# Energy Relations in Transformations from Three to Two-Dimensional Systems. I. The Latent Heat and Entropy of Spreading of Myristic and Pentadecylic Acids

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## 1. Introduction. Heats of Spreading and Freezing

By the application of a Clapeyron equation in the form

$$\Delta H = \lambda_{S \to F} = T(\partial f/\partial T)(a_F - a_S) \qquad (1)$$

it is possible to determine the latent heat of spreading $\lambda_{S \to F}$ of a solid S to form a film F upon an aqueous subsolution. Here $f$ is the film pressure at equilibrium between the crystals and the film and $a$ the area of the surface involved. In practice $a_S$ may be made sufficiently small to be negligible.

Since the values of the temperature required to give the same molecular area at equilibrium in a monolayer of either the 14 or the 15 carbon atom acid are not very different, it is apparent that the differences in the latent heats of spreading, at any given value of $a_F$, are almost entirely determined by the value $\partial f/\partial T$ of the slope of the $f$, $T$ curve.

Values of these slopes have been determined by Cary and Rideal,[1] who find $\partial f/\partial T$ to be practically the same for both myristic and pentadecylic acid, that is the $f$, $T$ curves are parallel, which is not in agreement with our data as presented later. The values of the latent heats of solidification or "settling" of these acids have been determined by King and Garner,[2] and these are, in kcal. per mole, 10.7 for the even (14 C) and 10.30 for the odd (15 C) acid if the solid is in the $\alpha$-form. The transformation $\alpha \to \beta$ of the odd acid evolves 1.20 kcal. per mole in addition.

Thus the tightness of binding of the molecules of the even (14 C) acid may be said to be 10.7 kcal. per mole greater in the crystals than in the three dimensional liquid, while for the odd (15 C) acid the value is 10.3 or 11.5 as has been stated. The effects of the small changes of volume are neglected.

All of the monolayers formed by these two acids are liquids in the ranges of $T$, $f$, and $a$ considered here. They may be classified as: I, Liquid, condensed; II, Liquid, intermediate (or transition); and III, Liquid, expanded.

In these liquid monolayers the energy of molecular binding may be assumed to be greater than in the three dimensional liquid on the basis of the orientation theory, which assumes intimate contact between the carboxyl groups and water molecules, both of which have powerful dipoles. On the basis of the reasoning given above the energy added as heat ($Q_F$) to produce a spreading of the material from the crystals over the surface of the liquid should for any of the solids be less than the heat of melting ($Q_M$), or (1) $Q_F < Q_M$.

**2. Apparatus and Methods.**—The film balance used for the measurement of film pressure, an improved form of that described by Harkins and Myers,[3] was of the general Adam–Jessop type, and was built in such a way as to give a high degree of accuracy in the measurements. For the determination of $\partial f/\partial T$ it is essential to have more accurate temperature control. The use of an air thermostat alone is not sufficient to determine closely enough the temperature of the film. The trough of stainless steel used to contain the subsolution was $80 \times 25 \times 0.5$ cm. with the bottom of the trough hollow, and water from a thermostat was circulated through the shallow reservoir in this bottom, so that the subsolution came rapidly to the thermostat temperature. Water from the thermostat was also circulated through the top of the metal box which inclosed the trough and underneath the trough, and the box was surrounded by an air thermostat.

In performing the experiments, two or three hundred small crystals of fatty acid, supplied by Drs. E. E. Reid and Jane D. Meyer, were placed on a clean surface of 0.01 $N$ sulfuric acid and the temperature of the air and the subsolution were equalized. Temperatures were read by means of thermocouples placed just above and just below the film-covered surface. The air within the film balance case was kept saturated with water vapor. This precaution was necessary for two reasons. At the higher temperatures if the air is not kept saturated, evaporation is rapid and the level of the subsolution in the film trough drops considerably in the course of an experiment, which introduces a proportionate error in the film pressures. Also rapid evaporation produces in the film-covered surface a temperature lower (by an unknown amount) than that measured with the thermocouples. The area included between the float and barrier of the film balance, which was available for spreading, was about 100 sq. cm. The criterion of equilibrium was constancy of film pressure within 0.1 dyne per cm. for ten to fifteen minutes. Attainment of equilibrium below 20° required about two hours but the time became rapidly less as the temperature was raised.

Since a considerable number of investigators

(1) A. Cary and E. W. Rideal, *Proc. Roy. Soc.* (London), **A109**, 328 (1925).

(2) Annie M. King and M. E. Garner, *J. Chem. Soc.*, 578 (1931).

(3) W. D. Harkins and R. J. Myers, *J. Chem. Phys.*, **4**, 716 (1936).

TABLE I

LATENT HEAT OF SPREADING OF MYRISTIC AND PENTADECYLIC ACIDS ON AN AQUEOUS SUBSOLUTION OF $pH$ 2

| Acid | Area per molecule at equilib. press., sq. Å. | $T$, °C. | Equilib. press., dynes per cm. | Entropy $(s)$, ergs per molecule per degree $\times 10^{-16}$ | Entropy $(S)$, cal. per mole per degree | Latent heat of spreading $(\lambda)$, kcal. per mole | Internal latent heat $(\lambda_i)$, kcal. per mole | State of film |
|---|---|---|---|---|---|---|---|---|
| Myristic | 22.3 | 12.5 | 9.8 | 14.7 | 21.3 | 6.07 | 5.79 | Condensed |
| | 23.4 | 14.8 | 11.4 | 15.4 | 22.3 | 6.46 | 6.08 | Intermediate |
| $(\partial f/\partial T = 0.662)$ | 23.6 | 9.5 | 7.7 | 15.5 | 22.5 | 6.40 | 6.13 | Condensed |
| | 25.7 | 16.6 | 12.5 | 16.9 | 24.5 | 7.14 | 6.69 | Intermediate |
| $(\lambda_{S \to L} = 10.7$ kcal. | 28.4 | 25.0 | 18.1 | 18.7 | 27.1 | 8.12 | 7.38 | Expanded |
| per mole) | 28.9 | 21.7 | 15.9 | 19.0 | 27.6 | 8.17 | 7.51 | Expanded |
| Pentadecylic | 20.9 | 25.0 | 20.6 | 10.8 | 15.7 | 4.67 | 4.17 | Condensed |
| $(\partial f/\partial T = 0.517)$ | 21.2 | 21.7 | 18.8 | 11.0 | 15.9 | 4.68 | 4.11 | Condensed |
| $(\lambda_{S_\alpha \to L} = 10.3)$ | 21.5 | 17.9 | 16.9 | 11.1 | 16.1 | 4.68 | 4.06 | Condensed |
| $(\lambda_{S_\beta \to L} = 11.5)$ | | | | | | | | |

have used the ring method in an attempt to determine the surface tension of a subsolution covered with an insoluble film, and since this method was applied by Cary and Rideal to determine the pressures of films in equilibrium with crystals of myristic, pentadecylic, and other acids, it is important to point out why this method fails. The film pressure is given by the equation

$$f = \gamma_S - \gamma_F$$

where $\gamma_S$ is the surface tension of the clean surface of the subsolution, and $\gamma_F$ the value when the film is present. However, at least with rings of the size in use, the ring method does not measure $\gamma_F$. This is due to the fact that, in order to meet the conditions of the theory of the method, the ring must be pulled completely from the liquid, and the maximum pull exerted gives the surface tension. Now at the instant when the maximum pull is exerted, the area of the surface inside the ring is much greater than when the surface is plane. Thus unless crystals of the solid are kept on the surface inside the ring, the surface tension found will be higher than the true tension for the film. The film pressure as determined will thus be too low; much too low if the film is initially condensed, considerably if expanded, and not very much if the film is in the intermediate (transition) state just above the pressure of the transition Intermediate → Expanded. Even if crystals are present inside the ring the time which elapses during the pulling of the ring from the surface is often insufficient to give equilibrium. In addition the weight of the crystals must be negligible or the method is inaccurate.

Values of the variable correction factor, which is essential if the pull on the ring is to be transformed into a surface tension, had not been de-

termined at the time of Cary and Rideal's work. The corrections cannot now be made because of insufficient data on the dimensions of the ring which they used.

The Wilhelmy method, used as a film balance in the form recommended by Harkins and Anderson,[4] should give fully as accurate results as those which we report in this paper, and this method is much more adaptable if temperatures much higher than 45° are to be used.

## 3.   Latent Heat and Entropy of Spreading of Monolayers

For myristic acid the magnitude of the slope $\partial f/\partial T$ as taken from Fig. 1 was found to be 0.662, while pentadecylic acid exhibited a much smaller value (0.517), or the difference between the two is 27% of the latter magnitude. The corresponding slopes found by Cary and Rideal are 0.568 and 0.552, so their work fails to exhibit a difference between the slopes.

The values of the entropy and of the latent heat of spreading are given in Table I. Pressure-area measurements on myristic and pentadecylic acids at several temperatures have been reported in another paper.[5] The areas given in Column 2 of Table I have been taken from the data of that paper for pressures read from the curves of Fig. 1. The relation between the latent heat and the molecular area of the film in equilibrium with the solid, is exhibited in Fig. 2, and is seen to be nearly linear. The complete relationship involves a three dimensional plot, since the temperature is also involved. The entropy of spreading increases with the molecular area, that is, with

(4) W. D. Harkins and T. F. Anderson, THIS JOURNAL, **59**, 2189 (1937).

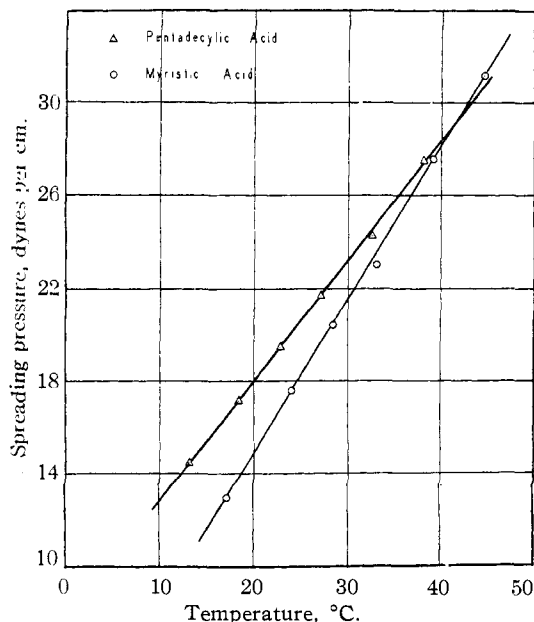(5) G. C. Nutting and W. D. Harkins, *ibid.*, **61**, 1180 (1939).

Fig. 1.—Equilibrium spreading pressures of crystals of myristic and pentadecylic acid on an aqueous subsolution at $p$H 2.



Fig. 2.—Internal latent heat of transformation from three-dimensional crystals to two-dimensional films on an aqueous subsolution at $p$H 2. The values for pentadecylic acid are in such a limited range of areas that the slope is uncertain, but it is certain that the values increase with molecular area as in the case of myristic acid.

the two dimensional "dilution" of the film. This is similar to the relation found in the vaporization of a liquid, since the entropy of vaporization increases as the concentration of the equilibrium vapor decreases.

The latent heat of spreading involves a work term $\int f\, da$ and, if this is subtracted, the internal latent heat is obtained. This gives the increment in molecular energy ($\lambda_i$) involved. Thus

$$\Delta E = \Delta H - W = \lambda_i = \lambda - f(a_F - a_S) =$$
$$\left(T\frac{\partial f}{\partial T} - f\right)(a_F - a_S) \quad (2)$$

The values for myristic acid given in Column 9 of the table show that $\lambda_i$ in calories per mole changes from 5800 at an area of 22.3 to 7500 at an area of 28.9 sq. Å. per molecule.

The entropy of spreading is found to vary from 14.5 to 19 $\times$ 10$^{-16}$ ergs per degree per molecule for myristic acid at areas from 22.3 to 28.9 sq. Å. per molecule. This would give, if a linear extrapolation is justified, about 26 $\times$ 10$^{-16}$ ergs per molecule per degree at 40°. With pentadecylic acid the entropy is about 11 at an area of 21 in the above units. These values may be compared with those for the entropy of vaporization of a normal liquid which follows Hildebrand's relation. Thus, for example, the values are 15.7 ergs per degree per molecule if the concentration of the vapor is 0.0201
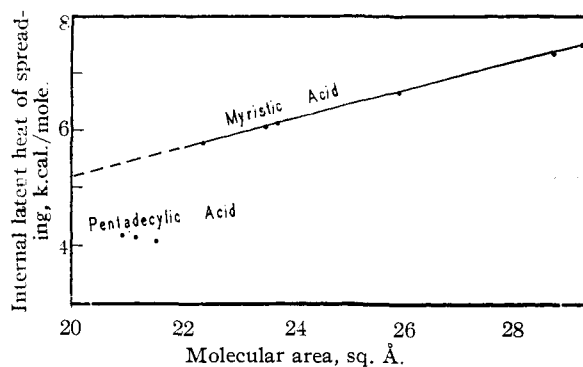
mole per liter,[6] and 18.8 if the concentration is 0.00507. These have been chosen at concentrations of the vapor which are associated with entropy values of the same order as those for spreading as cited above. From the rate at which the heat of spreading increases with the temperature it seems that at the melting point the value must still be below the heat of fusion. This means that the spreading of the material from a liquid lens gives off heat instead of absorbing it.

### 4. Summary

1. By the use of the equation $\Delta h = \lambda_{S \rightarrow F} = T(\partial f/\partial T)_a (a_F - a_S)$, the latent heats of spreading of crystals of myristic and pentadecylic acid to form a monolayer on 0.01 $N$ sulfuric acid have been determined. The measurements involved are the determination of the pressures of the film in equilibrium with the crystals at various temperatures, and that of the molecular area at each temperature and pressure.

2. The latent heats of spreading for myristic acid are found to increase with molecular area in an almost linear way, and rise from 6020 cal. per mole at 22.1 sq. Å. per molecule to 8060 cal. per mole at 28.7 sq. Å. The corresponding increase of entropy is from 14.5 to 18.9 $\times$ 10$^{-16}$ ergs per degree per molecule.

3. The latent heat of spreading is of the order of a thousand calories per mole less for pentadecylic (15 C) than for myristic (14 C) acid.

(6) W. D. Harkins, Proc. Nat. Acad. Sci., 5, 152 (1919).