ENERGY AND ENTROPY OF EXTENSION AND SPREADING OF MOBILE MONOLAYERS*

BY PROF. WILLIAM D. HARKINS, DR. T. FRASER YOUNG, AND EDWARD BOYD,
UNIVERSITY OF CHICAGO

THERMODYNAMICS reveals in two-dimensional systems a peculiar state of matter in which an extremely large amount of heat is required to increase the distance between the molecules by about thirty-five per cent without a change of temperature or of state. In three-dimensional systems at ordinary pressures these large amounts of energy are not used unless a change of state, as from liquid to gas, occurs.

In the period of the last fifty years, much work has been done on the pressure-area relations of mobile monolayers, that is films one molecule thick, particularly those of organic substances of the general type of pentadecylic acid, or on alcohol or amine, on the surface of water. On mercury or gallium the relations are undoubtedly the same, but the experimental difficulties when a liquid metal is involved are very great. If a barrier is placed between a clean water (or mercury) surface, and the same liquid covered by a film, a force acts on the barrier from the film toward the clean surface, and this force per centimetre is considered as the surface pressure (π). If the mean area per molecule of the monolayer is very large, as 100,000 A. of area (sq. A.), the film is a perfect two-dimensional gas. (Ten billion A. equal one square centimetre, or sixty-five million billion, one square inch.)

On compression this two-dimensional gas begins to change to a two-dimensional liquid (L_1) at an area of several hundred to several thousand sq. A., and is completely condensed to the liquid film at 40–50 sq. A. and a very low film pressure. Further reduction of area results in a rapid increase of film pressure, until the liquid (L_1) changes into a second liquid (L_2), which has very remarkable properties, in that it is at first very highly compressible, but becomes quite incompressible if the pressure is increased sufficiently.

At a molecular area of about 20.5 sq. A. the liquid

film freezes. The remarkable fact found by the application of thermodynamics in the present work is that there is no latent heat involved in this freezing, so it differs greatly in this respect from what is found in three dimensions. Thus a kind of 'ice' is formed which requires no heat to melt it.

Thermodynamical equations have been developed, which make it possible to determine the change in either energy or entropy of these two-dimensional layers (third dimension of the order of a ten millionth of an inch) on expansion or contraction. Thus if the films are stretched (expanded) they take up heat. The work shows that when a solid film is expanded at constant temperature, and undergoes transitions from solid to liquid (L_1), from liquid (L_1) to liquid (L_2), and then to gaseous film, almost all the heat is employed in two changes of area. As in three dimensions, a considerable amount of heat is utilized in the vaporization of the liquid (L_1).

The remarkable departure from the behaviour of ordinary three-dimensional matter is that in two dimensions at constant temperature:

- (1) No heat is required to melt the solid.
- (2) Very little heat is required to expand the liquid (L_1) so long as its molecules stay packed about as tightly together as in three dimensions.
- (3) There then ensues an expansion of this liquid film such that the intermolecular distance may increase by so much as thirty-five per cent. This occurs without a change of state, but nevertheless the heat absorbed is very great. For example, if the film consists of pentadecylic acid this extension of the film absorbs as much heat as is used in the evaporation of the same number of molecules of water at ordinary temperatures (11,000 calories per mole).
- (4) In the more expanded liquid state (L_2) the heat of expansion of the film is moderately high, but only a sixth as much per unit area as in the peculiar state described in (3).

* Substance of a paper read at the annual meeting of the U.S. National Academy of Sciences held during April 22–23.

BRITISH STANDARDS INSTITUTION

IN a paper read on April 2 to the London Branch of the Association of Mining Electrical Engineers, the significance of the work being carried on by the British Standards Institution was discussed by Mr. Percy Good, deputy director of the Institution. He began by paying a tribute to the foresight of British engineers who laid the foundations of a movement, which has spread to all industries and into practically every country. In Great Britain it is established on a truly democratic basis of self-government. Each industry as a whole governs for that industry; but due regard is taken as to the effect of any proposed change on other industries. Insistence on agreement

between the interests concerned before a standard is promulgated has as a rule resulted in wide acceptance.

The original standardizing committee grew to be a chartered institution with more than a thousand industrial and technical committees, the pressure for more standards being continuous. The fundamental principles which govern its operation are: (1) to prepare a standard only when those concerned with the production and use of the product and material in question agree that a standard is desirable; and (2) to issue a standard only if those chiefly concerned agree that a suitable draft has been produced.