

Although no experiments were performed to demonstrate the character of this exchange, the authors feel that it must certainly be heterogeneous, probably through a mechanism involving the simultaneous transfer of hydrogens in hydrogen bonds within groups of $N_2H_4-ND_3$ molecules. This explanation must not be too hastily accepted, however, because the absence of any pronounced super-conductivity of the hydrogen ion in hydrazine systems,² and the lack of tendency for ammonia and hydrazine to form mixed crystals³ argue against such a mechanism. The effect of small amounts of water on the formation of mixed crystals³ suggests that the observed exchange may have been due to water catalysis, although considerable care was taken to ensure the absence of water in the above experiments. Further experiments are desirable before more definite conclusions concerning the mechanism are attempted.

These observations were made during the

(2) P. Walden and H. Hilgert, *Z. physik. Chem.*, **A165**, 241 (1933).

(3) F. Friedrichs, *Z. anorg. allgem. Chem.*, **127**, 221 (1923).

course of a study of exchange reactions with deuterium which was supported by a grant from the Carnegie Institution of Washington.

DEPARTMENT OF CHEMISTRY

STANFORD UNIVERSITY RECEIVED FEBRUARY 18, 1938
STANFORD UNIVERSITY, CALIF.

Preparation of Barium Chlorite and Solubility of Silver Chlorite

By W. V. SMITH, K. S. PITZER AND W. M. LATIMER

Our attention has been called to the omission of two references which might properly have been included in our paper on silver chlorite.¹

Bruni and Levi² prepared pure barium chlorite and Levi³ reported values for the solubility of silver chlorite, which are in close agreement with our value at 25°.

(1) Smith, Pitzer and Latimer, *THIS JOURNAL*, **59**, 2640 (1937).

(2) Bruni and Levi, *Gazz. chim. ital.*, **45**, II, 169 (1915).

(3) Levi, *ibid.*, **53**, 525 (1923).

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF CALIFORNIA

BERKELEY, CALIF.

RECEIVED FEBRUARY 10, 1938

COMMUNICATIONS TO THE EDITOR

BENTONITE AS AN ADSORBENT IN THE PURIFICATION OF INVERTASE¹

Sir:

In the course of investigations on invertase we have developed, in the preparation of this enzyme, certain procedures which may be of value not only in connection with invertase but also in regard to other problems in biochemistry. Bentonite, a colloidal clay already well-known commercially, has been found to be an excellent adsorbent for invertase. Bentonite can be used, without preliminary treatment, in the undiluted autolysates from yeast. Both adsorption and elution can be carried out under conditions more favorable for the stability of invertase than those generally used with other clays. The optimal pH for adsorption is 4.1-4.3 while an acetate or phosphate solution of pH 5.3 or greater produces satisfactory elution. The amount of bentonite required for complete adsorption is relatively small and the five different samples of bentonite so far investigated have all

proved excellent adsorbents for invertase, yielding preparations of similar time values.

Invertase solutions with time values of 0.20-0.27 minute as expressed in the customary units² have been obtained by dialysis following a single bentonite treatment of various types of autolysates from bakers' yeast. Similar solutions have been prepared from unenriched brewers' yeast by a slight modification involving fractional adsorption on bentonite with 10-20% adsorption and loss in the first fraction. From enriched brewers' yeast (*i. e.*, yeast which has been allowed to ferment a sucrose solution) preparations have been obtained with time values of 0.15-0.18 minute. The invertase solutions thus prepared do not lose activity during dialysis or subsequent storage over a period of several months in the refrigerator.

The following describes a typical procedure. A fractional autolysate of bakers' yeast was prepared by treating 430 g. of yeast (time value, 34.3) at 30° with 43 cc. of ether, adding 43 cc. of toluene,

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) C. Oppenheimer, "Die Fermente und ihre Wirkungen," fifth edition, 1928, Vol. III, pp. 776-774.

430 cc. of water and 3.2 g. of sodium carbonate after the yeast had liquefied, and four hours after the addition of the ether filtering through filtercel with 80 g. of filtercel added to the mixture before filtration. The filtrate containing 7.7% of the invertase was discarded. To the residue was added 43 cc. of toluene and 430 cc. of water and autolysis was continued for five days at 20°. After filtration this autolysate was dialyzed immediately in Visking sausage casings. To a mixture of 80 cc. of 0.5% bentonite suspension and 27 cc. of a solution of pH 4.1 prepared by mixing 1 N acetic acid and 1 N sodium hydroxide, was added 265 cc. of this dialyzed autolysate which contained 7.53 units² of invertase per 100 cc. and had a time value of 2.24 minutes. The bentonite was separated by centrifuging, washed by stirring with 200 cc. of distilled water and again centrifuged. Ninety-two per cent. of the invertase was adsorbed. Elution was effected by shaking gently with three portions, 40, 30, and 20 cc., respectively, of an acetate solution of pH 5.7 prepared from mixtures of 0.1 N acetic acid and 0.1 N sodium hydroxide solutions. The three extracts represented 57.8, 13.2, and 3.6% of the invertase in the original autolysate and after dialysis had time values of 0.216, 0.215, and 0.278 minute and contained 10.5, 2.26, and 0.64 units, respectively.

NATIONAL INSTITUTE OF HEALTH
WASHINGTON, D. C.

MILDRED ADAMS
C. S. HUDSON

RECEIVED MARCH 17, 1938

ZINC SULFIDE AS AN ADSORBENT IN THE PURIFICATION OF INVERTASE¹

Sir:

In the preceding communication from this Laboratory, by Mildred Adams and C. S. Hudson, was described a method for purifying invertase solutions by adsorption on and subsequent elution from the colloidal clay "bentonite." A second excellent adsorbent has been found in zinc sulfide when precipitated directly in a solution of invertase under certain conditions; the resulting eluted and dialyzed enzyme solutions are of the same purity and stability as those obtained with bentonite. Adsorption of the invertase is carried out in an acetate buffer at about pH 4.4, and elution is effected with an ammonium phosphate buffer of pH 6.1; the solutions contain 1% sodium chloride to prevent the zinc sulfide from becoming colloidal. A typical preparation is recorded.

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

A bakers' yeast of relatively high invertase content was allowed to autolyze fractionally in the manner described in the preceding communication, and the first fraction discarded. The main autolysate was dialyzed in Visking sausage casings, and then represented 60% of the original invertase in the yeast. To 1940 cc. of this solution, containing 110.2 invertase units, was added 1940 cc. of water, 43.5 cc. of a 10% zinc acetate solution, 160 cc. of a buffer solution of pH 4.5 (made by mixing 2 N sodium hydroxide and 2 N acetic acid), and 450 cc. of a 10% sodium chloride solution. Hydrogen sulfide was bubbled through the solution, and the zinc sulfide separated by centrifuging; the supernatant liquid had a pH of 4.4, and contained only 6% of the invertase. The zinc sulfide was washed by shaking with 1500 cc. of a 1% sodium chloride solution and again centrifuged. The invertase was eluted by shaking with 400, 200, and 100 cc. portions, respectively, of a solution containing 1% sodium chloride and 1% mono- and dibasic ammonium phosphates such that it had a pH of 6.1. The combined extracts, after dialysis, contained 77.6 invertase units, and had a time value of 0.20 minute.

Zinc sulfide has been used in similar fashion in purifying the dialyzed autolysates of brewers' yeast of relatively low invertase content. With these solutions a fractional adsorption with zinc sulfide is necessary, 15-25% of the invertase being discarded in the first portion; adsorption and elution as described then produced invertase solutions of time value 0.21-0.22 minute.

These communications represent only a portion of the studies we have been making on invertase, but the use of the adsorbents may be of sufficient interest in the general field of biochemical purifications to warrant their earlier publication.

NATIONAL INSTITUTE OF HEALTH NELSON K. RICHTMYER
WASHINGTON, D. C. C. S. HUDSON

RECEIVED MARCH 17, 1938

CRYSTALLINE VITAMIN B₆

Sir:

Vitamin B₆ is that part of the vitamin B₂ complex [*Nature*, **133**, 498 (1934); *Biochem. J.*, **29**, 741 (1935)] responsible for cure of the "rat acrodynia" observed in young rats fed a vitamin B free diet supplemented with vitamin B₁ and riboflavin.

It has been shown [*Biochem. J.*, **30**, 304 (1936)] that vitamin B₆ can be adsorbed by fuller's earth from acid solution, eluted with Ba(OH)₂ and pre-

precipitated by phosphotungstic acid. In continuing this research, Peters' eluate [*Biochem. J.*, **27**, 225 (1933)] was used as a potent concentrate of B₆, in batches usually containing 10 to 50 thousand B₆ units. As the first step toward purification, vitamin B₆ was adsorbed on fuller's earth at pH 1.4, using 1 g. of earth to 10 units of B₆. Adsorption was repeated three times. The combined adsorbates were washed by grinding in a mortar with 2 ml. of 0.1 N hydrochloric acid per gram of fuller's earth used. The adsorbate was then eluted twice with 0.1 N barium hydroxide (12 ml. per gram of earth) by grinding in a mortar and letting stand overnight in the refrigerator. The filtrates were precipitated immediately with sulfuric acid and filtered. This filtrate was adjusted to pH 6.8 to 7 with 10% sodium hydroxide and evaporated to dryness. The residue was extracted five times with 95% ethyl alcohol, using 100 ml. each time, and the filtrate was evaporated to 50 ml. and treated with 450 ml. of ethyl acetate. After standing overnight in the refrigerator, the precipitate was filtered off and the filtrate evaporated to dryness. The residue was then taken up in 200 ml. of water, filtered, and the filtrate subsequently precipitated (1) with platinum chloride (activity remaining in the filtrate), then (2) with phosphotungstic acid (20% in 1 N sulfuric acid). The phosphotungstate was decomposed with barium hydroxide. The combined filtrates were precipitated with sulfuric acid, filtered, and the filtrate (neutralized with sodium hydroxide) evaporated to dryness. The residue was extracted several times with 95% ethyl alcohol to make 100 ml., filtered, and the extract precipitated with 400 ml. of ether and let stand overnight in the refrigerator. The ether was then filtered, evaporated, and the residue taken up in water. Activity of this concentrate corresponded to 20 to 100 γ of solids for one "rat day dose," with a total yield of 10 to 30% of the original strength. Repeated precipitation with phosphotungstic acid followed by regeneration gave aqueous solutions from which crystalline preparations were obtained having an activity of 5 γ per "rat day dose." Daily administration of 15 γ cured rat acrodynia in two weeks, of 5 to 10 γ in three to four weeks. Crystals were colorless rods of varying size, with rounded ends. They seemed to have a tendency to coalesce in rosetts or fan-shaped formations.

The curative influence of these crystalline preparations was confined to disappearance of the

specific skin symptoms. Growth was not promoted. Even the skin effect was not regularly attained unless a further supplement, corresponding to the so-called "filtrate factor" [*J. Biol. Chem.*, **114**, 109 (1936)], was added.

BABIES AND CHILDRENS HOSPITAL AND PAUL GYÖRGY
DEPARTMENT OF PEDIATRICS OF
WESTERN RESERVE UNIVERSITY
SCHOOL OF MEDICINE
CLEVELAND, OHIO

RECEIVED FEBRUARY 21, 1938

THE PRODUCTION OF AN ANTIRACHITIC PROVITAMIN FROM CHOLESTEROL

Sir:

It has already been reported [F. C. Koch, M. E. Koch and Ragins, *J. Biol. Chem.*, **85**, 141 (1929); Waddell, *ibid.*, **105**, 711 (1934); Hathaway and Lobb, *ibid.*, **113**, 105 (1936); Haman and Steenbock, *ibid.*, **114**, 505 (1936)] that the natural antirachitic provitamin D may be related to cholesterol rather than to ergosterol, and Windaus, Lettre and Schenck [*Ann.*, **520**, 98 (1935)] actually prepared from cholesterol by a number of difficult steps 7-dehydrocholesterol which upon irradiation with ultraviolet light acquired strong antirachitic properties.

If the precursor of the animal antirachitic provitamin is cholesterol, then its formation in the body may result from the partial dehydrogenation of the latter under the influence of dehydrogenating enzymes or under that of light in the presence of hydrogen acceptors. Some time ago we decided to test this view chemically by allowing cholesterol acetate to react with equimolecular proportions of hydrogen acceptors in the presence or absence of dehydrogenating catalysts and of light.

When cholesterol acetate, spectroscopically free from the antirachitic provitamin, was allowed to react with benzoquinone in a sealed tube at 120–130° for about two hours and the product subsequently freed from quinhydrone, unconverted quinone, etc., it was found to contain substantial quantities of 7-dehydrocholesterol. The crude mixture was then irradiated in pure ethyl ether with a quartz mercury lamp for four hours and the resulting product assayed biologically for us by Professors Robert S. Harris and J. W. M. Bunker of this Institute. They reported an antirachitic potency of considerably more than 6500 U. S. P. vitamin D units per gram, whereas a blank with our purified cholesterol acetate had a

potency of only about 2 U. S. P. vitamin D units per gram.

Some additional preliminary experiments are described in Table I. The 7-dehydrocholesterol was determined spectroscopically and the percentage conversion calculated from the results obtained. The absorption spectrum of our purified product showed two prominent absorption bands the peaks of which were at 269 and 281 $m\mu$, identical with those of 7-dehydrocholesterol and of ergosterol.

TABLE I
THE PARTIAL DEHYDROGENATION OF CHOLESTEROL
ACETATE

Dehydrogenating agent	$E_1^1\%$ at 269 $m\mu$	Conversion, %
Methylene blue + light (25°, 30 days)	6.5	2.3 ^a
Benzoquinone + Pd + light (25°, 30 days)	2.5	0.9
Benzoquinone + Pd (120–130°, 2 hrs.)	3.0	1.1
Benzoquinone (120–130°, 2 hrs.)	5.0	1.8
Benzoquinone (120–130°, 6 hrs.)	56.0	20.0
Chloranil (120–130°, 2 hrs.)	22.0	7.8(?)
Succinodihydrogenase (beef heart)	0.42	0.15

^a This gives the percentage of a purified material which was approximately one-tenth of the original crude product.

In the case of methylene blue the dehydrogenation was carried out in benzene solution which was rapidly stirred while it was exposed to light from a 250-watt lamp for thirty days. A similar experiment in benzene was performed without stirring using benzoquinone and palladium black. The succinodihydrogenase was prepared from beef heart in accordance with the method of Thunberg [*Biochem. Z.*, **285**, 48 (1933)].

This work is being continued actively in this Laboratory with cholesterol, stigmaterol, and sitosterol, using various hydrogen acceptors and dehydrogenating catalysts under diversified conditions, and a more complete report will be published in the future.

CONTRIBUTION NO. 166 FROM THE
RES. LAB. OF ORG. CHEM.
MASSACHUSETTS INST. OF TECH.
CAMBRIDGE, MASS.

NICHOLAS A. MILAS
ROBERT HEGGIE

RECEIVED MARCH 21, 1938

RESTRICTED ROTATION IN ETHYL ALCOHOL, ACETONE AND ISOPROPYL ALCOHOL

Sir:

The entropies given in Table I, column 2, were calculated from molecular data, assuming free rotation for the perfect gases at one atmosphere.¹

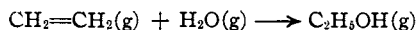
(1) Details will appear in a forthcoming publication by the authors.

TABLE I

	Temp., °K.	S Free rot.	S 3rd law	S Rest. rot.	Potentials
C ₂ H ₅ OH	351.6	73.1	69.7	69.7	3000, 9000
i-C ₃ H ₇ OH	355.4	82.6	78.3	78.3	3400, 3400 6000
(CH ₃) ₂ CO	329.2	73.3	72.6	72.6	1250, 1250

It is doubtful whether an error of more than 0.3 e. u. could result from the choice of the vibration frequencies, including those similar to the $2\nu_\alpha M$ vibrations in ethane. Column 3 of Table I lists the experimental third law entropies of the gases at their boiling points from thermal data down to 16°K. (Kelley). Column 4 gives the values of the entropy, calculated using the empirical restricting potentials in column 5 and the method of Pitzer.

Table II, column 2, gives ΔS values for the reaction



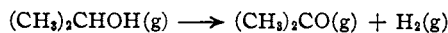
calculated from remarkably good equilibrium data²⁻⁴ using ΔH values from Rossini's accurate data on the heat of formation of ethylene, ethyl alcohol, and water.

TABLE II

Temp., °K.	ΔS Equilib. data	ΔS 3rd law	ΔS Free rot.	ΔS Rest. rot.
498	{ -31.13 -31.29	-31.27	-28.58	-31.27
548	-31.08	-31.16	-28.62	-31.16
593	-30.86	-31.13	-28.75	-31.13

The equilibrium data are probably reliable to about 5% in K , corresponding to 0.1 e. u. Column 3 gives values of ΔS calculated from the accurate experimental third law entropy data (see also Egan and Kemp), and heat capacities from the Raman frequencies (using the above restricting potentials for ethyl alcohol) to extrapolate above the boiling point. Columns 4 and 5 give, respectively, ΔS values from molecular data assuming free and restricted rotations with the above potentials.

Table III gives a similar comparison for the equilibrium



with the equilibrium data probably accurate to 7% or 0.15 e. u.

The results leave little doubt that neglect of potentials restricting internal rotations is the cause of the discrepancies in Table I, between values cal-

(2) Stanley, Youell and Dymock, *J. Soc. Chem. Ind.*, **53**, 105T (1934).

(3) Applebey, Glass and Horsley, *ibid.*, **56**, 279T (1937).

(4) Dodge and Bliss, *Ind. Eng. Chem.*, **29**, 19 (1937).

TABLE III

Temp., °K.	ΔS^\ddagger Equilib. data	ΔS 3rd law	ΔS Free rot.	ΔS Rest. rot.
457	27.44	28.39	25.34	28.39
475	27.56	28.37	25.40	28.37
491	27.73	28.35	25.47	28.35

$$\Delta H^\circ_{305} = 13,400 \text{ cal.}^\ddagger$$

culated using free rotation and the third law entropies, since the equilibrium data show the latter to be correct.

Kemp and Pitzer have demonstrated this for ethane and courageously predicted the discrepancies in other cases. *We agree with these authors that there is no reason to doubt the practical applicability of the Third Law.*

(5) Parks and Kelley, *J. Phys. Chem.*, **32**, 734 (1928).

(6) We wish to thank Professor G. B. Kistiakowsky for advance notice on this recently published value.

SCHOOL OF CHEMISTRY AND PHYSICS S. C. SCHUMANN
THE PENNSYLVANIA STATE COLLEGE J. G. ASTON
STATE COLLEGE, PENNSYLVANIA

RECEIVED FEBRUARY 23, 1938

HYDROGEN FLUORIDE AS A CONDENSING AGENT

Sir:

We have found that anhydrous hydrogen fluoride will promote the reaction between either olefins and benzene or aliphatic halides and benzene. The following reactions have been accomplished and others are in progress. We are continuing the work with other aromatic compounds.

All reactions were run in the liquid phase at 0° with stirring. The time required varied from two to twenty-four hours. Varying amounts of hydrogen fluoride were used without changing the results.

1. From the reaction of propylene and benzene two products were isolated. The one present in larger amount boiled at 149–150° at 730 mm., and gave an acetamino derivative that melted at 105–105.5°. Isopropylbenzene boils at 152° at 758 mm. and its acetamino derivative melts at 106°.

2. Isopropyl chloride gave indications of a reaction. Some material that boiled above 150° was produced. This formed an acetamino derivative, m. p. 166°, which may be the derivative of diisopropylbenzene.

3. Isobutylene formed two products. One was a liquid, b. p. 166.5–168° at 728 mm., the other was a crystalline solid, m. p. 77–78°. *t*-Butylbenzene boils at 168–170° at 760 mm. and di-*t*-butylbenzene melts at 78°.

4. *t*-Butyl chloride gave two products; one a liquid, b. p. 167–170°, and the other a solid, m. p. 77°. A mixed melting point of this solid and that formed in (3) was 76.5–77.5°. An acetamino derivative of the liquid melted at 169–170°. A dinitro derivative of the solid melted at 188°. The known acetamino derivative of *t*-butylbenzene melts at 170° and the dinitro derivative of di-*t*-butylbenzene melts at 191°.

5. Trimethylethylene formed two products, b. p. 188° and 262–265°.

6. *t*-Amyl chloride formed the same two products that were found in the reaction of trimethylethylene.

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

J. H. SIMONS
S. ARCHER

RECEIVED MARCH 8, 1938

THE PREPARATION AND PHOTOCHEMICAL OXIDATION OF 2,4-CHOLESTADIENE

Sir:

A further study of the method of preparation of 2,4-cholestadiene [H. E. Staveley and W. Bergmann, *J. Org. Chem.*, **1**, 575 (1937)] indicates that for consistent results it is desirable to use alumina which has been freshly reactivated by heating in a shallow pan at 200° for four hours. Activated Alumina, Grade A, 40 to 80 mesh (Aluminum Ore Co., East St. Louis, Ill.) is suitable. It is convenient to carry out the reaction in a small Pyrex retort. The preliminary heating should be continued for at least thirty minutes beyond the time when the droplets refluxing from the sides fail to crystallize when cooled locally by a jet of compressed air. Subsequent distillation yields 60 to 70% of a product having a specific rotation +90–100°. Distillation at higher temperatures (higher pressures) than previously recommended leads to the formation of cholesterol, m. p. 79.5–80°, $[\alpha]^{20D} -51.4^\circ$ in ether.

The isolation and purification of the 2,4-cholestadiene has been achieved by systematic fractional recrystallization from small amounts of ether. This is carried out in centrifugal filtration tubes [E. L. Skau, *J. Phys. Chem.*, **33**, 951 (1929); E. L. Skau and L. F. Rowe, *Ind. Eng. Chem., Anal. Ed.*, **3**, 147 (1931)] the yields being kept high by centrifuging at –78°. By this means a pure product is obtained, m. p. 68.5°, $[\alpha]^{25D} + 168.5^\circ$ in ether (30% yield from cholesterol). Comparison of the absorption spectrum and spe-

cific rotation of this product with those of the sample previously reported indicates quite definitely that the latter contained among other impurities a considerable amount of cholesterol.

Like ergosterol [A. Windaus and J. Brunken, *Ann.*, **460**, 227 (1928)] 2,4-cholestadiene in alcoholic solution adds oxygen in the presence of eosin and light to form a stable crystalline peroxide, m. p. 118.5–120.5°, $[\alpha]^{23D} + 52.8^\circ$ in chloroform.

Anal. Calcd. for $C_{27}H_{44}O_2$: C, 80.93; H, 11.08. Found: C, 80.72; H, 11.15.

A further study of these compounds is in progress.

This investigation is being aided by a grant from the International Cancer Research Foundation.

STERLING CHEMISTRY LABORATORY EVALD L. SKAU
YALE UNIVERSITY WERNER BERGMANN
NEW HAVEN, CONN.

RECEIVED MARCH 21, 1938

NEW BOOKS

The Carbon Compounds. A Textbook of Organic Chemistry. By C. W. PORTER, Professor of Chemistry in the University of California. Third revised edition. Ginn and Company, 15 Ashburton Place, Boston, Mass., 1938. viii + 495 pp. 16 × 24 cm. Price, \$4.00.

The earlier editions of this well-known book have been reviewed [Whitmore, *THIS JOURNAL*, **49**, 1391 (1927); **53**, 3195 (1931)].

"This book constitutes an outline of an elementary course in organic chemistry. Its scope is limited to fundamental principles and general reactions. The publishers have permitted frequent revisions and this policy has made it possible to keep the book in step with recent advances in the field of chemistry."

The present edition includes a new chapter on "Conjugation and Resonance" and a new chapter on "Optical Isomerism."

HENRY GILMAN

La Synthèse Totale en Chimie Organique. Mémoires de MM. Wöhler, Gerhardt, M. Berthelot, Le Bel, Van't Hoff, Jungfleisch, Ladenburg, Pasteur. (Organic Synthesis from the Elements.) Preface and Commentaries by MARCEL DELÉPINE. (Classiques de la Découverte Scientifique.) Gauthier-Villars, Éditeur, 55 Quai des Grands-Augustins, Paris 6, France, 1937. viii + 145 pp. 13.5 × 19 cm. Price, 21 francs.

The continuity of the present book depends so much upon the Commentaries of Professor Delépine that it seems proper to regard the work as his, a narrative history of the idea and of the fact of the synthesis of organic compounds from the elements, well documented and illustrated with quotations, often very long ones, from the original sources. While the editor-author agrees that many other illustrations might be found for his purpose, the principal points around which he has woven the narrative are as follows: the synthesis of urea by Wöhler and earlier investigations, the discovery of urea by Fourcroy and Vauquelin, the examination of the urine by Rouelle and by Bourdelin, some ideas before Berthelot on the synthesis of organic compounds, Gerhardt's earlier and later opinions, Berthelot's discussion in *La Chimie Organique fondée sur la synthèse*, his synthesis of stearin, of formic

acid, of acetylene, of ethylene, of alcohol, and of benzene structure theory (briefly), Van't Hoff on the formulas of structures in space, Le Bel on the relations which exist between the atomic formulas of organic substances and the rotatory powers of their solutions, Jungfleisch's synthesis of *d*- and *l*-tartaric acid from ethylene, Ladenburg's synthesis of coniine, asymmetric decomposition and total asymmetric synthesis. The result is an interesting and coherent account, a cross-section of the history of organic chemistry, which is all the more valuable because no adequate history of organic chemistry as a whole exists at present. The book is illustrated with portraits of Wöhler, Berthelot, Van't Hoff, Le Bel, Jungfleisch, Ladenburg, and Pasteur.

TENNEY L. DAVIS

Katalytische Umsetzungen in homogenen und enzymatischen Systemen. (Catalytic Reactions in Homogeneous and Enzymatic Systems.) By W. FRANKENBURGER, Ludwigshafen/Rhein. Akademische Verlagsgesellschaft m. b. H., Sternwartenstrasse 8, Leipzig C 1, Germany, 1937. xi + 444 pp. 22 figs. 15.5 × 24 cm. Price, RM. 34.80; bound, RM. 36.

This book, by one who contributed much to the modern ideas on catalysis, is a comprehensive survey of homogeneously and microheterogeneously catalyzed reactions.

It is somewhat disappointing that Dr. Frankenburger, who is an expert on heterogeneous catalysis, has not included heterogeneous reactions in the present volume; nevertheless the work covers a wide field. After a brief and rather non-mathematical introduction reviewing the general theories of reaction rates in elementary and complex reactions, the author discusses catalysis in gas reactions primarily from the point of view of reaction chain mechanism. Several typical reactions are dealt with in detail and the results of their kinetic analysis are presented clearly and yet not dogmatically. The next, and by far the longest, section deals with homogeneous catalysis in liquid mixtures. It is primarily a discussion of acid-base catalysis and of catalysis in oxidation reactions. One misses in the chapter on acid-base catalysis a unified statement of the general acid-base theory and yet its