ART. X.—*On the Classification of Organic Substances by Series;* by JAMES SCHIEL, of St. Louis.

THE progressive series which in 1842* I introduced into organic chemistry, have become the chief means of classification and of connecting organic substances generally. Several years after the introduction of the series, Gerhardt used them in the sense just mentioned in his Traité de Chimie and thereby contributed a great deal toward their general knowledge.† But the idea this distinguished chemist had formed of series was very imperfect, as is proved by the single fact that he ranged benzoic acid and acetic acid in what he called an isologous series (*Traité*, T. I, 127). As in the present state of chemical science, it is highly important that the principles of seriation be clearly understood, I will try to expound them in a more general and methodical manner than has been done hitherto.

The general formula of organic compounds containing carbon, hydrogen and oxygen is $\mathrm{C}_\alpha \mathrm{H}_\beta \Theta_\gamma$. By giving to γ successively the values 1, 2, 3, 4,... we may form the following series of oxydation:

$$(\mathrm{A})\quad \begin{array}{l} \mathrm{C}_\alpha \mathrm{H}_\beta \Theta \\ \mathrm{C}_\alpha \mathrm{H}_\beta \Theta_2 \\ \mathrm{C}_\alpha \mathrm{H}_\beta \Theta_3 \\ \mathrm{C}_\alpha \mathrm{H}_\beta \Theta_4 \\ \vdots \end{array}$$

From this all the series necessary for the classification of organic substances may be derived by putting $\alpha=n$ and $\beta=2n+2$, making β successively to decrease, the decrement being 2, 4, 6, 8,

* Annal. Liebig and Wöhler, July number, 1842.

† Gerhardt changed the name progressive into homologous, in the discovery itself of the series he has no share.

. . . By this we have the following series:

I. $\mathrm{C}_nH_{2n+2}\Theta$	II. $\mathrm{C}_nH_{2n}\Theta$	III. $\mathrm{C}_nH_{2n-2}\Theta$	IV. $\mathrm{C}_nH_{2n-4}\Theta$
$\mathrm{C}_nH_{2n+2}\Theta_2$	$\mathrm{C}_nH_{2n}\Theta_2$	$\mathrm{C}_nH_{2n-2}\Theta_2$	$\mathrm{C}_nH_{2n-4}\Theta_2$
$\mathrm{C}_nH_{2n+2}\Theta_3$	$\mathrm{C}_nH_{2n}\Theta_3$	$\mathrm{C}_nH_{2n-2}\Theta_3$	$\mathrm{C}_nH_{2n-4}\Theta_3$
⋮	⋮	⋮	⋮

and so forth.

Every general formula in one of these generic series represents special homologous series the members of which have the difference $n\mathrm{C}H_2$. When comparing the above series with the hydrocarburets known to exist in a free state, they will be found to represent different states of oxydation of these hydrocarburets.

Another kind of series is formed by making in the general formula $\alpha=n$ and $\beta=n$ and making β successively to decrease or increase, the increment or decrement being 1, 2, 3, 4, ... By this we form the series:

$$\text{(B.)}\quad \begin{array}{l} \mathrm{C}_nH_n\Theta_\gamma \\ \mathrm{C}_nH_{n\pm1}\Theta_\gamma \\ \mathrm{C}_nH_{n\pm2}\Theta_\gamma \\ \mathrm{C}_nH_{n\pm3}\Theta_\gamma \\ \vdots \end{array}$$

Every general formula here represents a series, the members of which are distinguished by $m\mathrm{C}H$ and which I therefore call *hemilogous* series. It is to be remarked that a hemilogous series whose general formula is $\mathrm{C}_nH_{n\pm1}\Theta_\gamma$, can only exist when n is an odd number, as the number of atoms of hydrogen entering into an organic compound is always an even number.* The hemilogous series are very useful for comparing the physical properties of organic substances.

I will now apply these principles of classification to three large classes or groups of substances, the hydrocarburets, the alcohols and the acids. The generic series formed by the first of these groups is the following:

C_nH_{2n+2} hydrurets of the radicals of the alcohols;
C_nH_{2n} the homologues of ethylen and the radicals of the alcohols;
C_nH_{2n-2} acetylen n=2; allyl n=6;
C_nH_{2n-4} thymen n=10;
C_nH_{2n-6} benzol n=6, toluol n=7, xylol n=8, cumol n=9, cymol n=10.
⋮
C_nH_{2n-1} stilben n=14;
C_nH_{2n-20} hydrocarburet found in the tar of Archangel n=19.

The maximum or minimum number of atoms of hydrogen which may be combined with n atoms of carbon cannot be deter-

* If one atom of nitrogen enters into the compound the atoms of hydrogen are an odd number, as nitrogen is triatomic. For this reason alone the formula of Quinine for instance, could not be written $C_{10}H_{12}N\Theta$, as chemists formerly used to do, but $C_{20}H_{24}N_2\Theta_2$ as it is written now for other reasons.

mined at present, but there is no hydrocarburet known to contain more than $(2n+2)$ and less than $2n-(n+2)=n-2$ atoms of hydrogen to n atoms of carbon.

The alcohols form several generic series:

Alcoholic series I.

$$C_nH_{2n+2}\Theta \text{ common alcohols of the type } \left.\begin{matrix} C_n{}' H_{2n+1} \\ H \end{matrix}\right\} \Theta$$

$$C_nH_{2n+2}\Theta_2 \text{ glycolic alcohols of the type } \left.\begin{matrix} C_n{}'' H_{2n} \\ H_2 \end{matrix}\right\} \Theta_2$$

$$C_nH_{2n+2}\Theta_3 \text{ glycerine `` } \left.\begin{matrix} C_n{}''' H_{2n-1} \\ H_3 \end{matrix}\right\} \Theta_3$$

$$\vdots$$

whether tetracid alcohols of the general formula $C_nH_{2n+2}\Theta_4$ and the type $\left.\begin{matrix} C_nH_{2n-2} \\ H_4 \end{matrix}\right\} \Theta_4$ can exist, is not known, as we know nothing certain about the existence of tetrabasic radicals. The polyethylenic glycols of the general formulas

$$C_nH_{2n+2}\Theta_4$$
$$C_nH_{2n+2}\Theta_5$$

are bibasic alcohols corresponding to the type $\left.\begin{matrix} (C_nH_{2n})_{m-1} \\ H_2 \end{matrix}\right\} \Theta_m$

Alcoholic series II.

$$C_nH_{2n}\Theta \text{ allylic alcohols of the type } \left.\begin{matrix} C_n{}'H_{2n-1} \\ H \end{matrix}\right\} \Theta$$

$$C_nH_{2n}\Theta_2 \text{ `` glycols `` } \left.\begin{matrix} C_n{}''H_{2n-2} \\ H_2 \end{matrix}\right\} \Theta_2$$

$$C_nH_{2n}\Theta_3 \text{ `` glycerine `` } \left.\begin{matrix} C_n{}'''H_{2n-3} \\ H_3 \end{matrix}\right\} \Theta_3$$

$$\vdots$$

of this series the only member known as yet is allylic alcohol $C_3H_6\Theta$ corresponding to the general formula $C_nH_{2n}\Theta$.

Alcoholic series III. IV. V.

$C_nH_{2n-2}\Theta$, $C_nH_{2n-2}\Theta_2$, etc.

$C_nH_{2n-4}\Theta$, $C_nH_{2n-4}\Theta_2$, etc.

$C_nH_{2n-6}\Theta$ the homologues of phenylic alcohol;

$C_nH_{2n-8}\Theta$ " cinnamylic alcohol.

The homologous series answering the general formula $C_nH_{2n-6}\Theta$ is

$C_6H_6\Theta$	phenylic	alcohol	boil.	point,	184°.
$C_7H_8\Theta$	benzoylic	"	"	"	204°.
$C_8H_{10}\Theta$	xylenic	"	"	"	220°.
$C_9H_{12}\Theta$	?				
$C_{10}H_{14}\Theta$	cuminic	"	"	"	243°.

as homologous with phenylic alcohol, the last member of this series, cuminic alcohol, ought to boil at 264°.

Forming a hemilogous series out of such of those alcohols as answer to the general formula $C_nH_{n+1}\Theta$ we have:

$Є_7H_8\Theta$ benzoylic alcohol, boil. point, 204°.
$Є_9H_{10}\Theta$ cinnamylic " " " 250°.

the difference in composition is here $2ЄH$, the difference in boiling point, 46°; to the difference $ЄH$ in composition there corresponds therefore a difference in the boiling points of 23°, and as to the difference $ЄH_2$ we mostly find a difference of 19°–20° in boiling points, the influence of the atom of H on the boiling point is in this case 3°. In a similar manner the influence of Є on the boiling point may be shown to be 26°, as benzoylic alcohol and cinnamylic alcohol differ by $Є+ЄH_2$ and $ЄH_2$ answers to 20°, we have $46°-20°=26°$. The influence of the single elements on the boiling point may thus be found by seriation and general laws deduced by comparing the different results obtained by this method. The acids form quite a number of generic series.

Series of Acids I.

$Є_nH_{2n}\Theta_2$ fatty acids $n=1$ to $n=30$.
$Є_nH_{2n}\Theta_3$ glycolic acid $n=2$.
$Є_nH_{2n}\Theta_4$ glyceric acid $n=3$ (isomeric with lactic acid.)
⋮

The acids of this generic series correspond to the first alcoholic series.

Series of Acids II.

$Є_nH_{2n-2}\Theta_2$
$Є_nH_{2n-2}\Theta_3$
$Є_nH_{2n-2}\Theta_4$
$Є_nH_{2n-2}\Theta_5$
⋮

The special homologous series deriving from this generic series are,

$Є_3H_4\Theta_2$ acrylic acid.	$Є_2H_2\Theta_3$ glyoxylic acid.
$Є_4H_6\Theta_2$ crotonic "	$Є_3H_4\Theta_4$ pyroracemic acid.
$Є_5H_8\Theta_2$ angelic "	⋮
etc. etc.	——
$Є_2H_2\Theta_4$ oxalic acid.	$Є_3H_4\Theta_5$ tartronic acid.
$Є_3H_4\Theta_4$ malonic "	$Є_4H_6\Theta_5$ malic "
$Є_4H_6\Theta_4$ succinic "	⋮
$Є_5H_8\Theta_4$ lipic "	——
etc. etc.	
$Є_4H_6\Theta_6$ tartaric acid.	$Є_6H_{10}\Theta_8$ mucic acid.
⋮	——

Series of Acids III.

$Є_nH_{2n-4}\Theta_2$
$Є_nH_{2n-4}\Theta_3$
$Є_nH_{2n-4}\Theta_4$
$Є_nH_{2n-4}\Theta_5$
⋮

From this generic series are derived:—

$Є_6H_8Θ_2$ sorbic acid.

$Є_4H_4Θ_4$ maleinic acid.
$Є_5H_6Θ_4$ itaconic "
$Є_6H_8Θ_4$?
$Є_7H_{10}Θ_4$ terebinic "

$Є_3H_2Θ_5$ mesoxalic acid.

$Є_6H_8Θ_7$ citric acid.

Acid series IV.

$Є_nH_{2n-6}Θ_2$
$Є_nH_{2n-6}Θ_3$
$Є_nH_{2n-6}Θ_4$
$Є_nH_{2n-6}Θ_5$
⋮

From this generic series we derive:—

$Є_6H_6Θ_2$ oxyphenic acid.
$Є_8H_{10}Θ_2$ terebentilic "

$Є_4H_2Θ_4$ mellitic acid.
$Є_3H_{10}Θ_4$ cholesteric "

$Є_5H_4Θ_3$ pyromucic acid.
$Є_6H_6Θ_3$ pyrogallic "
$Є_7H_8Θ_3$ ipecacuanic "
$Є_8H_{10}Θ_3$ ricinoleic "

$Є_6H_6Θ_5$ aconitic acid.*

Acid series V.

$Є_nH_{2n-8}Θ_2$
$ЄH_{2n-8}Θ_3$
$Є_nH_{2n-8}Θ_4$
$Є_nH_{2n-8}Θ_5$
⋮

From this generic series we derive:—

$Є_7H_6Θ_2$ benzoic acid.
$Є_8H_8Θ_2$ toluylic "
$Є_9H_{10}Θ_2$?
$Є_{10}H_{12}Θ_2$ cuminic "

$Є_8H_8Θ_6$ phenoxacetic acid.

$Є_5H_2Θ_5$ krokonic acid.
$Є_6H_4Θ_5$ comenic "
$Є_7H_6Θ_5$ gallic "
$Є_{24}H_{40}Θ_5$ cholic "
$Є_7H_6Θ_3$ salicilic acid.
$Є_8H_8Θ_3$ anisic "
$Є_9H_{10}Θ_3$ phloretinic acid.

* The radical of the tribasic aconitic acid $\left.\begin{matrix}Є_6'''H_3Θ_3\\ H_3\end{matrix}\right\}Θ_3$ may be derived from a hydrocarburet by substitution of H_6 by $Θ_3$, as acetic acid is formed by substitution of H_2 by $Θ$ in the radical $Є_2H_5$. The triacid alcohol or glycerin corresponding to aconitic acid would therefore be $\left.\begin{matrix}Є_6H_9\\ H_3\end{matrix}\right\}Θ_3$; it belongs to the alcoholic series II, answering to the general formula $Є_nH_{2n}Θ_3$, and the type $\left.\begin{matrix}Є_n'''H_{2n-8}\\ H_3\end{matrix}\right\}Θ_3$. This remark applies, *mutatis mutandis*, to other acids.

$\text{Є}_8H_8\Theta_4$ lecanoric acid. $\text{Є}_9H_{10}\Theta_4$ veratric acid.

Acid series VI.

$$\text{Є}_nH_{2n-10}\Theta_2$$
$$\text{Є}_nH_{2n-10}\Theta_2$$
$$\text{Є}_nH_{2n-10}\Theta_2$$
$$\vdots$$

Of the acids deriving from this generic series only a few are known as yet.

$\text{Є}_9H_9\Theta_3$ cumaric acid. $\text{Є}_7H_4\Theta_7$ mionic acid.

$\text{Є}_8H^6\Theta_4$ phtalic acid.
$\text{Є}_{24}H_{38}\Theta_4$ choloidic "
$\text{Є}_{25}H_{40}\Theta_4$ hyocholic "

From other known acids it is hardly possible to form series, as they stand mostly isolated; there is for instance only one acid —anemonic acid $\text{Є}_{15}H_{14}\Theta_7$—known as yet, which corresponds with the general formula $\text{Є}_nH_{2n-16}\Theta_7$.

The generic series of acids considered above may be ranged into one primitive series:

$$\text{Є}_nH_{2n}\Theta_{2x}$$
$$\text{Є}_nH_{2n-2}\Theta_{2x}$$
$$\text{Є}_nH_{2n-4}\Theta_{2x}$$
$$\text{Є}_nH_{2n-6}\Theta_{2x}$$
$$\text{Є}_nH_{2n-8}\Theta_{2x}$$
$$\text{Є}_nH_{2n-10}\Theta_{2x}$$
$$\vdots$$

where Θ_2^x means, that in order to form a generic series from one of these primitive formulas, Θ has successively to receive suffixed the numbers 2, 3, 4, ... x. It is easy to see that as every generic series, as for instance:

$\text{Є}_nH_{2n-2}\Theta_2$;	$\text{Є}_2H_2\Theta_2$,	$\text{Є}_3H_4\Theta_2$,	$\text{Є}_4H_6\Theta_2$	. . .
$\text{Є}_nH_{3n-2}\Theta_3$;	$\text{Є}_2H_2\Theta_3$,	$\text{Є}_3H_4\Theta_3$,	$\text{Є}_4H_6\Theta_3$	. . .
$\text{Є}_nH_{2n-2}\Theta_4$;	$\text{Є}_2H_2\Theta_4$,	$\text{Є}_3H_4\Theta_4$,	$\text{Є}_4H_6\Theta_4$	. . .
$\text{Є}_nH_{2n-2}\Theta_5$;	$\text{Є}_2H_2\Theta_5$,	$\text{Є}_3H_4\Theta_5$,	$\text{Є}_4H_6\Theta_5$	. . .
$\vdots$				

consists of two kinds of series, of which those lying on the horizontal lines are homologous series, and those lying on the vertical lines are series of oxydation, the primitive series therefore expresses a *seriation in a cube.*

It is worth observing that there may be series of isomeric substances running parallel to each other; such series may be called *homarithmical series.*