

the mean of the y 's, one characteristic of the least-squares principle.

The stretch of the springs in Fig. 3 varies. The line cd is drawn to make this more apparent. If all the observed y 's were on cd the stretch of each spring would be the same, l . But, Σl remains constant and hence, the fitted line takes a position such that the sum of the plus deviations equals numerically the sum of the minus deviations, or the algebraic sum of the deviations is zero, a second characteristic of the least-squares principle.

The essential characteristic, the sum of the squares of the deviations is a minimum, may be explained in terms of energy, as developed by Hersey.⁴ The coil spring with no initial tension and no stretch has no stored energy. As the spring is stretched the stored energy increases as the square of the stretch. In Fig. 2 the stretch of each spring is l and the stored energy of all the springs is Σl^2 . In Fig. 3 the stretch of the springs is variable, $l + \Delta$, where Δ is the deviation of the respective observed y from the fitted y . The stored energy of the springs is $\Sigma(l + \Delta)^2$, or

$$\begin{array}{ll} \text{for the } +\Delta\text{'s,} & \Sigma l^2 + 2 \Sigma l\Delta + \Sigma \Delta^2 \\ \text{for the } -\Delta\text{'s,} & \Sigma l^2 - 2 \Sigma l\Delta + \Sigma \Delta^2 \\ \text{for all } \Delta\text{'s,} & \Sigma l^2 \quad \quad + \Sigma \Delta^2 \end{array}$$

The $l\Delta$ terms cancel since l is constant and the sums of the $+\Delta$'s and $-\Delta$'s are numerically equal. The system comes to rest with stored energy at a minimum and since Σl^2 is constant it follows that $\Sigma \Delta^2$ is a minimum.

In reaching this equilibrium the wheel is rotated through an angle proportional to b . The b scale on the circumference of the wheel is linear, and dependent on the ratio of the x to the y spacing. In the diagram this ratio is 1.146, and 5° corresponds to .1 on the b scale ($1.146 \times 2 \times 3.1416 \times 5 \div 360 = .1$).

Three features of the least-squares principle of fitting the equation $y = a + bx$ are thus shown mechanically:

1. The fitted line cuts the center x at the mean of the y 's.
2. The algebraic sum of the deviations is zero.
3. The sum of the squares of the deviations is a minimum.

W. L. GAINES

J. R. PALFREY

AGRICULTURAL EXPERIMENT STATION
UNIVERSITY OF ILLINOIS

PALEOGEOGRAPHIC WALL MAPS

In practically all the present-day text-books of geology, more or less use is made of paleogeographic maps. These maps constitute a most excellent teaching device, but it is the opinion of the writer that the maps as published in most of the text-books are of but little value to elementary students. In all the text-books in use at the present time such maps are published in black and white and seas are shown by means of lined areas or some such device. All these devices so obscure the boundaries of land masses, political boundaries and so forth, which are also shown by black lines, that it is almost impossible to determine the relation of the seas to the present continents and political divisions. This difficulty is increased by the small scale necessarily used in the text-book publications. The result is that the average

student gets only a hazy idea of the paleogeography of the past in relation to the present-day continents, and even the exceptional student who endeavors to study out these maps is soon hopelessly lost in the maze of lines and boundaries and soon gives up in discouragement. Thus a very excellent teaching device is rendered practically useless. The difficulty of the small scale can be partially overcome by the use of lantern slides of these maps, but this is of little help, since the confusion of lines and boundaries still exists.

The writer has for some time been using a method of making paleographic wall maps which is both rapid and inexpensive and which gives maps on which students can see at a glance the position of past geographic features in relation to the present-day continents. An outline map of the continent in question is first made by tracing from a political wall map of suitable size the political boundaries and boundaries of land masses on tracing paper or tracing cloth. All boundaries are traced in black India ink with a lettering pen which makes a stroke of about an eighth of an inch wide. Lines of this width can usually be distinguished anywhere in the ordinary lecture room. Care should be taken not to use too much detail, but enough should be included so that no student will have any difficulty in locating any place on the map with regard to its present-day political boundaries or the boundaries of the land masses. From this outline map a large number of outline maps are prepared by tracing them on tracing paper of the kind used by architects in making preliminary plans of buildings. These outline maps are then used as needed in preparing paleographic maps of any period or epoch. Using the same kind of a lettering pen the boundaries of the seas are drawn in with some sharply contrasting color such as bright red. In this way the boundaries of the seas are never confused with the political and other boundaries drawn in black on the outline map. The areas of the seas are then roughly colored with soft blue chalk (not crayon) and then carefully rubbed with a small piece of cotton cloth. This rubs the color into the paper sufficiently that it is not rubbed off by handling and distributes the color evenly over the map. The seas now stand out in strong contrast to the land areas, and the political and other boundary lines are not in the least obscured by the coloring. As a result students grasp the situation immediately as soon as one of the maps is shown to them and get a clear conception of all the geographic features of the past with their relation to the present-day configuration of the continents. The tracing paper map when finished is mounted on muslin in the usual way and makes a very durable map. After the preliminary outline maps are made a

paleographic map can be made from any of the published maps in fifteen to twenty minutes. Since this method is both rapid and inexpensive, it is possible to have a large number of these maps illustrating not only periods but all important epochs of a period. The writer has found that not only do students grasp

many of the facts of historical geology better by this method but that its use greatly adds to the pleasure of both the student and instructor.

LERoy T. PATTON

DEPARTMENT OF GEOLOGY,
TEXAS TECHNOLOGICAL COLLEGE

SPECIAL ARTICLES

THE STRUCTURE OF VITAMIN A AND THE SYNTHESIS OF IONENES

THE brilliant investigations of the past two or three years, here as well as abroad, on the chemical nature of vitamin A, which culminated in the structural formula (I) proposed a year ago by Karrer, Morf and Schöpp,¹ have directed increasing attention to this compound and its remarkable properties.

An article, dealing with the constitution of vitamin A, by Heilbron, Morton and Webster,² which has just appeared, leads us to report immediately and briefly the results of our own recent studies of this problem.

Heilbron, Morton and Webster distilled vitamin A concentrate with finely powdered selenium and obtained 1,6-dimethylnaphthalene (VI) as one of the principal products. As a possible explanation of this reaction, they suggest the preliminary cyclization of the vitamin to a hydronaphthalene derivative (II), which then breaks down to ionene (III), for Ruzicka and Rudolph³ have shown that when ionene is distilled with sulfur 1,6-dimethylnaphthalene results and, as is well known, the action of sulfur in such distillations is similar to that of selenium.

It is obvious that, whatever the mechanism may be by which ionene is formed from the vitamin, the value of this observation of Heilbron, Morton and Webster's, in throwing light upon the constitution of the vitamin, depends upon the establishment of the constitution of ionene itself, and that is one of the phases of this vitamin problem which our organic laboratories at Columbia University have been studying for some time and which we believe that we have now brought to a successful conclusion, through the investigations of Dr. David Davidson and Messrs. Victor G. Fourman and Percy M. Apfelbaum.

Ionene was discovered by Tiemann and Krüger⁴ by the dehydration of *alpha*-ionone, or of a mixture of *alpha*- and *beta*-ionones. Later, Tiemann⁵ showed that it could be prepared also from *beta*-ionone.

On the basis of the products obtained from it by

¹ Karrer, Morf and Schöpp, *Helv. Chim. Acta.*, 14, 1434 (Dec., 1931).

² Heilbron, Morton and Webster, *Biochem. J.*, 26, 1194.

³ Ruzicka and Rudolph, *Helv. Chim. Acta.*, 10, 918 (1927).

⁴ Tiemann and Krüger, *Ber.*, 26, 2693 (1893).

⁵ Tiemann, *Ber.*, 31, 873 (1898).

oxidation, Tiemann and Krüger were disposed first to assign to ionene constitution (IV), but finally decided in favor of formula (V).

Three years later, Barbier and Bouveault,⁶ proposed the structure (III) as the more probable one for ionene, but cited no new experimental work in support of this opinion. Tiemann,⁷ in reply to Barbier and Bouveault, insisted upon the correctness of his own formula (V) and quoted his original oxidation experiments.

Baeyer and Villiger⁸ investigated the constitution of ionene, by their exhaustive bromination method, confirmed the existence of the carbon skeleton common to all three of the suggested ionene formulas, but threw no light upon the location of the double bonds.

Auwers and Eisenlohr,⁹ as the result of their study of the molecular refractivity of ionene, decided in favor of (IV) rather than (V), but apparently failed to consider (III) at all.

In the course of their researches in the naphthalene field, Ruzicka and Rudolph³ distilled ionene with sulfur, as noted above, and obtained 1,6-dimethylnaphthalene, using the Barbier and Bouveault formula (III) to illustrate the reaction. A year later, in his brochure¹⁰ on the sesquiterpenes, Ruzicka accepted the carbon skeleton of the ionene formula as proven, but the location of the double bonds as still unknown.

It is our belief that we have now cleared up this uncertainty, and established the complete constitution of ionene, by the results of the following investigations:

I. Mr. Fourman, by a careful study of the nitro, nitroamino and sulfo derivatives, the oxidation products of ionene itself and of its dinitro derivatives, has made it quite evident that the Barbier and Bouveault formula (III) for ionene is correct.

II. Davidson and Apfelbaum have now demonstrated the accuracy of this deduction by the synthesis of ionene through these steps:

⁶ Barbier and Bouveault, *Bull. soc. chim.* [3], 15, 1008 (1896).

⁷ Tiemann, *Ber.*, 31, 854 (1898).

⁸ Baeyer and Villiger, *Ber.*, 32, 2429 (1899).

⁹ Auwers and Eisenlohr, *J. prakt. Chem.* [2], 84, 61 (1911).

¹⁰ "Über Konstitution und Zusammenhänge in der Sesquiterpenreihe," *Fortschr. d. Chem., Phys. u. phys. Chem.*, 19, No. 5, p. 9 (1928).