CLXVIII.—*A Development of the Atomic Theory which Correlates Chemical and Crystalline Structure and leads to a Demonstration of the Nature of Valency.*

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THE morphotropic relationships observed between related chemical substances, fragmentary as they are, indicate convincingly that crystal structure is a function of chemical constitution, although no satisfactory suggestion as to the nature of this function has yet been made. Further, the simple character and wide applicability of the doctrine of valency suggests that valency is capable of a perfectly definite physical interpretation ; the failure of the numerous attempts which have been made to convert the doctrine of valency into a concept comparable in definiteness with the atomic theory does not weaken the conviction as to its possibility.

The determination of the nature of valency and of the connexion existing between chemical constitution and crystal form is a problem affecting the foundations of both chemistry and crystallography. By adopting a very simple fundamental conception as to the nature of the environment of the atoms in a chemical molecule which will be acceptable to the chemist and applying to it methods of treatment which will be acceptable to both crystallographer and chemist, we find ourselves able to offer a scheme, which, whilst in entire harmony with current views of molecular constitution, indicates quantitatively the relation of chemical constitution and crystalline form for any compound substance, and interprets valency as a simple volume relation.

The fundamental conception which forms the basis of the present work is briefly stated below, and this statement is followed by a discussion in which the conception is expanded or developed into a form susceptible of treatment by the geometrical methods of crystallography.

The Fundamental Conception.

Each chemical atom present in a compound occupies a distinct portion of space by virtue of an influence which it exerts uniformly in every direction.   The domain of a chemical molecule is the space-unit consisting of one or more of these distinct portions of space, obtained by homogeneously sub-dividing into units a homogeneous structure built up of the spheres of influence of a number of associated atoms. The form of aggregation of the spheres of influence of the atoms thus

associated in a molecule constitutes the stereometric arrangement of these atoms and thus the chemical molecule acquires a definite shape. A crystal is the homogeneous structure derived by the symmetrical arrangement in space of an indefinitely large number of spheres of atomic influence.*

Development of the Fundamental Conception.

A mechanical assemblage of the nature contemplated by the above fundamental conception may be a stable one if subject to the operation of two opposing influences acting between the atomic centres, namely, (1) a repellent force, which may be attributed to the kinetic energy of the atoms, (2) an attractive force of the nature of gravity. The simplest premise is that these, and no other opposing forces, are operative. The nature of the equilibrium in such an assemblage is represented by the hypothesis that space is filled by spheres of atomic influence which are in mutual contact at their boundaries ; for most practical purposes it suffices to regard the assemblage as in static equilibrium under the influence of the two opposing forces, although the spheres of atomic influence are doubtless the seat of considerable activity of movement.

It is noteworthy that the assumption of simultaneously operative attractive and repulsive forces acting between the atoms has been made in every serious attempt to visualise atomic and molecular action. Boscovich in 1758 premised that the atoms are held apart and at equilibrium distances as the result of an equilibrium established between the attractive and repulsive forces acting between them ; by postulating the existence of similar forces acting between the molecules of gases and liquids, van der Waals has more recently succeeded in accounting almost perfectly for the physical behaviour of fluids. The conclusion that the atoms appropriate distinct and characteristic portions of space in the manner now premised has been rendered unquestionable by the unique comparative work of Tutton on the alkali sulphates and double sulphates and the corresponding selenates. (Compare also Sollas, *Proc. Roy. Soc.*, 1898, **63**, 271.)

The attractive forces acting between the atoms will cause the portions of space which they respectively appropriate, supposed as spherical as possible, to be in contact one with another, at the

* The meaning attached to the term "homogeneous" in the present paper is indicated by the following definition : a homogeneous structure or assemblage is one in which every point or unit possesses an environment identical with that of an infinitely large number of other similar points or units in the assemblage if the latter is regarded as indefinitely extended throughout space (compare Barlow, *Min. Mag.*, 1897, **11**, 120 ; *Sci. Proc. Roy. Dubl. Soc.*, 1897, **8**, 528).

maximum number of points ; and as a result of this the atoms com-
posing a chemical molecule will lie as closely together as possible whilst
the molecules themselves will also pack closely together into the
minimum compass.   In other words, the spheres of influence of the
atoms composing a molecule will be forced into such relative positions
as will permit of the molecules themselves packing together closely.
The total effect produced is thus one corresponding to that of a
uniform compression exerted upon a concourse of elastic bodies in
contact, the necessary result of which would be to leave a minimum of
interstitial space.

Now the maximum closeness of packing of a number of similar
bodies is commonly attained in some homogeneous arrangement of
them, that is, in some arrangement in which the distribution of the
structural units is the same about every unit.   And, since all crystal-
line structures are homogeneous assemblages built up of certain units,
which units we conceive to be the chemical molecules, we develop from
our fundamental conception the view that a crystalline structure is a
close-packed, homogeneous assemblage of the spheres of influence of
the component atoms.

The close-packed, homogeneous assemblage of spheres of atomic
influence derived by the comparatively simple process of development
just indicated is partitionable, homogeneously, into cells which are all
exactly similar and each of which contains a chemical molecule.   The
essential feature of the new method of investigation introduced in the
present paper is the formation of close-packed assemblages corre-
sponding to different chemical compounds and the study of the par-
titionings of them which can be effected.   Inasmuch as the close-
packed assemblage must coincide in symmetry and relative dimensions
with the crystalline structure of the substance represented, our method
may be checked to a large extent quantitatively by reference to the
crystallographic measurements ; and since the assemblage itself can be
partitioned into units identical in composition, configuration, and shape
with the chemical molecule, the study of this partitioning at once
reveals a number of important geometrical properties of the molecule.
Many of these properties furnish immediate explanations of observed
peculiarities of chemical behaviour, such as those relating to tauto-
meric or isodynamic compounds, to substitution in aromatic nuclei, and
the like.   In the present work, the necessity never arises for intro-
ducing the common conception that, within the molecule, the portions
of space appertaining to different atoms overlap—that, like figure-
skaters associated in the production of some complex figure, the
different atoms follow paths which cross or interweave—and thereby
give rise to tautomerism and intermolecular change.   Further, the
ambit of this inquiry does not involve the assumption that the

individual atoms possess polarity, although the derived cluster or molecule may, and indeed often does, exhibit polarity as a consequence of the arrangement of the atoms.

The construction of close-packed assemblages representing molecular complexes by the packing together of the spheres of atomic influence of various elements naturally involves the assignment of specific volumes or diameters to the latter. It might therefore seem at first sight that fresh assumptions defining these volumes are necessary, and that these would be as axiomatic in character as is our fundamental conception ; this, however, is not the case, and for a reason which will be fully developed later, but which may be indicated briefly here.

On studying the methods by which one close-packed homogeneous assemblage of spheres may be converted, geometrically, by substitution of certain of its parts, into related close-packed homogeneous assemblages, geometrical properties governing the substitution become revealed which are of perfectly general applicability and which lead at once to a geometrical interpretation of valency. These geometrical properties are discussed later, but one must be noted here. It is that if some set of spheres in the assemblage is to be replaced by another set which is to occupy the same cavities, and in such a way that the new and also homogeneous assemblage shall retain the same general arrangement of parts and the same density of packing as the old one, the total solid volume of the substituting and substituted spheres must be almost the same. Thus, for instance, in the close-packed homogeneous assemblage representing benzene, groups are found of three hydrogen spheres, one of the three spheres belonging to each of three adjacent molecules ; if one-sixth of these groups are to be symmetrically replaced each by one nitrogen sphere, so as to produce the assemblage for triphenylamine, the sphere representing nitrogen must have about three times the volume of that representing hydrogen. If these relative volumes are chosen, the replacement can be effected so that close-packing and homogeneity are retained practically unimpaired ; if other relative volumes are assigned to the spheres representing nitrogen and hydrogen, the derived assemblage cannot be rendered homogeneous and as close-packed as before without such a re-arrangement of its parts that it no longer represents chemically the triphenyl derivative of ammonia.

The ordinary law of valency is thus merely an interpretation of a simple geometrical property of close-packed homogeneous assemblages of spheres ; the other aspects of valency, such as multivalency, the valency of compound radicles, etc., are, as will appear later, also directly traceable to simple geometrical properties of such assemblages.

To prevent misunderstanding, three remarks must at once be made concerning this application of geometrical principles. First, it is not to be supposed that the whole numbers by which we ordinarily represent the valency of the different elements stand precisely in the ratios of the volumes of the spheres of atomic influence; these numbers are merely approximations and the spheres of atomic influence of the univalent elements, for instance, are not quite the same. Indeed, peculiarities in the types of combination occurring between allied elements of the same valency may be traced to slight deviations from this geometrical interpretation of the valency numbers. Secondly, the volume ratios of the spheres of influence of different elements do not remain quite constant under changes of condition; thus, differences exhibited between the types of combination effected between two given elements at different temperatures may be traced to slight differences in the relative rate of increase of the volumes of the atomic spheres of influence as the temperature rises. Thirdly, in passing from compound to compound, the absolute magnitudes of the spheres of atomic influence often change considerably, although the relative magnitudes are but slightly affected.

These three remarks are not the direct outcome of the fundamental conception, but are the result of a consideration of the observed facts in the light of that conception. The third is of importance in connexion with the theory of molecular volumes, in that it indicates that the molecular volume is not an additive property which can be summed up from component atomic volumes in the simple manner attempted in the past. An example which will make this clear may be drawn from the data (p. 1699) relating to benzene and its derivatives containing halogen. It is there shown that, taking the spheres of atomic influence of carbon as of volume four, those of hydrogen, chlorine, and bromine, as of volume one, benzene and its per-halogen derivatives are characterised by presenting an almost identical spatial arrangement of the component spheres of atomic influence. Now this could not be the case if the atoms of carbon, hydrogen, chlorine, and bromine, in these compounds actually appropriated respectively the atomic volumes 11·0, 5·5, 22·8, and 27·8 stated by Kopp. The interpretation of the evidence adopted in this paper is that in benzene of molecular volume 77·4 and tetrabromobenzene of molecular volume 130·2, the sphere of influence of the carbon atom is about four times as large as those of either hydrogen or bromine; but that on introducing the bromine atoms into the benzene molecule the volumes of the spheres of influence of both carbon and hydrogen expand proportionally in the ratio of 77·4 : 130·2 (compare Thorpe, Trans., 1893, 63, 811).

The rational character of the conclusion now drawn is well illus-

trated by the axial ratios and molecular volumes of potassium and cæsium sulphates (Tutton, Trans., 1905, **87**, 1188).

K_2SO_4 .... Mol. vol. $= 64\cdot91.$ $a : b : c = 0\cdot5727 : 1 : 0\cdot7418.$
Cs_2SO_4 ....　　,,　$= 84\cdot58.$ $a : b : c = 0\cdot5712 : 1 : 0\cdot7531.$

It will be seen that in passing from potassium to cæsium sulphate the molecular volume increases by about one-third, whilst the axial ratios remain almost unchanged; it is inconceivable that this close adherence to the type would survive a large increase in size of only one constituent atom of the molecule, but if, as we now conclude, the substitution of cæsium for potassium merely expands the whole molecule uniformly from the volume 64·91 to 84·58, the spheres of influence of the atoms of different valency preserving the same ratios, the retention of the original crystalline structure would be expected.

During recent years much attention has been devoted to the study of the so-called " topic axial ratios " of crystalline substances, these values being calculated in the most general case of an anorthic substance from the axial ratios, $a : 1 : c$, the interaxial angles, a, β, and γ, and the molecular volume, V, by means of the formulæ,

$$\chi = \sqrt[3]{\frac{a^2 V}{c \sin a \sin \beta \sin \gamma}},\ \psi = \chi/a,\ \text{and}\ \omega = c\psi.$$

If proper axial directions are selected, and if proper multiples of the axial ratios are used in calculating the topic axial ratios, a', b', and c', and a'', b'', and c'' of two comparable substances, the ratios $a' : a''$, $b' : b''$, and $c' : c''$, represent the relative distances at which the units of the structures are distributed in space in the three axial directions, a, b, and c, respectively. The topic axial ratios, however, have no signification which assists in the detection of relationships between crystalline form and molecular constitution; and it is for this reason that their study has hitherto afforded no information on the subject which could not have been equally well derived from the consideration of the ordinary axial ratios.

For our present purpose, it is of service to learn for series of crystalline substances the dimensions of the molecule in three properly selected axial directions and its volume in terms of the dimensions and volume of the valency unit, which consists of the portion of space allotted to a univalent atom present in the molecule, half that occupied by a bivalent atom, one-third that occupied by a tervalent atom, &c. The volume occupied by the molecule, which is the sum of the volumes of the component spheres of atomic influence, may thus be taken as the sum of the valencies of the component atoms; this sum of the valencies we term the valency volume, W. The valency volume

thus derived involves the assumption that the spheres of atomic influ-
ence fill space without interstices.

The molecular dimensions referred to are given by the "equivalence
parameters," x, y, and z, calculated in the following manner from the
axial ratios and the valency volume.

$$x = \sqrt[3]{\frac{a^2 W}{c \sin \alpha \sin \beta \sin \gamma}}, \quad y = x/a, \text{ and } z = cy.$$

The equivalence parameters are naturally the products of the corre-
sponding topic axial ratios by $3 \sqrt{(W/V)}$.*

The axial directions to which crystalline substances are ordinarily
referred for descriptive purposes are not, in general, directions along
which occur the minimum distances separating the centres of the
structural units. Thus, one important type of cubic crystalline sub-
stances is that in which the centre points of the structural units lie at
both centres and angles of a cubic partitioning of space, and in this
system the distance separating centres of structural units is a minimum
along the trigonal axes, this separating distance being $\sqrt{3}/2$ of that
along the rectangular cubic axes ordinarily used. If, therefore, the
topic axial ratios or the equivalence parameters are to express the
minimum distances separating centres of structural units in the
crystal, they must be stated with relation to the appropriately selected
directions in which those minimum distances occur; in the particular
cubic system instanced above, the directions to be selected would be

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* For the information of non-crystallographic readers, it may be stated that crys-
talline substances are classified according to their symmetry in six systems, which
are themselves subdivided into thirty-two crystal classes. A crystalline substance
is characterised, first, by its symmetry, or the crystal class to which it belongs, and,
second, by stating the ratio $a : b : c$ between the lengths of the three edges of a
parallelopipedal figure from which the crystal structure may be regarded as built up;
the angles bc, ac, and ab, between the axial directions a, b, and c, are termed α, β,
and γ. Certain of these constants are, in general, fixed by the symmetry of the
crystal system, and the appended list states the crystal systems in order of symmetry
and those constants (marked ?) which are not defined by the symmetry and which
therefore have to be determined by goniometric measurement.

Cubic system	$a : b : c = 1 : 1 : 1$.	$\alpha = \beta = \gamma = 90°$.
Hexagonal system	$a : b : c = 1 : 1 : 1$.	$\alpha = \beta = \gamma = ?$.
Tetragonal system	$a : b : c = 1 : 1 : ?$.	$\alpha = \beta = \gamma = 90°$.
Orthorhombic system	$a : b : c = ? : 1 : ?$.	$\alpha = \beta = \gamma = 90°$.
Monosymmetric system	$a : b : c = ? : 1 : ?$.	$\alpha = \gamma = 90°$, $\beta = ?$.
Anorthic system	$a : b : c = ? : 1 : ?$.	$\alpha = ?$, $\beta = ?$, $\gamma = ?$.

The rhombohedral system is a subdivision of the hexagonal system, and the con-
stants appertaining to both are similarly stated; both of these systems are frequently
referred to axes of the form $a : a : a : c = 1 : 1 : 1 : ?$, the three equal axes a lying in
a plane at mutual inclinations of $120°$ and perpendicular to the c-axis.

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those of the trigonal axes of symmetry. Appropriate intercepts of the ordinary crystallographic axes will, however, serve for the pur- pose of dividing space into parallelopipedal cells equal in volume to the molecular or the valency volume, the three dimensions of the parallelopipedon giving the ratios of the minimum translations of the structure in the three axial directions. This, in most instances, suffices for purposes of comparing substances of similar crystalline structure, for, although the values compared do not necessarily express the minimum distances separating unit centres in the structure, they are similar functions of such distances.

The sets of equivalence parameters stated below will show that a method of calculation is now available which enables us to correlate the apparently very incongruent crystallographic data relating to series of compounds which may be regarded chemically as derived from the same parent substance.

The appended table gives the axial ratios and topic axial ratios (Gossner, *Zeit. Kryst. Min.*, 1904, **38**, 154) for the orthorhombic hexa-halogen derivatives of ethane, together with the corresponding equivalence parameters. Gossner's axial ratios (*loc. cit.*, 504) for the monosymmetric pentabromoethane, namely, $a : b : c = 0.8353 : 1 : 0.5655$, $\beta = 111°5'$, are also included, but have been transposed by making $a(001)$, $m(012)$, and $q(111)$; this gives $a : b : c = 0.5650 : 1 : 1.5590$, $\beta = 91°19'$, numbers which are more in accordance with the distorted orthorhombic character of the crystals. The length of the c-axis of pentabromoethane has been divided by five for the purposes of the following calculation of the equivalence parameters :

	$a : b : c.$	$V.$	$\chi : \psi : \omega.$	$W.$	$x : y : z.$
$CCl_3 \cdot CCl_3$	0·5677 : 1 : 0·3160	113·34	4·8713 : 8·5808 : 2·7115	14	2·4260 : 4·2733 : 1·3503
$CBr_2Cl \cdot CCl_3$	0·5612 : 1 : 0·3171	116·72	4·8760 : 8·6884 : 2·7551	14	2·4047 : 4·2849 : 1·3587
$CBrCl_2 \cdot CBrCl_2$	0·5646 : 1 : 0·3192	120·16	4·9647 : 8·7949 : 2·7520	14	2·4090 : 4·2669 : 1·3620
$CBr_3 \cdot CBr_3$	0·5639 : 1 : 0·3142	131·83	5·1099 : 9·0618 : 2·8472	14	2·4197 : 4·2911 : 1·3483
$CHBr_2 \cdot CBr_3$	0·5650 : 1 : 0·3118	126·46	$\beta=91°19'$	14	2·4294 : 4·2995 : 1·3406
Chlorobromonitro-phenol	1·0470 : 1 : 0·5994 $\beta=114°38'$	118·7	6·2043 : 5·9257 : 3·5519	38	4·2443 : 4·0537 : 2·4298
Dibromonitro-phenol	1·0302 : 1 : 0·5912 $\beta=114°37'$	121·1	6·2069 : 6·0249 : 3·5619	38	4·2179 : 4·0942 : 2·4205
Bromoiodonitro-phenol	1·0400 : 1 : 0·5802 $\beta=114°14'$	129·03	6·4133 : 6·1667 : 3·5779	38	4·2669 : 4·1028 : 2·3804

The second part of the table deals with Gossner's data (*Zeit. Kryst. Min.*, 1905, **40**, 84) for those derivatives of 1-chloro-3-bromo-5-nitro-6-hydroxybenzene in which the 1-chlorine atom is replaced by bromine and iodine.

Throughout the above two series the equivalence parameters are distinctly less variable than are the corresponding topic axial ratios, and in so far support our contention that the volumes of the spheres of atomic influence of hydrogen, chlorine, bromine, and iodine bear almost the same ratio to the corresponding molecular volumes. A

careful inspection of the above table will show, however, that the equivalence parameters have most advantage over the topic axial ratios, as a measure of the similarity of type of two allied substances, in those cases in which the molecular volumes differ most. It sometimes happens that the equivalence parameters preserve their constancy no better throughout a series of related compounds than do the topic axial ratios; this is only the case, however, when the molecular volumes are practically constant throughout the series. The values obtained by Jaeger (*Zeit. Kryst. Min.*, 1904, **38**, 595) for the six isomeric tribromotoluenes afford an example of this kind.

When dealing with a series of related compounds, it often happens that the observed axial ratios of one or more members of the series do not give directly equivalence parameters in harmony with those of the rest of the series: in these cases, the selection of certain simple multiples of one or both of the axial ratios, a/b and c/b, as a basis from which to calculate the equivalence parameters, generally brings the substance into agreement in this respect with the other members of the series. The selection of these multiples is arbitrary, in that it is made without other directing indication than an approximate knowledge of what values the equivalence parameters should possess; its arbitrary character is connected with the fact that the numerical values of the axial ratios themselves are arbitrarily fixed, in that it is usually possible, on the basis of the goniometrical examination, to assign to a crystalline substance several sets of indices and axial ratios, all of which have the same experimental justification. And amongst these alternative sets of axial ratios one, in general, leads, without previous reduction, to the deduction of equivalence parameters in harmony with those of other members of the series.

An inspection of the possible simple multiples which can be selected shows that in most of the cases now dealt with only one leads to the required conformity of the equivalence parameters; this fact is the ground for the selection of that particular multiple. Thus, in the previous table, the fact that the only simple way of bringing the equivalence parameters of pentabromoethane into congruence with those of the hexa-halogen derivatives is by taking one-fifth of the length of the c-axis in calculating the values of x, y, and z, determines the choice of this multiple.

It may, however, be contended that by suitable manipulation of the most unfavourable set of axial ratios, any desired result may be obtained, and, without further discussing this point, we may admit that if, in any particular case, it is found necessary to select fractional multiples of the recorded axial ratios in order to exhibit relationships between the equivalence parameters, the demonstrative value of that

case is diminished. For the elucidation of every important point we have therefore selected, from the mass of crystallographic data available, cases in which complex fractionation of the axial ratios is unnecessary. All, however, who are experienced in crystallographic measurement recognise that two independent observers very commonly assign different parametral schemes to the same substance, and it cannot therefore be legitimately urged that in any large proportion of instances the stated axial ratios can without reduction be taken as referring to the molecular unit itself. And the fact that it is possible, throughout this paper, to offer a complete argumentative sequence based on unmanipulated axial ratios fully justifies the quotation for illustrative purposes of a number of cases of the other kind.

It should perhaps be pointed out that the detection or indication of morphotropic relationships between two substances exhibiting the axial ratios, $a' : b' : c'$ and $a'' : b'' : c''$, is generally effected by showing a correspondence between one or more of the ratios a/b, c/b, or a/c in both. As the only numerical data available are thus the values a'/b', a''/b'', c'/b' and c''/b'', fallacy may well arise if too great advantage is taken of the fact that these ratios are simple fractional multiples of molecular dimensions in the several axial directions in the crystal structure. The extent to which the selection of simple multiples of the axial ratios may be legitimately applied is, however, much greater in the case of the equivalence parameters, because here the conditions are much more narrowly limited. Instead of having to select numbers which are consonant, as simple multiples, with the ratios a/b and c/b, we have here to satisfy the following much more rigid conditions. Given, for two instances, the axial ratios, $a' : b' : c'$ and $a'' : b'' : c''$, and the valency volumes, W' and W'', select such simple multiples, pa', qb', rc', ha'', kb'', and lc', of the axial ratios for the calculation of the equivalence parameters, x', y', z', x'', y'', and z'', as will satisfy the conditions that $x'y'z' = W'$, $x''y''z'' = W''$, $x'/pa' = y'/qb' = z'/rc$, $x''/ha'' = y''/kb''$ $= z''/lc''$, and will make one, two, or all of the values x', y', and z' equal to one, two, or all of the values x'', y'', and z''.

As a somewhat extreme instance of the method of treatment adopted we submit the following table, from which we conclude that the quantitative data referring to camphor and its orthorhombic halogen derivatives are wholly in accordance with the hypothesis as to molecular constitution now put forward ; in this series, the valency volume $W = 60$. The axial ratios for the hexagonal form of camphor, namely, $a : c = 1 : 1\cdot6202$, are thrown into the orthorhombic form of $a : b : c = 0\cdot8660 : 1 : 1\cdot6202$. In this table, as in others given later, the values of x, y, and z are tabulated in such an order as reveals the relation between the several sets.

Substance.	a : b : c.	Multiples of axial ratios selected.	x : y : z.
Camphor *	0·8660 : 1 : 1·6202		2·9943 : 3·4577 : 5·6021
a-Dibromocamphor † ...	0·7925 : 1 : 0·5143	$2a, 5c/3$	2·9959 : 3·4949 : 5·5395
β-Dibromocamphor † ...	0·9527 : 1 : 0·5186	$3b/5$	3·0107 : 3·4832 : 5·5308
a-π-Dibromocamphor ‡	0·6860 : 1 : 0·3323	$5a/4, 5c$	2·9498 : 3·4400 : 5·7156
β-Monobromocamphor §	1·0620 : 1 : 0·8220	$a/2$	2·9084 : 3·5382 : 5·6363

The above sets of figures show that the axial ratios of members of a series of related substances having the same valency volume may be interpreted by means of the equivalence parameters so as to indicate similarity of chemical structure.   Camphor and its various halogen derivatives may be supposed to have practically identical molecular configurations, and, in accordance with the views expressed above, should possess nearly identical relative molecular dimensions if really built up from spheres of atomic influence of the volumes four, two, and one ; the possibility of assigning almost the same set of equivalence parameters to all the members of the series is in entire harmony with this conclusion.   But before proceeding to a closer study of the assemblages representing chemical substances, it is desirable to demonstrate that the new kind of axial ratios render valuable service in   expressing   and   elucidating   morphotropic   and   constitutional relations between substances of different valency volumes.

The following table gives data for the orthorhombic d- ω- and dl- ω-bromocamphoric anhydrides (*Acta Soc. Scient. Fenn.*, 1896, **21**, 204) (the value of a being reduced to 2/3), for the monosymmetric d-π-bromocamphoric anhydride (Trans., 1897, **71**, 970) (the a value being reduced to 4/3), the orthorhombic d-camphoric anhydride and the orthorhombic addition compound of d-camphoric acid with acetone (Trans., 1896, **69**, 1696) (the axial lengths being unaltered).

Substance.	W.	a : b : c.	x : y : z.
d-ω-$C_{10}H_{13}BrO_3$	60	0·5920 : 1 : 0·5775	3·3145 : 3·2332 : 5·5988
dl-ω-$C_{10}H_{13}BrO_3$	60	0·5816 : 1 : 0·5799	3·2710 : 3·2615 : 5·6241
d-π-$C_{10}H_{13}BrO_3$	60	1·0835 : 1 : 1·6453	3·4985 : 3·2286 : 5·3125
$\beta = 88°59'30''$			
d-$C_{10}H_{14}O_3$	60	1·0011 : 1 : 1·7270	3·2654 : 3·2618 : 5·6331
d-$C_{10}H_{16}O_4, \frac{1}{2}(CH_3)_2CO$	74	1·2386 : 1 : 1·7172	4·0435 : 3·2646 : 5·6060

A very close approximation to agreement between the equivalence parameters is observed throughout the table ; the largest discrepancies are to be noted in the x and z values for the d-π-bromocamphoric anhydride, and the reason lies in the fact that the directions x and z are affected by the shear which gives the crystals their monosymmetric symmetry. But on comparing the values for the addition compound of camphoric acid and acetone with those of the previous substances, it is seen that

* des Cloizeaux, *Compt. rend.*, 1859, **48**, 1064.
† Zepharovich, *Zeit. Kryst. Min.*, 1883, **7**, 588.
‡ Kipping and Pope, Trans., 1895, **67**, 371.
§ Armstrong and Lowry, Trans., 1902, **81**, 1466

whilst the values y and z agree closely right through the table, the x value for the addition compound is much in excess of the other x values. This suggests that on introducing water and acetone into the close-packed assemblage representing camphoric anhydride, the new assemblage retains the y and z dimensions of the original one, and that the anhydride assemblage merely opens out in the direction of x to admit of the new components entering as a close-packed layer or pad between the two surfaces exposed.

The kind of relation thus shown to exist between the camphoric anhydride and the camphoric acid addition compound assemblages is of frequent occurrence, notably in the case of double salts and substances crystallising with the solvent. The interpretation of the relationship in the light of our fundamental conception with the aid of the equivalence parameters at once elucidates a number of mineralogical observations which, in spite of their important character, have hitherto remained without explanation. Thus, it has long been known that the monosymmetric mineral chondrodite, $Mg_3(SiO_4)_2, 2Mg(F)(OH)$, the orthorhombic humite, $Mg_5(SiO_4)_3, 2Mg(F)(OH)$, and the monosymmetric clinohumite, $Mg_7(SiO_4)_4, 2Mg(F)(OH)$, in each of which the angle $\beta = 90°$, are morphotropically related in such a way that, whilst the ratio a/b is practically the same in all, the ratio c/b is in the proportion of $5 : 7 : 9$ for the three substances respectively (Penfield and Howe, *Zeit. Kryst. Min.*, 1894, **23**, 78). On summing up the valency volumes of these substances, regarding the isomorphous constituents F and OH as present in equivalent proportion, the values 38, 54, and 70 are obtained ; these numbers are practically in the ratio of $5 : 7 : 9$. On calculating the equivalence parameters as in the appended table, it is seen that the values of x and y remain almost the same throughout the series, whilst z increases in the proportion stated ; the values of z/W are given in the last column.

Mineral.	W.	a : b : c.	x : y : z.	z/W.
Chondrodite......	38	$1\cdot08630 : 1 : 3\cdot14472$	$2\cdot4249 : 2\cdot2323 : 7\cdot0199$	$0\cdot18473$
Humite...........	54	$1\cdot08021 : 1 : 4\cdot40334$	$2\cdot4278 : 2\cdot2475 : 9\cdot8965$	$0\cdot18327$
Clinohumite......	70	$1\cdot08028 : 1 : 5\cdot65883$	$2\cdot4349 : 2\cdot2540 : 12\cdot7547$	$0\cdot18221$

The practical constancy of the values x, y, and z/W indicates that the increment of the series, Mg_2SiO_4, is introduced as a layer parallel to the directions a and b and perpendicular to the direction c, so that the dimension of the latter is the only one of the three which is materially affected ; it is further clear that the effect produced upon the c-axis by insertion of the group is proportional to its valency volume.

The increment of composition in the series is Mg_2SiO_4, the composition of forsterite ; by subtracting this increment from the composition of chondrodite, the residue $MgSiO_4$, $2Mg(F)(OH)$, is obtained ; this is the composition attributed to prolectite (Sjögren, *Zeit. Kryst. Min.*, 1896,

26, 103). The equivalence parameters and the axial ratios for the two latter minerals should thus be deducible from the data given for the above three ; the values calculated on this assumption and those actually observed are given in the following table. The determined length of the axis b has been halved in the numbers given for forsterite.

Prolectite, $W = 22$:

	a : b : c.	x : y : z.
Observed	$1 \cdot 0803 : 1 : 1 \cdot 8862$	$2 \cdot 3877 : 2 \cdot 2102 : 4 \cdot 1689$
Calculated	$1 \cdot 0822 : 1 : 1 \cdot 8500$	$2 \cdot 4292 : 2 \cdot 2446 : 4 \cdot 1526$

Forsterite, $W = 16$:

Observed	$0 \cdot 9296 : 1 : 1 \cdot 1714$	$2 \cdot 4492 : 2 \cdot 2769 : 2 \cdot 8691$
Calculated	$0 \cdot 9240 : 1 : 1 \cdot 1804$	$2 \cdot 4292 : 2 \cdot 2446 : 2 \cdot 8674$

It will be admitted that the agreement between the observed and calculated numbers is very close in view of the comparatively rough manner in which these two minerals have been characterised.

The above results may be summarised by saying that in the crystalline state the spaces occupied by the groups or radicles common to the several members of the series assume similar forms, and the amount of space occupied by any such radicle or group bears to the amount of space occupied by the whole molecule the ratio borne by the valency volume of the component group to the valency volume of the molecule. Results of a similar nature are repeatedly stated in the course of this paper, and it is claimed that these are observations of fact which must be accepted quite independently of any judgment which may be passed upon the theoretical views advanced to explain them.

The extent to which the present mode of treatment is independent of crystalline system is worthy of note ; the monosymmetric chondrodite becomes orthorhombic by the addition of Mg_2SiO_4, whilst the addition of the second increment of Mg_2SiO_4 reduces the symmetry to that of the monosymmetric clinohumite. This fact has interesting applications to the isomorphism and morphotropic relationships existing between naturally occurring silicates belonging to different crystalline systems.

That the same sort of relationship holds between salts containing various proportions of water of crystallisation is indicated by the following comparison of the tetragonal and orthorhombic nickel sulphates containing $6H_2O$ and $7H_2O$ respectively, and the two orthorhombic sodium carbonates containing $1H_2O$ and $7H_2O$ (from Rammelsberg, *Kryst-physik. Chem.*, I, 417 and 548).

It will be seen that on calculating the equivalence parameters, using the simple multiples of the axial ratios noted in the last column, two of the equivalence parameters remain nearly unchanged during the hydration of the salt; the whole effect of the introduction of the water of crystallisation can thus be thrown upon one of the three axial directions. That is to say, the water entering the structure may be regarded as forming a layer in the crystalline structure, and as being so symmetrically introduced as to affect but one axial direction. This same reasoning is applicable to a number of compounds containing water of crystallisation, but in some cases requires modification: for example, the introduction of water of crystallisation to form a cubic crystalline substance must take place symmetrically in the various equivalent directions throughout the assemblage.

It is instructive to notice that in passing from the tetragonal salt, $NiSO_4,6H_2O$, to the orthorhombic hydrate, $NiSO_4,7H_2O$, but very slight disturbance of the symmetry occurs; the orthorhombic salt, both in crystal habit and axial ratios, approximates closely to tetragonal symmetry.

The effect both of polymorphism and of the introduction of water of crystallisation is seen in the following table relating to the optically active *trans-π*-camphanic acids, $C_{10}H_{14}O_4$, which crystallises with $1H_2O$ in a monosymmetric and also in an orthorhombic form, and without water in an orthorhombic form (Kipping and Pope, Trans., 1897, **71**, 962).

	$a \ : \ b \ : \ c.$	Multiples of axial ratios taken.	$x \ : \ y \ : \ z.$	$W.$
$C_{10}H_{14}O_4, H_2O$ ...	$1\cdot9110 : 1 : 1\cdot4627$	$2b$	$4\cdot4514 : 4\cdot6588 : 3\cdot4072$	66
	$\beta = 69°5'$			
$C_{10}H_{14}O_4, H_2O$ ...	$0\cdot9158 : 1 : 0\cdot3551$	$2c$	$4\cdot2716 : 4\cdot6643 : 3\cdot3126$	66
$C_{10}H_{14}O_4$	$0\cdot9584 : 1 : 0\cdot7292$		$4\cdot2745 : 4\cdot4600 : 3\cdot2522$	62

The difference in crystalline form of the two hydrated modifications of the acid causes change in the dimensions in the directions a and c, those namely which are involved in the shearing process by which the monosymmetric system is derived from the orthorhombic; the direction b remains practically unaltered, so that the y-value is nearly the same for the first two substances. The removal of the molecule of water of crystallisation from the orthorhombic form causes practically no change in the x-value, and produces most alteration in the direction of the b-axis.

The mode suggested above of regarding molecular complexes such as double salts, compounds containing solvent of crystallisation, and the like, naturally directs attention to one aspect of molecular composition which has hitherto not been considered as of importance. Some simple numerical relation is found to subsist between the valency volumes of the two or more molecular components making up the system. This

simple relationship is most prominent in the double salts; the follow-
ing examples, typical of large classes of substances, to which the
valency volumes of the component complexes are appended, will
indicate the kind of relation observed.

$$K_2SO_4, Al_2(SO_4)_3, 24H_2O \quad .. \quad .... \quad \text{Valency volume} = 12 + 36 + 96$$
$$(NH_4)_2SO_4, Al_2(SO_4)_3, 24H_2O \quad ...... \qquad ,, \qquad \quad ,, \quad = 24 + 36 + 96$$
$$2KCl, CuCl_2, 6H_2O \quad .... \qquad ,, \qquad \quad ,, \quad = \; 4 + \; 4 + 24$$
$$K_2SO_4, CuSO_4, 6H_2O \quad .... \qquad ,, \qquad \quad ,, \quad = 12 + 12 + 24$$

In each of the above and in other cases representing double salts
the valency volumes of the component complexes are in a simple ratio
one to the other and to the total valency volume. In connexion with
these observations it may be remarked that the close-packing together
of two molecular surfaces evidently requires that the spacing of the
spheres of influence shall be congruent—in other words, that the dis-
tances separating corresponding parts on the one surface shall be
simple fractions of such distances on the other; and if this holds good
in the three principal plane directions, it involves a simple numerical
relation between the volumes of the associated complexes. The
applicability of this principle to cases where the water of crystallisation
is intercalated in isolated groups of one or more molecular complexes
so as to produce crystalline assemblages of the high symmetry
associated with the cubic or hexagonal systems, as in the alums, and
not inserted in layers, as in assemblages of lower crystallographic
symmetry, is more directly apparent.

The Partitioning of Close-packed Assemblages.

All symmetrical and homogeneous close-packed assemblages can be
partitioned in a symmetrical and homogeneous way into similar cells
or units. And, after an appropriate partitioning, the unit or cell
into which the close-packed assemblage is resolved represents in com-
position, constitution, and configuration the chemical molecule itself;
each cell of the partitioning is thus occupied by one chemical molecule,
and the partitioning is of such a nature that the cell walls do not
intersect any component sphere. Thus, one close-packed assemblage
of the general composition, C_nH_{2n-6}, can be partitioned symmetrically
into units of the composition, C_6H_6, and represents benzene; another
representing toluene can be partitioned into units of the composition
C_7H_8; and three others, representing the three xylenes, are partition-
able into units of the composition C_8H_{10}. In many cases the parti-
tioning which has to be resorted to for the purpose of resolving the
close-packed assemblage into the similar groups representing mole-
cules is, owing to geometrical reasons, of lower symmetry than the
original assemblage; the partitioning is therefore arbitrary, in that

it leaves unsevered some contacts between neighbouring spheres in the assemblage which are of precisely the same quality as others which it ruptures ; and some of the spheres left mutually attached after the partitioning have, previous thereto, no closer association than others which the partitioning allots to different molecules.   Many close-packed assemblages can be partitioned in two distinct ways, but so that the units resulting from both partitionings are constitutionally identical ; in other cases two distinct methods of partitioning are possible, and give rise to units or molecules exhibiting isomerism. Many of the peculiarities observed in the substitution of aromatic hydrocarbons are immediately traceable to this property of the corre-sponding close-packed assemblages.   Further, many other close-packed assemblages can be partitioned in two ways in such a manner that the units or molecules which result are constitutionally dissimilar ; these assemblages represent tautomeric or isodynamic substances, and, as will be shown in a later paper, the two kinds of unit produced represent in every way the two forms of the substances concerned.

For a close-packed assemblage to represent a particular substance, it must not only be a homogeneous one in which the spheres of influence of the component atoms are present in the proportions indicated by the molecular composition, but it should exhibit the crystalline symmetry of the substance ; moreover, groups of associated spheres of atomic influence should be recognisable in it, identical in composition and configuration with the chemical molecule itself.   And since the assemblage is a homogeneous arrangement of spheres of atomic influence grouped to form similar molecules, it must be homogeneously partitionable into space-units, all identical and each representing a chemical molecule in composition and configuration.   It is evident that isomerism introduces a complication ; as will be shown later, in cases where isomerism is possible and not traceable to varieties of partitioning of the same assemblage, several close-packed assemblages are obtainable corresponding in number and character to the various known isomerides ; these alternative assemblages are all close-packed, but not necessarily all equally densely packed.   We have therefore to derive these isomeric assemblages from others by a process of sub-stitution or distortion, and to show what provision can be made to ensure their separate and individual existence : that is, to indicate a method by which one assemblage can be geometrically prevented from lapsing into an alternative or isomeric assemblage merely because the latter happens to be slightly more densely packed.   The necessary condition in all cases is that the disposition in the homogeneous assemblage of the spheres of atomic influence with respect to one another is such that if represented by stacks of spheres of appropriate sizes, the arrangements presented are equilibrium arrangements in

close-packing.   An assemblage of spheres is described as close-packed if it cannot be caused to pack more closely by any process of shearing or distortion unaccompanied by "remarshalling" of its parts; the meaning attached to the term remarshalling is defined by the statement that an assemblage retains its original marshalling, after subjection to shearing or distortion, when no sphere of the assemblage has been shifted during the distortion past the narrowest part of one of the small apertures found between the other spheres immediately surrounding it.   This mode of considering close-packing permits of the existence in close-packed assemblages of groups of spheres or of radicles whose individual shape is such that the space occupied by the whole assemblage is greater than would be requisite if the constituent spheres were separately stacked or were differently arranged; in other words, there are in many cases several equilibrium arrangements in close-packing of the same set of spheres; these arrangements present slightly different densities of packing.   In the numerous cases discussed later it will be seen that the alternative arrangements provided correspond closely with the number and nature of the isomerides actually obtainable.

The geometrical idea of marshalling acquires further importance when it is considered that most of the available data of a quantitative character are crystallographic, and that by hypothesis the crystal structure is a close-packed assemblage of the molecules.   During the process of crystallisation the molecules, by the operation of the two forces previously referred to, would become closely and homogeneously fitted together, and be subject to such distortion or deformation as may be necessary for this purpose.   The nature of this distortion can, in many cases, be exactly traced, and is not of such a kind as leads to remarshalling.

The Representation of Molecular Complexes.

The purely mechanical view of molecular structure above foreshadowed is most conveniently depicted by a purely mechanical method. The statical equilibrium established in close-packed molecular assemblages as a result of the simultaneous attraction and repulsion of the atoms is expressed graphically in a very complete manner by representing each sphere of atomic influence by an elastic ball of appropriate diameter composed of soft, solid indiarubber, which, while deformable, is practically incompressible, a very considerable number of balls being employed, and the mass subjected to uniform pressure nearly sufficient to close up the interstices by flattening the spheres at the places of contact.   For practical purposes hard balls are more convenient to handle; if slightly flattened at the points of con-

tact, they represent sufficiently well the arrangement under con-
sideration.

If balls of appropriate magnitudes and appropriate degrees of
compressibility are selected, they can be grouped together and close-
packed under a general pressure so as to simulate accurately both
chemical molecules and assemblages of chemical molecules.

The Configuration of Aromatic Compounds.

It will be convenient at once to apply the geometrical principles
developed above to some particular series of chemical compounds, and
for this purpose we select a number of typical aromatic substances,
because these have been so completely examined crystallographically
as to allow of a direct control upon the validity of the methods which
we employ.

The problem involved in determining the configuration of the benzene
complex, stated in the terms introduced in the foregoing pages, is that
of finding an arrangement of spheres of two sizes, six of each, of
such a form as corresponds to the general properties of benzene, and of
such a configuration that an indefinitely large number of identical
groups of the kind can, without remarshalling, be close-packed so as
to give an assemblage exhibiting the crystalline symmetry of benzene.
The problem is very precisely defined, in that the known molecular
composition and the known relations between the six hydrogen atoms
in the molecule which are expressed in the isomerism of the di- and
tri-substitution derivatives, and also the known crystalline form, all
limit its solution ; to these conditions must be added that the
assemblage for benzene must be capable of conversion, by simple
substitutions in which the type of the units is not changed, into
assemblages which conform in chemical and crystallographic respects
to the properties of benzene derivatives and of other aromatic
hydrocarbons.   A further important limitation is imposed by the new
condition that the relative volumes of the spheres of atomic
influence composing the various assemblages must be directly pro-
portional to their fundamental valencies.

The solution of the problem is the following : Six spheres, each of
volume four, are placed in contact so that their centres lie at the
apices of a regular octahedron ; six spheres, each of about volume
one, are then placed in six of the eight similar hollows lying round
the octahedral group in such a manner that the two unoccupied
hollows are diametrically opposite each other.   The resulting
arrangement is shown in plan in Fig. 1 ; it is in certain respects similar
to some of the benzene configurations deduced from Werner's theory
(Bloch, *Theorie des Kohlenstoffatoms*, 1903, 72), and, like the latter,

leads to the derivation of three isomeric di-derivatives.   It indicates also the derivability of one, two, and three tri-derivatives from the para- meta- and ortho-derivatives of benzene respectively.   The configuration depicted is, in fact, in accordance with the general pro- perties of benzene, in so far as these are ex- pressed by the isomerism of aromatic com- pounds.

FIG. 1.

We have next to show how complexes in which the parts are marshalled as indicated can be close-packed so as to form a homo- geneous assemblage exhibiting the symmetry and axial ratios of crystalline benzene ; this is accomplished by the following series of numbered steps :
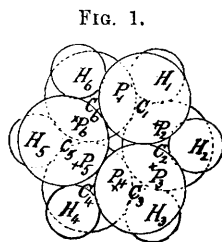
FIG. 2.
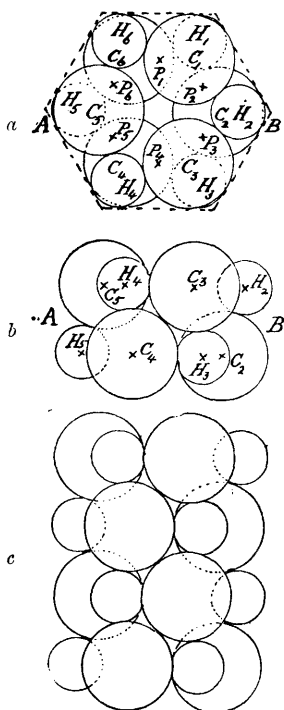
(1.) The complexes are piled vertically in close-packed columns, the faces in contact being those which do not carry small or hydrogen spheres ; in the column the individual complexes have the same orientation, and each small sphere is in contact with three larger ones.

(2.) The column thus obtained is slightly shortened by compression, so that the centres of the larger spheres separate until the smaller spheres touch four instead of three of them ; the arrangement which results, employing complexes of hard spheres, is shown in plan and elevation in Fig. 2, a, b, and c. The two sizes of spheres alternate regu- larly in the vertical column, as indicated in Fig. 2c, and a geometrical partitioning divides it into cells each containing two consecutive layers of the column, as shown in Fig. 2b.   The shortening of the column does not so distort it as to lead to remarshalling.

(3.) Columns thus built up are placed in contact side by side and similarly orientated so as to form walls having the direction C_1C_4 or C_2C_3 indicated in Fig. 3.

(4.) These walls are then packed side by side so as to fill space as shown in Fig. 3, and for the purpose of achieving the closest possible

packing of a number of walls, a, b, c, d, e, f, &c., the walls a, c, e must
be placed at a somewhat different level from the alternate walls, b, d, f;
the successive walls in the structure then interlock. The raising of
alternate walls with respect to the others is indicated in Fig. 3, and
other subsequent figures, by drawing the circles representing the one
level in single lines, and those representing another level in double
lines.

(5.) The closeness of the packing is further increased by again
slightly distorting each complex, without remarshalling; the nature
of this distortion will be realised on comparing Fig. 1, representing

FIG. 3.
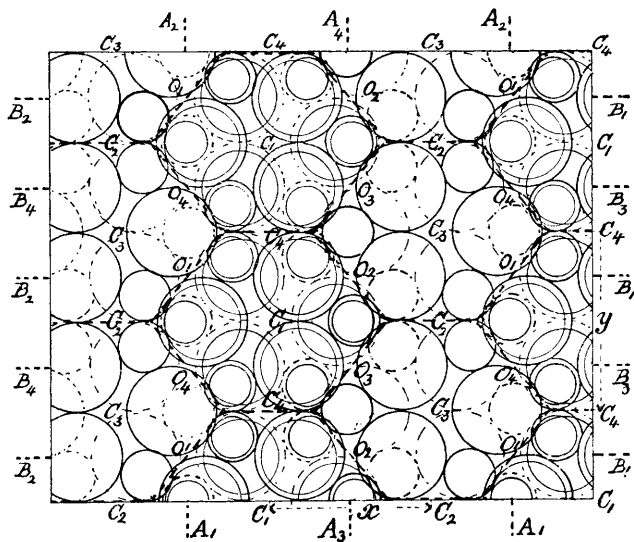
the undistorted complex, with Fig. 2a, showing the effect of the first
distortion involved in the shortening of the columns, and also com-
paring it with one complex of hexagonal contour in Fig. 3.   Fig. 4
indicates the effect of the second distortion on the elevation of the
columns.   The assemblage which has thus been obtained is that repre-
sentative of crystalline benzene.

The several distortions just above described are geometrically very
simple, and assist in the achievement of the closest possible packing of
the benzene complexes, with the aid of any distortion or shear which does
not involve a remarshalling of the parts of the complexes. We suggest
that no adjustment other than those described assists the close-packing,
and that the arrangement finally depicted in Fig. 3 is the most close-

packed possible. It remains now to show that this assemblage is strictly in accordance with the crystalline form of the hydrocarbon, and must therefore be regarded as representing the distribution in space of the atoms and molecules which make up benzene in the crystalline state.

Benzene crystallises in the holohedral orthorhombic system, and exhibits the axial ratios $a : b : c = 0\cdot891 : 1 : 0\cdot799$ (Groth); these values give, since the valency volume W is 30, the equivalence parameters $x : y : z = 3\cdot101 : 3\cdot480 : 2\cdot780$. The structure depicted in Fig. 3 is also holohedrally orthorhombic in symmetry, but, in order that it may correctly simulate the crystal structure of benzene, it must be possible to select three translation dimensions within it, which lie in directions parallel to the three axes of the orthorhombic symmetry, and for these translations, or simple multiples of them, to have the values of the equivalence parameters x, y, and z. The appropriate translation dimensions are shown in Figs. 3 and 4 ; and these drawings have been made to the scale of $x : y : z = 3\cdot101 : 3\cdot480 : 2\cdot780$. The length x is one-half a translation along the axis a, y is twice the diameter of a large or carbon sphere, and z is, as indicated in Fig. 4, very slightly less than the sum of the diameters of a large and a small sphere ; the product, $xyz = W$, is the minimum unit volume of the assemblage. The dimensions of the structure represented in Figs. 3 and 4, as well as the symmetry, are therefore in accordance with those of crystallised benzene.
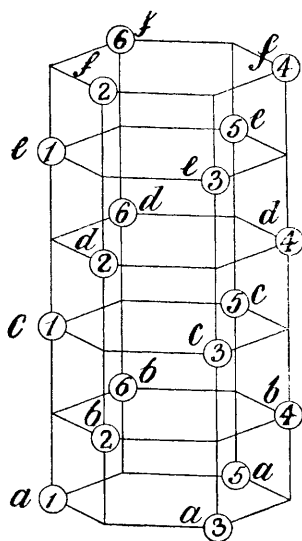
FIG. 4.
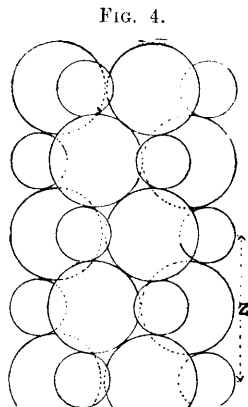
The type of homogeneous structure thus assigned to the benzene assemblage is that marked No. 54 of Barlow's list (*Zeit. Kryst. Min.*, 1894, **23**, 1), and is No. 14 of Sohncke's sixty-five systems with a centre of symmetry added. The positions of the different kinds of digonal screw axes (c) which lie perpendicular to the plane of Fig. 3 are marked C_1, C_2, C_3, C_4. The digonal screw axes (both a and b) which lie parallel to the plane of Fig. 3 pass midway between these axes ; their projections are marked A_1A_2, A_3A_4, B_1B_2, B_3B_4. The centres of symmetry lie on the axes whose projections, A_1A_2, A_3A_4, are shown on Fig. 3, and are found at the points where these axes intersect planes drawn perpendicular to the plane of the figure through the axes B_1B_2, B_3B_4 ; their projections are marked O_1, O_2, O_3, O_4. The axes C_1, C_2, &c., all lie in planes of symmetry which are perpendicular to the plane of Fig. 3, and both the other sets of planes of symmetry are planes of gliding-symmetry. The difference in level of the nearest identical

layers of two interlocked walls of columns is seen from Fig. 4 to be $z/4$, z being the prism-translation which represents the vertical or c-axis of the crystal.

Although the highly symmetrical configuration of the benzene molecule depicted in Fig. 1 undergoes some distortion, unaccompanied by remarshalling, when packed into the structure shown in Fig. 3, it must be concluded that the distorted configuration occurs only in the crystalline state. There is no need to suppose that this temporary distortion survives the disintegration of the assemblage consequent on destruction of the crystalline structure, so that, for purposes of chemical reaction, and when separated from close-packed association with its companion units, the symmetry of the molecule should be regarded as the highest which the complex representing it is able to assume without remarshalling of its component spheres. This is of universal application, and in this, and all other cases, the nature of the marshalling must be regarded as the characterising feature of the chemical molecule.

Fig. 5.

The objection may be taken to the benzene configuration now suggested which was raised against, and which proved fatal to, the solid configurations proposed by Ladenburg (see Lewkowitsch, Trans., 1888, **53**, 781; *Ber.*, 1883, **16**, 1576), namely, that all solid configurations of the benzene molecule lead to enantiomorphism amongst the di- and tri-substitution derivatives, an enantiomorphism which has not hitherto been discovered. This objection is, however, groundless as applied to the present work, and for the following reason. In the column represented as an element of the structure in Fig. 4, the hydrogen spheres lie three in each of a set of parallel planes represented by a, b, c, d, e, f, of Fig. 5 and at the numbered points. And in accordance with what has been explained above, the geometrical partitioning of the column involves the separation of any two of its consecutive layers to form a free molecule of the hydrocarbon; alternative partitionings are thus possible, giving as separate complexes the pairs of layers ab, cd, ef, or bc, de, fg. And if the hydrogen spheres, 1, 2, 3, 4, 5, and 6, are replaced in any symmetrical manner in the layers a, b, c, &c., of the column, so as to lead to enantiomorphism on partition-

ing into the units *ab*, *cd*, *ef*, the simultaneous occurrence in another column of partitioning into the units *bc*, *de*, *fg*, will lead to the production of units or molecules enantiomorphously related to the former, and the whole disintegrated structure will be externally compensated. Therefore, although many of the di- and tri-derivatives of benzene must possess enantiomorphous configurations, they could not exist in the non-crystalline state in an optically active form, because the alternative partitioning annuls the optical activity.

The benzene assemblage is thus one in which two distinct geometrical partitionings can be performed, each leading to a subdivision into identical benzene molecules. Such alternative partitioning is in many cases possible; as already indicated (p. 1690), in certain cases this leads to the production of alternative constitutions. In a later paper we shall show, for example, that the assemblage representative of phloroglucinol is partitionable in two ways, the one leading to the configuration of the symmetrical trihydroxybenzene, the other to that of the 1 : 3 : 5-triketohexamethylene. The possibility of such an alternative geometrical partitioning of the appropriate homogeneous assemblage affords an explanation of the existence of enolic and ketonic isomerides.

Without at present pursuing this particular aspect of alternative geometrical partitioning further, one application of it can at once be made which illustrates the kind of way in which the new method of formulating molecular structures elucidates certain obscure points in the behaviour of benzene derivatives. The numbering in Fig. 5 is that conventionally used for distinguishing the six hydrogen atoms in the Kekulé formula of benzene, and the possibilities of isomerism attending the formation of di-derivatives of the hydrocarbon can be conveniently traced on Fig. 5 with the aid of the numbering and lettering given. The production of a mono-substitution derivative C_6H_5X necessitates the replacement of one hydrogen sphere in each alternate layer *a*, *c*, *e*, *g*, or *b*, *d*, *f*, *h*, by the group *X*; the introduction of a second group *X* to give the derivative $C_6H_4X_2$ may be brought about in two generically distinct ways: the second group *X* may enter the column in the same layers in which the first group *X* was introduced, leaving the alternate layers still unsubstituted, and in this case a meta-di-derivative alone will be formed; or the second group *X* may be introduced into the alternate layers, into which the *X* groups did not originally enter, and then an ortho- or para-diderivative, or both, will be formed. A complete geometrical difference in kind thus exists between the derivation of the 1 : 3-di-derivative and that of the 1 : 2- and 1 : 4-isomerides; this is wholly in harmony with the observed chemical facts.

Further, suppose that the two substituting groups *X* are in-

troduced symmetrically into the column shown in Fig. 5 ; several geometrically distinct possibilities occur, but attention need here only be directed to one, namely, to the result obtained by substituting the hydrogen spheres a_1, b_4, c_3, d_6, e_5, f_2, g_1, h_4, &c., each by the group X. This type of substitution is highly symmetrical, and on subsequently partitioning the column, the units or molecules, a_1b_4, c_3d_6, e_5f_2, g_1h_4, all of the para constitution, result from the one kind of partitioning, whilst the other kind of partitioning leads to the production of the ortho-isomeride, b_4c_3, d_6e_5, f_2g_1, h_4i_3. The application, in different parts of the same assemblage, of the two partitionings leads to the simultaneous production of an ortho- and a para-di-derivative.

From the foregoing it will be seen that our method of regarding chemical structure is at once applicable to the facts summarised in the para-, ortho-, and meta-law ; it offers, in fact, a mechanism illustrating the facts that, if a meta-di-derivative of benzene is formed in any particular reaction, it is, in general, practically the sole product, whilst if an ortho-derivative is formed, it is, in general, accompanied by a large proportion of the para-isomeride (compare Armstrong, Trans., 1887, **51**, 258).

In deducing the above configuration for benzene we have dealt only with close-packed arrangements of spheres in contact ; these spheres are conceived merely as the regions of space inhabited by distinct atoms, and this method of treatment, as already indicated, does not represent the truth with precise accuracy. The real state of the assemblage is, as has been said, better represented by the packing of elastic spheres subjected to a general pressure so as practically to eliminate the interstitial space ; it is only for convenience of repre-sentation that interstitial spaces are shown in the diagrams. As the assemblages represented, in which interstitial space is shown, would be converted into the correct assemblages containing no interstitial space, if the spheres were supposed elastic and subjected to appropriate pres-sure, the validity of the argument is not affected, because the relative dimensions of the assemblages are practically unaffected by the pressure.

The same type of assemblage as has been assigned to benzene is in accordance with the crystallographic data for hexachloro- and hexa-bromo-benzene ; these are pseudotrigonal and have been described by Fels (*Zeit. Kryst. Min.*, 1900, **32**, 367) as monosymmetric with the following axial ratios :

$$C_6Cl_6, \ a : b : c = 2{\cdot}0993 : 1 : 4{\cdot}3220, \ \beta = 116°52'.$$
$$C_6Br_6, \quad ,, \quad = 2{\cdot}0903 : 1 : 4{\cdot}2620, \ ,, = 116°28'30''.$$

These axial ratios are simplified by changing the forms {100},

$\{001\}$, $\{10\bar{2}\}$, and $\{11\bar{1}\}$, to $\{\bar{1}01\}$, $\{100\}$, $\{101\}$, and $\{011\}$; this gives :

$$C_6Cl_6, \ a : b : c = 2 \cdot 1012 : 1 : 3 \cdot 8618, \ \beta = 87°49'45''.$$
$$C_6Br_6 \quad ,, \quad = 2 \cdot 0902 : 1 : 3 \cdot 8183, \ ,, = 87°18'.$$

On taking, in these values, $2a$ and $5b$, the equivalence parameters become compatible with those of benzene, namely :

$$C_6H_6, \ x : y : z = 3 \cdot 101 \quad : 3 \cdot 480 \quad : 2 \cdot 780, \quad \beta = 90°.$$
$$C_6Cl_6, \quad ,, \quad = 3 \cdot 0169 : 3 \cdot 5894 : 2 \cdot 7724, \ ,, = 87°49'45''.$$
$$C_6Br_6, \quad ,, \quad = 3 \cdot 0181 : 8 \cdot 6097 : 2 \cdot 7587, \ ,, = 87°18'.$$

So far as is known, benzene is not dimorphous, but it is interesting to notice that an alternative close-packed arrangement exists of units possessing the marshalling shown in Figs. 1 and 2 ; this alternative crystallographic arrangement of the units apparently occurs in the known crystalline modifications of some of the halogen derivatives of benzene.

The alternative arrangement referred to is of highly symmetrical marshalling, and may be regarded as consisting of layers of spheres one of which is depicted in Fig. 6, arranged one upon the other in rhombohedral symmetry ; any two successive layers are thus arranged as shown in Fig. 7a, and form one stratum of benzene complexes, the centres of the latter lying at the points A. Fig. 7b shows how the next stratum of two layers has to be superposed upon that of Fig. 7a : Fig. 7c, how the next stratum lies upon that of Fig. 7b ; this mode of superposition, which is designed so as to produce close-packing, leads to rhombohedral symmetry. The spheres of the fourth stratum, neglecting any slight distortion, come vertically over the corresponding ones of the first, and thus the first and fourth strata have the same projection. The centres of the small or hydrogen spheres do not lie exactly in the same planes as the large or carbon spheres of the same layer. The contour of the set of spheres con_ stituting one benzene unit or molecule grouped about the centre A in Fig. 7a will be easily distinguished and seen to be identical in marshalling with that of Figs. 1 and 2.

Benzene units or molecules of the marshalling depicted in Figs. 1 and 2 can thus be packed closely in two alternative modes, the one indicated in Fig. 3, the other in Figs. 7a, b, and c. The alternative assemblages thus indicated may be geometrically distinguished in the following way.

It is well known that an indefinitely large number of equal spheres can be close-packed in either cubic or holohedral hexagonal symmetry ; in the latter case, alternate triangularly arranged layers lie vertically over one another, and the two sets of alternate layers of which the
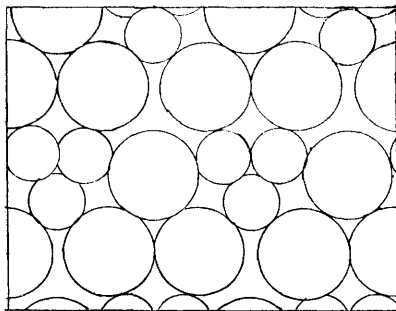
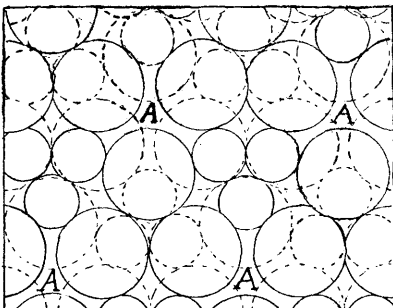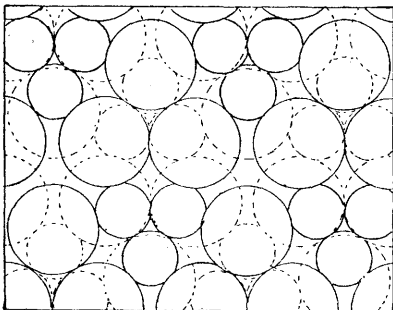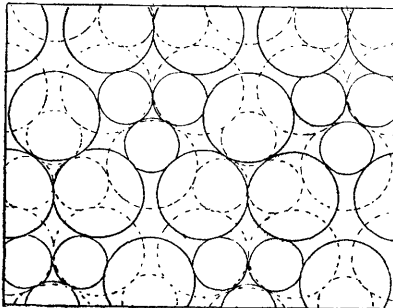BARLOW AND POPE:

FIG. 6.

FIG. 7a.

FIG. 7b.

FIG. 7c.

assemblage then consists are connected by coincidence-movements about hexagonal screw axes perpendicular to the plane of the layers (Barlow, *Sci. Proc. Roy. Dubl. Soc.*, 1897, **8**, 527). From either the cubic or the hexagonal close-packed arrangement one-fourth of the spheres can be symmetrically removed without impairing the symmetry ; each layer then presents the appearance shown in Fig. 8, and in both cases the assemblage can be regarded as made up of octahedral groups of six spheres, two layers combining to furnish a single stratum of groups as shown in Fig. 9. The number of cavities being twice that of the octahedral groups, if three smaller spheres, each having one-fourth the volume of a larger sphere, are squeezed into each cavity of an assemblage of either kind, the composition C_nH_n is attained, and since the carbon spheres occur in groups of six, the partitioning yields units of the benzene composition C_6H_6.

After this replacement of one-fourth of the spheres by sets of three small spheres in either the cubic or the hexagonal assemblage, a comparatively slight distortion or adjustment suffices to re-establish close-packing ; the appropriate distortion of the

hexagonal assemblage converts it into the benzene assemblage of Fig. 3, whilst the system derived from the cubic assemblage, by a slight distortion, yields the rhombohedral or nearly rhombohedral assemblage of Figs. 7a, b, and c. In the latter case the distortion consists in a compression in the direction of one of the four trigonal axes, the planes of the triads of small spheres remaining practically parallel to the planes of the layers.

A comparison of the diagrams will show that the benzene assemblage of hexagonal derivation (Fig. 3) and that of cubic derivation (Figs. 7a, b, and c) are geometrically closely related, in addition to being symmetrically partitionable into units of the same marshalling ; in both assemblages the smaller spheres are grouped in triads, each group being contained in a cavity surrounded by twelve of the larger spheres, and the three spheres of a group being attached to three
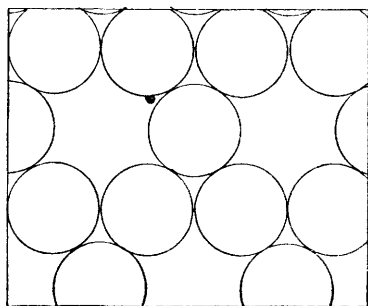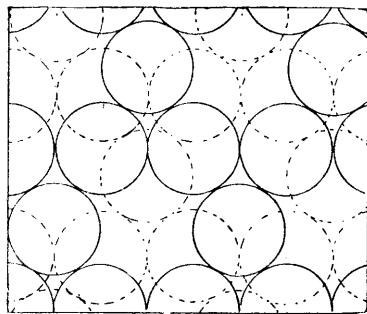
FIG. 8.   FIG. 9.

different benzene complexes. Among the prominent or singular points are found, in each case, the centres of the benzene complexes and the centres resembling them which are situated midway between six large spheres not belonging to the same complex and the centres of the cavities containing the smaller spheres. The other singular points of the two systems do not correspond.

In an undistorted assemblage, retaining complete rhombohedral symmetry, as in that represented in Figs. 7a, b, and c, the ratio of the equivalence parameters x and y corresponding to the x and y of crystalline benzene would be $0.8660 : 1$, this being the ratio between the lengths of the side and the perpendicular to the side in an equilateral triangle ; the value z would be rather less than in the case of the assemblage for benzene depicted in Fig. 3. The substitution of slightly different halogen spheres for hydrogen spheres in certain of the halogen derivatives of benzene will evidently affect the rhombohedral marshalling and lower the symmetry ; the departure from rhombohedral symmetry

may be expected to be somewhat pronounced. The values quoted
for the orthorhombic (O) and monosymmetric (M) benzene halogen
derivatives in the appended table, which is calculated from data given
by Fels (*Zeit. Kryst. Min.*, 1900, **32**, 358), seem to indicate that the
crystalline structure of these substances is one derived from the cubic
marshalling of the complexes just described.

	Crystal system.	β.	Multiples of axial ratios chosen.	Molecular volume.	$a : b : c$.	$x : y : z$.
1:4-C$_6$H$_4$Cl$_2$	M	100°25′	$a/2$	96·4	2·3366 : 1 : 1·3920	3·1306 : 3·6828 : 2·6457
1:4-C$_6$H$_4$Br$_2$	M	98 11½	$a/2$	104·4	2·4720 : 1 : 1·3774	3·2274 : 3·5966 : 2·6111
1:4-C$_6$H$_4$I$_2$	O	90 0	$b/2$	—	0·4342 : 1 : 0·3658	3·1402 : 3·6161 : 2·6419
1:2:4:5-C$_6$H$_2$Cl$_4$	M	99 26	$2c$	116·2	0·9041 : 1 : 0·3650	3·2414 : 3·5852 : 2·6169

Notwithstanding difference in crystalline system and accompanying
differences in the extent to which the assemblages are sheared in the
various directions, and the slight differences in the relative volumes
of the spheres of influence of hydrogen, chlorine, bromine, and
iodine, the respective x, y, and z values agree closely throughout the
series.

It will be seen from the foregoing that a close-packed homogeneous
assemblage has been derived which is entirely representative of our
chemical and crystallographic knowledge of benzene ; also that the
crystal symmetry of several of the halogen derivatives of the hydro-
carbon is almost identical with that of a close-packed assemblage of the
benzene molecular units having the alternative arrangement described.
Having thus given a detailed example of the methods of working
adopted, it will be convenient to summarise briefly as follows the
salient features presented by such close-packed equilibrium assemblages
as those depicted.

Any chemical compound can be represented by a close-packed and
homogeneously symmetrical assemblage of slightly deformed spheres
of the appropriate magnitudes, A, B, C, &c., in which the numerical
proportions of the different components are those of the spheres of
influence of the corresponding atoms present in the molecule of the
compound represented. In order to differentiate between organic sub-
stances having the same percentage composition but different mole-
cular weights or constitutions, a number of different close-packed
assemblages of the same composition have to be formed, the units of
which are different. Thus the several assemblages composed of
spheres representing carbon and hydrogen in equal proportion are
obtainable which correspond in number and properties to the hydro-
carbons of the empirical composition CH, and differ among themselves
both in the magnitudes and configurations of the units or molecules
into which they are partitionable. One, and only one, configuration of

unit represents acetylene ; another dipropargyl ; and a third, as shown above, represents benzene. Further, the comparison of numbers of close-packed assemblages representing organic compounds reveals the existence in different assemblages of compound groups identical in composition and configuration ; these component groups are the radicles known to organic chemistry, and the persistence of a particular type of structure as an element throughout widely differing assemblages characterises that particular structural element as a radicle. Again, the fragments of the close-packed assemblages which represent different radicles can be classified in homologous or related series according to their composition and symmetry ; the groups representing complex radicles, such as benzyl, benzoyl, acetyl, ethyl, &c., contain particular groups representing simpler radicles, such as phenyl, methyl, &c., precisely in accordance with our knowledge of those complex radicles.

If the substance under consideration is one of known crystalline form, it is found that the general symmetry of the close-packed assemblage is identical with that observed in the corresponding crystal. The axial ratios and interaxial angles of the latter are also compatible with the relative dimensions of the close-packed assemblage ; the correspondence also extends to the optical properties, to the twinning and to any so-called optical anomalies exhibited by the crystalline substance, these being paralleled by corresponding symmetrical structural features of the properly constituted assemblage. In very many cases close-packed assemblages of spheres representing a particular substance can be built up in two or more ways, each being in accordance with the chemical nature of the substance and partitionable into identical chemical molecules. The one of these assemblages can in some cases be distorted symmetrically in such a manner that it passes over into the other, the symmetrical distortion thus enabling a passage from one type of symmetry to the other. The alternative of symmetrical arrangement of the same set of units, whether achieved in this way or not, indicates polymorphism, and the different kinds of crystallographic symmetry actually exhibited by the substance are represented by the types and dimensions of the two or more close-packed assemblages.

Where, in consequence of the presence of the same units or radicles in two assemblages and a similar or partially similar arrangement of them, some of the translations or other dimensions are the same in both assemblages, difficulty is often experienced in detecting the similarity of dimension'; the difficulty is, in many cases, due to the axial directions chosen not corresponding in the two crystalline structures, similar directions not being immediately apparent from an inspection of the crystalline forms ; an instance bearing on this is found in the cases of hexachloro- and hexabromo-benzene, dealt with above. But when this complication does not arise, the relation between polymorphous iso-

BARLOW AND POPE :

merides is frequently seen to be of a very simple character.   This may
be illustrated by a comparison of the orthorhombic mineral gerhardtite,
$4CuO,N_2O_5,3H_2O$, with the synthetic monosymmetric compound of the
same composition, using the crystallographic data by Wells and Penfield
(*Zeit. Kryst. Min.*, 1886, **11**, 303).

$$4CuO,N_2O_5,3H_2O.$$
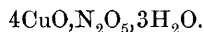
	β.	a : b : c.	x : y : z.	Density.
Natural	90°	0·92175 : 1 : 1·1562	3·1858 : 3·4562 : 3·9961	3·426
Synthetic ...	85°27′	0·9190 : 1 : 1·1402	3·1976 : 3·4794 : 3·9673	3·378

Notwithstanding the difference of crystalline system and of density,
it will be seen that relative lengths of corresponding dimensions in the
two structures, as indicated by the equivalence parameters $x : y : z$, are
almost the same. A slight shear of the orthorhombic structure would
bring its symmetry into congruence with that of the monosymmetric
one.   The monosymmetric mineral eudidymite, exhibiting $a : b : c =$
$1·7107 : 1 : 1·1071, \beta = 86° 14′ 30″$, and the orthorhombic epididymite with
$a : b : c = 1·7274 : 1 : 1·0680$, both of   which   have   the   composition
$NaBeHSi_3O_8$, are related in precisely the same manner as the fore-
going (Flink, *Zeit. Kryst. Min.*, 1894, **23**, 353).   Another instance of
similar kind is supplied by the rhombohedral and monosymmetric
forms of quinol, which are described in detail later (p. 1704).

The previously current views as to the constitution of benzene do not,
of course, lend themselves in any way to the detection of a connexion
between constitution and crystalline form, and although the discussion
of the initial problem has led to a result which agrees so well with the
mass of available qualitative and quantitative data that little doubt
can survive as to the general accuracy of the solution offered, it
is desirable that we should further consolidate our position by the
study of a typical set of substitution derivatives of benzene.   We
therefore proceed to the investigation of the three dihydroxybenzenes,
triphenylmethane and its derivatives, triphenylamine, naphthalene, and
anthracene, in order to show that, by adhering strictly to the mode of
procedure adopted in the case of benzene itself, it is possible to obtain
close-packed assemblages of the appropriate spheres whose types of
symmetry and relative axial dimensions are in agreement with our
chemical and crystallographic knowledge.   Although in some cases
the arrangement in the actual crystal may be other than that here
suggested, it is not probable that this frequently occurs, as it would
generally involve the existence of two arrangements for the same
molecular units, both very closely packed and both displaying sym-
metry of structure referable to the same one of the thirty-two crystal
classes, and having the same or interconvertible axial dimensions.

Quinol.

$$HO \cdot C {<}{\genfrac{}{}{0pt}{}{CH \cdot CH}{CH:CH}}{>} C \cdot OH.$$
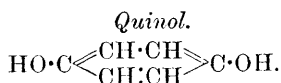
Quinol, or *p*-dihydroxybenzene, is dimorphous, and the first modification to which we direct attention is that which crystallises in the rhombohedral system and exhibits $a = 108° 4' 30''$; $a : c = 1 : 0.6591$ (Groth). The occurrence of the high rhombohedral symmetry is of importance, in that it imposes narrow limitations upon the nature of the close-packing of the molecules in the crystal structure and upon the configuration of the molecules themselves. The assemblage appropriate to quinol is derived from the benzene unit or molecule in the following manner.

Benzene complexes distorted as in Fig. 3 are arranged in mutual contact and similarly orientated upon the same plane in such a way that the centres of the complexes lie at the knots of an equilaterally triangular network. Triads of small spheres are observable in the plane layer thus obtained, just as in Fig. 3, but the three individual spheres forming a triad are no longer all in contact. Substitute now one sphere of each triad by a sphere of twice its volume, the substituted spheres being similarly situated throughout the plane layer of complexes, and being so selected as to conserve the digonal axis of rotation which passes through the centre of each benzene complex. The introduction of this larger sphere just about suffices to bring it into contact with the two smaller spheres of the same triad, but still leaves in the structure a gap bounded on one side by those two smaller spheres; this gap is filled by the introduction of another hydrogen sphere, which then makes contact, or nearly so, with five spheres of a face layer. This last inserted sphere is rather large for the narrowest part of the gap which it occupies, and will therefore project a little, either above or below the level of the hydrogen spheres; its position can, however, be so adjusted as still to conserve the digonal axes.

The arrangement now arrived at is indicated in Fig. 10, in which the two layers of spheres making up the one layer of complexes are respectively represented by continued and broken lines; the thick straight lines represent the projections of the digonal axes. Each of the broken line hexagonal cells indicated approximately outlines one quinol molecule or one unit of the structure.

Since the plane network formed by the centres of the original benzene complexes becomes in the quinol structure an equilaterally triangular one, successive layers of complexes identical with the first can be built up so that the set of digonal axes found in any one layer is at 120° with the set found in the next layer. The orientation of successive layers thus related is so chosen that the

system forms a series of screw-spiral; corresponding points in the first and fourth layers of complexes having the same projection on the plane parallel to the first plane layer. On thus stacking successive layers, the spheres of any layer may individually move up or down slightly in such a manner as to accommodate the contours of neighbouring layers. As the presence of spheres of different sizes makes the layers of different thicknesses in different parts, it is essential for close-packing that the layers should be so adjusted, one above the other, that thick portions of the one are superposed upon thin portions of the next; this is achieved by the adoption of the spiral arrangement described. The attainment of close-packing will be further assisted
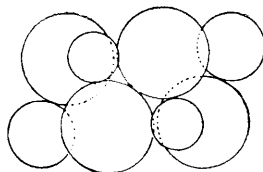
Fig. 10.
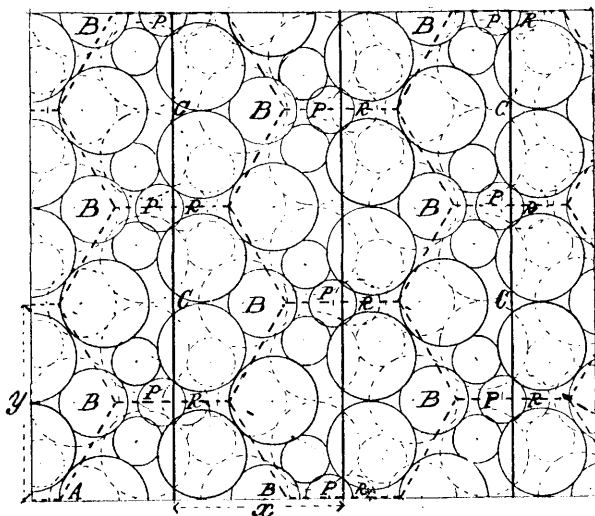
because, since the mass consists of elastic deformable spheres and is supposed subject to a general and uniform compression, a slight mutual adjustment of the relative positions of the component spheres will occur so as to produce increased closeness of packing; this change will be probably symmetrical, and therefore unlikely to alter the character of the general symmetry. In the present case it will not be necessary to indicate the precise nature of this adjustment, and the more so, as it consists merely in a slight movement, mostly up or down, of some sphere or spheres with respect to others in the layer. For the sake, however, of clearness, it will be well to state in general terms the nature of this mutual accommodation of the layers of an assemblage one to another, which can occur without the accompaniment of material rearrangement or remarshalling.

If an assemblage of elastic spheres, mutually in contact and subject to general compression, or some system of mutually repellent centres mechanically equivalent to it, is nearly but not quite closely-packed or in equilibrium, the assemblage will pass to a condition of equilibrium in close-packing by executing small relative mutual adjustments of its parts.   And if the original system is either symmetrical or so nearly symmetrical as to be capable of becoming completely so when equilibrium is ultimately reached, the resultant assemblage will be a symmetrical or homogeneous one ; in other words, the same conditions of equilibrium will continually repeat themselves throughout it.   And when it is considered that the spheres of influence, which, for purposes of simplicity, we are now treating statically, are certainly the seat of great dynamic activity, it must be concluded that the establishment of equilibrium as just indicated will be a very rapid process.   The question as to what equilibrium of composition must characterise a system in order that it may be capable of close-packing in homogeneous arrangement is discussed in a later chapter on valency.

FIG. 11.

It will be seen that the geometrical partitioning of the assemblage shown in Fig. 10 resolves it into units or molecules of the para-constitution, in which the spheres of intermediate size representing oxygen are diametrically opposite each ot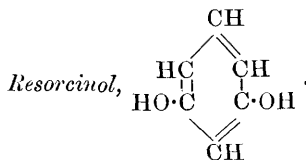her on a line passing through the centre of the molecule (Fig. 11).   The hydroxylic hydrogen spheres are not shown in Fig. 11, because their precise position is not fixed by the symmetry ; it is not immediately apparent what precise course is taken by the walls of the partitioning which separates the assemblage into molecular units.

The assemblage depicted in Fig. 10 as appropriate for quinol possesses trigonal symmetry, and in addition has digonal axes perpendicular to and intersecting the trigonal axes ; the digonal axes are those already described, and also an equal number which lie midway between and parallel to them.   It is identical in kind with that attributed to quinol on the basis of the goniometrical examination, with the exception that it possesses no centres or planes of symmetry ; the assemblage is thus an enantiomorphous one, and is of type 46 or 47 of Barlow.   The type of symmetry of the measured crystals of quinol and of the structure described and figured above being identical, with the exception that the indicated enantiomorphism has not been detected, it remains to show that the axial ratios of the crystals are compatible with the dimensions of this structure and that attributed above to benzene.

On substituting $3a/4$ for a in the axial ratios for quinol, the latter become $a : c = 1 : 0\cdot8788$, and, throwing these into the ortho-rhombic form of $a : b : c = 0\cdot8660 : 1 : 0\cdot7610$, and calculating the equi-valence parameters, taking the valency volume $W = 34$, the values $x : y : z = 3\cdot2238 : 3\cdot7227 : 2\cdot8330$ are obtaine l.   Fig. 10 is drawn to the same scale as the benzene assemblage, employing these parameters ; the value of z is, as it should be, a trifle greater than in the case of the hydrocarbon.

The principal dimensions of the monosymmetric form of quinol become nearly identical with those of the rhombohedral form if the fractions of the axial ratios suggested by Arzruni (*Physik. Chem. d. Kryst.*, 1893, 227) are adopted, for then $a/3 : b : c/2 = 0\cdot8683 : 1 : 0\cdot7790$, $\beta = 107°$, are obtained.   Two of these axial values are identical with those of the rhombohedral form, and the third, namely, the c-value, corresponds to an oblique measurement expressing nearly the same thickness of stratum as is indicated by the corresponding perpendicular axis c in the trigonal form.   The equivalence para-meters, $x : y : z = 3\cdot2526 : 3\cdot7459 : 2\cdot9184$, $\beta = 107°$, are obtained from the axial data modified as above ; in comparing these values with those of the rhombohedral form it should be noted that $2\cdot9184 \times sin\ 107° = 2\cdot7909$, a quantity very near to the z-value of $2\cdot7800$ for benzene.

It is suggested that the assemblage of the monosymmetric form of quinol is composed of layers of the same nature as those present in the rhombohedral assemblage depicted in Fig. 10, which there-fore applies to both forms, but that the disposition of succeeding layers is different.   The arrangement in the case of the rhombohedral form is that derived from the holohedral hexagonal arrangement of the benzene complexes, whilst in the monosymmetric form the layers are so deposited one on the other that a plane of symmetry passes through the centre of each benzene complex perpendicular to the digonal axis.   In other words, the two assemblages assigned to quinol precisely parallel the two attributed above to benzene ; one of these is found in the crystalline hydrocarbon itself and its per-halogen derivatives, and the other in its di- and tetra-halogen deriva-tives.

$$
\textit{Resorcinol,}\quad
\begin{array}{c}
\text{CH} \\
\diagup\ \diagdown \\
\text{HC}\qquad\text{CH} \\
\| \qquad\quad | \\
\text{HO·C}\qquad\text{C·OH} \\
\diagdown\ \diagup \\
\text{CH}
\end{array}\ .
$$

In order to obtain a homogeneous assemblage isomeric with that representing quinol, but in which the two hydroxyl groups are in the meta-positions as in resorcinol, layers differing distinctly,

though not greatly, from those indicated in the former case must be
employed. An assemblage representative of the structural features of
resorcinol is shown in Fig. 12, in which, as in the case of the quinol
assemblage shown in Fig. 10, each considerable gap among the large
spheres of a layer is occupied by three of the smallest or hydrogen size
and one of the medium or oxygen size. In Fig. 12 the projection of
one half of the double layer of spheres or single layer of benzene
complexes is represented by broken lines, the other half, which is
either above or below the first, being indicated by continuous lines;
the exigencies of the packing do not allow of the centres of all the

Fig. 12.
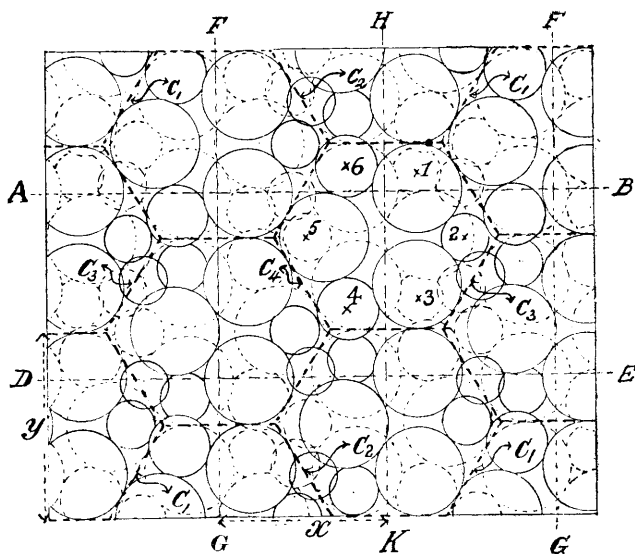
spheres in a layer lying quite in the same plane, and the extent of this
deviation is indicated by a slight overlapping in parts of the projection.
The hydroxylic hydrogen sphere in particular is, just as with quinol,
prevented from attaining the level of the others by being rather large
for the narrower parts of the gap into which it must be inserted, and
therefore projects above the others.

As before, the assemblage can be geometrically partitioned into
hexagonal prisms with identical contents as indicated in the figure;
the hexagons are, however, not now regular. The molecule is derived
as before by associating, in accordance with the partitioning, a group
of spheres of one layer, whose centres are contained within a single
prism, with a corresponding group in the layer immediately above or

below, whose centres are contained in the same prism. The exact nature of the attachment of the hydroxylic hydrogen atom is, as in the case of quinol, left undetermined by the symmetry ; but, if the centres of these hydrogen atoms lie all slightly above or slightly below the planes of the respective layers, the system possesses digonal screw axes perpendicular to the plane of the diagram through all such points as C_1, C_2, C_3, C_4, the translation component of which is $z/_2$, where z is a translation of the system in a direction perpendicular to the plane of the diagram. Two sets of planes of gliding-symmetry perpendicular to the plane of the diagram are also present, and are marked AB, DE, and FG, HK, in Fig. 12. The symmetry about the digonal axes is manifest if the system formed by the continuous line circles is rotated as a whole through $180°$ about any one of the points C_1, C_2, &c., when all its parts come to coincidence with the system formed by the broken line circles.

The system displays hemimorphous orthorhombic symmetry of the type $53\,B_4$ in Barlow's list and $12\,a$ of Fedoroff ; it is therefore identical in crystallographic symmetry with the crystals of resorcinol which Calderon described as belonging to the hemimorphous orthorhombic system and as having the axial ratios $a : b : c = 0·9123 : 1 : 0·5876$. It remains now to show that these axial dimensions are compatible with the figured structure.

On substituting c by $4c/3$ in the axial ratios given above, the values, $a : b : 4c/3 = 0·9123 : 1 : 0·7835$, are obtained, and, since $W = 34$, the equivalence parameters are $x : y : z := 3·3055 : 3·6233 : 2·8388$. It is interesting to note that the value z, which represents a translation perpendicular to the plane of Fig. 12, is practically identical with the corresponding value for quinol. The applicability of the above set of axial ratios is shown as before by drawing the figure representing the assemblage to the scale adopted for benzene, using the above equivalence parameters.

$$Catechol, \quad \begin{array}{c} CH \\ HC \quad C·OH \\ HC \quad C·OH· \\ CH \end{array}$$
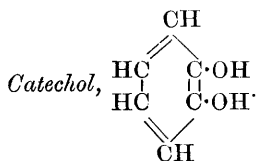
Catechol, or o-dihydroxybenzene, is monosymmetric with the axial ratios $a : b : c = 1·6086 : 1 : 1·0229$, $\beta = 85°45'$ (Beckenkamp, *Zeit. Kryst. Min.*, 1900, **33**, 599). These values may be transposed by writing a_1 for b, b_1 for c, and c_1 for $a/2$, and then become $a_1 : b_1 : c_1 = 1 : 1·0229 : 0·8043$, $\gamma = 85°45'$; the valency volume, $W = 34$, as before, and the equivalence parameters are $x : y : z = 3·4605 : 3·5398 : 2·7833$.

The values of y and z thus obtained differ but little from those of benzene, and, in harmony with this, benzene complexes in which the ortho-substitution of two oxygen and two hydrogen spheres for two hydrogen spheres has been made can be fitted together to form columns and walls just as in the case of the benzene assemblage; the walls can be placed at different levels so as to pack together more closely, but their relative positions must not, as is the case with benzene, be such as to produce digonal axes in the directions a and c. If, however, the digonal axis which passes through the middle of each unit taken alone is made the direction of the b-axis in the assemblage, the fitting together of the walls being effected consistently with this, monosymmetric symmetry will result.

The direction of a in the axial ratios stated is possibly ill-chosen, but, premising that the other two axial directions have been correctly located, and that their dimensions are as indicated, a different choice for the direction a would cause no change in the dimensions indicated as the mean thickness of the walls. And thus, the selection of any other axial direction for the a-axis, as according better with the construction of the assemblage, will accord equally well with the constants b and c or x and z. The extent to which one wall is sheared upon the next is in any case probably not the same as in benzene, owing to the conditions being complicated by the changed configuration of the molecular complexes.

Without tracing the precise form of the catechol assemblage, a diagrammatic representation of the symmetry of the system, in which the shear is not taken into account, is given by Fig. 13, which thus shows merely the mutual disposition of the hexagonal cells using the equivalence parameters stated above, and without indicating how the walls are fitted together. The proper sizes of the various spheres on the benzene scale are not employed, but only their correct relative orders of magnitude.

For purposes of comparison it is convenient to resume the data concerning the dihydroxybenzenes in the accompanying table.

|	Crystal system.	$a\ :\ b\ :\ c$	$x\ :\ y\ :\ z$
Quinol	Rh.	$\alpha = 108°4'30''$	$3\cdot2238 : 3\cdot7227 : 2\cdot8330$
,, ...	Mo.	$2\cdot6050 : 1 : 1\cdot5580$ $\beta = 107°$	$3\cdot2526 : 3\cdot7459 : 2\cdot9184$
Resorcinol	Or.	$0\cdot9123 : 1 : 0\cdot5876$	$3\cdot3055 : 3\cdot6233 : 2\cdot8388$
Catechol	Mo.	$1\cdot6086 : 1 : 1\cdot0229$ $\beta = 85°45'$	$3\cdot4605 : 3\cdot5398 : 2\cdot7833$

Triphenylmethane, $(C_6H_5)_3CH$.

The stable modification of triphenylmethane belongs to the hemimorphous orthorhombic system with $a : b : c = 0\cdot5716 : 1 : 0\cdot5867$

(Hintze, *Zeit. Kryst. Min.*, 1884, **9**, 546) ; the labile form is also
orthorhombic, and gives $a : b : c = 0.7888 : 1 : 0.6959$ (Groth, *Zeit. Kryst.
Min.*, 1881, **5**, 478).

An assemblage appropriate for the stable modification of triphenyl-
methane is derived by disposing three benzene complexes (Fig. 2)
triangularly and similarly orientated in the same plane, and replacing
the single triad of hydrogen spheres by one sphere of the volume used for
carbon in such a way that the latter makes contact with the three com-
plexes and has its centre in the same plane as the other spheres of the
layer. The large complex (Fig. 14) now has the composition and consti-
tution of the triphenylmethyl radicle, and a column of such double layers
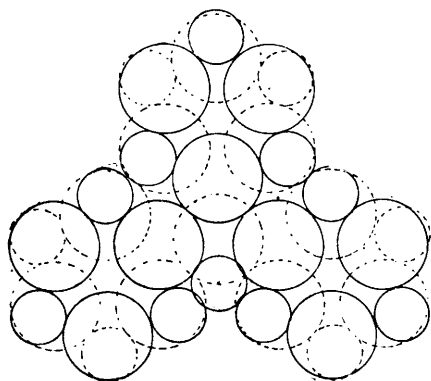
FIG. 13.
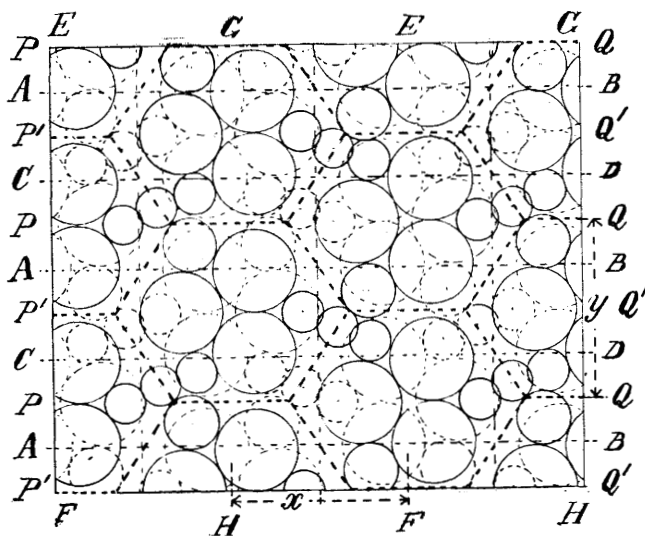
can be built up, just as in the case of benzene (Fig. 4), and consists of
alternating single layers of two kinds. The packing of the benzene
complexes about the central and last inserted carbon sphere in the
assemblage can, however, be made closer by effecting a slight adjust-
ment and then inserting an additional set of hydrogen spheres in the
numerical proportion of one to each triad of benzene complexes, in the
manner shown in Fig. 15. The centre of the last added hydrogen
sphere is not exactly in the plane containing the centres of the
original spheres, but lies a little above or below that plane, because
the available space is rather too constricted in the plane of these
centres, whilst there is still space above and below. This condition is
indicated by the added hydrogen spheres overlapping their neighbours

slightly, as shown in the plan of the complete structure given in Fig. 16.   Each of the last added hydrogen spheres is in contact with either, but not with both, of the methylic carbon atoms belonging to the layers immediately above
and below.

After a further slight adjustment which does not involve remarshalling, the composite columnar groups thus constituted can be aggregated so as to form linear serrated walls.   Each of these walls, as in the case of resorcinol, consists of alternate single layers of the two kinds represented by continuous and broken line circles.   Finally, the walls thus composed can be fitted together and inter-

Fig. 14.

locked by being placed at different levels, just as in the case of benzene, and in the manner represented in Fig 16.   The nature of the geometrical partitioning by means of which the structure is divided into identical molecules is indicated by the thick broken lines in the figure, the slight protrusion of some of the spheres of a molecule beyond the prism boundary of its space-unit being only apparent, and accounted for by the interlocking.

Fig. 15.

It is not suggested that the diagram presents great accuracy, but it suffices to show the possibility of combining such molecular complexes as those of triphenyl-methane so as to form a close-packed assemblage, and, as before, some slight mutual adjustment of the relative positions diagrammatically indicated is all that is necessary to produce statical equilibrium of such an assemblage as the one proposed. This obviously trivial change can be made so as not to alter the character of the symmetry, and
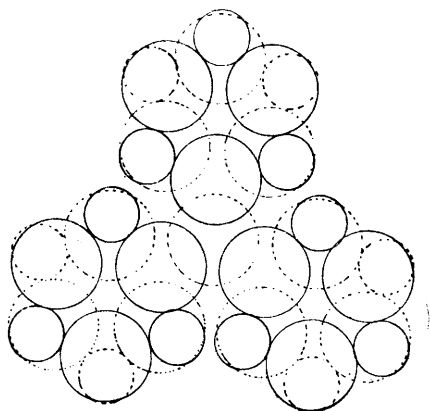
5 U 2

may, indeed, be regarded as negligible. If the methane hydrogen spheres last inserted in the structure lie all slightly above or slightly below the general planes of their respective layers, digonal axes exist perpendicular to the plane of Fig. 16 through the points marked C_1, C_2, C_3, C_4; these are the only ones which can be present. Planes of symmetry exist perpendicular to the plane of the diagram

FIG. 16.
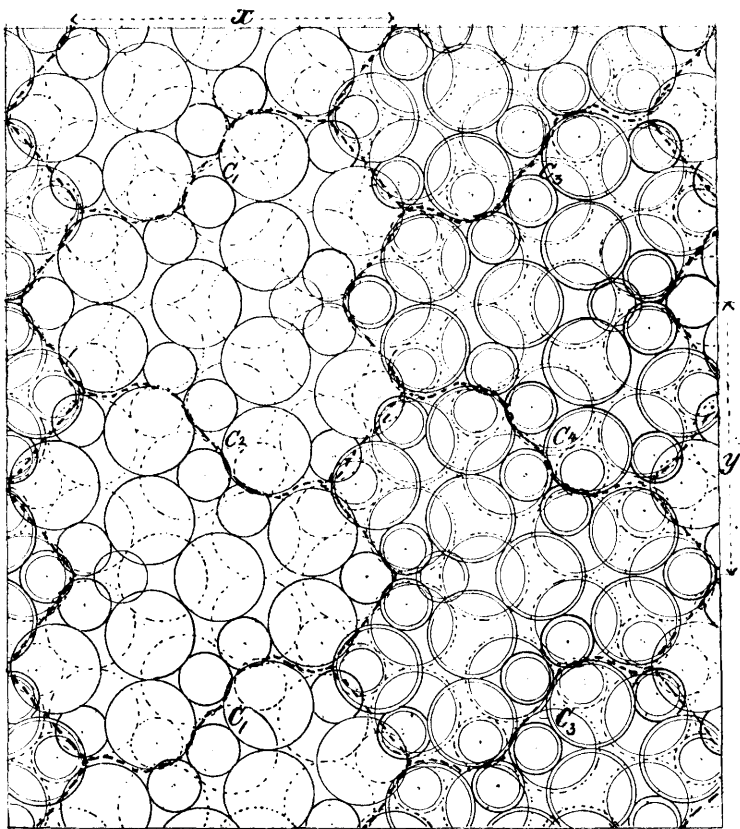
and at right angles to the direction of extension of the walls of complexes; they pass midway between the rows of digonal axes. Consequent on the existence of these planes and axes of symmetry, there are also present planes of gliding-symmetry; these are perpendicular to the plane of the diagram, and bisect the walls in the direction of their extension. The direction of the shift in these is perpendicular in the plane of the diagram, namely, in the direction of the axis b or y.

The structure displays hemimorphous orthorhombic symmetry, and is of the type marked 56 B_3 in Barlow's list and 6h in that of Fedoroff, and the crystallographic symmetry is thus identical with that assigned by Hintze to the stable form of triphenylmethane.   That, in addition to this identity in symmetry, the axial ratios of the hydrocarbon also agree with the dimensions of the assemblage, may be shown as follows: The valency volume of triphenylmethane is 92, and, on taking in the axial ratios given above, $b/2$ and $4c/9$, so that $a:b:c = 1\cdot1432:1:0\cdot5216$, the equivalence parameters, $x:y:z = 6\cdot1317:5\cdot3637:2\cdot7973$, are obtained; these numbers have been used for drawing Fig. 16 to the same scale as Fig. 3 for benzene.   It will be seen that the value $x = 6\cdot1317$ is about twice the corresponding value $x = 3\cdot1001$ for benzene, and that $z = 2\cdot7973$ for triphenylmethane is slightly greater than $z = 2\cdot780$ for benzene.   The unique position of the methane hydrogen sphere is observable in other cases, and is perhaps accountable for the facility with which this atom is exchanged or replaced.

Another arrangement of the same complexes, very similar to the one just described, is possible, which also exhibits hemimorphous orthorhombic symmetry, and which is perhaps the more probable of the two; it is obtained as follows:

Instead of placing the complexes which lie on the same

FIG. 17.

vertical line in the diagram on the same level, let those lying on the same horizontal line be so placed; the plane assemblage of complexes thus consists of horizontal strings on two levels, as shown diagrammatically in Fig. 17. On laying down succeeding layers, let the orientation of each string be reversed so that digonal screw axes pass perpendicular to the plane of the diagram through all points A, A', B, B'; planes of symmetry pass horizontally through the axes A, A', B, B', and planes of gliding-symmetry pass midway between points A, A' and between points B, B'.   The adjustment of the parts in a complex has to be slightly different from that obtaining in the case previously described, in order that the axial ratios may be those stated; the form of complex requisite is that approximately indicated in Fig. 18.

The labile orthorhombic form of triphenylmethane with $a:b:c = 0\cdot7888:1:0\cdot6959$ has probably not been so exactly measured as the stable modification, but on selecting the multiples 3$b/2$ and 5$c/2$,
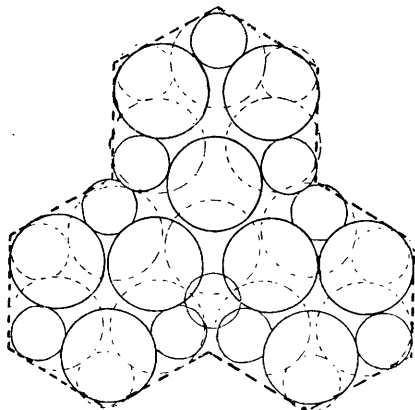
1716   BARLOW AND POPE:
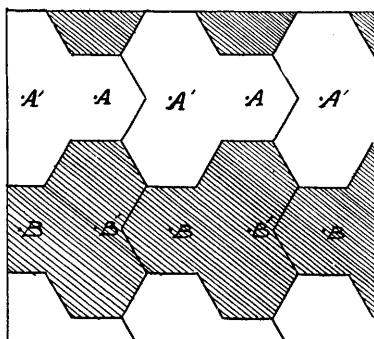
and exchanging a and c, the equivalence parameters, $x:y:z=$ $6 \cdot 1738 : 5 \cdot 3231 : 2 \cdot 7995$, result : these agree closely with the corresponding values given for the stable modification. Holohedral orthorhombic symmetry may be attained by the introduction of additional digonal screw axes whose projections are vertical lines in the diagram, and which reverse the orientation of alternate walls of complexes; or the symmetry may be similarly heightened by some other analogous method.

Since the height of one double layer composing a plane of packed triphenylmethane complexes, namely, $z = 2 \cdot 7973$, is about the same as the corresponding dimension, $z = 2 \cdot 780$, in the benzene assemblage, and since the contour and dimensions of one triphenylmethane complex in the assemblage are nearly identical with those of a plane arrangement of three benzene com-

Fig. 18.

plexes, it should be possible to arrange a plane assemblage consisting of triphenylmethane and benzene complexes in equal numbers in close order, and then to form a close-packed assemblage by piling up the layers thus obtained. And it is doubtless as a result of such a process as this that triphenylmethane and benzene yield the crystalline compound,

$$(C_6H_5)_3CH, C_6H_6,$$
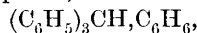
which is rhombohedral with $a : c = 1 : 2 \cdot 5565$ (Hintze, *Zeit. Kryst. Min.*, 1884, **9**, 545).

The alternative arrangement of the benzene molecular complexes, that, namely, which is derived from a cubic assemblage and described on p. 1699, is evidently more likely than the rhombic benzene arrangement to lend itself to the derivation of the rhombohedral symmetry of the substance in question. Accordingly, we find that a mixed assemblage composed of equal numbers of triphenylmethane and benzene complexes fulfilling the required conditions is obtainable from the alternative form of benzene arrangement in the following manner :

Partition a layer of benzene complexes of the latter assemblage into a mixture of triplets and single complexes, as indicated diagrammatically in Fig. 19 ; exchange the triplets for triphenylmethane complexes,

assigning to these the three different orientations possible in a symmetrically distributed manner; the result is a highly symmetrical layer having trigonal symmetry about axes perpendicular to it.   Pile such layers one upon the other in such a way that corresponding points such as A, A, A ; B, B, B; C, C, C, respectively, lie on staircase spirals whose axes are perpendicular to the plane of the diagram through O', O'', O''' ; this would be represented by the superposition of the diagrams a, b, and c. The result will evidently be an assemblage whose dimensions are very compatible with those of the second benzene arrangement. The symmetry of the assemblage depicted is that of the crystal class No. 18, and the data furnished by Hartley and Thomas (this vol., p. 1019) show that the compound $(C_6H_5)_3CH,C_6H_6$, crystallises in class 17 or 18.

In order to show that the axial ratios of the crystalline double compound are in harmony with this view, it must be first pointed out that, dividing c by three, and multiplying throughout by 0·8660, the axial ratios are obtained in orthorhombic form as $a:b:c = 0.8660:1:0.7380$; these figures are almost identical with those of p-di-iodobenzene given on p. 1702, namely, $2a:b:2c = 0.8684:1:0.7306$.   Now the valency volume, W, of the

FIG. 19.

double compound is $92 + 30 = 122$, and, since its magnitude is about that of four benzene units, the values a and b may each be multiplied by two so as to be about double the corresponding values for the
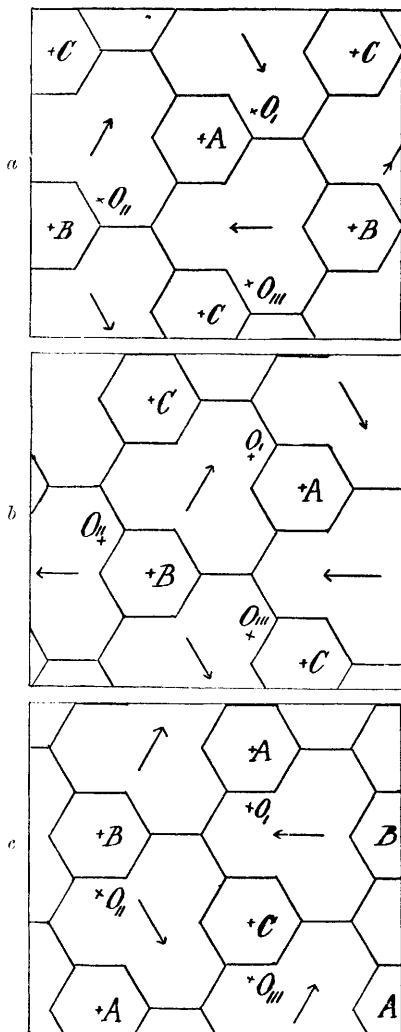
benzene form; the equivalence parameters then become $x:y:z = 6\cdot2824 : 7\cdot2545 : 2\cdot6769$. These figures indicate a slight increase in the z value as compared to that of the p-di-iodobenzene, namely, $z = 2\cdot6419$; this may be traced to the introduction of the methane residue, CH.

Whilst the character of the triphenylmethane assemblage is such that by a rearrangement of the kind suggested cavities of the shape and size of the benzene unit can be readily produced, complexes of other shapes and sizes could not be so easily intercalated. And in harmony with this it is known that the hydrocarbon does not form addition compounds with fatty substances nor with homologues of benzene, but does so with thiophen, pyrrole, and aniline, all substances possessing the hexagonal contour of benzene (Hartley and Thomas, *loc. cit.*, 1014). Compatibility of solid contour appears to be a determining factor in the production of other and similar addition compounds. Thus, v. Baeyer found (*Ber.*, 1905, **38**, 589) that p-tri-iodotriphenylcarbinol forms an addition compound with benzene. The picrates of aromatic hydrocarbons are also probably similarly constituted to the compound, $CH(C_6H_5)_3, C_6H_6$, as intercalations of two compatibly shaped groups.

FIG. 20.
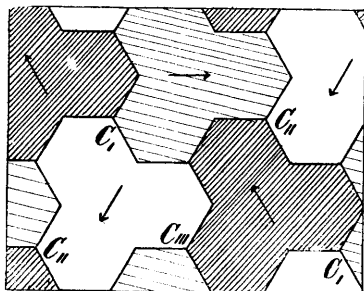
Triphenylmethyl Bromide, $(C_6H_5)_3CBr$.

Triphenylmethyl bromide is rhombohedral with $a:c = 0\cdot7843$ (Hintze, *Zeit. Kryst. Min.*, 1884, **9**, 549), and on writing the axial ratios in the orthorhombic form of $a:b:c = 0\cdot8660 : 1 : 0\cdot7843$, a great resemblance to the constants of benzene becomes apparent. W is 92, and when $2a$ and $3b/2$ are taken in order to make the space-unit commensurate with the molecular complex of triphenylmethane, the equivalence parameters $x:y:z = 6\cdot1671 : 5\cdot3411 : 2\cdot7932$, values nearly identical with those for triphenylmethane, are obtained. The manner in which triphenylmethane complexes of the form represented in Fig. 18 can be arranged in rhombohedral symmetry is indicated in Fig. 20; trigonal screw axes occur perpendicular to the plane of the diagram through C_i, C_{ii}, C_{iii}, and the three different levels at which the complexes lie are indicated by the absence of shading and by the light and dark hatching. The type

of symmetry is that numbered 42 and 43 in Barlow's list and 15 and 16 in that of Sohncke ; three different orientations of the complexes are involved, as indicated by the arrows.

Triphenylcarbinol, $(C_6H_5)_3C\cdot OH$.

The replacement of the bromine atom in triphenylmethyl bromide by a hydroxyl group to form triphenylcarbinol involves the insertion into the assemblage of an oxygen sphere of volume two and a hydrogen sphere of volume one in place of the bromine sphere of volume one.   A consideration of Fig. 16 shows that but little change need result to the assemblage by this substitution ; the oxygen sphere will take the place of the bromine sphere, and the forcing apart of the structure necessary for this will be accompanied by an enlargement of the triangular space below the bromine sphere such as will allow of the insertion of another hydrogen sphere. Some mutual adjustment of parts is required to re-establish close-packing, but the axial dimensions, notwithstanding this, need experience but slight change.

Triphenylcarbinol is rhombohedral with $a : c = 1 = 0.6984$ (Groth, *Zeit. Kryst. Min.*, 1881, **5**, 479), and on stating this ratio in the orthorhombic form the value $a : b : c = 0.8660 : 1 : 0.6984$ is obtained ; selecting the multiples $4a/3$ and $3c/4$, and calculating the equivalence parameters, the values $x : y : z = 6.2053 : 5.3763 : 2.8162$, are obtained, W being 94 ; so far as these numbers can be interpreted, it would seem that on substituting hydroxyl for bromine or hydrogen in the corresponding compounds, the structures are enlarged in nearly the same proportion in each of the three directions.
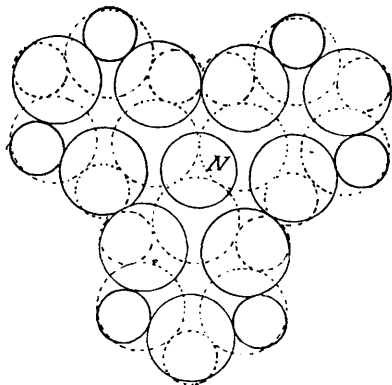
Triphenylacetic Acid, $(C_6H_5)_3C\cdot COOH$.

Triphenylacetic acid is monosymmetric with $a : b : c = 0.8346 : 1 : 0.9250$, $\beta = 42°34'30''$ (Groth, *Zeit. Kryst. Min.*, 1881, **5**, 483) ; morphotropically the crystals are nearly rhombohedral, and, for comparison with the substances previously discussed, it is convenient to change the indices of certain forms, making $c,(101)$ and $r,(001)$.   We then get $a : b : c = 0.5646 : 1 : 0.6161$, $\beta = 90°12'30''$, and on calculating the equivalence parameters from these values, taking $2a$ and $3c/4$, we obtain $x : y : z = 6.5083 : 5.7639 : 2.6657$, W being 100. These valency parameters are quite compatible with those of the series of halogen derivatives of benzene given above, the introduction of the large carboxyl group affecting the parameters x and y and leaving the z value practically the same as in the cases referred to.

Triphenylamine, $(C_6H_5)_3N$.

If, in the derivation of the complexes and columns representing the triphenylmethyl radicle, the group of three benzenoid hydrogen spheres, instead of being replaced by a carbon sphere of volume four, is replaced by a nitrogen sphere of volume three, close-packing and homogeneity can be retained in accordance with the simple valency law previously briefly stated and without the addition of another hydrogen sphere. The assemblage appropriate to triphenylamine is thus immediately obtained, and consists of complexes of the form shown in Fig. 21, packed together in a manner so similar to that which represents triphenylmethane that a separate figure is unnecessary. Triphenylamine is monosymmetric with $a : b : c = 0.9913 : 1 : 1.4119$, $\beta = 88°38'$ (Arzruni, *Zeit. Kryst. Min.*, 1877, **1**, 451), $W = 90$, and, on taking $2a$ and $3c/2$, the equivalence parameters $x : y : z = 5.8835 : 5.5079 : 2.7781$, are obtained ; the z-value is practically that of benzene and triphenylmethane, and the x and y values differ but slightly from those for the latter substance, as would be anticipated; the introduction of the nitrogen sphere necessarily causes less spreading of the complexes in the plane of Fig. 14 than that of a carbon and a hydrogen

FIG. 21.

sphere. A slight shear given to the triphenylmethane assemblage in the plane containing the directions x and z would degrade the orthorhombic symmetry of that assemblage to the monosymmetric symmetry of triphenylamine.

For purposes of reference it will be convenient to collect the data referring to the above substances in which three phenyl groups are associated in the following table :

Substance.	Crystal system.	Fractions of axial ratios selected.	$x : y : z$	Auxiliary fractions.
Triphenylmethane :				
Stable form	Or	$b/2,\ 4c/9$	$6\cdot1317 : 5\cdot3637 : 2\cdot7973$	$3a/2,\ 4c/3$
Labile ,, ...	,,	$3b/2,\ 5c/2$	$6\cdot1738 : 5\cdot3231 : 2\cdot7995$	$5c/4,$
$(C_6H_5)_3CH,C_6H_6$	Rh.	$c/3$	$6\cdot2824 : 7\cdot2545 : 2\cdot6769$	—
Triphenylmethyl				
bromide	,,	$2a,\ 3b/2$	$6\cdot1671 : 5\cdot3411 : 2\cdot7932$	none
Triphenylcarbinol	,,	$4a/3,\ 3c/4$	$6\cdot2039 : 5\cdot3727 : 2\cdot8143$	$2a/3,\ c/2$
Triphenylacetic acid ...	Mo.	$2a,\ 3c/4$	$6\cdot5085 : 5\cdot7639 : 2\cdot6657$	$2b/3,\ 4c/3$
		$\beta = 90°12'30''$		
Triphenylamine	,,	$2a,\ 3c/2$	$5\cdot8835 : 5\cdot5079 : 2\cdot7781$	$4a/3,\ 3c/4$
		$\beta = 88°38'$		

Notwithstanding the larger size of the molecular unit containing three phenyl groups, the great resemblance of the corresponding structures to the benzene assemblage indicates that the type of the latter might be closely adhered to in the crystalline forms of these derivatives ; and for converting the benzene assemblage into that appropriate to triphenylmethane one axis is multiplied by two and another by three over two. It is of great significance, as supporting the argument concerning fractionation of the axial lengths (p. 1683), that if, in the case of all these triphenyl-derivatives, one axial length is multiplied by two and another by three over two, the further reduction operation which has to be performed on the resulting axial ratios, before they yield equivalence parameters, is much more simple in character than the total reduction operation. This is seen on comparing the last column of the above table, in which is indicated the reduction necessary after one axial length has been multiplied by two and another by three over two in order to secure the conformity of equivalence parameters obtained, with the more complex reduction operation which has to be performed upon the original axial ratios to obtain the same result (column 3).
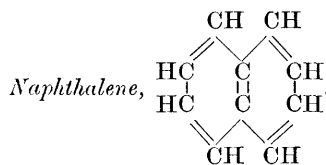
Naphthalene,

Our knowledge of the chemical constitution of naphthalene is summarised by deriving the configuration of one of the columns in the assemblage representing it from that of benzene (Figs. 1 and 2), in the manner shown in plan and elevation in Fig. 22. A little consideration of this figure will show that the configuration offered fulfils the requirements of a structural formula for naphthalene, as deduced from the isomerism of its derivatives, in just the same way as in the case of benzene.

1722   BARLOW AND POPE:

According to Groth, naphthalene crystallises in the holohedral monosymmetric system showing $a : b : c = 1\cdot3777 : 1 : 1\cdot4364$, $\beta = 57°11'$, the forms (001), ($\bar{2}$01), (110), (11$\bar{1}$), and a perfect cleavage on (001) (Negri, *Zeit. Kryst. Min.*, 1896, **25**, 410).

Complexes of the kind shown in the figure can be packed in columns just as can the benzene complexes, and an assemblage is derivable which is in accordance with the crystallographic properties of naphthalene ; as, however, we are at present engaged upon the crystallographic examination of a number of simple naphthalene derivatives, we propose to leave the further discussion of the nature of the naphthalene assemblage until this work is completed.

Fig. 22.

Anthracene,
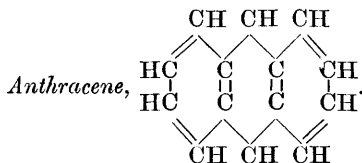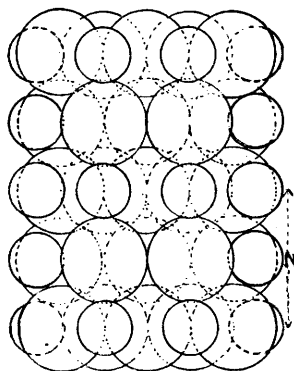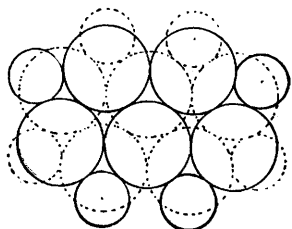
The application to the complex representing naphthalene of the process by which that complex was derived from the one representing benzene can be made in two ways, leading to the production of complexes which are in entire harmony with current knowledge of the constitution of anthracene and phenanthrene respectively. The configuration representing anthracene is shown in plan in Fig. 23, and examination will show that it is in agreement with the known isomerism of derivatives of the hydrocarbon. Units of this kind can be packed to form a close-packed assemblage in accordance with the crystal form of anthracene ; we shall, however, deal later with the packing of these units in connection with naphthalene.

An inspection of the models representing the molecular configurations of the aromatic hydrocarbons, benzene, naphthalene, and anthracene reveals a great resemblance of parts ; thus, regarded in one direction they all present the same aspect, that, namely, which is represented in the elevation depicted in Fig. 2 *b*. The specific properties associated with the aromatic substances are doubtless attributable to this likeness in configuration. This will naturally also apply to such substances as thiophen, pyridine, &c.

The Nature of Valency.

Having illustrated the way in which chemical substances can be
formulated as close-packed assemblages, and having demonstrated that
the method has the unique advantage of closely correlating molecular
structure and crystalline form, it will be convenient to direct attention
to certain well-marked geometrical properties of close-packed assem-
blages. From the way in which triphenylmethane, ȉtriphenylamine,
&c., have been derived from benzene, it is clear that some sort of
relationship exists between close packing and valency, although the
precise nature of that relationship is not immediately obvious.

We have now to show that close-packed assemblages of spheres of
different sizes, held in stable equilibrium as described, are characterised
by the possession of three general geometrical properties, and to demon-
strate that these ȉproperties are merely the geometrical expression of
chemical valency. The three properties in question refer (1) to
equality of valency, (2) to the
valency relations of atoms or
radicles of different valency vol-
umes, and (3) to multivalency.

FIG. 23.

On Equi-valency.

From a homogeneous close-
packed assemblage of spheres,
similarly environed single
spheres, or groups of two,
three, or more, can be removed homogeneously so as to leave a
residual set of spheres which, although homogeneous, is no longer
close-packed. The cavities which have been produced, being homo-
geneously arranged, are similar and identically related, and can
thus be re-occupied by a different set of identically similar groups
of spheres or single spheres. The packing of the new assemblage
thus derived can, like that of the original assemblage, be made
very close without any remarshalling of the unremoved spheres, if
such general deformation and local adjustment occur as will adapt
the shapes of the cavities to the shapes of the new contents, but
leave the cavities of about the same relative volumes as before the
process of exchange. Under these conditions and provided the dis-
tortion is not extreme, an intimate morphological relation of the
nature described later will exist between the original and the derived
assemblages.

The essential condition for close-packing is that each sphere of an
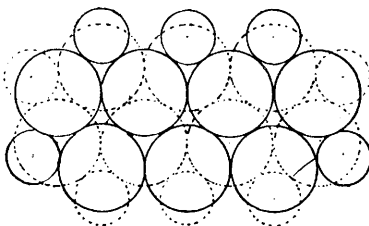
assemblage of spheres shall be in actual contact with or in close juxta-
position to a relatively large number of spheres ; in other words, that
only a small part of that shell-shaped portion of space immediately
surrounding any sphere shall consist of interstices. And the provision
that the cavities vacated preserve approximately their original magni-
tude ensures that the framework in which they occur merely suffers
such slight alteration in the density of its packing as is involved in
the change of shape of the cavities consequent on the latter being
packed with fresh contents ; in fact, the shell-shaped portion of space
immediately surrounding each cavity is about as densely packed
with spheres after substitution as before, and consists of the same
spheres.

It is possible, however, to retain a high degree of closeness of pack-
ing if the removal of spheres as just described is followed by an
equivalent introduction of other spheres to fill the vacant cavities.
The geometrical property of close-packed homogeneous assemblages
which is here concerned may be formally stated in the following terms.
If in a close-packed assemblage of spheres, single spheres or groups of
two or more, selected homogeneously, are replaced homogeneously by
other groups of spheres in such a way that the resulting assemblage
is close-packed without resorting to remarshalling, the replacing
group is practically of the same relative magnitude as the group re-
placed, and possesses the same fundamental valency.

This geometrical property of close-packed homogeneous assemblages
is the obvious analogue of an important class of observed facts relating
to isomorphism, morphotropy, valency, and chemical substitution.

Thus, on replacing in a compound an atom of an element by another
belonging to the same group in the periodic system, the resulting com-
pound is ordinarily isomorphous with the first ; the two elements of the
same group are represented by spheres of atomic influence of so nearly
the same size as compared with the sphere volumes of other constituents
that the one replaces the other without, in general, leading to a change
of crystalline system. It is convenient to show how closely the one
sphere of atomic influence must approximate in size to that of an
isomorphous element by the following table dealing with the series of
alkali sulphates and selenates which have been so accurately measured
by Tutton (Trans., 1905, **87**, 1188) ; the equivalence parameters are
calculated on the assumption of the pseudo-hexagonal structure made by
Tutton :

	$V.$	$W.$	x : y : $z.$
K_2SO_4	64·91	12	2·2109 : 2·1977 : 2·8463
Rb_2SO_4	73·34	12	2·2049 : 2·1899 : 2·8648
Cs_2SO_4	84·58	12	2·2003 : 2·1826 : 2·8777
K_2SeO_4	71·67	12	2·2207 : 2·2083 : 2·8204
Rb_2SeO_4	79·94	12	2·2147 : 2·1957 : 2·8412
Cs_2SeO_4	91·09	12	2·2112 : 2·1900 : 2·8524

It is observable that slight, though appreciable, disturbances attend the substitution of potassium by rubidium or cæsium or of sulphur by selenium.   The distortion of the assemblage thus indicated would be produced if the spheres of atomic influence of potassium, rubidium, and cæsium, or of sulphur and selenium, differ slightly in relative magnitude.   The phenomena observed in connection with isomorphism, of the nature noted above, and especially those of polymorphism, indicate that, under the same external conditions, two elements do not appropriate spheres of atomic influence which bear precisely the same ratio to the molecular magnitude. Further, many facts connected with the relative stability of analogous compounds, such, for instance, as that of the chlorine compounds of the nitrogen group of elements, NCl_3, PCl_3, $AsCl_3$, &c., lead to a similar conclusion ; at the same time, the differences are not of such a magnitude as to lead to a difference of valency or, what is the same thing, not so great as to necessitate a remarshalling when an atom of the one replaces an atom of the other element in a compound.

It would seem that for two elements to be isomorphously replaceable one by the other, their spheres of atomic influence must be much more nearly of the same magnitude than if they are merely to possess the same valency.   This is distinctly indicated by the more considerable changes produced in the equivalence parameters by the mutual replacement of hydrogen, potassium, and sodium, univalent elements which are not isomorphous ; it is illustrated by the following table :

	a : b : c.	Multiples of axial ratios taken.	x : y : z.
Picric acid (orthorhombic) :			
$C_6H_2(NO_2)_3 \cdot OH$	$0 \cdot 9370 : 1 : 0 \cdot 9740$		$3 \cdot 5587 : 3 \cdot 6994 : 3 \cdot 7981$
Potassium picrate (orthorhombic) :			
$C_6H_2(NO_2)_3 \cdot OK$	$0 \cdot 9420 : 1 : 1 \cdot 3520$	$3c/4$	$3 \cdot 5238 : 3 \cdot 7407 : 3 \cdot 7932$
Amidosulphonic acid (orthorhombic) :			
$NH_2 \cdot SO_3H$	$0 \cdot 9948 : 1 : 1 \cdot 1487$		$2 \cdot 2933 : 2 \cdot 3053 : 2 \cdot 6481$
Potassium amidosulphonate (orthorhombic) :			
$NH_2 \cdot SO_3K$	$0 \cdot 9944 : 1 : 0 \cdot 7097$	$5c/3$	$2 \cdot 2704 : 2 \cdot 2832 : 2 \cdot 7006$
Phthalic acid (monosymmetric), $\beta = 86°21'$:			
$C_6H_4(CO_2H)_2$	$0 \cdot 7080 : 1 : 1 \cdot 3452$		$2 \cdot 5801 : 3 \cdot 6442 : 4 \cdot 9022$
Potassium phthalate (orthorhombic) :			
$C_6H_4(CO_2K)(CO_2H)$ ...	$0 \cdot 6705 : 1 : 1 \cdot 3831$	$2a, c/2$	$2 \cdot 5409 : 3 \cdot 6742 : 4 \cdot 9272$
Sodium phthalate (orthorhombic) :			
$C_6H_4(CO_2Na)(CO_2H)$ ...	$0 \cdot 7262 : 1 : 1 \cdot 4197$		$2 \cdot 5756 : 3 \cdot 5468 : 5 \cdot 0353$

On replacing hydrogen by potassium or sodium, much more deformation of the assemblage occurs than when potassium replaces rubidium or cæsium; the incompatibility of pattern between the original and derived assemblages in the former case accounts for the non-formation of isomorphous mixtures between an acid and its alkali salt, or between a potassium and a sodium salt of the same metal. If this is really a true statement of the case, it would be expected that two elements of the same valency, which cannot replace each other isomorphously in simple compounds, might do so in more elaborate complexes, because the distortion produced by replacing one sphere of atomic influence by another markedly different in size would be less considerable in the larger than in the smaller complex. We thus find that whilst the equivalent elements tin, lead, and platinum do not replace each other isomorphously in their simple compounds, they do so in more complex compounds; thus the three salts, $K_2Sn(OH)_6$, $K_2Pb(OH)_6$, and $K_2Pt(OH)_6$, are isomorphous (Zambonini, *Zeit. Kryst. Min.*, 1906, **41**, 53).

The change of relative magnitude of the spheres of atomic influence as any vertical column in the periodic table is descended is frequently indicated in the axial ratios of the binary compounds. Thus the axial ratios $a : c$, of the hexagonal minerals, zincite, ZnO, greenockite, CdS, and wurtzite ZnS, are $1 : 1\cdot6219$, $1 : 1\cdot6218$, and $1 : 1\cdot6004$ respectively; this indicates that the spheres of atomic influence of zinc and cadmium, or of sulphur and oxygen, have not the same relative magnitudes, but the identity of the axial ratios of zinc oxide and cadmium sulphide suggests that the relative volumes of the spheres of atomic influence of zinc and cadmium are in the same ratio as are those of oxygen and sulphur.

We may conclude that the geometrical interpretation of the periodic law is possibly that in any vertical column of the periodic classification of the elements the magnitudes of the spheres of atomic influence change slowly and in the same direction as the column is descended; in passing from one vertical column to the next, however, the general magnitude of the spheres of atomic influence changes so considerably as to amount to a change of valency or, in other words, to necessitate remarshalling when an atom belonging to one column is replaced by an atom belonging to another.

One important practical bearing of the first geometrical property is the simple interpretation which it affords of a whole class of morphotropic relations which have hitherto resisted explanation, those, namely, in which a close crystallographic relation subsists between substances derived one from the other by replacing one group by another, dissimilar in form and kind. Thus the following anorthic minerals :

$$a \; : \; b \; : \; c.$$

Albite, $NaAlSi_3O_8$ ...... $0·6335 : 1 : 0·5577$, $\alpha=94°\ 3'$, $\beta=116°29'$, $\gamma=88°\ 9'$
Anorthite, $CaAl_2Si_2O_8$ ... $0·6347 : 1 : 0·5501$, $\alpha=93°13'$, $\beta=115°55'$, $\gamma=91°12'$

although greatly different in type of composition, are morphotropically so closely related that they form the plagioclases by isomorphous mixture.   They have, however, the same valency volume, namely, 32, and by removing from the albite assemblage the group NaSi, of valency volume 5, it can be replaced without remarshalling, and indeed with but little disturbance of the crystalline structure, by the group CaAl, of the same valency volume.   Similarly,

Olivine, Mg_2SiO_4, $a : b : c = 0·465 : 1 : 0·586$, and

Chrysoberyl, Al_2BeO_4, $a : b : c : = 0·470 : 1 : 0·680$,

have the same valency volume, exhibit a similar morphotropic similarity, and are derived, one from the other, by the same kind of substitution. A number of cases of isomorphously replaceable groups occurring amongst minerals have been discussed by Prior (*Min. Mag.*, 1903, **13**, 217), and all of these appear to be embraced by the conclusions derived above and in the following pages.

It is clear from the foregoing that neither a replaced group or radicle, nor one which replaces, in a homogeneous assemblage, necessarily consists of spheres which are all of the same magnitude. Thus, the nitro-group, NO_2, can replace the methyl group, CH_3, in the manner indicated, the valency volume of both being seven.   When, as in this case, there is a marked difference in shape between the substituting and substituted groups some considerable discrepancy between the crystal forms is to be expected, although a marked resemblance may still be observed.   The orthorhombic substances, aceto-p-toluidide, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3$, and p-nitroacetanilide,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3,$$
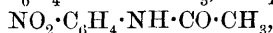
differ in constitution in that the nitro-group of the one is replaced in the other by a methyl group of the same valency volume.

	a	: b :	$c.$	Multiples of axial ratios taken.	x	: y	: $z.$
Aceto-p-toluidide	$0·6313$	: 1 :	$0·3288$		$2·073$	: $3·980$	: $6·304$
p-Nitroacetanilide ...	$1·0445$	: 1 :	$0·8889$	$2a,\ 3\frac{1}{2}c$	$2·001$	: $4·178$	: $6·223$

The close morphotropic relationships noticed by Zirngiebl (*Zeit. Kryst. Min.*, 1902, **36**, 117) between the following pairs of compounds are all similar instances of the application of the first geometrical property of close-packed homogeneous assemblages :

(1) Ammonium iodate, and ammonium fluoriodate,

$$NH_4IO_3 \text{ and } NH_4IF_2O_2.$$
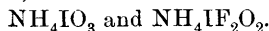
(2) The stable and labile o-sulphobenzoic chlorides,

$$C_6H_4 {<} {CO \cdot Cl \atop SO_2 \cdot Cl} \text{ and } C_6H_4 {<} {SO_2^- \atop CCl_2} {>} O.$$
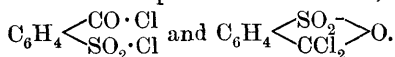
(3) Phthalic acid, and o-sulphobenzoic acid,

$$C_6H_4(CO_2H)_2 \text{ and } C_6H_4(CO_2H)(SO_3H).$$

(4) Benzoic acid, and benzenesulphonic acid,

$$C_6H_5 \cdot CO_2H \text{ and } C_6H_5 \cdot SO_3H.$$

(5) Sulphoacetic acid, $CH_2(CO_2H)(SO_3H)$, and methionic acid, $CH_2(SO_3H)_2$.

The latter cases are particularly interesting as showing that a carbon atom of valency volume four, is replaceable by a sulphur and an oxygen atom, each of valency volume two, in such a way that the marshalling of the assemblage remains unchanged, and even that corresponding features of the crystalline structures are distinctly recognisable. It is thus indicated that the sulphur in a sulphonic acid is fundamentally bivalent. As will be shown later, the necessity never arises for attributing to sulphur a fundamental valency other than two.

The process of replacing an oxygen and a sulphur sphere, each of volume two, by one carbon sphere of volume four, as involved in certain of the above cases, must be expected to lead to so considerable a change in the shape of the cavity within which the operation is performed as will greatly obscure the morphotropic relations between the two geometrical assemblages ; it is thus found that, although the morphotropic relations are distinctly observable, considerable disturbance of the axial ratios and equivalence parameters attends the passage from one to the other of the related compounds.

A word may be said as to the resulting effect when, instead of refilling the gaps produced in a homogeneous assemblage in the manner described, these gaps are closed up by the residual assemblage shrinking together so as to pass to a condition of equilibrium. In order that a homogeneous assemblage of spheres of two or more kinds may exhibit maximum closeness of packing, each component sphere must occur surrounded by a shell of other spheres the density of arrangement throughout which must be a maximum. And if several similarly placed equal spheres are removed from the assemblage and the remaining structure closes up and passes to an equilibrium condition of maximum closeness of packing, it will commonly be found that the component spheres will no longer all be surrounded by shells of spheres equally densely disposed to those composing the original assemblage ; and even if the main bulk of the derived assemblage is as densely packed as at first, the assemblage will at isolated points present packing of less density.

The cases quoted above have been selected as illustrations because the simplicity of the crystallographic relationships enables them to be followed quickly, but in most instances the crystallographic relationship is not immediately obvious, being masked by a change of crystalline

symmetry or by an unfavourable choice of axial directions.   Notwith-
standing this, the relationship is always present, although its detection
may involve the kind of investigation used in the foregoing study of
benzene, the dihydroxybenzenes, &c.   That so considerable a crystallo-
graphic difference as that between the rhomhohedral and monosym-
metric forms of quinol involves no difference in marshalling of the
components of the molecule has been already shown, and complication
of this nature has in most cases to be dealt with.

Another kind of application of the first geometrical property has
been illustrated in the derivation of the assemblage appropriate to
triphenylamine from that of benzene (p. 1720), by the symmetrical
replacement of groups of three hydrogen spheres each by one nitrogen
sphere.   We shall show, in a later paper, that the method here used is
also of perfectly general application, so that, for instance, the assemb-
lage for tetramethylmethane may be derived from that of methane by
the symmetrical replacement of groups of four hydrogen spheres, each
by one carbon sphere.

The Relations between Equivalent Radicles of Different Valency Volumes.

The second of the geometrical properties referred to, and which is
of importance as indicating the valency relations existing between
radicles of the same valency but different valency volumes, may be
best realised by the consideration of the following process.

Select a unit—not necessarily a minimum one, but one which
includes a considerable number of spheres—in a close-packed homo-
geneous assemblage of spheres of various magnitudes which is in
stable equilibrium under the postulated conditions of external pres-
sure, &c.   Partition this assemblage into such units by mere geo-
metrical surfaces, and derive from it an analogous assemblage in the
following manner.   Withdraw a number of equal and similarly
situated spheres, one from each space unit or cell of the partitioning,
and, ignoring the partitioning, which has now served its purpose,
enlarge similarly the cavities thus left vacant so that they can just
contain equal spheres of considerably larger size than those removed ;
the enlargement necessitated by the introduction of those larger
spheres is to be so conducted as to conserve the original marshalling.

The second geometrical property is that, under the above conditions,
in order that the modified assemblage, like that from which it was
derived, shall be close-packed and homogeneous, some definite number
of additional spheres of a particular size must be inserted with the
large spheres in each cavity produced in the space unit ; the number
of the accompanying spheres to be thus introduced is dependent on

5 x 2

their size and on those of the substituting and substituted spheres.
The nature of this interdependence of sphere magnitude is experiment-
ally found to be a simple one.   If a sphere of volume m (an atom of
valency m) is replaced by one of volume $m + n$ (valency $m + n$), one or
more additional spheres (atoms) having the total volume n (valency n)
must be simultaneously inserted in order that close-packing may be
re-established without remarshalling ; the bearing of this result on
chemical substitution is indicated by the interpolated words.   Thus, on
replacing a hydrogen atom in the benzene molecule by chlorine, since
the substituted and substituting atoms have the same valency and are
therefore represented by spheres of about the same relative size, the
cavity in the close-packed assemblage vacated by the hydrogen sphere
can be so nearly filled by the chlorine sphere, that small deformations
or adjustments unaccompanied by remarshalling suffice to restore the
close-packing temporarily disturbed by the substitution ; the order of
the change in the crystallographic dimensions produced by these
deformations is indicated by the table of equivalence parameters
of benzene and its per-halogen derivatives given on p. 1699.   If, how-
ever, one hydrogen atom in the benzene molecule is replaced by a
carbon atom, the higher valency of the latter necessitates the intro-
duction with it of other atoms, the sum of the valencies of which is
three, the difference between the valency of carbon and of hydrogen,
if close-packing is to be re-established without remarshalling ; thus
three hydrogen atoms, giving toluene—one nitrogen atom, giving benzo-
nitrile—or one hydrogen and one oxygen atom, giving benzaldehyde—
or some other set of atoms of which the valency volume is three, must
be inserted together with the carbon atom, for without this close-
packing cannot be secured without remarshalling.

The existence of the second geometrical property may be sufficiently
explained for our present purpose in the following manner.   Any
sphere in a close-packed assemblage is in immediate contact with a
number of others, which form, as it were, a shell or envelope about
it ; if the sphere in question is replaced by one considerably larger, a
gap or gaps are formed in the enveloping shell of spheres, which can-
not be closed as a result of deformation or adjustment unaccompanied
by remarshalling.   If a sphere of volume m is replaced by one of
volume $m + n$, however, the resulting gap in the enveloping shell
can be so filled by a sphere or spheres of the total volume n that the
resultant assemblage can regain its original close-packing by the mere
operation of slight deformations and adjustments unaccompanied by
remarshalling.   The great flexibility of structure displayed by close-
packed assemblages of spheres naturally assists materially in bringing
about this result.

Much of the work detailed in the previous pages, in which it is

shown that the properties of close-packed equilibrium assemblages of spheres are in complete harmony with the crystallographic and constitutive properties of chemically related substances, is so much cumulative evidence of the existence of the geometrical property now under discussion. For, whenever a chemical compound is derived by substitution from some parent substance, the relation between the two compounds is expressible in terms of the valencies of the substituted and substituting groups ; and the replacement of an atom by another of higher valency is necessarily accompanied by the introduction of additional atoms in obedience to the valency law.

The mode of operation of the second geometrical property will be seen by a comparison of the methods by which the assemblages for triphenyl-amine and triphenylmethane were derived (pp. 1711, 1720) from that of benzene. In the former case, by application of the first geometrical property, a group of the three hydrogen spheres of volume three was replaced by a nitrogen sphere of volume three, so that close-packing was retained without remarshalling. But, on forcing a carbon sphere of volume four into the cavity vacated by the group of three hydrogen spheres, the resulting enlargement of the cavity led to the production of a gap in the enveloping shell of spheres, and this proved just large enough to accommodate an additional hydrogen sphere ; the latter had, therefore, to be inserted in order that close-packing might be restored without remarshalling. A little considera-tion will show that the derivation of the dihydroxybenzenes from benzene, and of triphenylcarbinol from triphenylmethane, also involve the application of the second geometrical property.

The cases cited above will suffice for our present purpose, without more formal proof of the accuracy of the way in which the property has been stated. We may now proceed to show that the second geometrical property at once elucidates a number of hitherto very obscure crystallographic relationships, and thereby amass further circumstantial evidence in support of the geometrical interpretation of valency.

The crystalline forms assumed by sodium nitrate and calcium carbonate as calcite are highly distinctive, and are so closely similar as to make it impossible to doubt that the crystal structures and the marshalling are identical ; although no explanation has been hitherto available of this identity of crystal structure existing between two substances of such dissimilar type, it now appears that the similarity is a result of the second geometrical property of close-packed homogeneous assemblages. For, if in the rhombohedral structure of crystalline sodium nitrate, $NaNO_3$, the univalent sodium atom sphere of volume one is replaced by the bivalent calcium atom sphere of volume two, a gap will be produced in the shell of spheres

enveloping the metallic atom sphere in the assemblage ; this can only be filled by the insertion of one additional valency or volume unit if close-packing is to be restored without remarshalling. The additional valency unit is provided by replacing the nitrogen sphere of volume three by a carbon sphere of volume four, and the assemblage, after this double modification, can regain close-packing without undergoing remarshalling. The derived calcium carbonate assemblage retains so closely the marshalling of the original sodium nitrate assemblage that the two exhibit almost identical crystalline forms ; the similarity extends even to the unique mode of gliding-twinning, to the cleavage, and to the abnormally high double refraction.

An exactly similar relationship to the above exists between the orthorhombic forms of calcium carbonate and potassium nitrate ; the equivalence parameters of all four substances are given in the following table.

	$W.$		$x : y : z.$
$NaNO_3$, rhombohedral......	10	$\alpha = 102°47'$	$2\cdot2092 : 2\cdot2092 : 2\cdot2092$
$CaCO_3$, ,, ...	12	$\alpha = 101°55'$	$2\cdot3398 : 2\cdot3398 : 2\cdot3398$

		$a : b : c.$	
KNO_3, orthorhombic	10	$0\cdot5910 : 1 : 0\cdot7011$	$1\cdot7079 : 2\cdot8898 : 2\cdot0260$
$CaCO_3$, ,, ...	12	$0\cdot6224 : 1 : 0\cdot7206$	$1\cdot8615 : 2\cdot9909 : 2\cdot1553$

It is important to notice that in these cases, in passing from the substance of valency volume ten to that of twelve, the structure or assemblage is expanded in all three axial directions ; it is not possible to say that the molecular increase affects one axial direction to an appreciably different extent from the others ; this should be attributed to the fact that the shapes of the contents of corresponding cells are similar in the cases compared.

Another interesting case arises in connexion with the crystallographic similarity between the monosymmetric alkali salts of methanedisulphonic acid, $CH_2(SO_3H)_2$, and iminosulphonic acid, $NH(SO_3H)_2$, which has been pointed out by Zirngiebl (*Zeit. Kryst. Min.*, 1902, **36**, 117). On replacing the tervalent nitrogen atom in iminosulphonic acid by a quadrivalent carbon atom, an additional hydrogen atom has to be simultaneously inserted into the assemblage in order that close-packing without remarshalling may occur. The following data suffice to show that this case is of the same character as that of calcite and sodium nitrate.

	$W.$	$\beta.$	$a : b : c.$	$x : y : z$
$CH_2(SO_3K)_2$	24	$89°49'$	$1\cdot6160 : 1 : 0\cdot9362$ (take $2b$)	$4\cdot0604 : 2\cdot5126 : 2\cdot3523$
$NH(SO_3K)_2$	22	$88°41'$	$1\cdot6636 : 1 : 0\cdot9604$	$3\cdot9877 : 2\cdot3970 : 2\cdot3021$

A somewhat similar relationship holds between the monosymmetric p-nitrobenzenesulphonic chloride and amide (Benedicks, *Zeit. Kryst. Min.*, 1903, **37**, 285) ; the replacement of the chlorine sphere of volume

one by a nitrogen sphere of volume three involves the insertion into the assemblage of two additional hydrogen spheres, forming the sulphon-amide, for the purpose of restoring the close-packing without re-marshalling.

	β.	$a : b : c.$	$x : y : z.$
$NO_2 \cdot C_6H_4 \cdot SO_2Cl$	$105°39'$	$1\cdot3042 : 1 : 1\cdot1369$	$3\cdot1955 : 4\cdot9002 : 2\cdot7855$
$NO_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$ ...	$100°12'$	$0\cdot6501 : 1 : 0\cdot5184$	$3\cdot3650 : 5\cdot1762 : 2\cdot6833$

The case for which data are given in the following table is of importance because all the substances are orthorhombic and the series is four members in length.

	$W.$	$a : b : c.$	$x : y : z.$
C_6H_6	30	$0\cdot8910 : 1 : 0\cdot7990$	$3\cdot1010 : 3\cdot4800 : 2\cdot7800$
$C_6H_5 \cdot NH_2, HBr$	36	$0\cdot7230 : 1 : 0\cdot8180$	$3\cdot2178 : 3\cdot9337 : 2\cdot8441$
$C_6H_5 \cdot NH_2, NBr, CdBr_2$	40	$0\cdot7943 : 1 : 0\cdot3044$	$3\cdot2268 : 4\cdot4168 : 2\cdot8067$
		(take $5/4b, 3c$)	
$C_6H_5 \cdot NH_2, HNO_3$	44	$0\cdot6265 : 1 : 0\cdot5727$	$3\cdot1126 : 4\cdot9682 : 2\cdot8453$

It will be seen that the successive replacement of hydrogen in benzene by NH_2 and the insertion of HBr, and $CdBr_2$ or HNO_3, all take place in accordance with the second geometrical property of close-packed assemblages, and that the main effect of the insertion of the various groups falls upon the direction y in the benzene assemblage. The directions x and z in the benzene assemblage are but little changed by the substitutions. The lengthening of one of the three axes which accompanies the substitution of the ammonium bromide residue for hydrogen in benzene is not often observed in cases in which the ammonium radicle replaces an atom of a univalent metal such as potassium ; it commonly happens that the axial ratios are practically unchanged by such a substitution as the latter, just as is the case when the group CaC replaces NaN in the rhombohedral sodium nitrate. We purpose dealing later in detail with the relation between salts of ammonium and the alkali metals, and for the present merely call attention to the case of the orthorhombic potassium and ammonium vanadylthiocyanates (Steinmetz, *Zeit. anorg. Chem.*, 1904, **41**, 686), in which the replacement of potassium by ammonium affects two of the equivalence parameters (x and z), leaving the third (y) practically unaltered.

	$W.$	$a : b : c.$	$x : y : z.$
$K_2(VdO)(CNS)_4, 5H_2O$	63	$0\cdot9163 : 1 : 0\cdot5469$	$4\cdot5902 : 5\cdot0095 : 2\cdot7397$
$(NH_4)_2(VdO)(CNS)_4, 5H_2O..$	75	$0\cdot9910 : 1 : 0\cdot6070$	$4\cdot9508 : 4\cdot9957 : 3\cdot0324$

It is interesting to notice in connexion with the question of ter- and quinquevalent nitrogen compounds that, whilst the occurrence of benzo-nitrile, $C_6H_5 \cdot C\vdots N$, is accounted for on p. 1730, the isomeric phenyl-carbylamine, $C_6H_5 \cdot N\vdots C$, may be derived, by the application of the first geometrical property, from aniline hydrobromide by replacing

the four univalent atoms associated with the nitrogen atom by a carbon atom.

An instance illustrative of the effect of salt formation is found in the comparison of camphoroxime and its hydrobromide: both these substances are monosymmetric, camphoroxime giving

$$a : b : c = 1 \cdot 0252 : 1 : 0 \cdot 6073, \ \beta = 80°18'$$

(*Zeit. Kryst. Min.*, 1889, **15**, 402), and its hydrobromide,

$$a : b : c = 1 \cdot 4699 : 1 : 1 \cdot 0796, \ \beta = 80°41'$$

(Trans., 1897, **71**, 1048). On transposing the indices of the forms present on the oxime by changing (100) to (101), (101) to (001), (101) to (100), and (110) to (111), and similarly changing in the crystals of the hydrobromide, (001) to (101), (101) to (100), ($\bar{3}$02) to (001) and (011) to (111), the axial values become comparable and the following results are obtained :

	a : b : c.		x : y : z.
$C_{10}H_{16}{:}N{\cdot}OH$	$1{\cdot}2766 : 1 : 1{\cdot}8571$	$\beta = 85°18'$	$3{\cdot}7935 : 2{\cdot}9716 : 5{\cdot}5155$
$C_{10}H_{16}{:}N{\cdot}OH, HBr$..	$1{\cdot}3356 : 1 : 1{\cdot}9599$	$\beta = 85°56'$	$3{\cdot}8797 : 2{\cdot}9048 : 5{\cdot}6932$

The close approximation of the equivalence parameters indicates that not only is the marshalling of the assemblage unchanged by the passage from the oxime to its hydrobromide, but that the dimensions of the assemblage are but slightly altered. The addition of the elements of hydrogen bromide scarcely alters the values x and y, but appreciably increases the value of z.

Orthosulphobenzoic acid, $o\text{-}C_6H_4(SO_3H)(CO_2H)$, yields a stable and a labile acid chloride, to which the constitutions, $o\text{-}C_6H_4(SO_2Cl){\cdot}COCl$ and $o\text{-}C_6H_4{<}^{SO_2}_{CCl_2}{>}O$, must be attributed ; its imide is saccharin, $o\text{-}C_6H_4{<}^{SO_2}_{CO}{>}NH$, to which the axial ratios, $a : b : c = 2{\cdot}7867 : 1 : 1{\cdot}7187$, $\beta = 76°8'30''$, have been assigned (Trans., 1895, **67**, 986). These axial ratios may be transposed by a simple change of indices to $a : b : c = 1{\cdot}3565 : 1 : 0{\cdot}4298, \beta = 85°57'$. All these substances are related through the second geometrical property in the manner shown in the following table :

	a : b : c.	β.	Multiples of axial ratios taken.	x : y : z.
Acid	$0{\cdot}6678 : 1 : 1{\cdot}2074$	$90°$	$4a, 2b$	$2{\cdot}5708 : 3{\cdot}8496 : 4{\cdot}6481$
Labile chloride......	$1{\cdot}8103 : 1 : 2{\cdot}0997$	$90°$	$2a, 3b$	$2{\cdot}5727 : 3{\cdot}6773 : 4{\cdot}4377$
Stable ,, ...	$1{\cdot}8555 : 1 : 2{\cdot}0067$	$89°27'$	$2a, 3b$	$2{\cdot}4770 : 3{\cdot}7025 : 4{\cdot}5800$
Saccharin	$1{\cdot}3565 : 1 : 0{\cdot}4298$	$85°57'$	$2b, 3c$	$2{\cdot}5183 : 3{\cdot}6857 : 4{\cdot}7521$

The equivalence parameters are related in the same kind of way as those of the similarly related substances dealt with above ; but, apart from this, the values for the acid and the labile chloride on the one hand, and for the stable chloride and saccharin on the other, seem

particularly closely related. This would appear to indicate that the labile chloride is the true acid chloride, whilst the stable chloride is the dichloroanhydride of the acid.
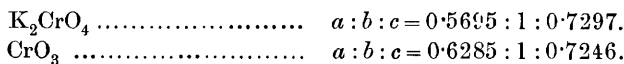
The effect on the equivalence parameters of introducing homologous radicles into the molecule is well illustrated by Tutton's measurements (Trans., 1890, **57**, 714) of the 1-alkyl-3-diphenyl-5-phenylpyrrholones, having the constitution $\dfrac{\mathrm{CH{:}CPh}}{\mathrm{CPh_2 \cdot CO}}{>}\mathrm{NX}$, in which X represents either methyl, ethyl, or propyl. The methyl and ethyl derivatives are anorthic and isomorphous, and the ethyl derivative crystallises also in monosymmetric forms isomorphous with the propyl compound ; the data for these substances are included in the following table :

X.	W.	Crystal system.	$a\ :\ b\ :\ c.$	$x\ :\ y\ :\ z.$
Methyl	116	A	$0{\cdot}9059 : 1 : 0{\cdot}8695$	$4{\cdot}9092 : 5{\cdot}4192 : 4{\cdot}7120$
			$a = 79°52',\ \beta = 86°3',\ \gamma = 70°26'$	
Ethyl	122	A	$0{\cdot}9120 : 1 : 0{\cdot}9524$	$4{\cdot}8928 : 5{\cdot}3649 : 5{\cdot}1095$
			$a = 78°48',\ \beta = 89°10',\ \gamma = 68°2'$	
Ethyl	122	M	$1{\cdot}6898 : 1 : 1{\cdot}9579$	$5{\cdot}6273 : 3{\cdot}3302 : 6{\cdot}5200$
			$\beta = 86°54'$	
Propyl	128	M	$1{\cdot}8060 : 1 : 1{\cdot}8821$	$6{\cdot}0577 : 3{\cdot}3542 : 6{\cdot}3129$
			$\beta = 86°17'$	

It is seen that in the passage from the methyl to the anorthic ethyl derivative, the x value remains nearly unchanged, the y value diminishes slightly, and the z value increases so as to carry the whole effect of the increased valency volume ; similarly, in the passage from the monosymmetric ethyl- to the propyl-derivative, the y value remains almost constant, the z value diminishes slightly, whilst the x value increases so as to bear the effect of the increase of W and the diminution of the z value. No attempt has been made here to bring the anorthic and monosymmetric substances into harmony ; but it is clear, from the above changes of the equivalence parameters, that the directions a, b, and c in the anorthic substances are roughly identical with the directions b, c, and a respectively in the monosymmetric compounds and that it would not be difficult to calculate from the data given what directions are absolutely equivalent in the two types of symmetrical assemblage.

As the second geometrical property of close-packed assemblages is obviously a reversible one, further extensions of the method of substitution which it involves can be made. Thus, if one-fourth of the oxygen spheres are homogeneously removed throughout the assemblage of potassium chromate, two additional valency or volume units must also be removed in order that close-packing without remarshalling may be possible ; when this is done, the residual skeleton, CrO_3, is obtained. The observed axial ratios for potassium

chromate and chromium trioxide are found to be nearly the same, namely :—

$$K_2CrO_4 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad a : b : c = 0{\cdot}5695 : 1 : 0{\cdot}7297.$$
$$CrO_3 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad a : b : c = 0{\cdot}6285 : 1 : 0{\cdot}7246.$$

The simplicity of the chemical and crystallographical substitution relations exemplified by the cases dealt with above justifies the hope that before long the relative nature of the assemblages affected by all inorganic compounds will be traceable as a complete scheme exhibiting the relations holding between them.

Multivalency.

The well-known law that the several valencies of multivalent elements in general differ by two or multiplies of two has hitherto successfully evaded all attempts to attach to it a physical signification ; the recurrence of two and its multiples in this connexion has, however, received a geometrical interpretation in the last few pages. It has been shown that the insertion of an atom of valency $m + 1$ into the space vacated in the assemblage by atoms of the total valency m necessitates the simultaneous introduction of an additional atom of valency 1 into the enveloping shell of atoms if the close-packing is to be restored without remarshalling.   This process is equivalent to inserting an atom of valency 1 into the space already occupied by an atom of valency m, when the gap produced in the shell enveloping the two atoms must be filled by the insertion of an additional atom of valency volume 1.   The atom of valency m will under these conditions function as having the valency $m + 2$, although its sphere of influence retains the volume appropriate to an atom of valency m.   Similarly, if two atoms of valency 1 are forced into the cavity along with the original atom of valency m, one or more atoms of the total valency volume 2 must be inserted into the enveloping shell for the preservation of close-packing without remarshalling, and in this case the original atom of valency m functions as one of valency $m + 4$.   Thus, the relation between the compounds CsI, CsI_3, CsI_5 or CsI_7, and CsI_9 (Abegg and Hamburger, *Zeit. anorg. Chem.*, 1906, **50**, 403) seems clearly indicated ; the sphere of atomic influence or the fundamental valency of cæsium and of iodine is 1 in each of these compounds. Ammonium chloride, NH_4Cl, also must be regarded as derived by inserting into the ammonia assemblage a monovalent atom of volume 1, when a gap is produced in the shell of spheres originally surrounding the nitrogen sphere which can be filled up so as to restore close-packing without remarshalling by the insertion of another sphere of volume 1 ; in the ammonium salts the nitrogen atom thus has the fundamental

valency 3.   Examples bearing upon this are quoted in connexion with the aniline salts (p. 1733) and the vanadylthiocyanates (p. 1733).

The limitation of the valencies to m, $m + 2$, $m + 4$, &c., must be expected only when the fundamental valency m, stated as a whole number, expresses closely the volume of the sphere of atomic influence of the element. But it has been already pointed out (p. 1726) as probable that the spheres of atomic influence of elements in the same vertical column of the periodic table change in volume slightly as the column is descended : although the valency, stated as a whole number, remains the same. Discrepancies should therefore arise of the nature illustrated by the following example. Sulphur yields with chlorine the compounds S_2Cl_2, SCl_2 and SCl_4, and, in general, as this element exhibits only bi-, quadri- or sexa-valency, it may be concluded that its sphere of atomic influence has very closely the volume 2, compared with that of chlorine as 1, or oxygen as 2. Molybdenum, in the same vertical column, should have a sphere of atomic influence somewhat different from this, and we accordingly find that molybdenum forms the compounds $MoCl_2$, $MoCl_3$, $MoCl_4$ and $MoCl_5$. There seems here a clear indication that, the sphere of atomic influence of chlorine having the volume 1, that of molybdenum is between 2 and 3, for then close-packing might be attained in an assemblage containing twice or thrice as many atoms of chlorine as of molybdenum, and the insertion of two more halogen atoms into each unit of the partitioning in these assemblages in accordance with the second geometrical property would in this event again lead to the production of close-packed assemblages. The fact that the compounds SF_5 and MoF_6 can be formed probably indicates that the sphere of atomic influence of fluorine is slightly smaller than that of chlorine.

In this connexion one necessary consequence of assigning somewhat different volumes to the spheres of atomic influence of two elements of the same valency may be noted. The simple compounds of such elements might differ in type and crystalline form to such an extent that chemical analogies would be difficult to follow ; in the more complex compounds, however, built up by the operation of the second geometrical property, the differences in volume of the spheres of influence would exercise less effect than in the simple compounds. It is to be expected, therefore, that very dissimilar elements of the same valency would behave dissimilarly in their simple compounds, but would conform more to the same type in their compounds of considerable molecular complexity. This is illustrated by the fact that the equivalent metals lead and platinum exhibit ordinarily but little analogy, whilst their complex compounds, $K_2Pb(OH)_6$ and $K_2Pt(OH)_6$, are actually isomorphous.

So far as the present inquiry has extended, it has not been found

necessary to attribute to the same element under different conditions of combination spheres of atomic influence of different volumes ; that is to say, elements such as sulphur and nitrogen always exhibit the fundamental valencies 2 and 3 respectively, and the higher valencies are merely expressive of the operation of the second geometrical property of close-packed homogeneous assemblages. It remains to be ascertained whether in every case the facts accord with the attributing of one particular fundamental valency to each known element. It is, however, very important that the necessity does not arise for attributing to nitrogen a higher fundamental valency than 3, and that in many per- and proto-metallic salts all known facts accord with the assumption of one, and only one, fundamental valency to the metal.

Thus it will probably be agreed that the formation of the compound KI_3 is not due to potassium becoming tervalent, but to the production of a molecular compound between potassium iodide and iodine. But thallous iodide, TlI, which is isomorphous with potassium iodide, can be converted into thallic iodide, TlI_3, which is isomorphous with the compounds RbI_3 and CsI_3 (Wells and Penfield, *Amer. J. Sci.*, 1894, **47**, 463 ; Abegg and Maitland, *Zeit. anorg. Chem.*, 1906, **49**, 340), thus :—

$$RbI_3 \quad .... \quad a:b:c = 0\cdot6858 : 1 : 1\cdot1234$$
$$CsI_3 \quad ...... \; .... \quad a:b:c = 0\cdot6824 : 1 : 1\cdot1051$$
$$TlI_3 \quad .... \quad a:b:c = 0\;6828 : 1 : 1\cdot1217$$

So that thallic iodide, in which the metal is tervalent, is isomorphous with substances of corresponding molecular composition in which the metal is apparently univalent ; the parallel between thallic iodide and the periodides of the alkali metals affords strong presumptive evidence in favour of the explanation of multivalency advanced in the present paper.

There are, as is well known, limitations to the extent to which different elements exhibit multivalency ; thus, carbon seems always to be quadrivalent, but sulphur and nitrogen show changeable valency. This difference is traceable to the nature of the partitioning occurring in close-packed assemblages ; it is convenient to deal with this particular aspect of the partitioning as a third geometrical property of close-packed homogeneous assemblages. This third property is that, on the introduction, in accordance with the second geometrical property, of additional spheres beyond the numerical proportions required by the fundamental valencies of spheres already present, the resulting close-packed assemblage may be, in general, partitioned in two distinct ways ; the one way partitions the assemblage into units representing two different compounds, in each of which the

fundamental valencies alone are involved; the other partitions the assemblage into identical units, and in this case some particular atom of valency m functions as of valency $m + 2$ or $m + 4$ in accordance with the second geometrical property. It is frequently found practically that only one of the two kinds of partitioning is operative under a given set of conditions, although, in certain cases, both occur simultaneously ; thus, the quaternary ammonium salts or ammonium salts exist in solution partly as such, partly as the tertiary amine or ammonia and alkylammonium or hydrogen salt.

The precise nature of the principle which determines whether partitioning of the second kind, into identical units, or of the first kind, into two kinds of units, will occur in any given case cannot yet be determined ; it appears to be somewhat akin to the principle which determines polymorphism and largely dependent on temperature conditions, as in the case of ammonium chloride, which at ordinary temperatures is partitionable into units, NH_4Cl, of the one kind, but which at high temperatures is partitionable only into two kinds of units, NH_3 and HCl. The same kind of behaviour is exhibited by some carbon compounds, for triphenylmethyl bromide, under certain conditions, gives a stable periodide, $(C_6H_5)_3CBr,I_4$ (*J. Amer. Chem. Soc.*, 1898, **20**, 790), analogous to the periodides of ammonium and alkali iodides. The whole question of the magnitude and form of the units produced when a given homogeneous assemblage breaks up, or in other words, the question as to which links break most easily and which survive, is an extremely obscure one. It would seem that as disruption proceeds, small spheres are at a disadvantage as compared with larger ones ; perhaps they are moved more violently, and thus their contacts, which are necessarily fewer than those of the larger spheres, are more easily broken. The third geometrical property of close-packed homogeneous assemblages is intimately connected with the whole question of chemical action ; and with this we propose to deal later.

The Crystalline and Amorphous States.

The present work indicates that the chemical molecules assume such shapes when arranged in a crystal structure as can be close-packed in homogeneous assemblage ; and configurations are assigned to chemical molecules, built up from the spheres of influence of the component atoms which are in entire accordance with our chemical knowledge of the substances considered. A slight difference necessarily exists, however, between the conditions of the molecule in the crystalline state and in an amorphous or unconstrained condition.

Within the crystal the molecule is subject to the action of symmetrically disposed restraining forces identical in kind with those which

endow it with its characteristic shape ; the molecule under this action
will therefore necessarily experience a definite though slight deforma-
tion whilst entering as a unit into a crystalline assemblage.   But
when the constraining forces are removed by the disintegration of the
crystalline structure, it is to be expected that the molecule will assume
a rather more symmetrical shape than before.   The differences in con-
figuration which may thus arise have been illustrated in the case of
benzene ; the free and unconstrained molecule will have the structure
shown in Fig. 1, and this, in the crystalline structure, assumes the
slightly distorted form which is shown packed in the assemblage in
Fig. 3.

Apart from such comparatively slight differences as these, the
arrangement of the atomic spheres of influence within the molecule
must be regarded as nearly identical in both the amorphous and
crystalline states, although in the former case the relative situations of
the molecules necessarily display more or less heterogeneity ; the
possible changes in configuration of the molecule are controlled by the
condition that, for the substance to preserve its chemical individuality,
the marshalling of the parts of the molecule must be the same in all
states.

Even in liquids, however, many indications are given that the
molecules, from time to time, and from place to place, transitorily
assume a homogeneous arrangement throughout tracts which, on a
scale of molecular dimensions, are of considerable extent.   The
doubly-refracting liquids, or so-called liquid crystals, which now form
a large class of substances, can only have their origin in wholesale
homogeneity of arrangement throughout spaces of molecularly great
volumes.   Much of the uniformity and symmetry characterising the
chemical behaviour of fluid substances can be explained by assuming
the existence of this fragmentary homogeneity of arrangement, liable
though it must be to continual destruction and reconstitution.   The
well-known influence of surfaces and of catalytic agents upon chemical
action can be easily formulated as due to an arranging effect produced
by the surface or catalyst leading to the transitory formation of a
complex assemblage which immediately undergoes partitioning into
two distinct assemblages in accordance with the third geometrical
property of close-packed assemblages.

It must be concluded that, in crystals, the arranging process without
which crystallisation cannot occur precedes the act of solidification,
a film being present at the surface of the growing crystal which,
although not yet solidified, is, owing to the presence of the symmetri-
cally-constituted surface, homogeneously arranged like the substance
of the solid crystal.   This film will, in general, be of microscopic thin-

ness, although thick when regarded molecularly. The process of crystallisation involves not only the complete homogeneous arrangement of the molecules, but incidentally also their deformation, and this deformation will naturally differ in extent in different substances ; the varying amount of deformation which has to be effected in the molecules of different substances during crystallisation may well be a responsible factor in determining the very different speeds of crystallisation observed amongst chemical substances.

The Crystalline Forms of the Elements.

During the present investigation no occasion has arisen for discriminating between the forces which hold the parts of the molecule together and those as a result of which the separate molecules are held together. That such a necessity actually exists is indicated by the fact that those elements, such as sulphur, which are most liable to allotropy occur in several crystalline modifications of low symmetry, whilst most of the others are obtainable only in crystalline modifications of high symmetry. In the cases of crystalline elements, which are at present regarded as composed of identical atoms, it is conceivable that the nature of the packing may be modified by the existence of grouping of the identical spheres of influence of the atoms so as to form molecular aggregates.

Thus, there are two distinct ways in which the closest-packed cubic assemblage of equal spheres can be partitioned into tetrahedral groups of four spheres. In the one partitioned assemblage all the groups are found similarly orientated, whilst in the other one half of the groups display an orientation opposite to that of the remaining half. If a nucleus is formed of the latter arrangement, which has the higher symmetry of partitioning, and this nucleus is caused to grow in accordance with the former or less symmetrically partitioned arrangement, twinning of the mass is brought about which precisely simulates the twinning of diamond (compare Sollas, *Proc. Roy. Soc.*, 1901, **67**, 493 and Barlow, *Sci. Proc. Dub. Roy. Soc.*, 1897, **8**, 542).

The crystallographic properties of diamond are thus capable of explanation on the assumption that the molecule consists of four atoms tetrahedrally arranged.

Groups of eighteen equal spheres representing carbon atoms can, however, also be built up by the stacking together in trigonal symmetry of three groups of six, each arranged as in benzene ; the arrangement is that of the nine spheres, *a*, in one plane of Fig. 24 associated with the nine spheres marked in dotted circles in the figure, and in which the three benzenoid carbon complexes are grouped about

the blackened triangular segment. The graphic formula of such a complex is that of the triple naphthalene ring, and the complexes may be close-packed as indicated in the figure, in which the letters, *a*, *b*, *c*, *d*, *e*, *f*, and *g* refer to the carbon spheres composing one layer of different groups. The assemblage has rhombohedral symmetry, and is thus compatible with the rhombohedral or pseudo-rhombohedral crystalline symmetry of graphite, and an assemblage partitioned into these 18-membered groups might on oxidation be expected to yield mellitic and oxalic acids just as does charcoal and also, with previous formation of graphitic acid, graphite. This suggestion does not, however, without some additional hypothesis, throw any light on the low density of graphite as compared with diamond.
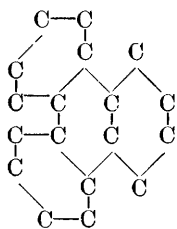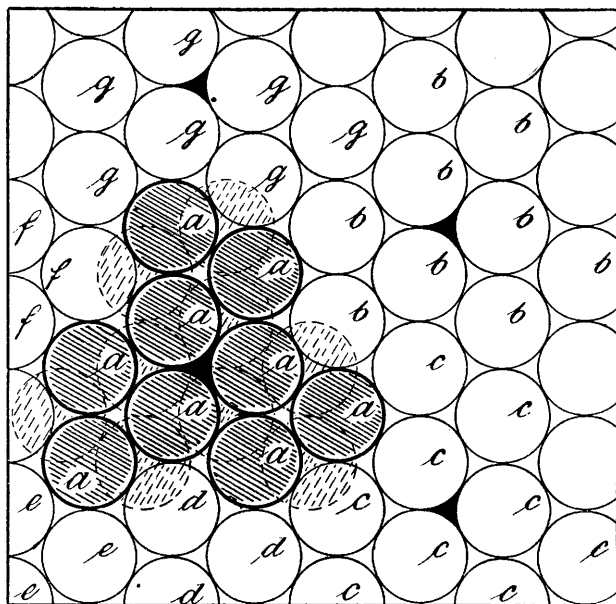
Fig. 24.

Other ways of partitioning a cubic closest-packed assemblage of equal spheres may perhaps also find parallels among the elements ; for example, that into groups of eight spheres arranged rhombohedrally. Thus the molecule of sulphur apparently contains 8 atoms (Beckmann, *Zeit. anorg. Chem.*, 1906, **51**, 96), and certain of the crystalline modifications of this element exhibit axial ratios which indicate that

they probably originate from some distortion of a cubic arrangement. The monosymmetric fourth modification of sulphur, with $a:b:c = 0.99575 : 1 : 0.99983$, $\beta = 84°14'$ (Muthmann, *Zeit. Kryst. Min.*, 1890, **17**, 345), approximates very closely to cubic symmetry.

Conclusion.

Before concluding this paper, it is desirable, for the sake of clearness, briefly to indicate further results which have been obtained, and which we hope shortly to publish in detail.

In one of the homogeneous assemblages of spheres, each representing a carbon atom, one-half of the spheres can be homogeneously replaced, each by four hydrogen spheres; the substituted assemblage is then partitionable into units or cells of the composition CH_4, and having the tetrahedral marshalling attributed to methane by van't Hoff and Le Bel. If in this methane assemblage one hydrogen sphere is removed symmetrically from each cell or unit of the partitioning, and close-packing restored by shrinking the assemblage together, the subsequent partitioning resolves the assemblage into units of the composition C_2H_6, each having the marshalling attributed to ethane by van't Hoff and Le Bel. By the further removal of hydrogen spheres and the re-establishment of close packing by the process of closing-up, homogeneous assemblages representative in number and characteristics of all the normal paraffins can be derived, and by appropriate substitutions effected in these assemblages arrangements entirely representative of all the other open chain paraffins can be deduced.

If, in the ethane assemblage, a hydrogen sphere is removed from each methyl group and the assemblage shrunk together in a particular symmetrical manner so as to close up the cavities, an assemblage is produced which may be partitioned into units of the composition C_2H_4; the units have the plane configuration attributed by Wislicenus to ethylene, and the assemblage is characterised by geometrical peculiarities representative of unsaturation or the presence of an ethylenic bond. From this assemblage others can be derived by substitution equal in number, and corresponding in properties, to the open chain olefines. The further removal of hydrogen spheres from the ethylene assemblage leads to the production of an assemblage representing acetylene, and this by appropriate substitution can be converted into others representing the homologues of acetylene. These assemblages exhibit a geometrical peculiarity representative of the presence of a triple or acetylenic bond.

Although the crystalline forms of the aliphatic hydrocarbons are unknown, ample crystallographic data relating to simple fatty compounds are available, and with the aid of these the conclusions briefly

described above have been verified.   The geometrical peculiarities which are the analogues of an ethylenic and an acetylenic bond suggest that the spheres between which the double or triple bond is operative are not closely surrounded by other spheres, and that when a carbon sphere is in a state of saturated combination the shell of spheres enveloping it will be found to have a maximum density of packing.

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