tives. In most of these cases there is a definite but somewhat diffuse scattering at very small angles. Equatorial maxima run out from this halo like small arrowheads, but in spite of ingenuity in obtaining the very sharpest possible patterns, it has been impossible to resolve these equatorial streaks into a series of individual spots. There are, however, some very interesting characteristics of this phenomenon which seem worth recording.

Fig. 1*a* is a diagrammatic representation of the

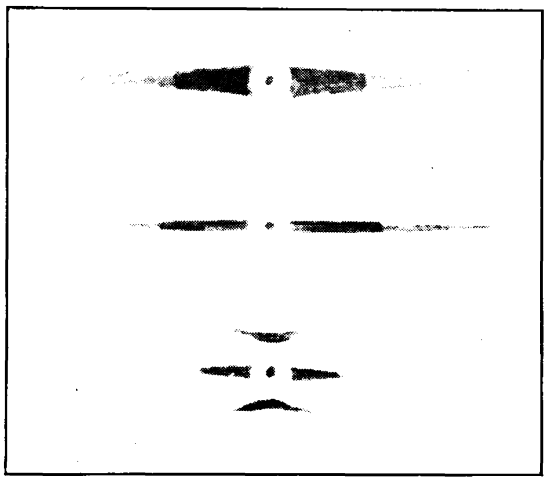

FIG. 1. Diagrams of diffraction effects at very small angles of fiber pattern. (*a*) Native ramie. (*b*) Mercerized ramie dried under tension. (*c*) Regenerated cellulose rayons (nitro, cuprammonium, viscose).

innermost part of a diffraction pattern for native ramie. A continuous streak runs along the equator from the central spot of the pattern, which is widest at the smallest angles and tapers gradually to a nearly constant width of blackening on the film. The greatest intensity seems to be reached at a spacing of about 40 A.U., followed by a rapidly diminishing intensity down to about 20 A.U. The obvious explanation of this pattern seems to be that a whole range of lateral spacings between macromolecules, crystallites or micelles occurs. The greater this spacing is, that is, the smaller the angle, the less perfect is the longitudinal arrangement along the length of the chains in the crystallites so that the resulting diffraction effect is increasingly more diffuse or wider.

In Fig. 1*b* is represented the innermost part of the pattern of mercerized cellulose dried under tension so that the greatest preferred orientation can be gained. The same equatorial streak can be observed as with the original native ramie, but now it is very sharp and uniform in width until it merges with the trace of the undiffracted beam. The marked effect, therefore, of pulling the chains more nearly parallel to each other is directly indicated.

Fig. 1*c* represents an entirely new finding for rayon. With the most careful technique involving very small pinholes, careful blocking of the primary beam, vacuum camera and similar details, we find for all regenerated cellulose rayons, including nitro, cuprammonium and viscose, the production of a very sharp equatorial streak and very definitely a first layer line on either side from which can be measured a fiber identity period of 154 A.U. Acetate rayons do not give this pattern but only a fairly diffuse general scattering around the central spot. The progression in regularity of structure from native ramie to mercerized ramie when dried under tension and then to commercial rayons seems to be clearly indicated by these curious unresolved diffraction maxima at very small angles.

G. L. CLARK
E. A. PARKER

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS

SECONDARY INCREASE OF LENGTH OF STRETCHED CHILLED RUBBER[1]

DURING some work on "frozen" crude rubber, we have noted that stretched samples behave in a curious way that may have significance in attempts at explaining the rubbery state.

It is well known that crude rubber becomes hard and opaque at low temperatures, and is then said to be "frozen" or "boardy." It exhibits most of the phenomena associated with true crystallization; for instance, a development of well-marked, strongly birefringent granules, a decrease in volume during freezing and an incipient formation of crystal nuclei at a low temperature before contraction in volume begins.

In the current investigation we have noted the following strange behavior of crystallizing samples. When a piece of crude rubber, for example, a strip about 5 mm wide and 2 mm thick, is stretched moderately, cooled to $-25°$ C. and maintained at that temperature, it first becomes hard and then during a few hours the length of the stretched piece increases about 4 per cent. A strip of rubber, stretched and nailed to a board, rises to form an arc between the points of attachment. This secondary elongation is roughly independent of the amount of stretch if the increase in length has been between 20 and 300 per cent. We have observed it with smoked sheet, pale crepe, milled pale crepe and with smoked sheet that has been swelled slightly by benzene to remove strains, and thoroughly dried. It is absent or feeble with vulcanized rubber

[1] Publication approved by the director of the National Bureau of Standards of the U. S. Department of Commerce.

or with rubber that has been stretched to the degree at which it displays marked resistance to further elongation. The elongation does not occur with unstretched rubber. The effect is not simply a component of the volume changes which occur on stretching or freezing, but is opposite in direction and has at least four times the magnitude which such volume changes would produce. Measurements have not yet been made of the change of volume accompanying the elongation. By analogy with the contraction of stretched rubber on heating, it seems probable that this phenomenon is related to the Gough-Joule effect, and that the increase in length is accompanied by a lateral contraction of such magnitude that the volume decreases.

Available evidence indicates that rubber hydrocarbon consists of very long molecules. When rubber is stretched, these molecules tend to be oriented parallel to the direction of elongation, so that, when freezing begins, a crystalline axis has already been established. The crystals are correspondingly oriented. During freezing a time comes when enough molecules have fallen into crystalline spacing to harden the sample and relieve the stresses that produced stretching. As more molecules move into the crystalline arrangement, the spacings at right angles to the stretch become less, the long directions of the molecules become more strictly parallel to the axis of stretch, and the sample is elongated. This explanation is supported by unpublished evidence regarding crystal growth at approximately – 25° C.

W. HAROLD SMITH
CHARLES PROFFER SAYLOR
NATIONAL BUREAU OF STANDARDS

SCIENTIFIC APPARATUS AND LABORATORY METHODS

POTENTIAL MEASUREMENTS IN OXIDO-REDUCTION MIXTURES[1]

IN the series "Studies on Oxidation-Reduction,"[2] Clark has described the apparatus used for potential measurements of oxido-reduction dyes in various ratios of oxidant and reductant. The mounting of the potentiometer and the gas purification being left out of consideration, the principle of this apparatus is briefly the following.

Reductant is sucked out of the reduction vessel into a reservoir. Here the hydrogen gas still present is removed from the reductant by passing nitrogen through it. Now a burette may be filled from the reservoir, so that measured quantities of reductant may be introduced into the electrode vessel. We then found that this apparatus might quite well be simplified, while retaining the principle according to Clark, by leaving out the reservoir and substituting the burette for it. At the same time the number of taps is in this way reduced from 6 to 3, as is apparent from the figure (Fig. 1). During the numerous determinations of oxido-reduction curves executed with this apparatus, it has continually proved to answer the purpose easily. This may justify this short communication.

The apparatus is used in the following manner: Via A, three-forked tap X (T shape) and B the electrode vessel C may be made free from oxygen by passing nitrogen through it. *Via* G and three-forked tap Y the nitrogen may be led through burette D and then either to the electrode vessel (*via* three-forked tap Z with double boring) or to the reduction vessel M, first

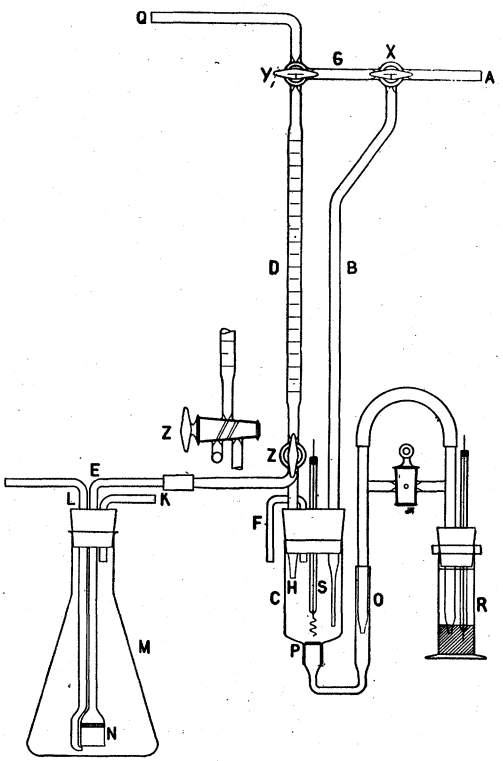

FIG. 1

driving away the oxygen and after reduction the hydrogen. The stream of hydrogen passes to M *via* L. By connecting Q with a water spout air pump, the reductant may directly be sucked into burette D, after being freed from hydrogen in the reduction vessel. This takes place under overpressure of nitrogen in M *via* a tube of communication with L which has not been drawn in the figure. After the burette has been filled,

[1] From the Histological Laboratory of the University of Amsterdam. Director, Professor Dr. G. C. Heringa.

[2] No. 3, pp. 31–36, U. S. Government Printing Office, Washington, 1928.