the effect of oceanic edge currents would be expected to be of shorter range at shorter periods, this would not give a negative gradient in variation energy, it would only reduce the excess at Eskdalemuir. The effect might be caused by the presence of a more highly conducting region beneath Eskdalemuir, which would reduce the coastal energy enhancement at all periods.

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PHYSICS

Circulation within Monolayer Films on Aqueous Substrates at Low Surface Pressures

ALTHOUGH at high surface pressures, up to about 20 dynes/cm², films of long chain fatty acids on water form uniform monolayers, at zero surface pressure the film is no longer uniform but has been described by some authors as consisting of "islands" held together by the van der Waals forces of cohesion between the hydrocarbon chains[1]. An examination with an electron microscope of surface films of stearic acid prepared at a surface pressure of 3 dynes/cm² has provided some evidence that these irregularly shaped islands exist[2].

Radio-tracer studies of oleic acid and other films on water have revealed an interesting phenomenon lending credence to the existence of islands. An apparent circulation of large film elements in a regular periodic manner has been observed. Although oleic acid is usually considered to be "insoluble" in water, surface films after spreading to a pressure of 5–20 dynes/cm² do proceed to dissolve at a rate which is a function of the surface concentration. As the diffusion process continues the surface pressure drops substantially and radioactive counting of the remaining surface film gave the results shown in Fig. 1.

The experiments were conducted as follows. A 'Pyrex' glass dish 9 cm in diameter was cleaned and placed in a polyethylene holder. Distilled water (50 ml.) was then added to give a water depth of 0·8 cm. A Baird–Atom model 821*B* counting tube, 3 cm in diameter, was placed over the dish, and the background radioactivity counted for 1 h in 10 min intervals. The entire apparatus was suspended on a heavy steel plate attached by springs to a frame in order to block out vibrations. Finally, a measured amount of radioactive oleic acid in hexane was spread on the water surface with an Alga micrometer syringe. The counting rate was monitored for 24 to 170 h.

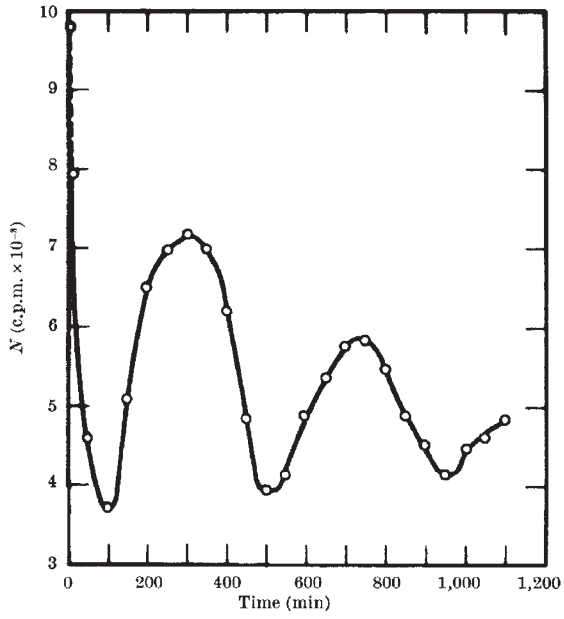

Fig. 1. Counting rate of a 50 Å²/molecule oleic acid film versus time.

In many of the experiments, such as that shown in Fig. 1, an oscillatory character was discovered in the counting rate. The oscillations were attributed to an instability in the system termed the Marangoni effect[3]. As the surface film diffuses into the water, the film remaining on the surface begins to form islands, a process which simultaneously gives rise to tension gradients engendered by the following mechanism.

At equilibrium there would be islands but no surface tension gradients, because the islands would be surrounded by surface active molecules and smaller islands acting more or less individually, but nevertheless present in sufficient numbers so as to maintain a constant surface pressure over the entire surface. Thus at the start of the experiment we have a picture of islands amid a distribution of smaller film segments without surface tension gradients. If we permit molecular transfer by diffusion from the surface into the bulk, then it is easy to picture a situation in which the loss of a few molecules from an island into bulk will have little effect on the local surface pressure whereas the diffusion into the bulk of some of the individually acting molecules will result in a local increase in the surface tension, thus inducing a gradient. Indeed, it is our opinion that the diffusion from the surface into the bulk of surface active material existing as a configuration of islands surrounded by molecules will be inherently unstable and always exhibit the Marangoni effect.

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Transport Processes and the Chemical Potential

MELEHY[1,2] has proposed a theory of transport phenomena, based on a claim that the chemical potential for each constituent is not a constant everywhere in a system which is in thermodynamic equilibrium. He argues that the usual proof of its constancy everywhere is invalid, and that, in any case, its consequences are contrary to experiment. For example he states[1] that the net work in transferring a particle between two points, whatever the gravitational or electrostatic potential difference may be, would be zero on the usual theory, that is, the transfer would be at constant energy. Some consequences would be the denial of the existence of such effects as the Peltier effect and the necessity in thermal equilibrium for the conduction bands to line up throughout a crystal containing a non-degenerate p–n junction.

I criticized[3] his theory, using a new method to validate again the constancy of the chemical potential, $\mu_i + \varphi$, throughout a system at thermodynamic equilibrium; μ_i