DISCUSSION AND CORRESPONDENCE

THE SEMI-CENTENARY OF WILLARD GIBBS' PHASE LAW (1876–1926)

THE issue of the *Chemisch Weekblad*, of September 18, 1926, published by the Netherlands Chemical Society, is of particular interest to American scientists. Thanks to the interest in the history of science by the editor of that periodical, Dr. W. P. Jorissen, at Leyden, we are reminded in these pages of what science owes to Josiah Willard Gibbs, who occupied the chair of mathematical physics at Yale from 1871 until his death in 1903.

Doubtless this man has been the greatest scientific genius produced by the United States of America. His paper "On the Equilibrium of Heterogeneous Substances," published in 1876 in the Proceedings of the Connecticut Academy, has not only governed to a great extent the development of chemistry since 1886 but it has also included a program for the future. When J. D. van der Waals at Amsterdam had grasped the deep significance of Gibbs's work and after he had drawn Bakhuis Roozeboom's (then in Leyden, later in Amsterdam) attention to its importance, the phase law was very readily developed. Almost all branches of chemistry to-day are reaping the fruits of the accomplishments of this deep genius of New Haven, who through his modesty was so little known even to his countrymen.

The detailed treatment of this part of the history of science would yield a most fascinating narrative, full of variety and stimulation to our future generations. Not only this issue of the *Chemisch Weekblad* and the list of books and pamphlets on the phase law and its applications added to it by Dr. Jorissen but also Donnan's discourse held in September, 1924, on the occasion of the centenary celebration of the founding of the Franklin Institute, as well as Lash Miller's paper in the *Chemical Reviews* (January, 1925), would supply abundant material. The jubilee issue of the *Chemisch Weekblad* commemorates at the same time the fact that twenty-five years ago F. A. H. Schreinemakers, to whom the development of the phase law owes so much, was appointed a professor in the University of Leyden.

After a short historical introduction of W. P. Jorissen, Henry Le Chatelier (Paris) gives a paper on "L'oeuvre de J. Willard Gibbs." Wilhelm Ostwald (Grossbothen, Germany) informs us why he translated Gibbs's papers into German. J. D. van der Waals, Jr. (Amsterdam), son of J. D. van der Waals, treats Gibbs's influence on the theory of mixtures; W. Lash Miller (Toronto) "The Fundamental Equation of Willard Gibbs." F. A. H. Shreinemakers expresses his gratitude and deep appreciation towards his friend and teacher, Bakhuis Roozeboom, who passed away too soon; Gustav Tammann (Göttingen) gives us an insight into the development of metallurgy. Norway is represented by J. H. L. Vogt (Trondhjem) who pictures the significance of Gibbs's life work for petrography, and J. J. van Laar (Holland) gives a paper on a "Limiting Case in Phase Equilibria." J. W. Terwen (Delft, Holland) calls our attention to the significance of the phase law to the study of allotropy; F. G. Donnan (London) to the influence of Gibbs's work on industry.

The issue closes with a paper of F. A. Freeth (Hartford, England) on "The Scientific Work of F. A. H. Schreinemakers" and Miss W. C. de Baat's (Leyden) personal reminiscences of the time during which Schreinemakers was a professor at Leyden.

The whole issue of the *Chemisch Weekblad* (illustrated with seven portraits) may be considered as a publication worthy of the man to whose genius science is so deeply indebted.

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ANN ARBOR, MICH.
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SECOND ORDER STARK EFFECT IN HYDROGEN

THROUGH the kindness of Dr. T. Takamine, I received some information about very accurate experimental determinations of the second order Stark effect in hydrogen, carried out by Professor M. Kiuti. Unfortunately this material came too late to be used in my article on the Stark effect (*Phys. Rev.*, *28*, p. 695, 1926), therefore, I should like to make these beautiful observations available to a larger public through the agency of SCIENCE.

Professor Kiuti measured the shift of the central ⊥ component of $H\gamma$ in very strong electric fields and obtained the following results:

(1) Result of most recent experiments:

Field	Shift	Shift reduced to 100,00 volt/cm
140,000 volt/cm	.64 Å	.33 Å
156,000 "	.67 "	.28 "

(2) Result of previous experiments (*Japanese Journal of Physics*, *4*, p. 13, 1925):

Field	Shift	Shift reduced to 100,00 volt/cm
95,000 volt/cm	.35 Å	.39 Å
103,000 "	.33 "	.31 "
107,000 "	.39 "	.34 "
124,000 "	.57 (?)	.33 (?)
161,000 "	.67 "	.26 "

(3) Professor Kiuti makes the following remarks:

(a) It appears that the effect is rather large at weaker fields, so that it is possible that the shift is not quite proportional to the square of the field. However, the degree of accuracy of these measurements does not permit to assert it definitely.

(b) The weighted means of the most reliable observations is

Field	Shift
100,000 volt/cm	0.28 Å

(c) The field was here calculated theoretically. If Stark's value is extrapolated, the field becomes 5 per cent. less, increasing the shift in the same proportion.

In order to compare Professor Kiuti's measurements with our theory, it will be necessary to compute the theoretical shift more accurately than it has been done heretofore. The formula given in my paper (*l. c.*) for the shift is

$$\Delta_2\lambda = \frac{D^2\lambda^2}{16\mu^3 hc}\left(\frac{h}{2\pi e}\right)^6 [S(m, n, s) - S(m', n', s')],$$

$$(1) \quad S = (m+n+s)^4 [17(m+n+s)^2 - 3(m-n)^2 - 9s^2 + 18s + 10].$$

D is the strength of field, m, n, s are quantic integers, while the rest of the symbols are used in the customary sense. Substituting the most accurate available values of μ, e, h, we find the numerical factor

$$(2) \qquad \Delta_2\lambda = 5.16 \cdot 10^{-18} D^2\lambda^2 (S - S'),$$

if D is expressed in kilovolt/cm, λ in Å.

The component observed by Professor Kiuti is in reality a superposition of two lines. The first is given by the quantic numbers $m = n = 1$, $s = 3$; $m' = n' = 0$, $s' = 2$, the second by $m = n = 2$, $s = 1$; $m' = n' = 0$, $s' = 2$. Accordingly, the first gives the shift 0.246 Å, the second 0.268 Å. The first line is responsible for 81 per cent. of the total intensity, while the share of the second is 19 per cent. We obtain, therefore, for the center of gravity the shift

$$\Delta_2\lambda = 0.251 \text{ Å}.$$

This is the theoretical value in the new theory which must be compared with 0.28 Å found by Professor Kiuti experimentally.

It is interesting to compute the values resulting from our old theory (*Ann. der Phys.*, 51, p. 168, 1916) with the same accuracy. The only difference is in the expression of the function S: the terms $18s + 10$ in formula (1) must be omitted. We obtain the following results: Shift of the first line 0.208 Å, shift of the second line 0.252 Å, shift of the center of gravity

$$\Delta_2\lambda = 0.217 \text{ Å}.$$

We see that the experiments agree decidedly better with the new theory than with the old one. Perhaps the accuracy of the observations is not yet sufficient to make the decision in favor of the new theory conclusive. It seems, however, that such a decision is well within the reach of experimental possibilities.

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UNUSUAL CARBONIFEROUS CEPHALOPODS

TEXT-BOOKS of geology point to the Ordovician as the time of great development of the straight cephalopods and declare that "these predaceous masters of the sea attained a length of twelve to fifteen feet, and had a maximum diameter of twelve inches." They further indicate that, with the rise of coiled forms, orthoceracones waned rapidly, although they were still common and relatively large in the Silurian, and not unknown in the Devonian. Carboniferous orthoconic cephalopods, however, are reputed to be rare and invariably small. That this is not always the case is evidenced by the discovery of large orthoconic forms in the Fayetteville shale of Arkansas, a formation of upper Mississippian (Chester) age. These fossils, which recently have been described in detail by the writer,[1] are remarkable for several reasons.

In the first place, they attained a length of at least four feet and must have had a diameter of ten inches. *R. solidiforme,* the holotype of the new genus *Rayonnoceras* (M. C. Z., No. 2326–30) has a diameter of six inches *posterior* to the living chamber, while another specimen, in the University of Arkansas Museum, has a diameter of nearly eight inches, *although the shell is still septate.* An ordinary collection of specimens of species of *Rayonnoceras* will contain individuals as large or larger than those in the usual Ordovician group of cephalopods. An examination of the literature shows that in only one other case have large straight cephalopods been discovered in the Carboniferous. Sowerby[2] described *Orthoceras gigantea* from the red limestone of Castle Espie, Ireland, as attaining a length of two feet. McCoy[3] later described the same species as *Actinoceras giganteum,* and reported its maximum (reconstructed) length as four feet. With the exception of this Irish species, no other Carboniferous cephalopod even approaches the Fayetteville specimens in size. There are also cases where orthoconic Carboniferous

[1] Croneis, C., *M. C. Z. Bull.*, LXVII, No. 10. (1926.)

[2] Sowerby, *Min. Conch.*, 81. (1818.)

[3] McCoy, *Carb. Fos. Ire.*, 11. (1844.)