investigated at room temperature and a pressure of about 0.01 mm. on evaporated layers of nickel, palladium and platinum. It was found that there is a stable layer of hydrogen on the catalysts which is not removed by pumping at room temperature and which exchanges readily with molecular hydrogen or deuterium. The rate of this exchange is equal to the rate of the para-hydrogen conversion on nickel, but is smaller on palladium and platinum. It is shown that the amount of ex-changeable hydrogen in the stable layer can be taken as an indication of the number of active centers on the catalyst. This number is 10^{14} to 10^{15} cm.$^{-2}$ and shows that a great fraction of the apparent catalytic surface is active. The various possible mechanisms for the conversion of para-hydrogen and the exchange are discussed and their bearing on other exchange, hydrogenation and isomerization reactions considered.

Fluorochlorobromomethane

BY KENNETH L. BERRY[1,2] AND JULIAN M. STURTEVANT

In connection with recent theories of optical activity,[3] an optically active pentatomic molecule would be of considerable interest. Attempts have therefore been made to resolve fluorochlorobromoethane, perhaps the most readily obtainable of the few such substances having potential optical activity. During this work several physical properties of this substance have been determined.

Swarts[4] attempted to resolve this substance by fractional crystallization of the complex it forms with salicylide, but without success. He was also unsuccessful[5] in attempts to decarboxylate optically active fluorochlorobromoacetic acid to yield the active substituted methane.

Preparation and Purification.—Ethyl chloroacetal was prepared by the addition of chlorine to vinyl acetate in alcohol solution according to the method of Filachione.[6] Bromination[7] of the chloroacetal, followed by hydrolysis, yielded chlorodibromomethane. This latter halide on treatment with antimony trifluoride and bromine gave fluorochlorobromomethane[4] in fair yield, though contaminated with considerable amounts of higher and lower boiling halides. The crude product was washed at 0° with very dilute alkali followed by water, dried over calcium chloride, and fractionated from phosphorus pentoxide through a 48-cm. vacuum-jacketed column packed with glass helices. The main fraction was collected between 36.3 and 36.8°, and was stored in sealed ampoules in the dark. Over-all yields of approximately 25% were obtained.

Anal. 0.2097 g. gave 0.4693 g. AgCl + AgBr; calcd. 0.4711 g. AgCl + AgBr.

One hundred and forty grams of material boiling at 36.3–36.8° was refractionated, and the middle cut of 65 g. was again fractionated to give a 37 g. fraction boiling at 36.11–36.18° (cor.) (756.0–756.2 mm.). This sample was used for the determination of physical properties. It remained perfectly colorless when sealed in an ampoule and stored in the dark.

Physical Properties.—The fusion curve of fluorochlorobromomethane, which was observed in an apparatus similar to that described by Skau,[8] showed the 36.11–36.18° fraction to be quite pure. The melting point was found to be −115° (cor.).

The density was determined dilatometrically from 0 to 25°, and can be represented in this range by the equation ($t = °C.$)

$$d_t = 1.9771 - 2.51 \times 10^{-3}t - 2.03 \times 10^{-5}t^2 + 3.3 \times 10^{-7}t^3 \quad (1)$$

A Pulfrich refractometer was employed to determine the refractive dispersion of fluorochlorobromomethane in the visible spectrum at 0.5, 10.0 and 20.0°. The data were fitted to an equation of the form recommended by Tilton[9] ($\lambda =$ wave length in microns)

$$n^2 = a^2 - k\lambda^2 + \frac{m}{\lambda^2 - l^2} \quad (2)$$

(1) The material in this communication constitutes part of a dissertation submitted by Kenneth L. Berry to Yale University in partial fulfillment of the requirements for the Ph.D. degree, June, 1940.

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(3) Kuhn, *Z. physik. Chem.*, **B31**, 23 (1936); Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937); Condon, Altar and Eyring, *ibid.*, **5**, 753 (1937).

(4) Swarts. *Bull. acad. roy. Belg.*, [3] **26**, 102 (1893).

(5) Swarts, *ibid.*, [3] **31**, 28 (1896); *ibid.*, Memoirs Couronnes, **54**, 54 (1896).

(6) Filachione, THIS JOURNAL, **61**, 1705 (1939).

(7) Jacobsen and Neumeister, *Ber.*, **15**, 601 (1882).

(8) Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).

(9) Tilton, *Bur. Standards J. Research*, **17**, 046 (1936).

The constants for this equation listed in Table I reproduce the data within the experimental accuracy from λ 0.7065 to λ 0.4047.

TABLE I

THE CONSTANTS OF EQUATION (2)

Temp., °C.	a^2	k	m	l^2
0.5	2.0083	0.00432	0.01175	0.01832
10.0	2.0041	.01828	.00873	.03954
20.0	1.9778	.00610	.01082	.02256

The Lorenz–Lorentz molecular refractivities for the sodium D line are $R_{0.5} = 19.24$, $R_{10} = 19.26$, $R_{20} = 19.31$. Using the atomic refractivities[10] of carbon, hydrogen, chlorine and bromine, one finds the atomic refractivity of fluorine at λ 0.5893 and 20° to be 0.956.

Attempted Resolution.—Three types of procedure for accomplishing the resolution of fluorochlorobromomethane suggest themselves: (a) formation of solid addition compounds with optically active substances; (b) utilization of vapor pressure differences in asymmetric solvents; and (c) selective adsorption on optically active adsorbents. Limitations of time have not permitted an extensive investigation of these proce-

(10) "Organic Chemistry, An Advanced Treatise," edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1739.

dures, though indications of positive results were obtained with the first method.

It was found that digitonin[11,12] forms an insoluble digitonide with fluorochlorobromomethane. This digitonide cannot be dried and characterized since it very readily loses its volatile component. The halide was added to an aqueous alcoholic solution of digitonin at 0°; after vigorous shaking the mixture was centrifuged, and the precipitate was then warmed to 55° under a slow stream of air to sweep the vaporized halide into a dry-ice-cooled receiver. The distillates thus obtained had rotations varying from zero to +0.15° (1-decimeter tube). The irreproductibility of the results, and the poor recovery of the very expensive digitonin make further experiments along this line seem unpromising.

Summary

Fluorochlorobromomethane was prepared in pure form, and its boiling point, melting point, density and refractive dispersion determined. Inconclusive results were obtained in attempts to resolve the substance through its insoluble digitonide.

(11) Windaus and Weinhold, Z. physiol. Chem., **126**, 299 (1923).
(12) Windaus, Klänhardt and Weinhold, ibid., **126**, 308 (1923).

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The Pressure–Area–Temperature and Energy Relations of Monolayers of Octadecanenitrile

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1. Introduction

Until recently only three liquid phases have been known to exist in monolayers. These are (1) the liquid expanded or L_1 phase, (2) the intermediate or I phase, and (3) the liquid condensed or L_2 phase. Any one of these may exist at low pressures, and therefore may be designated as a low pressure liquid phase. Recently a new liquid $LS^{1,2}$ phase has been discovered, but is found to exist only at high film pressures, since it is formed by a transition from the liquid condensed (L_2) phase when the pressure is raised to a sufficiently high value. Except at the lowest temperatures at which this new phase is formed, the transition

(1) W. D. Harkins and L. E. Copeland, J. Chem. Physics, **10**, 272 (1942).
(2) L. E. Copeland, W. D. Harkins and G. E. Boyd, ibid., **10**, June (1942).

is of the second order, so at the transition point the molecular area is the same in the high pressure LS phase as in the low pressure L_2 phase. However, by increase of pressure the area for the LS phase may be reduced below any possible area, for the given temperature, at which the L_2 phase may exist. This new high pressure phase has been found to form in monolayers of the normal long chain paraffin alcohols, but its lower limiting molecular area is 19.98 sq. Å., since below this it transforms into the "solid" or S phase.

At the highest pressure at which a low pressure liquid alcohol monolayer is stable, its molecular area may be below that possible for the stable existence of the high pressure liquid phase. Thus at 2.85° and 14 dyne cm.$^{-1}$ the molecular area for octadecanol is 19.8 sq. Å., the lowest area