The Melting Point Diagram for the System *meso–dl-* **Diethyl Glycol.**—Known mixtures of pure *dl* and *meso* glycols sealed in small melting point tubes were heated slowly under constant agitation in a water-bath, the temperature of which was raised at the rate of 1° per five minutes. The temperatures at which the last particle of solid disappeared were recorded as the melting points and are plotted in Fig. 1. The composition of the eutectic mixture is 21.5% *meso-* and 78.5% *dl*-glycol and that of the glycol mixture (m. p. 50.4°) obtained from the hydrogenation of divinyl glycol 52% *meso* and 48% *dl*.

The divinyl glycol separated from the glycol mixture formed during the reduction of a mixture of acrolein and crotonaldehyde according to the method of Lespieau and Weimann[2] gave the same mixture of diethyl glycols as that from acrolein alone.

It may therefore be concluded that the pinacolic reduction of acrolein gives equal quantities of *meso-* and *dl-* divinyl glycol.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA AT LOS ANGELES
LOS ANGELES, CALIFORNIA   RECEIVED FEBRUARY 8, 1943

COMMUNICATIONS TO THE EDITOR

THE THERMODYNAMICS OF STYRENE (PHENYL-ETHYLENE), INCLUDING EQUILIBRIUM OF FORMATION FROM ETHYLBENZENE

Sir:

We have measured the heat capacity of styrene from 15 to 300°K., the heat of fusion, and the vapor pressure. The latter is represented between 0 and 60° by the equation

$$\log_{10} p_{mm.\ Hg} = -2604.67 T^{-1} - 2.57692 \log_{10} T + 15.90485$$

The calculation of the entropy is summarized in Table I.

TABLE I
ENTROPY OF STYRENE

0–15°, 2 × $D(123/T)$	0.56
15–242.47°, solid	36.82
Fusion, 2617/242.47	10.79
242.47–298.16°, liquid	8.61
Liquid at 298.16°	56.78 ± 0.3 cal./deg. mole
Vaporization, 10390/298.16	34.85
Compression, $R \ln 6.19/760$	−9.56
Ideal gas at 1 atm.	82.07 cal./deg. mole

Since the reaction forming styrene from ethylbenzene is of considerable interest, we have calculated the equilibrium constant at various temperatures by thermodynamic methods. Measurements of the vapor pressure of ethylbenzene from 0 to 60° lead to the equation

$$\log_{10} p_{mm.\ Hg} = -2959.08 T^{-1} - 5.8 \log_{10} T + 25.25883$$

and hence to a heat of vaporization of 10,100 cal./mole at 298.16°K. Combining this value with the observed pressure, 9.58 mm., and with the entropy of liquid ethylbenzene[1] we find for S^0_{298} 86.39 cal./deg. mole in the gas.

(1) Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1547 (1930).

The heat of the reaction

$$C_6H_5CH_2CH_3 = C_6H_5CH=CH_2 + H_2$$

is calculable from the heats of hydrogenation of styrene and ethylbenzene.[2] Making reasonable assumptions regarding ΔC_p, we find for the temperature range 381–1000°K.

$$\log_{10} K = -5657.9 T^{-1} - 6.3779 - 0.0008804 T + 4.3687 \log_{10} T$$

Values of the equilibrium constants calculated from this equation are tabulated in Table II.

TABLE II
DEHYDROGENATION OF ETHYLBENZENE TO FORM STYRENE

T, °K.	$-\log_{10} K$
381	10.26
400	9.48
500	6.30
600	4.15
800	1.41
1000	−0.27
(1500)	(−2.52)

Available data on the pyrolysis of ethylbenzene indicate that near-equilibrium yields were obtained at 425–550°,[3] but not at higher temperatures[4] where, however, the situation is obscured by numerous side reactions.

The details of the calorimetric work will be

(2) Dolliver, Gresham, Kistiakowsky and Vaughan, *ibid.*, **59**, 831 (1937).

(3) Sergienko, *Compt. rend. acad. Sci.* (U. R. S. S.), **26**, 69–72 (1940); Oblad, Marschner and Hurd, THIS JOURNAL, **62**, 2066 (1940).

(4) Dobryanskiĭ, Uchenyi, Zapiski, Leningrad, Gosudarst. Univ. im. A. S. Bubnova, Ser. Khem. Nauk I, No. 1, 105 (1935); Dobryanskiĭ, *et al.*, Trans. Exptl. Research Lab. "Khimgas," Materials on Cracking and Chem. Treatment of Cracking Products (U. S. S. R.), **3**, 1 (1936); Zal'kind and Bulavskiĭ, *Plasticheskie Massui*, No. 3, 9 (1935).

presented later, together with a discussion of the molecular structure.

DEPARTMENT OF CHEMISTRY   LESTER GUTTMAN
UNIVERSITY OF CALIFORNIA   EDGAR F. WESTRUM, JR.
BERKELEY, CALIFORNIA   KENNETH S. PITZER
            RECEIVED OCTOBER 19, 1942

AN AMYLASE INHIBITOR FROM CERTAIN CEREALS

Sir:

In the course of an investigation of the action of salivary amylase on native wheat starch granules, it was observed that starch degradation did not occur when the wheat berry was crushed in a solution of human saliva. Degradation was rapid when starch prepared from similar grain was thus treated, but it again was inhibited by adding to it the wash liquid obtained during starch extraction.

Further studies indicated that wheat grain contains a water-soluble, protein-like substance which has a powerful inhibitory action on salivary, pancreatic, and most bacterial amylases. The substance inhibits the action of these enzymes both on gelatinized and native (raw) starch. No inhibition was observed with two commercial amylase preparations, supposedly of bacterial origin, nor with fungal nor cereal malt amylases. The sensitive amylases varied in their response; under comparable conditions equal amounts of the inhibitor gave reductions in starch dextrinization rates of 82% for salivary amylase, 48% for bacterial amylase, and 23% for pancreatic amylase.

The inhibiting substance is soluble in water and in dilute salt and dilute ethanol solutions but insoluble in petroleum ether. High levels of ammonium sulfate or of ethanol give precipitates that are active when redissolved in water. The substance is retained by a cellophane dialysis membrane. In water solution it is quite thermostable, being little affected by temperatures up to 90°. However, autoclaving for thirty minutes at 15 lb. pressure causes complete loss of inhibiting properties.

Reaction of the inhibitor with the amylase is reversible; differential alcohol solubilities have been utilized to separate a combination of the two into active inhibitor and active amylase.

The inhibitor was found in all samples of wheat and rye tested and one of similar properties in certain of the sorghums. Amylase inhibitors could not be detected in barley, oats, maize, rice, or most of the sorghums.

The inefficiency of human saliva as a hydro-lytic agent for digestion of the starch of wheat or rye or of their flours may be of pronounced physiological significance. As far as starch is concerned, the recognized high nutritive value and digestibility of these cereals must be attributed to actions in regions of the digestive tract other than the mouth. The finding likewise has industrial significance, since bacterial amylases may be used as "pre-malting" agents in the current expansion of alcohol production from grain. Indications are that at least certain bacterial amylase preparations, while entirely satisfactory for pre-malting corn, would not be as applicable in the liquefaction of unautoclaved wheat mashes.

Experimental data relative to the above discussion are being prepared for publication and work in progress is designed to provide additional information relative to the nature and mode of action of the inhibiting substance.

DEPARTMENT OF AGRICULTURAL CHEMISTRY
UNIVERSITY OF NEBRASKA   ERIC KNEEN
LINCOLN, NEBRASKA   R. M. SANDSTEDT
            RECEIVED MAY 10, 1943

STEROLS. CLIV. SAPOGENINS. LXVI. THE SAPOGENIN OF *TRIGONELLA FOENUM-GRAECUM*

Sir:

In the course of our plant studies during the past year we have found two hundred new sources for steroidal sapogenins. Among the plants investigated was *Foenugreek* seed, *Trigonella Foenum-Graecum*. Recently, Soliman and Mustafa [*Nature*, **151**, 196 (1943)] have reported that the sapogenin fraction from this plant contains an unknown sapogenin, m. p. 198°, of the composition $C_{27}H_{42}O_3$, having one free hydroxyl group and two inert oxygen atoms. These authors state the sapogenin "belongs to the sarsasapogenin group of sapogenins and its structure is now the subject of study."

We wish to report that we have identified the sapogenin of *Trigonella Foenum-Graecum* as diosgenin, m. p. and mixed m. p. 202° (*Anal.* Calcd. for $C_{27}H_{42}O_3$: C, 78.2; H, 10.2. Found: C, 78.3; H, 10.1). Acetylation with boiling acetic anhydride gave diosgenin acetate, m. p. and mixed m. p. 199° (*Anal.* Calcd. for $C_{29}H_{44}O_4$: C, 76.3; H, 9.7. Found: C, 76.2; H, 9.5).

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STATE COLLEGE, PENNA.   CLARENCE H. RUOF
            RECEIVED APRIL 12, 1943

STEROLS. CLV. SAPOGENINS. LXVII. PENNO-GENIN, NOLOGENIN AND FESOGENIN, THREE NEW SAPOGENINS FROM *BETH* ROOT

Sir:

We have investigated the steroidal sapogenin fractions from *Beth* root collected at seven different localities during the past two years. One of these lots was obtained from S. B. Penick and Company. We have found that diosgenin accounts for 35–60% of the total steroidal sapogenin fractions. From the mother liquors of the crystalline diosgenin acetate was obtained kryptogenin acetate [Marker and co-workers, THIS JOURNAL, **65**, 739 (1943)], m. p. 154°, in 20–40% yields. Hydrolysis of the mother liquors from kryptogenin acetate gave a new steroidal sapogenin having the composition $C_{27}H_{42}O_4$, m. p. 247°, which we have named Pennogenin. *Anal.* Calcd. for $C_{27}H_{42}O_4$: C, 75.3; H, 9.8. Found: C, 74.9; H, 10.0. The yields of the latter varied from 10–20% of the total sapogenin fractions. Two of the oxygen atoms are present as hydroxyl groups, one of which acts with boiling acetic anhydride to form a monoacetate, m. p. 200°. *Anal.* Calcd. for $C_{29}H_{44}O_5$: C, 73.7; H, 9.4. Found: C, 73.6; H, 9.6. Pennogenin shows no ultraviolet absorption for a free carbonyl group. Prolonged treatment of pennogenin (I) with ethanolic hydrochloric acid gives kryptogenin (II). We propose structure I for pennogenin.

I. Pennogenin

II. Kryptogenin
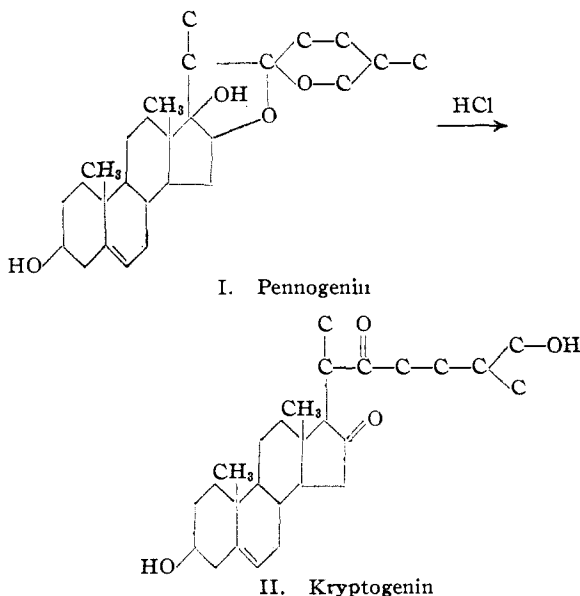
In each of the sapogenin fractions isolated from the seven different sources of Beth root, the three above products accounted for over 85% of the total crystalline sterols.

The mother liquors from pennogenin, however, contain relatively smaller amounts of two new sapogenins, m. p. 265 and 180°, which we have named nologenin and fesogenin, respectively. Both give precipitates with alcoholic digitonin and give tests for unsaturation.

Nologenin, having the composition $C_{27}H_{44}O_5$, was isolated from the crude crystalline pennogenin fraction. *Anal.* Calcd. for $C_{27}H_{44}O_5$: C, 72.3; H, 9.8. Found: C, 72.3; H, 9.5. Boiling acetic anhydride formed a diacetate, m. p. 180°. *Anal.* Calcd. for $C_{31}H_{48}O_7$: C, 70.0; H, 9.1. Found: C, 70.0; H, 9.2. Although its solubility and melting point correspond to those of chlorogenin, the two compounds are readily differentiated by their analyses and the melting points of their acetates.

Fesogenin having the composition $C_{27}H_{40}O_3$ was isolated from the mother liquor of the crude crystalline pennogenin fraction. *Anal.* Calcd. for $C_{27}H_{40}O_3$: C, 78.6; H, 9.8. Found: C, 78.3; H, 9.8. Catalytic hydrogenation using palladium–barium sulfate catalyst gave dihydrofesogenin, m. p. 213°. *Anal.* Calcd. for $C_{27}H_{42}O_3$: C, 78.2; H, 10.2. Found: C, 77.8; H, 10.2. Reduction with sodium in alcohol gave tetrahydro-fesogenin, m. p. 240°. *Anal.* Calcd. for $C_{27}H_{44}O_3$: C, 77.8; H, 10.7. Found: C, 77.6; H, 10.6. These reduction experiments indicate a conjugated system. The details of the isolation work and structure proof will be given in a forthcoming issue of THIS JOURNAL.

We thank Parke, Davis and Company for their help.

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RECEIVED APRIL 20, 1943

STEROLS. CLVI. SAPOGENINS. LXVIII. THE STEROIDAL SAPOGENIN FROM *BALANITES AEGYPTICA* (WALL.)

Sir:

Kon and Weller [*J. Chem. Soc.*, 800 (1939)] have reported the isolation of a new steroidal sapogenin, nitogenin, from the kernels of *Balanites aegyptica* (Wall.). Its properties have been described as follows: m. p. 201°, $[\alpha]_D$ −112° in chloroform, *Anal.* C, 77.6; H, 10.5; acetate,

m. p. 192°, *Anal.* C, 76.1; H, 10.0; benzoate, m. p. 229°, *Anal.* C, 78.2; H, 9.1. This material differed from tigogenin and sarsasapogenin by direct comparison. However, the authors failed to note its similarity to diosgenin. Thus, diosgenin isolated from *Dioscorea tokora* [Fujii and Matsukawa, *J. Pharm. Soc. Japan*, **56**, 408 (1936)] has the following properties: m. p. 200°, $[\alpha]^{19}D$ −119° in chloroform, *Anal.* Calcd. for $C_{27}H_{42}O_3$: C, 78.2, H, 10.2.; acetate, m. p. 190°, *Anal.* Calcd. for $C_{29}H_{44}O_4$: C, 76.3; H, 9.7.; benzoate, m. p. 237°, *Anal.* Calcd. for $C_{34}H_{46}O_4$: C, 78.7; H, 9.0.

We have obtained a sample of palm kernels identified for us as *Balanites aegyptica*. The sapogenin fraction contained diosgenin as its principal constituent. The identification was made by the melting point and mixed melting point determinations on the free genin, 206°; acetate, 200°; and benzoate, 238°. Catalytic reduction of its acetate gave tigogenin acetate, m. p. and mixed m. p., 202°. A mixture containing the latter and the original acetate melted 186°.

We thank Parke, Davis and Company for their help.

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RECEIVED APRIL 21, 1943

thors.[3] The values of h and g established by Stonehill and Berry are, however, not final. The fundamental constants given by Birge[4] differ somewhat from, and supersede, those listed by Childs and used by Stonehill and Berry in their calculations. On the basis of the Birge constants $e = 4.8025 \times 10^{-10}$ e. s. u. (instead of Childs' 4.803×10^{-10}), $k = 1.38047 \times 10^{-16}$ erg/°C. (instead of 1.379×10^{-16}), $N = 6.0228 \times 10^{23}$ (instead of 6.028×10^{23}), $T_0 = 273.16$ (instead of 273.18) and on the basis of Wyman's[5] value 78.54 for the dielectric constant of water at 25° we find $h = 0.5091$ and $g = 0.3286 \times 10^8$. Calling d and t the ratios $D/78.54$ and $T/298.16$ we have, in general

$$h = \frac{0.5091}{(dt)^{3/2}} \text{ and } g = \frac{0.3286 \times 10^8}{(dt)^{1/2}}$$

The revised constant l for the osmotic coefficient formula

$$1 - G = l z_1 z_2 \sqrt{I} \cdot \sigma(ga\sqrt{I})$$

is 0.3908 for water at 25° and, in general

$$l = 0.3908/(dt)^{3/2}$$

(3) On the basis of the constants tabulated by Fowler in his 'Statistical Mechanics" (Cambridge University Press, 1936) Van Rysselberghe and Eisenberg (THIS JOURNAL, **61**, 3030 (1939), **62**, 451 (1940)) and Eisenberg (Thesis, Stanford University, 1942) used the values $h = 0.5059$ and $g = 0.3287 \times 10^3$.

(4) Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

(5) Wyman, *Phys. Rev.*, **35**, 623 (1930).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON
EUGENE, OREGON   PIERRE VAN RYSSELBERGHE
RECEIVED FEBRUARY 19, 1943

FURTHER REVISION OF THE CONSTANTS OF THE DEBYE-HÜCKEL THEORY

Sir:

In a recent note Stonehill and Berry[1] have published revised values for the constants h and g in the Debye–Hückel expression for the logarithm of the activity coefficient of a z_1,z_2-valent electrolyte in aqueous solution at 25°

$$\log_{10} \gamma = \frac{-h z_1 z_2 \sqrt{I}}{1 + ga\sqrt{I}} - \log_{10}(1 + 0.018\Sigma m_i)$$

On the basis of the physical constants tabulated by Childs[2] they find $h = 0.5103$ and $g = 0.3290 \times 10^8$. They indicate some of the possible implications of this change from the values $h = 0.5065$ (or 0.5056) and $g = 0.3287 \times 10^8$ (or 0.3288×10^8) based on the old values of the fundamental constants and used so widely by numerous au-

(1) Stonehill and Berry, THIS JOURNAL, **64**, 2724 (1942).

(2) Childs, "Physical Constants," Methuen, London, 1939.

CONSTANTS OF THE DEBYE-HÜCKEL THEORY

Sir:

In accordance with the revised constants of Birge quoted in the preceding Communication of Dr. Van Rysselberghe, the equations of Scatchard and Epstein[1] for the Debye–Hückel limiting-law expressions in terms of concentrations in moles per kilogram of water should also be revised to give

$$\ln \gamma_k / z_k^2 \sqrt{\mu} = 1.1244 [1 + 0.15471 (t/100) + 0.03569 (t/100)^2 + 0.02389 (t/100)^3]$$

$$\ln \gamma_k / z_k^2 \kappa = 3.470 \times 10^{-8} [1 + 0.10194 (t/100) + 0.04269 (t/100)^2 + 0.00976 (t/100)^3]$$

$$\kappa/\sqrt{\mu} = 0.3240 \times 10^8 [1 + 0.05217 (t/100) - 0.00916 (t/100)^2 + 0.00888 (t/100)^3]$$

in which γ_k is the ratio of the activity of the k'th ion species to its molality, z_k is its valence, t the centigrade temperature, μ the ionic strength,

(1) G. Scatchard and L. F. Epstein, *Chem. Rev.*, **30**, 211 (1942).

and κ has its usual significance in the Debye theory. The equations are valid for aqueous solutions at one atmosphere from 0 to 100°C.

In terms of the quantities given by Dr. Van Rysselberghe the first equation gives

$$2.3026h/\sqrt{\rho_0} = 3l/\sqrt{\rho_0}$$

and the third equation gives $g/\sqrt{\rho_0}$, if ρ_0 is the density of water at the temperature t.

NEW BOOKS

New Technical and Commercial Dictionary—Spanish, English—English, Spanish. Compiled by ANTONIO PEROL GUERRERO, Industrial Engineer, Escuela Central de Ingenieros, Madrid; Chief Editor, Editorial Tecnica Unida. The Chemical Publishing Company, Inc., 234 King Street, Brooklyn, New York, N. Y., 1942. ix + 600 pp. 15.5 × 23.5 cm. Price, $10.00.

Now when at last we are becoming conscious that from south of the Rio Grande to the Antarctic the population of this hemisphere speaks Spanish and that therefore we must learn this language to become better neighbors, the publication of Spanish–English dictionaries is especially welcome. The New Commercial Technical Dictionary of Spanish–English and English–Spanish compiled by Sr. Antonio Perol Guerrero has been written for the use of engineers, business men, and military men. It is undoubtedly a heavy task, that of writing a technical dictionary of so wide a scope. As a consequence, the dictionary is somewhat deficient in words related to industrial trades (metal smith, ship fitter, copper smith, pipe fitter, pattern maker, moulder, etc.). There are in the Spanish–English section some errors of spelling (*azurar* instead of *azuzar*, *cretaneo* instead of *cretaceo*, *húmico* instead of *húmido*, *reactico* instead of *reactivo*, *juga* instead of *jugo*, *respiradore* instead of *respiradora*) and repetitions, which may be corrected in the next edition. The third section of the book contains useful conversion tables of weights and measures.

E. S. GUZMAN BARRON

Preparacion de Productos quimicos y quimicofarmaceuticos. (Preparation of Chemical and Chemical-Pharmaceutical Products.) Volumes I and II. By Professor C. A. ROJAHN, University of Halle. Translated and considerably amplified by Professor Francisco Giral, Chief of the Departments of Organic Synthesis in the "Laboratorios Hormona," Mexico. Editorial Atlante, S. A., Mexico, D. F. xxxix + 1002 pp. 17.5 × 24 cm. Price, $11.00.

This book of preparations of chemical and pharmaceutical products was written by Professor Rojahn for the benefit of students of pharmacy; Professor Giral on translating the book from German into Spanish has also had the same aim in view. To make the book of practical use to Latin-American pharmacists, Professor Giral has used the pre-

scriptions of purity given by the U. S. Pharmacopeia. In these two volumes, an imposing array of methods of preparation of inorganic and organic compounds is given, all of them described with simplicity and clarity. The author was well aware of the lack of explanation of the reactions going on in those preparations and has defended in the foreword his method of presentation. Professor Giral has remedied in part this lack by providing excellent notes, added when compounds of biological interest are described. The reader would welcome more of these notes. An interesting feature of the book is that the methods selected are those requiring the least amount of laboratory material. In the section on organic compounds, some preparations of biological importance could be added (e. g., keto acids, phosphorylated carbohydrate derivatives), whereas in the section on inorganic compounds, a number of them could be dispensed with. If in the next edition Professor Giral eliminates those preparations of no practical utility and increases the number of supplementary notes, the quality of the book will be greatly improved.

E. S. GUZMAN BARRON

Quantitative Analysis. A Theoretical Approach. By WILLIAM RIEMAN, III, PH.D., Associate Professor of Chemistry, Rutgers University, JACOB D. NEUSS, PH.D., Research Chemist, Merck and Co., and BARNET NAIMAN, PH.D., Assistant Professor of Chemistry, College of the City of New York. Second edition. McGraw-Hill Book Company, Inc., 330 West 42nd St., New York, N. Y., 1942. xi + 496 pp. 66 figs. 15.5 × 23.5 cm. Price, $3.50.

According to the Preface, the revision of the first edition (reviewed in THIS JOURNAL, **59**, 1410 (1937)) has involved addition of some new procedures, the consistent use of the Brönsted acid–base concept, and development of the solubility product and related ideas using activities instead of concentrations. The theoretical material, explanatory mathematical parts and experimental procedures all are well written and readable; the book is well designed and executed from the mechanical side, being practically free from typographical errors and style faults (other than the omission of periods after some abbreviations and not others).

Although no longer than the average of such texts, it is composed of 29 chapters plus an appendix, and contains a