therefore seems probable that the adsorption is a combination of activated and van der Waals adsorption favoring the former for initial stages but changing in ratio progressively to the latter as successive increments of gas are added to the surface. This is in agreement with the conclusion of Benton and White[5] based upon indirect experimental evidence.

The technique worked out in detail for carbon monoxide on copper should be applicable to other gas-solid combinations at −183°. For reasons given in the introduction, direct experimental measurements of heats of adsorption are needed at low temperatures on chromium oxide. The technique described above is now being applied to the latter adsorbent.

Our thanks are due to the Committee on Grants-in-Aid of the National Research Council for supplying funds for technical assistance in this work.

Summary

1. A method has been described for the direct measurement of the differential heats of adsorption of carbon monoxide on copper at −183°.

2. The differential heats are of the order of 8 kcal. per mole in the initial stages, and decrease to 3 kcal. in the later stages of the adsorption.

3. The results seem to indicate that a considerable part of the adsorption for the initial increments of gas is of the activated type even at the low temperature of −183°.

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[5] Benton and White, THIS JOURNAL, 54, 1385 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

X-Ray Diffraction Studies of Built Up Films[1]

BY G. L. CLARK AND P. W. LEPPLA

The development by Langmuir and Blodgett[2] of a technique for the preparation of foliated films of any desired number of molecular layers permits for the first time the study of x-ray diffraction effects produced by a known number of planes. Clark, Sterrett and Leppla[3] reported distinct diffraction patterns from nine or more layers of stearates prepared by Blodgett's method. Langmuir and Schaefer[4] have since shown by chemical analysis of the unimolecular layer skimmed from solutions containing calcium or barium ions that the built up films vary continuously in composition from pure acid at *p*H 2 to pure soap at *p*H 11. In view of the fact that the soaps and the acids crystallize in different systems, and since, furthermore, several modifications of the fatty acids are known, the structure of the composite built up films was investigated by diffraction methods.

Experimental.—Films were prepared of stearates of lead, calcium and barium by means of a motor-driven device to ensure freedom from vibration and the highest possible perfection of the individual layers. To eliminate the necessity for oscillating the specimen in the path of the x-ray beam, curved surfaces were used as originally proposed by Trillat.[5] For the measurement of the long spacing, *d*, a radius of 15 mm. was employed. To each order corrections were applied for the actual position of the origin of the diffracted spot. To increase the intensity of the pattern for the study of films of only a few layers, the radius was increased to a maximum of 50 cm. Copper Kα radiation was used.

A double lining of lacquer overlaid with paraffin was used in the brass trough to prevent contamination of the solutions with copper ions. For the measurement of *p*H an antimony electrode was employed.

Since films do not adhere to glass at low *p*H, lacquered surfaces were used in the acid range. Molecules adhere to glass or metal by their polar groups and exist in an odd number of layers. On lacquer the hydrocarbon end of the chain is attached to the surface and the films exist in an even number of layers.

Composition of the Surface Film.—Unimolecular stearate films were skimmed from the surface of dilute calcium, barium and lead salt solutions at varying hydrogen-ion concentrations, the material air-dried, packed into tiny cells and transmission diffraction patterns registered. Side spacings characteristic of both the acid and the soap appeared in each case, the intensities indicating complete agreement with Langmuir and Schaefer's[4] conclusions.

Structure of the Built Up Films.—From the mechanism of the transfer process the gross structure readily may be inferred to be the alternating

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[1] From a thesis presented by P. W. Leppla to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1936. Presented before the 91st meeting of the American Chemical Society, Kansas City, Mo., April, 1936.

[2] Blodgett, THIS JOURNAL, 57, 1007 (1935).

[3] Clark, Sterrett and Leppla, *ibid.*, 57, 330 (1935).

[4] Langmuir and Schaefer, *ibid.*, 58, 284 (1936).

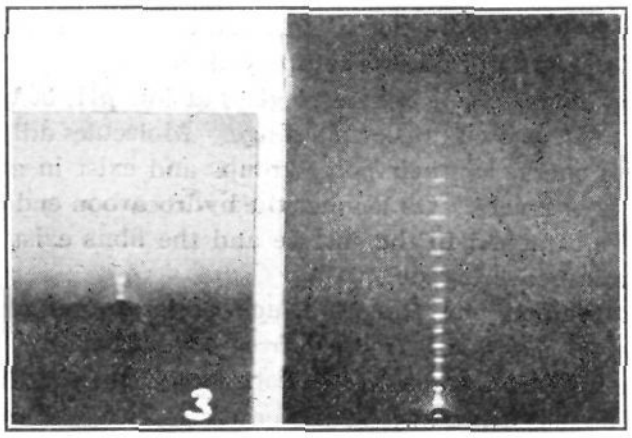
[5] Trillat, *J. phys. radium*, [6] 10, 32 (1929).

type common to fatty acids and derivatives. In the ordinary crystal modification of stearic acid the chains are tilted at about 27° from the normal to the base and *d* is about 40 Å. In stearates of divalent metals the chains are perpendicular or very nearly so to the base and *d* is approximately 50 Å. The spacings observed for built up films and for ordinary preparations are given in Table I.

TABLE I

		Å.
Stearic acid	Built up film	39.7 ± 0.2
	Melted on glass	39.5 ± .2
Calcium stearate	Built up film	49.4 ± .2
	Powder by transmission	50.0 ± 0.5
Lead stearate	Built up film	49.6 ± .2
	Powder by transmission	49.7 ± .5

Based upon the spacing observed and the relative intensities of the odd and even orders, it was concluded that the structure of the composite films varies *discontinuously* with the *p*H, being that of the acid below *p*H 3 and that of the soap above *p*H 6. As might be expected from the difference in lattice energies, the stearates power in imposing the soap structure on the film is the greater, and films containing even a relatively high proportion of the acid still have the structure of the soap. At intermediate hydrogen-ion concentrations a pattern was obtained characterized by low intensity of the higher order reflections, indicating a distorted transition structure. Lead stearate films at *p*H 4 gave a totally different pattern indicative of an entirely distinct configuration.



3 layers 50 layers

Fig. 1.—Diffraction patterns of built up films of lead stearate.

By an ingenious method of interference of monochromatic light, Blodgett[2] has measured the over-all thickness of calcium stearate films, obtaining 48.8 Å. per double layer. It has been suggested that comparison of such measurements with those of x-ray diffraction affords a direct approach to absolute x-ray wave length values. No significance can be attached to the discrepancy between Blodgett's value and those of this investigation since different samples of stearic acid were employed, and it has been shown adequately that *d* values for fatty acids vary greatly with the purity of the specimen, and for at least three polymorphic structures.

Pure stearic acid films were transferred to lacquered surfaces from perchloric acid solutions of *p*H 2 to 5. Two side spacings appeared on the photographic film in a position indicating that all the chains were tilted in the same direction, sloping down with respect to the plane in which the surface was raised and lowered during the transfer process.

Intensity Measurements.—The use of a large radius of curvature resulted in such high intensities that good patterns were obtained from as few as three layers of lead stearate. Figure 1 is a reproduction of such a pattern secured in three-fourths hour from a Philips Metalix tube operating at 28 kv. and 25 ma., as compared with a pattern for 50 layers.

From a series of films with increasing numbers of layers the data shown graphically in Fig. 2 were obtained. The intensities were read from micro-

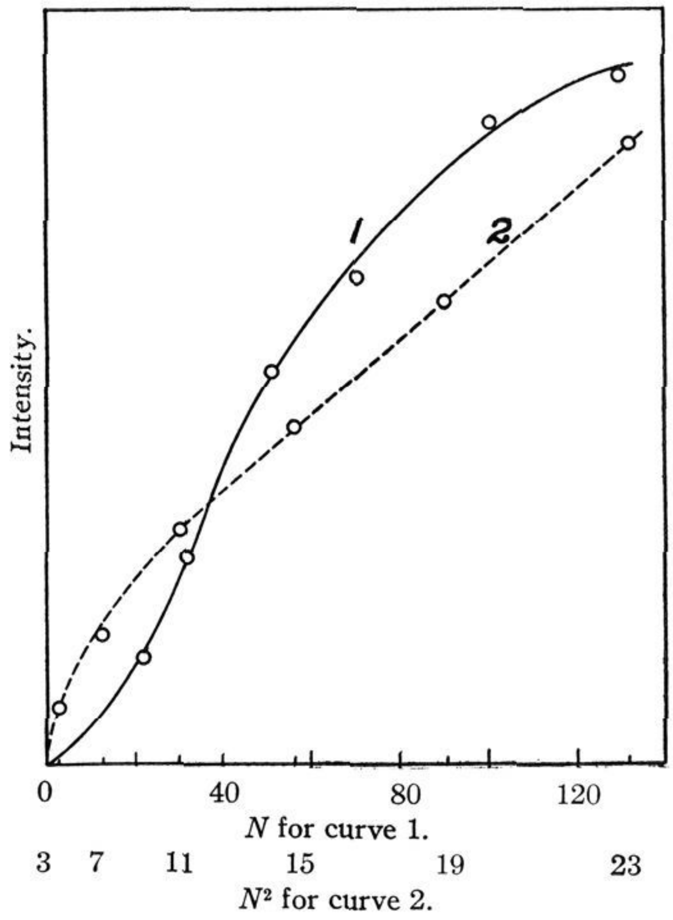


Fig. 2.

photometer traces and a blackening curve established from similar films developed simultaneously. In the experimental series the exposure time was varied systematically from one minute to one hour to keep the blackening between 25 and 50%. If intensities of interferences for the thinnest films are plotted against the *square* instead of the first power of the number of layers, the points between ten and thirty layers fall on a straight line. This is characteristic of an ideally imperfect diffracting medium. From a greater number of layers the intensity falls off, the upper layers shielding those below from the x-ray beam. Thus the irregularity of the first layers applied has become smoothed out and the planes approach perfection.

Test of the Laue Particle Size Equation.—The theoretically derived equation, $B = b + (0.9\ \lambda/D \cos \theta/2)$[6] has been used to calculate particle size in the colloidal range from the observed breadth of x-ray interferences. Until now it has been impossible to test the equation because of a lack of a comparison method. The expression is equally valid for the thickness of a built up film. The results of line breadth measurements are given in Table II. In general, agreement of observed and calculated values is good except for very thin films where the excess broadening observed is attributed to the previously mentioned distorted nature of the first layers applied.

TABLE II

Number of layers	Broadening Obsd.		Av.	Calcd.
3	0.21	0.28	0.25	0.186
4	.27	.17	.22	.139
5	.10	.16	.13	.112
6	.15	.10	.13	.093
7	.04	.05	.05	.080
8	.06	.05	.06	.070
9	.05	.08	.06	.062
10	.05	.02	.04	.056
17	.04	.02	.03	.035
20	.02	.03	.03	.028
25	.01	.03	.02	.022
30	.02	.02	.02	.019
35	.02	.02	.02	.016

Summary

The structures of Blodgett's composite films of stearic acid and stearates have been investigated by x-ray diffraction methods. The structure and hence the thickness have been found to be that of the constituent present in greater proportion. The *d* spacings agree closely with those of the crystalline material.

Intensity measurements have been made from successively increasing numbers of planes and the degree of perfection inferred therefrom.

Laue's particle size equation has been tested by the use of films of known thickness.

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(6) B = breadth of interference at points of half-maximum intensity; b = apparatus constant for minimum width under experimental conditions; λ = x-ray wave length; θ = diffraction angle for given interference; D = size of particle, or thickness of film.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Reactions of Nickel Carbonyl with Oxides of Nitrogen[1]

BY J. C. W. FRAZER AND WM. E. TROUT, JR.[2]

M. Berthelot[3] passed nitric oxide into nickel carbonyl and obtained a solid product. Subsequent admission of small amounts of oxygen to the reaction vessel produced another solid. Berthelot characterized both solids as complex compounds but did not give analyses. Some confusion has arisen in the literature concerning these experiments, apparently due to the mistaken translation of "bioxyde d'azote" as nitrogen peroxide.[4] Attempts to determine the nature of the solids have not been wholly successful.[5,6]

This paper reports further observations concerning the reactions of nickel carbonyl with oxides of nitrogen.

Experimental

Nitrogen Peroxide and Nickel Carbonyl.—Nitrogen peroxide and nickel carbonyl reacted exothermally at temperatures as low as −78°. The reaction was carried out

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(1) Abstract of a dissertation submitted by Wm. E. Trout, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University.

(2) Present address: Department of Chemistry, Mary Baldwin College, Staunton, Virginia.

(3) Berthelot, *Compt. rend.*, **112**, 1343 (1891); *Bull. soc. chim.*, **7**, 431, 434 (1892).

(4) Muhlert, *Chem. Zentr.*, Vol. II, 1063 (1892); Gmelin–Kraut, "Handbuch d. anorg. Chem.," Heidelberg, Carl Winter, 1909, Vol. V, p. 107; Mellor, "Comprehensive Treatise of Inorganic Chemistry," Longmans, Green and Co., London, 1928, Vol. VIII, p. 546.

(5) Mond and Wallis, *J. Chem. Soc.*, **121**, 32 (1922).

(6) Reihlen, Gruhl, Hessling and Pfrengle, *Ann.*, **482**, 161 (1930).