

the solutions on which the rotations were determined. Table III summarizes the analytical results.

TABLE II

	Cholestenone	Testosterone propionate	Testosterone benzoate
Enol ethyl ethers			
Freshly prepd. material	83.5-85, clear 95	143-150	Soften 175, 181-192
Mixed with free ketone	69-70	103-133	Soften 130, 156-168
Recl. CHCl <sub>3</sub> from rotn.	70-81	...	185-189
Mixed with free ketone	80-81	...	186-190
Rotation M. p., °C.			
Initial	-102.3	-140	-42.5
Final	+87.7	+88	+143
Free initial ketone	+87	+88	+148

TABLE III

## FORMULAS AND ANALYSES

Enol ethyl ethers	Cholesterol	Testosterone propionate	Testosterone benzoate
Formulas	C <sub>27</sub> H <sub>48</sub> O	C <sub>21</sub> H <sub>36</sub> O <sub>3</sub>	C <sub>23</sub> H <sub>36</sub> O <sub>3</sub>
Carbon, %	{ Calcd. 84.46 Found 84.2	{ Calcd. 77.42 Found 76.89	{ Calcd. 80.00 ...
Hydrogen, %	{ Calcd. 11.65 Found 11.53	{ Calcd. 9.67 Found 10.12	{ Calcd. 8.57 ...
C <sub>2</sub> H <sub>5</sub> O, %	{ Calcd. 10.92 Found 9.77	{ Calcd. 12.09 ...	{ Calcd. 10.71 Found 10.25

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### THE QUANTITATIVE DETERMINATION OF AMINO ACIDS

Sir:

One of the methods frequently employed for the estimation of individual amino acids in protein hydrolysates involves the selective precipitation of the respective amino acids in the form of salts. It is the object of such methods to precipitate as much of the salt as possible, 100% isolation being the ultimate goal. Unfortunately, most of the salts that are precipitated selectively are not precipitated quantitatively. Such an incomplete precipitation may be used to advantage, however, in a newly developed analytical principle which permits a rather precise determination of individual amino acids. It depends upon the fact that the amount of an amino acid salt precipitated at equilibrium is a function of the concentration of its ions in solution.

In order to demonstrate this, let us assume that an acidic reagent, RH, forms, with an amino acid, A, the binary salt, AH·R. In many cases the so-called solubility product of the participating ions was found to be approximately a constant.

$$[\text{AH}^+] \times [\text{R}^-] = \text{const.} \quad (1)$$

Figure 1 illustrates an experiment in which in-

creasing amounts  $r'$ ,  $r''$ ,  $r'''$  of the reagent are added to several equal portions of a solution, each containing  $Y$  moles of amino acid. In each sample a precipitate is formed. Were it completely insoluble, the course of precipitation would follow the straight line OB. In reality, however, the precipitation follows a hyperbolic curve passing through the points  $C'$ ,  $C''$ ,  $C'''$ ,  $C''''$ .

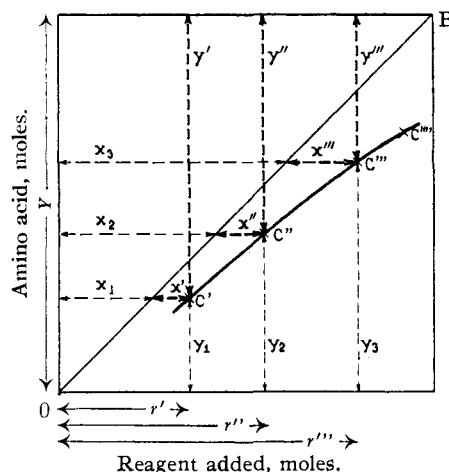


Fig. 1.—Determination of amino acids by means of the solubility product.

The precipitate obtained with an amount of reagent  $r'$  contains equivalent amounts  $x_1$  of the reagent, and  $y_1$  of the amino acid; the amounts  $x'$  of the reagent and  $y'$  of the amino acid remain in solution. Similarly, in a precipitation with an amount of reagent  $r''$  the amounts  $x''$  and  $y''$  remain in solution. From equation (1) it follows that

$$x' \times y' = x'' \times y'' = x''' \times y''' \quad (2)$$

Experimentally we have found the requirements of equation (2) to be fulfilled satisfactorily for the precipitation of proline by rhodanilic acid [M. Bergmann, *J. Biol. Chem.*, **110**, 471 (1935)], of glycine, alanine and leucine by dioxypyridic acid [M. Bergmann, *ibid.*, **122**, 569 (1938)], and of tyrosine by dioxanilic acid. In all cases where equation (2) is valid, the amount  $Y$  of an amino acid can be determined in a solution of unknown content. For this purpose equation (2) may be written in the following manner:

$$x'(Y - y_1) = x''(Y - y_2) = x'''(Y - y_3) \quad (3)$$

In equation (3) all values, with the exception of  $Y$ , may be determined experimentally.

In order to demonstrate the precision of such determinations, we report the following analyses:

	Present, mole	Found, mole
Glycine	0.0100	0.0103
L-Alanine	.00297	.00300
L-Leucine	.00255	.00260
L-Proline	.00420	.00435

The results obtained by the application of this

type of analysis to protein hydrolysates will be reported elsewhere.

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## NEW BOOKS

### **Fortschritte der Photographie.** (Progress in Photography.)

Edited by E. STENGER, Berlin-Charlottenburg, assisted by H. STAUDE, Berlin-Tempelhof. Vol. V. of "Ergebnisse der angewandten physikalischen Chemie." Akademische Verlagsgesellschaft m. b. H., Sternwartenstrasse 8, Leipzig, Germany, 1938. xiv + 415 pp. 78 figs. 16.5 × 24 cm. Price, RM. 33; bound, RM. 35.

Modern photography dates back to the introduction of the silver bromide-gelatin emulsion in the eighth decade of the last century. Since that time, there has been no basic change in the photosensitive material of the plate, film and paper—silver halides dispersed in gelatin. During the sixty years that the silver bromide-gelatin emulsion has been known, no substitute has been found which in any way approaches it in sensitivity to light, adaptability to varied purposes, and ability to reproduce tones satisfactorily.

The study of the photographic process by the methods of scientific research received its first important impetus in England in the hands of Hurter and Driffield in 1890, and Sheppard and Mees in the first decade of the present century. These investigators laid the foundations for the quantitative interpretation of the action of light on the plate and film. At the same time, the pioneer work on spectral sensitization was done in Germany, and extensive study of the development process was made in Germany and France. It was not until the years following 1918, however, that systematic research in Europe and the United States produced information which permitted clarification of the basic principles governing the action of light on the emulsion. These studies were made largely in the research laboratories of the photographic manufacturing concerns, particularly the Eastman Kodak Company in this country, the Agfa Company in Germany, and the British Photographic Research Association in England.

In Germany alone has the photographic process been the object of much research in the Universities. In reading the book under review, one is struck by the opportunities offered by photography as a subject for research in the Universities of this country. Even in those fields where the plate or film is used as an instrument for research on other subjects, many of the results are open to doubt because the investigator displayed lack of knowledge of the

capabilities and limitations of his tools. With the increasing use of photography as an instrument, there is growing need for courses of study in its principles. If these were associated with research on some of the infinity of unsolved problems, much of the misuse of photography in its applications to science and industry would eventually be avoided, and the results could not fail to be applied to an improvement of the product.

The photographic literature is singularly diluted by a large proportion of perfectly useless papers, written by people having no broad appreciation of the field, or no scientific training to guide their practical approach. It is very difficult for those not closely associated with scientific research in the subject to select the valuable material from that of doubtful basis. The book under review should provide a reliable guide for them. It is edited by Dr. Erich Stenger, head of the photographic and photochemical department of the Berlin Technische Hochschule, with particular assistance from Dr. H. Staude, who was trained at Dresden under Dr. Robert Luther, dean of German photographic research, and aided by a number of other competent co-workers. The book aims at surveying recent progress in the important fields of photographic research, and has succeeded singularly well. It is the most useful of the photographic textbooks which have appeared in recent years, considered from the point of view of those interested in the scientific aspects. It presupposes a moderate chemical and physical knowledge on the part of the reader. Its perusal will provide an excellent understanding of the state of knowledge of the subject up to the summer of 1937, for it covers not only the scientific and photographic publications, but the patent literature as well.

The first Chapter, compiled by W. Meidinger, treats of the photolysis of crystals of the alkali and silver halides, and of the latter in the presence of gelatin, as in the photographic emulsion, and closes with a survey of theories of the latent image. Progress in the technique of making photographic emulsions is handled by H. Socher, while H. Staude deals with the nature of developers and the theories of their action, and the problems of hypersensitizing, desensitizing, fixing, washing and drying. There is a very comprehensive survey by K. Meyer of recent research in photographic sensitizing dyes, in which field so much progress has been made in the past ten years, and which has been largely responsible for the recent outstanding ad-