XLVI.—*On an Application of Mathematics to Chemistry.* By ALEXANDER CRUM BROWN, M.D., D.Sc.

(Read 18th February 1867.)

Prefatory Note, added June 24, 1867.

Since reading this paper, I have seen Sir BENJAMIN BRODIE'S paper on "The Calculus of Chemical Operations," read before the Royal Society of London.

The two papers resemble one another, merely in being applications of mathematical language to chemistry. They entirely differ in method, object, and result.

I may here mention, what I have omitted to state explicitly in the paper, that I have no idea of attempting to substitute a functional notation for that in common use. I only propose to use a functional notation to express certain general and serial relations in those cases where the common atomic notation is inconvenient or obscure.

The full application of Mathematics to Chemistry can only be made when a fundamental physical hypothesis is discovered, from which, by means of mathematical methods, results may be deduced which coincide with the observed facts of chemistry. In the meantime, however, a profitable application of mathematics may be made in another direction. Mathematics is the science by means of which consequences are deduced from laws; and although we have not, as yet, discovered the laws of chemistry, we have what may represent them,—approximate generalisations. To these we can apply mathematical methods, or at least we can express them in mathematical language.

I.—*Definition of Symbols.*

The objects of chemical study are of two classes—1st, substances; and 2d, processes performed on these substances. In this paper I shall represent the former as operands, and the latter as operators; where the contrary is not specially mentioned, a single operand symbol will be used to indicate one molecule, or chemical unit of a homogeneous substance.

An operator ϕ is defined by the chemical equation or equations connecting a , and $\phi \cdot a$, a being a molecule of a substance, and $\phi \cdot a$ the result of applying the process ϕ to it. Thus if the chemical equation be $a + \text{KHO} = \phi \cdot a + \text{H}_2\text{O}$, the process ϕ as applied to a , is the union of a with a molecule of caustic potash and the simultaneous elimination of a molecule of water.

II.—Combination of Symbols.

The sign $+$ will be used in a purely enumerative sense, to connect operands. Thus, $a + b + c + \&c.$, means one molecule of a , and one of b , and one of c , &c. In the same way na means n molecules of a , the sign $+$ and numerical multipliers never being used to indicate combination.

Many chemical processes are capable of being applied either to *one* molecule or to several simultaneously. Thus, if ϕ be defined by the equation $a + \text{NH}_3 = \phi \cdot a + 2\text{HCl}$, or by a series of equations equivalent to this, ϕ may be performed either on one molecule containing two atoms of chlorine, or on two molecules, each containing one. In the latter case, a becomes $a + b$, and $\phi \cdot a$ becomes $\phi \cdot (a + b)$, here ϕ is not performed on a and on b , but on $(a + b)$; that is, partly on a and partly on b , so that $\phi \cdot (a + b)$ is not equal to $\phi \cdot a + \phi \cdot b$. The distributive law does not, therefore, hold good here. $(a + b)$ is, however, the same as $(b + a)$, and generally we may change the order of operands connected by the sign $+$.

In $\phi \cdot (a + b + c + \&c.)$, when $a, b, c, \&c.$ are identical, we have $\phi \cdot na$, and just as $\phi \cdot (a + b + c + \&c.)$ is not equal to $\phi \cdot a + \phi \cdot b + \phi \cdot c + \&c.$, so $\phi \cdot na$ is not equal to $n \phi \cdot a$; in other words, the commutative law of multiplication does not hold good for operators and numerical multipliers.

If a new process ψ be performed on the operand $\phi \cdot a$, there are two ways in which it may act; 1st, the process ψ may act *independently* on a , thus if $a = \text{CH}_4$, and ϕ be the replacement of H by COHO, and ψ the replacement of H by Cl, ϕ

and ψ may act independently, giving chloracetic acid, ; or the $\psi \cdot (\phi \cdot a)$

new operator ψ may act on that part of the molecule which has been introduced by the process ϕ , giving in the instance above the acetate of chlorine,

$(\psi \cdot \phi \cdot a)$ may therefore have two quite distinct meanings,

and it will be advisable to have two forms of notation for it. I shall represent the first by $\left. \begin{smallmatrix} \phi \\ \psi \end{smallmatrix} \right| a$, and the second by $\psi \cdot \phi \cdot a$, the complex operator $\psi \cdot \phi$ being in the case cited above, the replacement of H by COHO, in which the H is replaced by Cl, and may, therefore, properly enough be said to be the operator ϕ , acted on by ψ .

In the first case, which may be called the *vertical multiplication of operators*, I

shall assume for the present, that as the operators act independently, their order may be varied without change of meaning, and that the commutative law of multiplication applies.* In the second case, which may be called the *horizontal multiplication of operators*, it is obvious that the order cannot be changed without changing the meaning,—here then the commutative law does not apply, $\phi \cdot \psi \cdot a$ being in general different from $\psi \cdot \phi \cdot a$.

III.—The Laws of positive Integral Indices, as applied to Operators.

In the case of vertical multiplication, we may represent $\left. \begin{smallmatrix} \phi \\ \phi \end{smallmatrix} \right| \cdot a$ by the symbol $\phi^{21} \cdot a$, $\left. \begin{smallmatrix} \phi \\ \phi \end{smallmatrix} \right| \cdot a$, by $\phi^{31} \cdot a$, &c., and generally, it is obvious, that $\left. \begin{smallmatrix} \phi^m \\ \phi^n \end{smallmatrix} \right| \cdot a = \phi^{m+n1} \cdot a$ and $(\phi^m)^n \cdot a = \phi^{mn1} \cdot a$, when m and n are positive integers.

In horizontal multiplication, $\phi \cdot \phi \cdot a$, may be written $\phi^2 \cdot a$, $\phi \cdot \phi \cdot \phi \cdot a$, $\phi^3 \cdot a$, &c., understanding that $\psi \cdot \phi^n \cdot a$ is merely a contraction for $\psi \cdot \phi \cdot \phi \cdots \phi \cdot a$, and also, that $\phi^n \cdot \psi \cdot a$ is $\phi \cdot \phi \cdots \phi \cdot \psi \cdot a$; in other words, that the complex operator ϕ^n always acts by means of the ϕ at the extreme right of the series, and that an operator acting on it always acts upon the ϕ at the extreme left. With these assumptions, we at once see that the laws of indices $\phi^m \cdot \phi^n \cdot a = \phi^{m+n} \cdot a$, and $(\phi^m)^n \cdot a = \phi^{mn} \cdot a$, hold good also in the case of horizontal multiplication when m and n are positive integers.

It also follows from these assumptions, that if $\phi^n = \psi$, $\psi \cdot \phi = \phi^{n+1}$, but $\phi \cdot \psi$ may have several values, one of which is ϕ^{n+1} , for in $\phi \cdot \phi^n$, the action of ϕ is restricted to a particular part of ϕ^n , while no such restriction is made in the case of $\phi \cdot \psi$. Thus, if a be ammonia, and ϕ the replacement of H by CH_3 , $\phi^2 \cdot a$ is ethylamine, and $\phi \cdot \phi^2 \cdot a = \phi^3 \cdot a$ is propylamine; but if we put $\phi^2 = \psi$, $\phi \cdot \psi \cdot a$ may be either propylamine ($\phi^3 \cdot a$) or isopropylamine ($\phi^{21} \cdot \phi \cdot a$). The graphic formulæ will make this more obvious.

* It is not by any means certain that this is true, even in the case of the simplest operands; it is almost certain that it is not true in the case of complex operands; but as we have not sufficient data to enable us to form a theory connecting the order in which operators are applied to a molecule with the parts of the molecule upon which they act, I have provisionally assumed the simplest possible law.

ψ being here the replacement of H by C_2H_5 , $\phi \cdot \psi$ is the replacement of H by C_2H_5 , in which H is replaced by CH_3 ; ϕ^2 on the other hand, is the replacement of H by CH_3 in which H is replaced by CH_3 and $\phi \cdot \phi^2$, is the replacement of H by CH_3 in which H is replaced by CH_3 in which H is replaced by CH_3 .

IV.—On Negative Integral Indices as applied to Operators.

Without contradicting any previous assumption, we may define the symbol ϕ^{-1} by the equation $\phi \cdot \phi^{-1} \cdot a = a$, or $\phi \cdot \phi^{-1} = 1$. It is at once obvious that $\phi \cdot \phi^{-1} = \phi^{-1} \cdot \phi$, for if ϕ be the replacement of A by B, ϕ^{-1} is the replacement of B by A, and $\phi \cdot \phi^{-1}$ is the replacement of B by A, in which A has been replaced by B, that is, the replacement of B by B, and similarly $\phi^{-1} \cdot \phi$ is the replacement of A by A; it is different, however, in the case of vertical multiplication, $\left. \begin{smallmatrix} \phi^{-1} \\ \phi \end{smallmatrix} \right| \cdot a$ is not necessarily equal to a , for $\left. \begin{smallmatrix} \phi^{-1} \\ \phi \end{smallmatrix} \right| \cdot a$ expresses the replacement of A by B in one part of the molecule, and of B by A in another part of it, and it is only in particular cases that these two processes will leave the molecule unchanged, $\left. \begin{smallmatrix} \phi^{-1} \\ \phi \end{smallmatrix} \right| \cdot a$ must, of course, be *isomeric* with a .

$\left. \begin{smallmatrix} \phi^{-1} \\ \phi^{-1} \end{smallmatrix} \right| \cdot a$ is from the last chapter $(\phi^{-1})^{21} \cdot a$, and no confusion will arise by writing this $\phi^{-21} \cdot a$, as the only other meaning which this symbol could have would be $(\phi^{21})^{-1} \cdot a$, and this would be defined by the equation $\phi^{21} \cdot (\phi^{21})^{-1} \cdot a = a$, which could only mean $\left. \begin{smallmatrix} \phi \cdot \phi^{-1} \\ \phi \cdot \phi^{-1} \end{smallmatrix} \right| \cdot a$, giving as the equivalent for $(\phi^{21})^{-1}$, the expression $(\phi^{-1})^{21}$. We have thus, generally, $\left. \begin{smallmatrix} \phi^{-m1} \\ \phi^{-n1} \end{smallmatrix} \right| \cdot a = \phi^{-(m+n)} \cdot a$, and

$(\phi^{-m1})^{n1} \cdot a = \phi^{-mn} \cdot a$. An expression, $\left. \begin{smallmatrix} \phi^{p1} \\ \phi^{q1} \\ \phi^{r1} \\ \&c. \end{smallmatrix} \right| \cdot a$ (where $p, q, r, \&c.$ are any in-

egers, positive or negative) can then always be reduced to the form $\left. \begin{smallmatrix} \phi^m \\ \phi^{-n} \end{smallmatrix} \right| \cdot a$, by adding all the positive indices to form m , and all the negative indices to form n .

In the case of horizontal multiplication, we have at once $(\alpha \cdot \beta \cdot \gamma \dots \nu)^{-1} \cdot a = \nu^{-1} \dots \gamma^{-1} \cdot \beta^{-1} \cdot \alpha^{-1} \cdot a$, and therefore $(\phi^n)^{-1} = (\phi^{-1})^n$, and we may, therefore, write this ϕ^{-n} ; and as $\phi \cdot \phi^{-1} \cdot a = a$, we have $\phi^2 \cdot \phi^{-2} \cdot a = \phi^{-2} \cdot \phi^2 \cdot a = a$; and, generally, $\phi^m \cdot \phi^{-n} \cdot a = \phi^{m-n} \cdot a$; also $(\phi^{-m})^n \cdot a = \phi^{-mn} \cdot a$ and

$(\phi^m)^{-n} \cdot a = \phi^{-mn} \cdot a$; or, the ordinary laws of indices hold good in horizontal multiplication where m and n are any integers, positive or negative.*

V.—*Fractional Indices as applied to Operators.*

The symbols $\phi^{\frac{1}{n}}$ and $\phi^{\frac{1}{n}}]$ may be defined thus $(\phi^{\frac{1}{n}})^n \cdot a = a$ and $(\phi^{\frac{1}{n}}])^n \cdot a = a$.

When ϕ is of the form ψ^n , the first expression will have a real meaning, and so will the second when ϕ is of the form $\psi^{\frac{1}{n}}$. In the opposite case, $\phi^{\frac{1}{n}}$ and $\phi^{\frac{1}{n}}]$ are purely imaginary operators, and it is only when n of them are multiplied together in the first case horizontally, and in the second vertically, that they acquire a meaning. It may, however, be useful to break up an operator into imaginary factors. Thus, if ϕ be the replacement of three atoms of hydrogen by one of nitrogen, $\phi^{\frac{1}{3}}$ is the replacement of H by $\frac{1}{3}$ N, and where the 3 H atoms replaced by N have different positions in a molecule, it may be convenient to express it in this way. Thus, if a be benzol, ψ the replacement of H by NH_2 , and ϕ the replacement of 3 H by N, we may express diazobenzol by $\phi^{\frac{1}{3}} \cdot \psi \cdot a$; thus indicating that the process ϕ is performed on $\psi \cdot a$, so that $\phi^{\frac{1}{3}}$ acts on ψ , and $\phi^{\frac{1}{3}}$ on a .

In the same way, an operator may be broken up into imaginary factors which are not identical; thus, if ϕ be the replacement of N by O'' and HO , we may put $\phi \cdot a = \frac{\alpha}{\beta} \cdot a$ where α is the replacement of $\frac{2}{3}$ N by O'' , and β the replacement of $\frac{1}{3}$ N by HO .

VI.—*On Chemical Groups and Series.*

Those groups which in a former paper (*Trans.* xxiv. 331) I have called chemical genera, and which are characterised by containing a particular radical, the *generic* radical, may each be represented by a generic formula $\phi \cdot X$, where ϕ is an operator introducing the generic radical, and X a molecule or group of

* There is an obvious and important difference between direct and inverse operators, which I may mention here.

If we represent as direct those operators only which express direct processes which can be performed so as to get $\phi \cdot a$ by acting on a , it is plain that if ϕ includes the physical conditions of the process, $\phi \cdot a$ can have only *one* value. It may have a number of conceivable values, and it is the business of the experimental chemist to find out which of these is the real one; but $\phi^{-1}a$ may have more than one *real* value, for ϕ^{-1} is not restricted to mean *one* actual process capable of being performed, but any process, such that $\phi^{-1}a$ shall be by the process ϕ (performed on the part of the molecule, introduced or modified by ϕ^{-1}) reproduce a . Thus, if ϕ be the addition of H_2 , and a be alcohol, $\phi^{-1}a$ may represent either aldehyde or oxide of ethylene, for both of these give a when treated by the process ϕ . Examples of this kind might be multiplied to any extent.

molecules on which ϕ can act. Thus, if ϕ be the replacement of H by COHO, the monocarbon acids, the dicarbon acids, and the tricarbon acids, have the formulæ $\phi \cdot X$, $\phi^2 \cdot X$, $\phi^3 \cdot X$, respectively.

I shall only consider further the application of this method to two other kinds of series, which we may call *functional chemical series*. The first consists of terms of the form a , $\phi \cdot a$, $\phi^2 \cdot a$, $\phi^n \cdot a$. Here the successive terms are produced by the repetition of the process ϕ *independently* on a , and we may call such series *independent functional series*. We have instances of this in the series CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 ; NH_4I , $\text{NH}_3\text{CH}_3\text{I}$, $\text{NH}_2(\text{CH}_3)_2\text{I}$, $\text{NH}(\text{CH}_3)_3\text{I}$, $\text{N}(\text{CH}_3)_4\text{I}$; C_2H_2 , C_2H_4 , C_2H_6 , or in the so-called homologues of benzol C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$, $\text{C}_6\text{H}_4(\text{CH}_3)_2$, &c. In all these series we have a common difference between successive terms, and we may observe that all such series necessarily consist of a *definite* number of terms, for the process ϕ can only be performed *independently* on a a definite number of times. If we put $a = \phi^{-n} \cdot b$, where b is not of the form $\phi^{-1} \cdot x$, n is the number of times ϕ can be performed independently on a , and $n + 1$ is the number of terms in the series.

The other form of functional series is a , $\phi \cdot a$, $\phi^2 \cdot a$, $\phi^n \cdot a$. In this the successive terms are derived by the repetition of ϕ on that part of the molecule which was introduced or modified by the previous performance of ϕ , and we may call such a series a *successive functional series*. In order that such a series may be possible, it is necessary that a be of the form $\phi^{-1} \cdot b$, and that ϕ be of the form $\phi^{-1} \cdot \psi$; in other words, that ϕ can be applied once to a and once to ϕ . We have examples of this kind of series in "homologous" series, such as NH_4I , $\text{NH}_3(\text{CH}_3)\text{I}$, $\text{NH}_3(\text{CH}_2\text{CH}_3)\text{I}$, &c.

Here the law of derivation of successive terms does not, as in the independent functional series, contain in itself a determination of the number of terms of which the series consists, except where ϕ diminishes the weight of the molecule on which it acts. In this case, however, by inverting the series, we find that there are an indefinite number of terms before a , so that by inversion, if necessary, all such series may be reduced to the form a , $\phi \cdot a$ $\phi^n \cdot a$, where a is not of the form $\phi \cdot x$, and is, therefore, the first term.

In a series of this form, if ϕ does not involve x in the expression $\phi \cdot x$, we have a common difference in weight and composition. This is the case in "homologous" series. If ϕ involve x , there cannot, of course, be a common difference; this case will, however, be examined in a subsequent part of this paper.

There are two varieties of the successive functional series—1st, Where ϕ is a simple addition; and, 2d, Where ϕ is a replacement. In the first, the radical (or radicals) necessarily artiad, must be such that it (or they) can be again added to that part of the molecule which has been introduced or modified by the first ϕ . We have an example of this kind of series in the polymers of acetylene,

where ϕ consists in the addition of the radical C_2H_2 This series may be represented in several different ways, and we do not as yet know which is the true one. I append graphic formulæ of two of these ways, to illustrate my meaning—

The second of these is the form proposed by KEKULÉ, and appears on the whole to be the most probable.

In the other variety of successive functional series, ϕ is the replacement of one or more radicals by one or more new radicals. Let the replaced radical or group of radicals, be represented by Γ , and the replacing radical or group of radicals by Λ , and we at once see, first, that Γ and Λ are equivalent; and, second, that Λ must contain Γ , as the process is capable of repetition. When ϕ in $\phi \cdot x$ is independent of x , the difference between Λ and Γ is constant (as indeed Λ and Γ are themselves constant throughout the series), and is the common difference of the series. This is the case in "homologous" series. As an example, we may

take the series of the fatty acids. The formula of one of them is

where R is of the form C_nH_{2n+1} ; and taking any of the series of substances through which it is connected with the next higher member of the series, such as

we see that Γ is O'' and $(HO)'$, and Λ is H' , H' , and $(COHO)'$. Λ thus contains Γ , and the process is capable of repetition. The common difference is here CH_2 , but there are instances of series probably of the kind we are now considering (although we cannot at present trace the relation between successive terms) in which we have other common differences. Thus the carbonates, oxalates, and

mesoxalates, form a series in which the common difference is CO. In the series—methylic alcohol, ethylenic glycol, glycerine, erythrite, the unknown body $C_5H_5(HO)_5$, and mannite, as also in the series tartronic acid, tartaric acid, the unknown trioxypyrotartaric acid, and mucic acid, we have a common difference of $CH(HO)$. It is quite possible that relations may be discovered between the successive terms of these and similar series, which will show that they are successive functional series; and indeed homology has been assumed upon less evidence in cases where the common difference is the usual one CH_2 , as for instance in the series of bases $C_nH_{2n-5}N$ (pyridine, picoline, &c.).

It is instructive to compare *successive* functional series with the *independent* functional series isomeric with them. Thus, ammonia, methylamine, dimethylamine, trimethylamine, with ammonia, methylamine, ethylamine, propylamine: or benzol, toluol, xylol, pseudocumol, &c., with benzol, toluol, ethylbenzol, propylbenzol, &c. KEKULÉ, to whom we are greatly indebted for clearness of conception of the structure of the aromatic bodies, calls both of the last-mentioned series “homologous;” as the word “homologous” has never, as far as I know, been strictly defined, there can be no objection to this; but if we call the series C_6H_6 , $C_6H_5(CH_3)$, $C_6H_4(CH_3)_2$, &c. homologous, we must apply the same term to the series ammonia, methylamine, dimethylamine, &c. It will be observed, that while no *three* successive terms of an *independent* functional series can belong to the same *successive* functional series, *any* two successive terms may. For $\phi^{n+1} \cdot a$ and $\phi^{n+2} \cdot a$ are $\phi^{n+1} \cdot a$, and $\phi^{n+2} \cdot a$, and these are the initial terms of the series $\phi^{n+1} \cdot a$, $\phi^{n+2} \cdot a$, $\phi^{n+3} \cdot a$, &c. Thus, methylamine, dimethylamine, and trimethylamine, are not in successive series, but methylamine and dimethylamine are the initial members of the series which continues methyl ethylamine, methyl propylamine, &c.

If we restrict the term “homologous series” to successive functional series having the common difference CH_2 , we see that one substance may be the starting point of several homologous series. In this sense, NOAD’s toluic acid and α toluic acid are both homologues of benzoic acid. The one series being, benzoic acid, methyl benzoic acid (NOAD’s toluic acid), ethyl benzoic acid, propyl benzoic acid, &c.; the other being benzoic acid, α toluic acid, the acid $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot COHO$, &c.

When ϕ in the expression $\phi \cdot x$ involves x , it is obvious that there can be no common difference in the series a , $\phi \cdot a$, $\phi^2 \cdot a$, $\dots$, $\phi^n \cdot a$.

Such series have not been specially examined, but examples can easily be suggested; for instance, let ϕ be the series of processes by which acetic acid is successively converted into acetone, acetic acid, and isobutyric acid; then ϕ can again be applied to the last mentioned acid, giving isobutyron, isobutyronic acid, &c., thus giving rise to a series of acids, having the formulæ,—

Acetic Acid.

Isobutyric Acid.

Unknown Third Term.

is formally the first term of the series, although as the

formic ketone is unknown, we cannot directly prove the relation.

It is, however, unnecessary to dwell longer on such series ; it is sufficient to point out the probability of their existence, in order to show that a common difference is not an essential character of successive functional series.