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Chemistry. — "EYKMAN'S *Refractometric Investigations, in Connection with the Presentation of the Edition of his Works.*" By Prof. A. F. HOLLEMAN.

(Communicated in the meeting of January 25, 1919).

Though EYKMAN devoted about twenty-five years of his life to refractometric investigations of organic compounds, and collected in the course of these researches a tremendous amount of material, arriving at very important conclusions from this material, his work in this interesting region has, nevertheless, remained pretty well unknown. This is chiefly owing to the way in which he published it.

At first choosing for this purpose the *Berichte der deutschen chemischen Gesellschaft*, he afterwards wrote a number of treatises in the *Recueil*; but by far the greater part of his papers appeared exclusively in the *Chemische Weekblad*.

The researches of his pupils were up to now only laid down in Theses for the Doctorate.

For foreign chemists, who are only by exception conversant with the Dutch language, it was, therefore, practically impossible, to get acquainted with EYKMAN'S researches.

It further appeared, when his posthumous papers were put into my hands by his brother, our fellow-member Chr. EYKMAN, that these contained still a voluminous material of facts which had not yet been published at all.

In order to render his ideas and experimental results more generally accessible, it was necessary to collect his refractometric researches and publish them as a whole. This publication has been rendered possible by the financial help of the *Hollandsche Maatschappij der Wetenschappen*, which in this has proved itself worthy of its high traditions.

In the now published work: *Recherches réfractométriques de feu J. F. EYKMAN*, are found in the first place a biography and a summary of his researches in this region. Then follow the papers from the "*Berichte*", which contain among others his researches on the displacement of the double bindings in the side chains of aromatic compounds towards the nucleus. This displacement gives rise to a considerable increase of the molecular refraction and dispersion.

In his papers in the *Recueil* he described the refractometer constructed by him with constant deviation of 40° , which is obtained by rotation of the prism round a vertical axis. This apparatus has further an appliance, by means of which measurements of the refraction up to a temperature of about 150° can take place with ease for which reason it is to be preferred for organic-chemical researches to all other refractometers. Also his pycnometers are described there.

It is further demonstrated in these papers that the refractometric value of the group CH_2 is constant for the most divergent homologous series, if only the first three terms of these series are left out of consideration, for which this value is either greater or smaller.

Besides they contain the derivation of EYKMAN's formula for the molecular refraction. Hitherto the formula of GLADSTONE and DALE: $\frac{n-1}{d} \cdot P = \text{const.}$ was generally used for this, in which n represents the index of refraction, d the specific weight of the liquid substance, and P the molecular weight. After the formula $\frac{n^2-1}{n^2+2} \cdot \frac{P}{d}$ had been derived by LORENTZ by a theoretical way, this formula got to be almost exclusively used. The formulae of GLADSTONE and DALE and of LORENTZ do not present a constant value, however, for large ranges of temperature (e.g. of 100°); but those of the former descend, while the theoretical formula gives ascending values.

Taking into account that G. & D's formula may also be written: $\frac{n^2-1}{n+1} \cdot \frac{P}{d}$, and that accordingly the difference between the two formulae refers only to the denominator, EYKMAN tried by an empirical way to find a formula that also has constant values for large ranges of temperatures, and he found it in the expression $\frac{n^2-1}{n+0.4} \cdot \frac{P}{d}$. This rendered it, therefore, possible, to directly compare measurements which have been made at very divergent temperatures.

The papers in the *Chemisch Weekblad* treat two problems of great importance for organic refractometry, viz.: the cyclic compounds and unsaturate substances. As far as the former is concerned, he comes to the result that the number of C-atoms in the nucleus has a considerable influence on the refraction, which also extends over the refractometric values which CH_2 -groups have in the side chain.

In reference to the unsaturate compounds he proves by means of an exceedingly copious material, that there can be no question of a constant increment for the double binding, which BRÜHL intro-

duced, for that the double binding can exert a very divergent influence on the refraction, and especially on the dispersion of unsaturate compounds.

Among the posthumous papers there were the refractometric determinations of more than 350 compounds, which had not yet been published, among which almost complete series of homologues. That EYKMAN did not publish these himself I attribute chiefly to the fact that he could less and less bring himself to prepare his results for the press. Possibly, too, he wished to wait till some series had become still more complete, or to repeat some measurements before their publication. In view of these surmises it may seem somewhat bold to make results public which the master himself thought fit to withhold still. Besides, however, the fact mentioned just now, there is another circumstance that justifies publication. It is the comparison of the measurements made at the same substances which were carried out by him in many successive years. Then there appears to exist an almost perfect agrément in the values in almost all cases. In fact all his work gives the impression of having been executed with scrupulous care, also as regards the purity of the compounds.

It is to be regretted that the material left behind consists almost exclusively of tables, without any commentary. I have tried to supply this defect by adding a review to every series of measurements of homologues, for the rest fully realising the difficulty of this task, which certainly would have been accomplished by the master himself in a much better way. I have set myself the task to interpret the results in these reviews as much as possible in the same spirit as speaks from EYKMAN'S works, which often give evidence of entirely different views from those embraced by most chemist who work in this field, in the hope that those who are more competent in this kind of researches will judge that I have succeeded in giving the right interpretation.

The measurements left behind comprise compounds from the following homologous series: saturate hydrocarbons, alcohols $C_nH_{2n+1}OH$, alkylhaloids, aliphatic and cyclic amines, acid $C_nH_{2n}O_2$ and their esters, saturate aldehydes and ketones, unsaturate hydro-carbons, unsaturate acids, plurivalent alcohols, pluribasic acids, hydroxy-acids, aldehydic and ketonic acids, derivatives of carbonic acid, cyclic compounds, aromatic hydro-carbons, phenols, aromatic amines and aromatic acids.

This posthumous material confirms on one side for the greater part the conclusions at which EYKMAN had already arrived by the

aid of what had been published by him, but it tests them by a number of compounds hitherto unknown; on the other side some new points of view have come to light. Among these we may mention the influence of the bifurcation of the carbon chains, the further differentiation of the atomic refraction of oxygen, the influence of stereo-isomery, and the closer inquiry into the dispersion of the organic compounds.

This entire posthumous work shows with great evidence that there can be no question of constant atom refractions, not even for carbon. Though the variations in the atom refractions of this element are often pretty insignificant, it yet does not constitute an exception to the general rule that the atom refractions are *not* constant.

EYKMAN's work aims at no less than a total revision of the refractometry of organic compounds; he has treated in a masterly way all the fundamental questions in this region, thanks to his great gifts of research and his amazing energy, which have fortunately remained unaffected under the depressing feeling of neglected merit.

Amsterdam, January 1919.