condition is not satisfied, or the electrolyte content is much higher than in the bulk solution, in a film element at some distance from the lower border. Evidence has already been presented to show that electrolyte is accumulated in the film liquid,<sup>7</sup> and this is confirmed by the analysis of the present results.

If the equilibrium condition,

$$\Delta P = P_R + P_A + P_H = 0, \quad (3)$$

is satisfied in every element of the film at rest, it is possible to estimate the actual electrolyte concentration in the film liquid. This is because the thickness that satisfies eqn (3) is determined almost completely by the electrolyte concentration in

the film liquid. Results of such calculations (fig. 5) show that a very steep concentration gradient in the film liquid is required to explain the thickness profile on this basis.

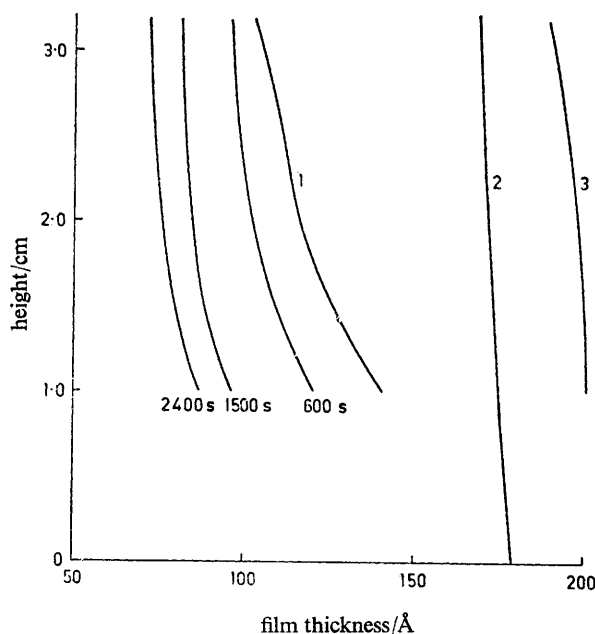


FIG. 4.—Thickness of a film stabilized with  $1.6 \times 10^{-6} \text{ mol cm}^{-3}$  cetyltrimethylammonium bromide and  $2.84 \times 10^{-5} \text{ mol cm}^{-3}$  sodium bromide in apparent rest (1) and after heating for the time indicated. Curve 2 is the calculated “equilibrium” film thickness for an electrolyte concentration of  $3 \times 10^{-5} \text{ mol cm}^{-3}$ , curve 3 the thickness of a film after slowly draining to apparent rest in 7 h. Original temperature  $29.1^\circ\text{C}$ .

From the response of a film to a small change in temperature, however, it may be concluded that eqn (3) is *not* in general satisfied in every film element, and also that the actual concentration gradient in the film liquid is less steep in this case (see fig. 5). The important observation is here that small temperature differences between the film and the bulk liquid result in immediate and reversible variations of film thickness. The greater part of the measured rate of film thinning (fig. 6) must be due to evaporation of water from the film surfaces, which proceeds at a rate determined by the diffusion coefficient  $D$  in the gas phase and the distance  $x$  to the region of condensation. The resulting rate of film thinning is

$$-\frac{dh}{dt} = \frac{18D}{RTx} \Delta p, \quad (4)$$

where  $\Delta p$  is the excess water vapour pressure of the thin film. In a first approximation, the excess vapour pressure is determined by the temperature difference only:

$$\Delta p = (Qp_0/RT^2)\Delta T, \quad (5)$$

where  $Q$  is the heat of evaporation of water at room temperature and  $p_0$  its equilibrium vapour pressure. The value of  $\Delta T$  was estimated from temperature measurements

by means of a set of thermistors, placed in the gas phase a few mm from the film. The actual temperature of the film element will be somewhat lower but even then application of eqn (4) and (5) shows that the observed rate of film thinning can be explained as a result of evaporation of water from the film, followed by diffusion of water vapour over a distance  $x$  of a few cm, and condensation on the surface of the bulk liquid.

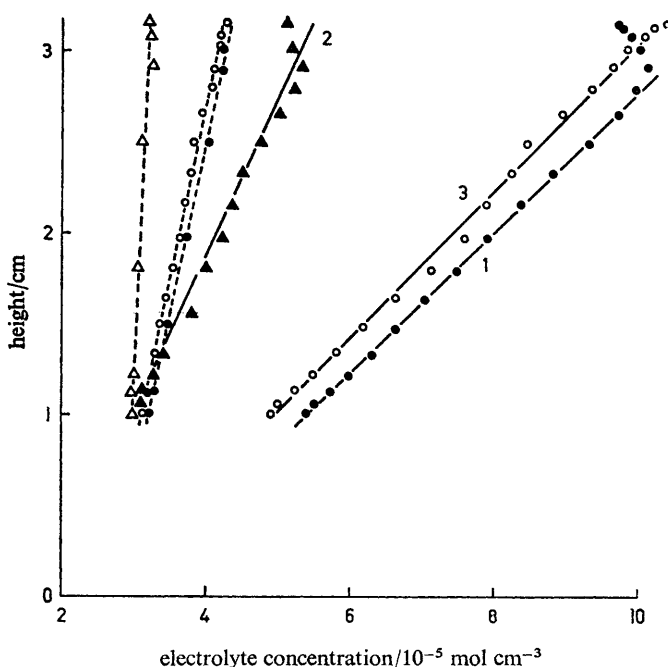


FIG. 5.—Electrolyte concentration as a function of the height for a film in apparent rest stabilized with  $3 \times 10^{-5} \text{ mol cm}^{-3}$  sodium lauryl sulphate (curve 1),  $1.5 \times 10^{-5} \text{ mol cm}^{-3}$  sodium lauryl sulphate and  $1.5 \times 10^{-5} \text{ mol cm}^{-3}$  sodium bromide (curve 2),  $1.6 \times 10^{-6} \text{ mol cm}^{-3}$  cetyltrimethylammonium bromide and  $2.84 \times 10^{-5} \text{ mol cm}^{-3}$  sodium bromide (curve 3) for  $\Delta P = 0$  (full lines) and for  $\Delta P = -2g\Delta c$  (dashed lines).

A possible contribution from extension to the thinning of films on warming was studied by suspending a thick film from the black film, using a technique that has already been described in connection with film elasticity measurements.<sup>6</sup> The rate of descent of the border line between the black and the thick film was practically unaffected by the change in temperature. It is concluded therefrom that downward motion of the border line is only determined by the usual drainage processes in the film, and there is no appreciable contribution from an extension of the black film. Fig. 7 shows a typical result of such measurements.

Evaporation of water from a film element results in increased solute concentrations, and therefore in decreased surface tension and water vapour pressure. The thickness of the element, at any time during the establishment of the water vapour pressure equilibrium, is determined not only by its decreased volume but also by expansion or contraction resulting from other equilibration processes. In order to clarify the behaviour of the film element under these circumstances, it is necessary to realize that eqn (3) is not the only condition to be satisfied in complete thermodynamic

equilibrium. There are several other conditions, which may conveniently be distinguished according to the characteristic time associated with the corresponding equilibration process. For any film element at any given time, some of these conditions may already be satisfied because the equilibration processes take less time than the age of the element. Other processes may require much more time, in particular because an equilibration process may proceed at very different rates in the plane of the film and perpendicular to that plane.

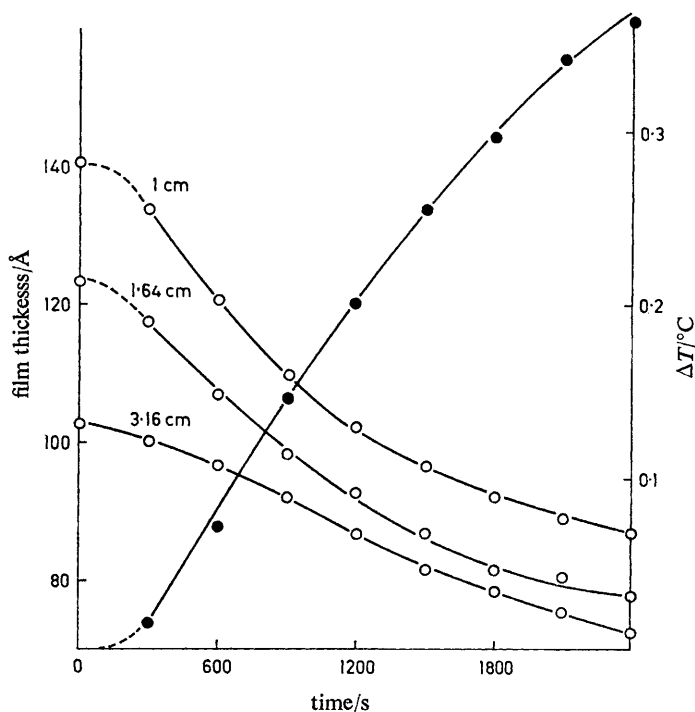


FIG. 6.—Increase in temperature (●) and the resulting decrease in film thickness (○) measured at three indicated heights in the film as a function of time. The film is stabilized with  $1.6 \times 10^{-6}$  mol  $\text{cm}^{-3}$  cetyltrimethylammonium bromide and  $2.84 \times 10^{-5}$  mol  $\text{cm}^{-3}$  sodium bromide. Original temperature 29.1°C.

For the present discussion, the most important equilibrium conditions and the corresponding equilibration processes are: (i) Uniformity of temperature and of chemical potentials of all components *in a film element*, including the contacting gas layer. Equilibration occurs by diffusional transport between film liquid and surfaces<sup>8</sup>; the characteristic time is much less than a milli-second.

(ii) Uniformity of surface (or film) tension along the entire surface. A simple experiment demonstrating the rapidity of this process was already described by Gibbs,<sup>1</sup> and later experience<sup>6</sup> has shown that the time required is of the order of milliseconds. The mechanism by means of which a thin film satisfies these two equilibrium conditions simultaneously consists of adjusting the thickness of the film elements, by expansion or contraction. Flow of film liquid with respect to its surface does not contribute significantly to changes in film thickness in so short a time.

(iii) Uniformity of temperature, and of chemical potentials of all volatile components, *in the whole system*. This is achieved in a time of the order of seconds, by

evaporation, diffusion in the gas phase and condensation. The process and the characteristic time for thermal equilibration are similar.

(iv) Mechanical equilibrium in the direction perpendicular to the plane of the film, i.e., between disjoining pressure and hydrostatic head. This is the condition expressed by eqn (3). The main process by means of which this equilibrium is established consists of flow of film liquid with respect to the surface,<sup>5</sup> and the characteristic time is of the order of many hours.

(v) Uniformity of chemical potentials of non-volatile components in the whole system. Diffusion of non-volatile components along the film proceeds about  $10^5$  times slower than diffusion in the gas phase, and therefore the chemical potentials of such components may not be uniform in a large film unless it has been left undisturbed for at least several days.

During equilibration, as required by conditions (iii) to (v), the equilibrium conditions (i) and (ii) remain *permanently* satisfied. Moreover, the thickness of an element of the film, of given composition, is already completely determined by conditions (i) and (ii), irrespective of whether any further equilibrium conditions are satisfied.

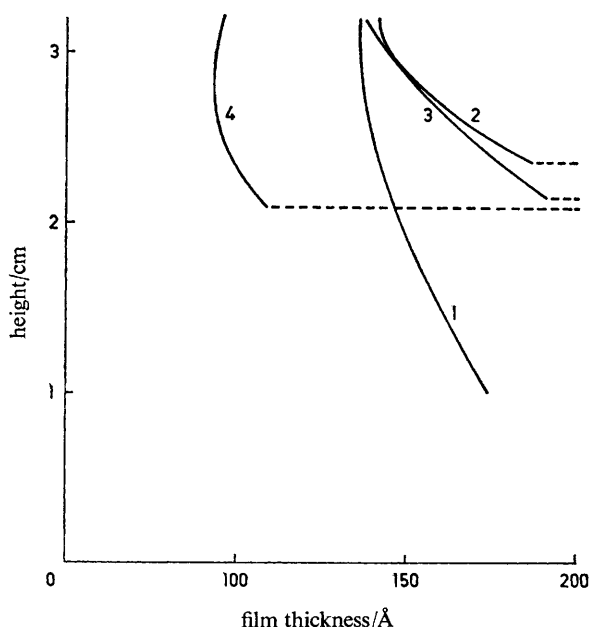


FIG. 7.—Thickness of a film stabilized with  $1.5 \times 10^{-5}$  mol cm $^{-3}$  sodium lauryl sulphate and  $1.5 \times 10^{-5}$  mol cm $^{-3}$  sodium bromide in apparent rest (1), 30 s after loading with a thick film (2) and after further draining for 760 s when the temperature is kept constant (3) or when the film is heated (4).

The interpretation of the film thickness measurements reported in fig. 3 and 4 must, therefore, be based on the supposition that condition (v) is, in general, *not* satisfied, even if the thickness profile remains unchanged during several hours. The liquid composition of the element may differ appreciably from that of the bulk liquid, and even from that of other film elements. The actual composition of the element at a given time is determined by the accumulated effects of processes (i)–(v) since the birth of the elements, and a full description of these effects is not possible at present.



That the composition of a film element depends upon the states through which it has passed during its production is shown by curve 3 in fig. 4. This curve relates to a slow-draining film, made from an aged solution, and which required 7 h to attain a state of apparent rest.

It is evident that the composition of a film element during the measurement reported in fig. 3 and 4 is determined by conditions (i)-(iii) being satisfied, and this composition will, in general, not be such that  $\Delta P$  of eqn (3) will vanish. The excess pressure  $\Delta P$  gives rise to flow of film liquid with respect to the surfaces.<sup>5</sup> The resulting rate of thinning in a part of the film with area  $a^2$  is then

$$-dh/dt = 8\Delta P\delta_w^3/3\eta a^2. \quad (6)$$

An evaluation of the magnitude of this effect requires an estimate of  $\Delta P$  for which we need the electrolyte content in the film liquid. The values shown in fig. 5 cannot be used for this purpose, because they are based on the supposition  $\Delta P = 0$ . If it is assumed that equilibrium condition (iv) need not necessarily be satisfied in a film element in a state of apparent rest, it is still possible to estimate the electrolyte concentration in the film element from condition (iii) expressing the uniformity of the chemical potential of water. In principle, it would also be possible to use condition (ii) for this purpose. This is the condition stating that the film tension in the element at height  $H$ , as determined by the composition and thickness of the element, should be equal to the equilibrium surface tension of the bulk solution corrected for the weight of the film suspended from the element. The use of this condition would require extremely accurate data on the relation between surface tension and composition, which are not available at present. Therefore, the remaining part of this paper will be confined to a discussion of the water vapour equilibrium in a film at apparent rest.

If the electrolyte content in the film element is higher than in the bulk solution by an amount of  $\Delta c$ , this will reduce the chemical potential of water by an amount that is approximately determined by

$$\Delta\mu_w = -2RTvg\Delta c. \quad (7)$$

Here,  $g$  is the osmotic coefficient of the solutes and  $v = 18 \text{ cm}^3 \text{ mol}^{-1}$ . For a film at rest the temperature is assumed to be uniform, and uniformity of the chemical potential of water requires that the pressure in the film liquid is higher than in the surrounding atmosphere by an amount of  $\Delta P$  given by

$$\Delta\mu_w = v\Delta P. \quad (8)$$

Assuming that the excess pressure in the film liquid is due to the terms appearing in eqn (3), it is possible to calculate the value of  $\Delta c$  that satisfies eqn (7) and (8) for any film thickness  $h$ . Results are shown in fig. 5. The rate of thinning due to liquid flow can now be found by inserting the resulting  $\Delta P$  in eqn (6). For a reasonable value of the surface area (several  $\text{cm}^2$ ) this gives a rate of thinning of one Å in a day.

It is concluded that the thickness of a film element at some distance from the border is not determined by disjoining pressure equilibrium but by vapour pressure equilibrium of volatile components. It is hoped that further work along these lines will provide information about the meaning of "pressure" in a thin film.

Thanks are due to Mr. Th. C. Kouters for skilful execution of the experiments.

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