been measured and the activity coefficient of 0.01 *m* hydrobromic acid determined in lithium bromide solutions.

2. From a combination of the data obtained from the two cells and from the known activity coefficients of lithium bromide, the dissociation of water in lithium bromide solutions has been calculated.

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# Further Discussion of the Surface Tension of Film-Covered Liquids at Saturation

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The surface tension[1] $\sigma_{13}$ registered at saturation vapor pressures by a liquid covered with a film is given by

$$\sigma_{13} = \sigma_{12} + \sigma_{23} \tag{1}$$

This equation must be interpreted differently for a film of monomolecular thickness from that for a film of such thickness that its interior possesses the properties of a phase in mass. In the latter case, two surfaces of discontinuity exist, and hence two surface tensions $\sigma_{12}$ and $\sigma_{23}$, but in the former case the value $\sigma_{13}$ cannot be interpreted in terms of $\sigma_{12}$ and $\sigma_{23}$, *per se.* The lowering of the surface tension of the liquid by the molecules of the monomolecular film is to be explained by the closer packing of the film molecules as a two-dimensional phase[2] according to the familiar conceptions developed by Langmuir.

The amount of lowering of the surface tension by a given number of film molecules when packed in the form of a monomolecular film would be different from that when packed as a polymolecular film of the same area, and since in the former case all the film molecules would be in closer contact (in fact, they would be in direct contact) with the molecules of the supporting liquid, it follows that the monomolecular film would cause the greater lowering of the surface tension for the same number of molecules per unit area, *i. e.*, for the same value of the film density; hence the monomolecular film is of greater stability, and by condensation from the vapor probably never becomes a thicker film with an interior having,

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(1) Bartell, Case and Brown, THIS JOURNAL, **55**, 2769 (1933).

(2) For a two-dimensional phase, the fundamental thermodynamic equation would be

$$d\epsilon = t d\eta - f ds + \mu_1 dm_1 + \mu_2 dm_2 + \ldots \tag{2}$$

where in place of the $-p dv$ term of a three-dimensional phase (J. Willard Gibbs, equation 86), we have $-f ds$; the $f$ is the two-dimensional outward pressure exerted by the molecules of the film in the plane of the film. The monomolecular film is to be considered as a part of the surface of discontinuity of the liquid, the fundamental equation of which (Gibbs, equation 501) contains a $+\sigma ds$ term instead of the $-f ds$ term above. These terms differ in sign because the natural tendency (to minimum potential energy) for the monomolecular film is to *expand* in area, whereas, for the surface of a liquid, to *contract.* It follows that the greater the value of $f$ of the monomolecular film, the lower will be the value of $\sigma$.

at saturation, the properties of a phase in mass. But if we *start* with a thick film, then it would be unstable with respect to a finite variation, and upon a small disturbance would break up into a monomolecular film of lowered surface tension with the excess film liquid gathered in the form of lenses. This is illustrated by the curves given in Fig. 1, the ordinates of which denote surface tension values, and the abscissas the film densities, expressed, for example, in molecules per unit area. The curve NOA represents (in a general way) the case for films which always remain monomolecular in thickness, and the curve NOB (the curves may start curving concavely downward immediately from N instead of O) represents the case for films that gradually increase in thickness until at saturation vapor pressures the interior of the film attains the properties of a phase in mass. The authors[3] who have dealt with the problem of lens formation on film-covered surfaces have given a curve of the type shown in Fig. 2 (inset), which shows the relation of the surface tension values to *film thicknesses*, and it was necessary, in the explanation of the phenomena of the instability of thick films and lens formation, that the curve based on such coördinates possess a minimum in order to show the region of instability, the region indicated by DE. If, however, the true curve is the one for a film that always remains monomolecular in thickness, and the experimental evidence[4] is (unlike that for polymolecular films[5]) very conclusive for this, then by using the density of the film, or the area occupied per molecule, instead of the indefinite and for the case of

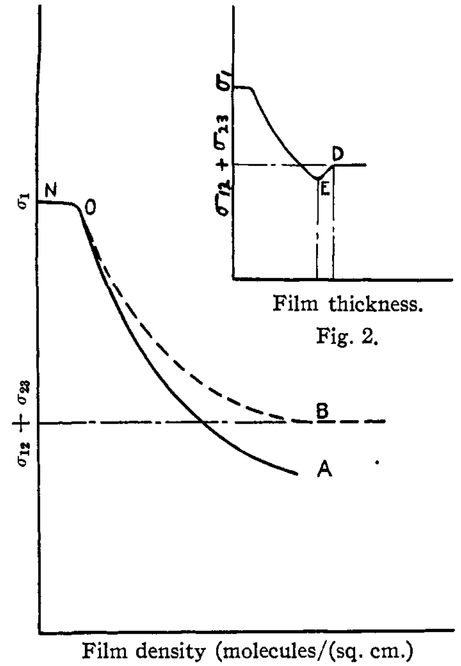

Fig. 2.

Fig. 1.—General relationship of surface tension to film density; curve NOA for a monomolecular film, NOB for a polymolecular.

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(3) Hardy, *Proc. Roy. Soc.* (London), **A86**, 610 (1912); **88**, 313 (1913); Bouasse, "Capillarité," Librairie Delagrave, Paris, 1924, pp. 356–360.

(4) Adam, "Physics and Chemistry of Surfaces," Oxford University Press, 1930, p. 29; Bouhet, *Ann. Phys.*, [10] **15**, 5 (1931).

(5) Cassel [*Trans. Faraday Soc.*, **28**, 177 (1932)] has obtained evidence that the film of carbon tetrachloride molecules adsorbed on the surface of mercury, attains at the saturated vapor pressure a density 3.6 times that of carbon tetrachloride in bulk, and because of the symmetry of this molecule, this result for a film thickness would represent the most accurate yet obtained for plane surfaces by calculation from surface tension lowering, were it not for the possible formation of capillary-active impurities by the contact of the organic halogen compound with mercury. This would cause the result to appear higher than the true value.

monomolecular films, erroneous coördinate, of film thickness, a curve without such a minimum is obtained, which is in accord with experimental facts. Moreover, a discontinuity will exist *between* the true curve NOA, and the curve NOB, given by a thick film. On the basis of this discontinuity, the instability of thick films and the formation of lenses on the film-covered surface are more logically illustrated in accordance with the existence of monomolecular films at saturation, as shown by the fundamental work of Devaux and Langmuir.

As indicated in Fig. 1, the value of $\sigma_{13}$ equal to $\sigma_{12} + \sigma_{23}$ is a limiting value for a thick film, and this, as shown in the fundamental work of Hardy,[3] is not in accord with the phenomena of lens formation by spreading liquids. But monomolecular films are strictly in accord with the phenomena, since the value of $\sigma_{13}$ equivalent to that given by $\sigma_{12} + \sigma_{23}$ is not a limiting value; instead, it represents merely a point on the surface tension–film density curve, for with further increase in the number of molecules per square cm. of film, $\sigma_{13}$ falls to a lower value, and when it does, a lens of the liquid constituting the film can exist in equilibrium with the film. But the formation of lenses indicates a condition of supersaturation, and if we consider the film being formed by condensation from the saturated vapor under isothermal conditions, no lenses would appear on the film-covered surface; that is, the surface tension $\sigma_{13}$ registers the value equal to $\sigma_{12} + \sigma_{23}$ at saturation vapor pressures. If $\sigma_{13}$ falls lower than the value of $\sigma_{12} + \sigma_{23}$, the density of the monomolecular film, *i. e.*, the number of molecules per square cm. of film, must become greater than when $\sigma_{13} = \sigma_{12} + \sigma_{23}$, which means that the vapor pressure will also be greater; greater, that is, than for the film liquid in bulk (since the film liquid in the form of a film in bulk would also register the tension given by equation (1) above), and it is under these supersaturated conditions that a convex lens, or a dew of lenses, of the film liquid can exist in equilibrium with the film.

## Summary

The surface tension value $\sigma_{13} = \sigma_{12} + \sigma_{23}$ registered at saturation vapor pressures by a liquid covered with a film is discussed for films of monomolecular and polymolecular thickness; the significance of the equation for the surface tension at saturation being very different for the two types of films.

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