ture. Altman and Kedrinskii[2] reported a reaction between ethylene oxide and ethanol in the presence of $H_2SO_4 \cdot H_2O$ as a catalyst at room temperature and atmospheric pressure, with 70% yield of ether in three hours. Brönsted, Kilpatrick and Kilpatrick[3] studied the kinetics of the hydrolysis of ethylene oxide in aqueous solution and found the reaction to proceed mainly as a basically catalysed reaction.

A very small steric factor accompanied by a comparatively high value of the activation energy would account for the present results. The work of Altman and Kedrinskii indicated a predominantly ionic mechanism for the liquid phase reaction. A very small steric factor for the gas phase reaction is in agreement with the deductions of Bawn concerning association reactions.[4] Apparently the formation of ether derivatives of ethylene oxide must occur through an ionic mechanism, in order to account for the rates of reactions in the liquid phase at room temperatures, or as heterogeneous reactions.

(2) Altman and Kedrinskii, *Trans. Exptl. Research Lab. Khemgas, Materials on Cracking and Chemical Treatment of Cracking Products, U. S. S. R.*, **3**, 34 (1936).
(3) Brönsted, *et al.*, THIS JOURNAL, **51**, 428 (1929).
(4) Bawn, *Trans. Faraday Soc.*, **31**, 1536 (1935).

HOWARD UNIVERSITY
WASHINGTON, D. C.   RECEIVED DECEMBER 31, 1938

Note on the Adsorption of Gases by Graphite. II

BY ARTHUR B. LAMB AND EDWIN N. OHL

Recently,[1] in connection with the study of the adsorption of gases by graphite, data were presented showing that at 0° and at −195.2° hydrogen is adsorbed much less by the pure graphite formed as pseudomorphs on heating crystalline silicon carbide to a very high temperature, than it is on ordinary Acheson graphite. Thus, at 300 mm. pressure and −195.2°, the adsorptions were 0.83 ± 0.01 on Acheson graphite and 0.18 ± 0.01 cc. per gram on the pseudomorphs, the ratio being 4.6 ± 0.3. In this connection it was also stated that the adsorptions of dichlorodifluoromethane (Freon) and of carbon dioxide at 0° on these pseudomorphs "were so slight as to be no greater than our errors of observation."

These very slight adsorptions of dichlorodifluoromethane and of carbon dioxide were somewhat surprising because these gases had been found to be moderately adsorbed on Acheson

(1) Lamb and Ohl, THIS JOURNAL, **60**, 1287 (1938).

graphite at 0° (0.96 ± 0.02 cc. of CCl_2F_2 and 0.17 ± 0.01 cc. of CO_2 per gram at 300 mm.) so that on the basis of the above ratio (4.6) of the adsorptions of hydrogen on these two varieties of graphite, a small but nevertheless measurable adsorption on the graphite from silicon carbide would have been expected. However, as this anomaly appeared to have no important bearing on our main thesis it was not studied further.

Dr. P. H. Emmett has now in a private communication kindly called attention to these surprisingly small adsorptions and has also pointed out that if these gases were indeed so very slightly adsorbed by the graphite from silicon carbide, it might be argued plausibly that the observed, relatively large adsorption of *hydrogen* on this graphite was due to the presence in it of some extra porosity, accessible to hydrogen but not to dichlorodifluoromethane or carbon dioxide, which is not present in Acheson graphite; an inference exactly contradictory to our conclusion based on other evidence.

In view of this possible inference we have reexamined our measurements of the adsorption of these gases on the graphite from silicon carbide. We find that the results obtained in these measurements were unusually irregular, those with dichlorodifluoromethane being particularly so, and for no apparent reason. The adsorptions observed with carbon dioxide were indeed small but were clearly greater than the experimental error.

In the hope of securing more definite evidence in this matter we have now repeated these measurements with especial care on a fresh sample of the pseudomorphic graphite derived from silicon carbide. The new data are in general agreement with those previously obtained but are far less erratic. They are shown graphically in Fig. 1 along with comparable data given previously[1] for carbon dioxide and Freon at 0° on ordinary Acheson graphite.

It can be seen from curves No. 2 and 4 of the figure that the adsorptions of these gases, while small, are by no means negligible, being 0.22 ± 0.01 cc. for Freon and 0.032 ± 0.01 cc. for carbon dioxide, at 300 mm. pressure. These adsorptions, compared with the corresponding values for these gases on Acheson graphite given above, yield the ratio 4.4 ± 0.3 and 5.2 ± 0.5, respectively. These ratios are practically identical with the ratio obtained for hydrogen on these two varieties of graphite at −195.2° and 300 mm. pressure, so

that there is now no discrepancy between the two sets of data and additional support is given to our prior conclusion that these pseudomorphs from silicon carbide do not contain any inner porosity accessible to hydrogen but not to carbon dioxide or Freon beyond that present in ordinary graphite.
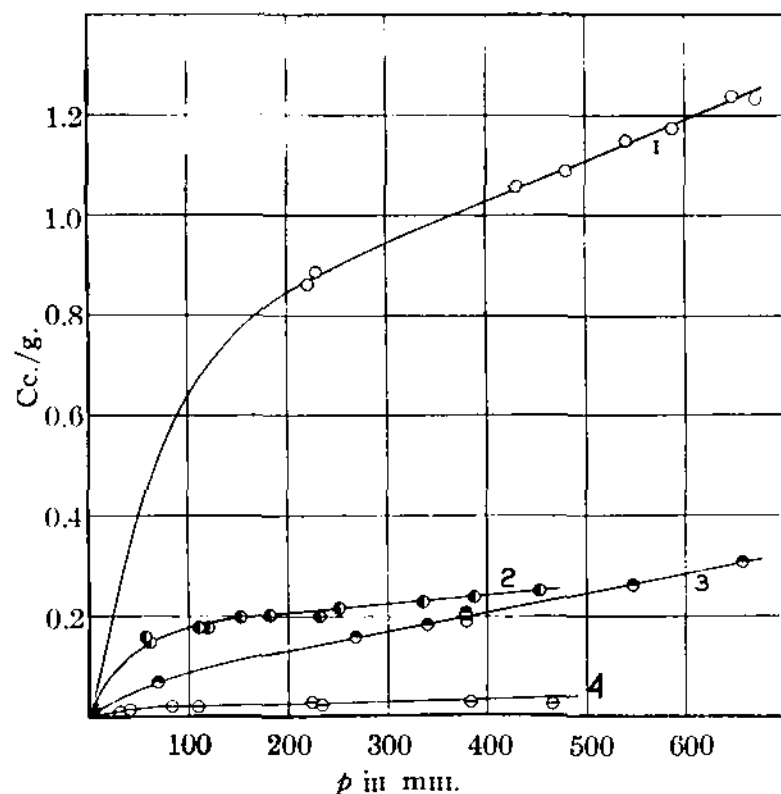

Fig. 1.—Adsorption at $0.0°$: 1, O, CCl_2F_2 on graphite; 2, ◐, CCl_2F_2 on SiC carbon; 3, ◓, CO_2 on graphite; 4, ⊖, CO_2 on SiC carbon.

It is also of interest that these two varieties of graphite should show so nearly the same relative adsorptive capacities at the same pressure over so considerable a temperature range and with these quite different gases.

CHEMICAL LABORATORIES
HARVARD UNIVERSITY
CAMBRIDGE, MASS. RECEIVED DECEMBER 23, 1938

A Modification of the Schlieren Method for Use in Electrophoretic Analysis

BY L. G. LONGSWORTH

The scale and schlieren methods have both been used for the determination of the refraction gradients that arise in electrophoretic and ultracentrifugal analysis.[1,2] With proper conditions either method yields a graph of the gradient, dn/dx, in a thin horizontal layer of the column as a function of the position, x, of the layer. With the scale method, however, this graph is obtained

(1) Lamm, Nova Acta Reg. Soc. Sci. Upsaliensis, Series IV, 10, No. 6 (1937).

(2) Tiselius, Särtryck Svensk Kem. Tidskrift, 50, 58 (1938).

by a laborious comparison of the scale photographs. The schlieren method may be modified to record this graph rapidly and automatically as will be shown below.

The schlieren method, as applied to electrophoretic analysis, may be described with the aid of Fig. 1. An image of the horizontal slit S,
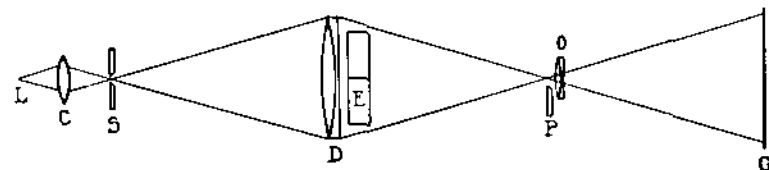

Fig. 1.

illuminated by the lamp L and condenser C, is formed by the lens D in the plane P. An opaque diaphragm with a sharp horizontal upper edge is placed in this plane and may be moved vertically. The camera objective O is focussed on the electrophoresis cell E and forms an image of this on the photographic plate G. If refraction gradients, i. e., electrophoretic boundaries, are present in the cell E the pencils of light through these gradients are deflected downward. With the diaphragm adjusted to intercept these deflected pencils, the regions at G conjugate to the boundaries in the cell appear as dark "schlieren" bands. Using corrected lenses and a narrow slit S the edges of the schlieren bands are quite sharp. The displacement of the diaphragm from the position of the undeviated slit image is proportional to the refraction gradient at positions in the cell E conjugate to the edges of the schlieren bands.
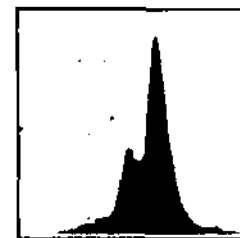
The modification of the schlieren method I have used consists in masking the cell image at the photographic plate by a narrow vertical slit and driving the plate horizontally past this slit as the diaphragm is progressively raised to the position of the undeviated slit image. One thus obtains on the plate a transparent area whose contour is a graph of the refraction gradient dn/dx versus the position x. Figures 2 and 3 (p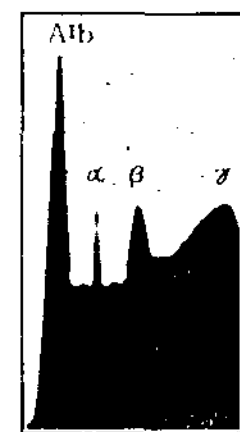ositive prints) were obtained in this manner. Figure 2 was obtained in the electrophoresis of a 0.5% solution of an egg albumin preparation and indicates

Fig. 2.

Fig. 3.