Prof. C. Schorlemmer on the Normal Paraffins. [Nov. 20,

X1. "On the Normal Paraffins. Part III." By C. Schorlemmer. F.R.S. Professor of Organic Chemistry in Owens College. Manchester. Received August 2, 1879.

The isomeric monochlorides, obtained from the normal paraffins existing in petroleum, yield by the abstraction of hydrochloric acid a mixture of olefines, one portion of which readily combines with hydrochloric acid in the cold, whilst the other unites with it only on heating.\*

The chlorides formed in the cold boil with partial decomposition and at a lower temperature than the others, which distil without undergoing any change, and have the general formula

. 
$$CH_3$$
— $CHCl$ — $C_nH_{2n+1}$ .†

They are therefore derived from the olefines of the series

$$CH_1 = CH - C_nH_{2n+1}$$
.

Similar results have been obtained by Le Bel.1

The constitution of the olefines combining with the acid in the cold is not yet known. They are possibly not derived from normal paraffins, but from isomerides, which cannot be separated from the former by distillation. On the other hand their formation can also be explained without making this assumption. This question can only be decided by using an absolutely pure paraffin.§

For this purpose, normal hexane from mannite was selected, which possibly might yield three isomeric monochlorides:

- (1.) CH<sub>3</sub>—CH<sub>3</sub>—CH<sub>3</sub>—CH<sub>3</sub>—CH<sub>3</sub>—CH<sub>3</sub>Cl
- (2.) CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CHCl—CH<sub>3</sub>
- (3.) CH<sub>3</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CHCl—CH<sub>3</sub>—CH<sub>3</sub>

The formation of the first two has already been proved. The following seemed capable of determining whether the third is also produced. By the abstraction of hydrochloric acid three hexylenes might be formed :-

The first of these does not combine with cold hydrochloric acid; the second is the hexylene obtained from secondary hexyl iodide.

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* "Journ. Chem. Soc.," 1873, p. 319.
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Le Bel and Wassermann have found that cold hydrochloric acid has no action on it, from which it follows that, if normal hexane from mannite vields a hexvlene combining with hydrochloric acid in the cold, it could be only diethylhexylene, which could be easily identified by conversion into ethylpropyl carbinol and oxidising it, when only propionic acid should be formed.

This was my programme; the results were, however, quite unexpected.

The hexylene obtained by decomposing the hexyl chlorides was left in contact with cold fuming hydrochloric acid for some weeks. The whole of it combined and the hexyl chloride thus formed boiled constantly and without the least decomposition at 124-125°. It was converted into the alcohol, which on exidation yielded only acetic acid and butyric acid, and consequently is methylbutyl carbinol. We have, therefore, the remarkable fact, that two hexanes exist, which must be regarded as normal compounds, and therefore according to our present theory, to be identical. This is, however, not the case. I have already in my first paper pointed out some other differences existing between the two hexanes, but left the question open, whether these are caused by impurities contained in the hexane from petroleum, or whether we have here a case of fine isomerism, for which an explanation has to be found.\* I believe the results of my present research speak strongly in favour of the latter view.

For several reasons I am inclined to believe that petroleum consists chiefly of an inextricable mixture of isomeric and homologous paraffins, in which, however, the normal hydrocarbons preponderate. This would certainly explain why it is so difficult to isolate from it bodies having a constant boiling point,+ but not the differences exhibited by the two hexanes.

A continuation of these researches has already been commenced. My friend Thorpe, who has made the most interesting discovery that the terebinthinate exudation of Pinus Sabiniana contains a large quantity of normal heptane, thas kindly offered me to join him in the chemical investigation of this hydrocarbon. At the same time we shall compare it with other "normal" heptanes from different sources.

XII. "The Geometric Mean, in Vital and Social Statistics." By Francis Galton, F.R.S. Received October 21, 1879.

My purpose is to show that an assumption which lies at the basis of the well-known law of "Frequency of Error" (commonly expressed

<sup>+</sup> Morgan, ibid., 1875, p. 301.

<sup>† &</sup>quot;Bull. Soc. Chim.," (2), xxviii, p. 460.

<sup>§ &</sup>quot;Journ. Chem. Soc.," 1875, p. 306.

<sup>|</sup> Hecht, "Deut. Chem. Ges. Ber.," xi, p. 1152.

<sup>\* &</sup>quot;Phil. Trans.," vol. clxii, p. 119.

<sup>† &</sup>quot;Journ. Chem. Soc.," 1875, p. 306.

<sup># &</sup>quot;Journ. Chem. Soc.," 1879, p. 296.

1879.7

by the formula  $y=e^{-h^2x^2}$ ), is incorrect in many groups of vital and social phenomena, although that law has been applied to them by statisticians with partial success and corresponding convenience. Next, 1 will point out the correct hypothesis upon which a Law of Error suitable to these cases ought to be calculated; and subsequently I will communicate a memoir by Mr. Donald McAlister, who, at my suggestion, has mathematically investigated the subject.

The assumption to which I refer is, that errors in excess or in deficiency of the truth are equally probable; or conversely, that if two fallible measurements have been made of the same object, their arithmetical mean is more likely to be the true measurement than any other quantity that can be named.

This assumption cannot be justified in vital phenomena. For example, suppose we endeavour to match a tint; Fechner's law, in its approximative and simplest form of sensation=log stimulus, tells us that a series of tints, in which the quantities of white scattered on a black ground are as 1, 2, 4, 8, 16, 32, &c., will appear to the eve to be separated by equal intervals of tint. Therefore, in matching a grey that contains 8 portions of white, we are just as likely to err by selecting one that has 16 portions as one that has 4 portions. In the first case there would be an error in excess, of 8; in the second there would be an error in deficiency, of 4. Therefore, an error of the same magnitude in excess or in deficiency is not equally probable in the indement of tints by the eye. Conversely, if two persons, who are equally good judges, describe their impressions of a certain tint, and one says that it contains 4 portions of white and the other that it contains 16 portions, the most reasonable conclusion is that it really contains 8 portions. The arithmetic mean of the estimates is  $\frac{4+16}{9}$ or 10, which is not the most probable value. It is the geometric mean 8 (4:8: \*8:16) which is the most probable.

Precisely the same condition characterises every determination by any of the senses; for example, in judging of the weight of bodies and of their temperatures, of the loudness and of the pitch of tones, and of estimates of lengths and distances as wholes. Thus, three rods of the lengths u, b, c, when taken successively in the hand, appear to differ by equal intervals when a:b::b:c, and not when a-b=b-c. In all physiological phenomena, where there is on the one hand a stimulus and on the other a response to that stimulus, Fechner's law may be assumed to prevail; in other words, the true mean is the geometric.

The same condition of the geometric mean appears to characterise the majority of the influences, which, combined with those of purely vital phenomena, give rise to the events with which sociology deals. It is difficult to find terms sufficiently general to apply to the varied topics of sociology, but there are two categories of causes, which are

of common occurrence. The one is that of ordinary increase, as exemplified by the growth of population, where an already large nation tends to become larger than a small one under similar circumstances, or when a capital employed in a business increases in proportion to its size. The other category is that of surrounding influences, or "milieux" as they are often called, such as a period of . plenty in which a larger field or a larger business yields a greater excess over its mean yield than a smaller one. Most of the causes of those differences with which sociology are concerned, and which are not purely vital phenomena, such as those already discussed, may be classified under one or other of these two categories, or under such as are in principle almost the same. In short, sociological phenomena. like vital phenomena are, as a general rule, subject to the condition of the geometric mean.

The ordinary law of Frequency of Error, based on the arithmetic mean, corresponds, no doubt, sufficiently well with the observed facts of vital and social phenomena, to be very serviceable to statisticians, but it is far from satisfying their wants, and it may lead to absurdity when applied to wide deviations. It asserts that deviations in excess must be balanced by deviations of equal magnitude in deficiency therefore, if the former be greater than the mean itself, the latter must be less than zero, that is, must be negative. This is an impossibility in many cases, to which the law is nevertheless applied by statisticians with no small success, so long as they are content to confine its application within a narrow range of deviation. Thus, in respect of stature, the law is very correct in respect to ordinary measurements. although it asserts that the existence of giants, whose height is more than double the mean height of their race, implies the possibility of the existence of dwarfs, whose stature is less than nothing at all.

It is, therefore, an object not only of theoretical interest but of practical use, to thoroughly investigate a Law of Error, based on the geometric mean, even though some of the expected results may perhaps be apparent at first sight. With this view I placed the foregoing remarks in Mr. Donald McAlister's hands, who contributes the following memoir.

XIII. "The Law of the Geometric Mean." By Donald McAlister, B.A., B.Sc., Fellow of St. John's College, Cambridge. Communicated by Francis Galton, F.R.S. Received October 21, 1879.

Suppose we have before us a large number of measurements. They may either be all approximations to the true value of a single unknown quantity, or may refer to the several members of a large class. The