ϵ_1 and B with ϵ_2 and also A with ϵ_2 and B with ϵ_1. The factor two must be removed. Using $\sigma = 10^{-7}$ cm. (this is within reason for such a large molecule) and $N = 6.83 \times 10^{18}$ molecules/cc. from the mean experimental pressure for the first 10 minutes, and substituting in equation (1) one gets

$$\frac{(2\pi)^{1/2}(6.83 \times 10^{18})^2(10^{-14})}{15!} \left(\frac{2 \times 8.3 \times 10^7 \times 571}{58}\right)^{1/2} (51.1)^{15} e^{-51.1}$$

or the rate of activation is 1.07×10^{20} molecules per cc. per second. Comparing this with the observed rate of decomposition which is 1.67×10^{15} molecules per cc. per second one finds that the maximum rate of activation is about 100,000 times larger than the observed rate of decomposition.

It is clear, that with what the writer believes to be a very conservative estimate of the complexity of the molecule azo-methane, here is another case of a uni-molecular reaction where activation by collision proves adequate to sustain an ample supply of active molecules.

[1] NATIONAL RESEARCH FELLOW.

[2] *Proc. Roy. Soc.*, **113**, 571, 1927.

[3] *J. Amer. Chem. Soc.*, **49**, 912, 1927.

[4] *Ibid.*, **49**, 28, 1927.

[5] This expression first appeared in a paper by B. Lewis and E. K. Rideal, *J. Amer. Chem. Soc.*, **48**, 2553, 1926.

[6] *Proc. Nat. Acad. Sci.*, **13**, 188, 1927.

ON X-RAY DIFFRACTION PATTERNS FROM LIQUIDS AND COLLOIDAL GELS

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Great interest is being displayed now in the interpretation of the X-ray diffraction patterns which are obtained from non-crystalline substances. When monochromatic X-rays, defined by pinholes, pass through liquids, gels, glasses, etc., the diffracion pattern is registered as one or more broad rings or haloes on the photographic film. There has been considerable controversy over the significance of these "amorphous" rings, but Zernicke and Prins[1] have recently deduced mathematically, with great success, that the broad rings are indicative of the natural distance of nearest approach of molecules in disordered thermal agitation, rather than of regularity of arrangement of atoms in molecules, chance lattice formation, crystal fragments, etc. Excellent new experi-

mental evidence has been obtained by Stewart and Morrow[2] on primary normal alcohols, which show two spacings for the liquids, one corresponding to the length and the other to the cross section (essentially constant) of the molecules, in every way analogous to the results with crystals. Raman and Sogan[3] have sought to obtain information concerning geometrical forms of molecules from the sharpness of the rings as a measure of homogeneity in X-ray scattering by comparison of the patterns of cyclohexane (sharp) and hexane (diffuse).

Most of the calculations of spacings have heretofore been made upon the basis of the Ehrenfest formula $a = \dfrac{7.72\,\lambda}{4\pi \sin \theta}$, $2\,\theta$ being the angle of the diffracted cone of rays. This formula was derived for the condition of regularity of spacings of atoms in molecules and has given results agreeing with spacings calculated from molecular weights and densities, assuming spheres, even for monoatomic liquid argon. However, recent developments should give weight to the classical Bragg equation $n\lambda = 2d \sin \theta$, which gives results about 0.81 as great as the Ehrenfest formula.

New practical significance in these "amorphous" patterns has been sought in the attempt to discover, for example, the structure of unstretched rubber. The fact that stretched rubber yields sharp, crystal-like, fiber patterns requires explanation in terms of original structure. Hauser and Rosbaud[4] have measured the spacings of the haloes for ordinary latex films as 14.88 A.U. (inner ring) and 6.05 A.U. (outer ring). They find also that metastyrol gives the same spacings. This is verified by Hünemörder[5] who shows also that for liquid styrol the outer ring appears in the same position but the inner ring observed in polymerized metastyrol is missing. Katz[6] has measured the haloes for the following pairs of substances, unpolymerized and polymerized: isoprene and rubber, styrol and metastyrol, dicyclopentadiene and cyclopentadiene-rubber, acrylic acid and polymerized acid, liquid and polymerized china wood oil. Upon the basis of eye measurement of diffraction ring diameters he comes to the conclusion that there is no change in spacings upon polymerization.

It seems of interest to present a few of the observations on X-ray patterns for amorphous substances made in the writers' laboratory. These tend to show that very important information of practical bearing can be obtained on rubber and its substitutes, nitrocellulose, gelatine, linseed oil, china wood oil, resins, varnishes, etc. In all cases the films have been photometered so that on the curves the exact centers of the broad bands are easily located. For unstretched rubber latex films the spacings calculated by the Ehrenfest formula from the two principal rings (second order faint rings appear in addition) are 6.03 and 14.76 A.U., in fair agreement with Hauser and Rosbaud. When, however, the rubber is very carefully purified by a process of fractional solution and evacuation

to constant weight, the spacings are 5.97 and 11.15 A.U., a profound change in the inner ring. Intermediate values up to 14.76 A.U. have been observed with solvent swelling.

With nitrocellulose of the same composition the following quantitative results are typical for the spacings of the inner and outer rings, respectively, calculated by the Bragg formula:

	FRESH	AGED (LIGHT)	AGED (HEAT)
Untreated, dry	{ 7.18 A.U.	{ 7.17 A.U.	{ 6.98 A.U.
	{ 4.02	{ 4.05	{ 3.92
Dry, residual solvent present	{ 9.30	{ 9.32	{ 7.86
	{ 4.47	{ 4.47	{ 4.31
Oil softener added	{ 7.34	{ . . .	{ . . .
	{ 4.31	{ 4.39	{ 4.39

The swelling or combination of molecules with solvent or oil has a much greater effect on the X-ray pattern than aging, even though the nitrocellulose film may become very brittle.

Contrary to the results of Katz, distinct though usually small differences in spacings are observed with china wood oil and linseed oil during polymerization and drying. The following remarkable results on china wood oil were obtained by careful measurement of the photometric curves; they are expressed as percentage change related to the spacings of the raw liquid oil calculated by the Bragg formula:

	INNER RING	OUTER RING
Raw liquid	8.5 A.U.	4.4 A.U.
Raw dry film (oxidation at room temperature)	+6%	+1%
Raw gel (polymerized by heat)	+3%	+2%
Prepared liquid	+12%	+16%
Prepared dry film	+13%	+ 6%

The prepared liquid in this case consisted of china wood oil heated with Venice turpentine and thinned with pure turpentine. The film dries with a crystalline finish which is, however, only a pseudo-crystalline, wrinkled skin. The increase in spacings (decrease in ring diameters) in every case including drying over those of the raw oil is remarkable. Combination with solvent molecules and polymerization are both definitely indicated. No indication has been found in these patterns of long spacings such as are obtained with solid carbon-chain compounds. It is possible that diffraction rings corresponding to these long spacings may be so close to the central direct-beam trace on the photographic films that they are not defined. This is particularly true where Mo-Kα rays have been used instead of rays from·a copper target.

Similar results have been obtained with cumar, resins, varnishes, etc. In all cases it is clear that the "amorphous" ring diagrams may yield very important theoretical and practical results in terms of fundamental space

array of molecules or aggregates acting as units, polymerization, the swelling of gels and changes during aging. X-ray science has reached the stage wherein it may analyze all matter in any form whatsoever.

[1] *Zeit. Physik,* **41,** 184 (1927).
[2] These Proceedings, **13,** 222 (1927).
[3] *Nature,* **119,** 601 (1927).
[4] *Kautschuk,* Jan., 1927, p. 17.
[5] *Ibid.,* Mar., 1927, p. 106.
[6] *Zeit. physik. Chem.,* **125,** 321 (1927).

THE EFFECT OF TUBERCLE BACILLI AND THE CHEMICAL FRACTIONS OBTAINED FROM ANALYSIS ON THE CELLS OF THE CONNECTIVE TISSUES IN RABBITS

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Under the auspices of the Research Committee of the National Tuberculosis Association, we have been making some of the biological tests of the proteid and phosphatid fractions which have been isolated from human tubercle bacilli. Two specimens of water-soluble proteids, 304 and 903, were received from Prof. Treat B. Johnson of Yale University and two phosphatid fractions, A-3 and A-4, from Dr. R. J. Anderson of the same laboratory. The effects of these chemical fractions are to be expressed in terms of the same phagocytic mononuclear cells as are involved in the infection itself.

In the study of infections, in general, increasing emphasis is being laid on the part played by the phagocytic mononuclear cells of the connective tissues. All the investigators who are employing the method of tissue culture find evidence of the transformation of fibroblasts and monocytes into macrophages, and the reverse, and hence tend toward the view that these mononuclear cells are of one strain and that any differences in their morphology and activity are due to environment.

In our work, with living tissues taken directly from the animal for supravital studies, we have found differences in the reaction of clasmatocytes and monocytes to tubercle bacilli, which seem to indicate a distinction of cellular response. In supravital studies, neutral red affords the advantage of a chemical indicator; its range in pH is from 6.8 to 8; toward the acid side it is a brilliant scarlet; its alkaline reaction is yellow. The optimum dilution of the dye, when it is to be used as a physiological indicator, is tested in normal blood by the scarlet reaction of the granules