

*Crystallographic relations of allied substances traced
by means of the law of valency-volumes.*

By W. BARLOW, F.R.S.

[Read November 2, 1915.]

A WORD of explanation as to the nature of valency-volumes: The existence of the law of valency-volumes involves the conclusion that each chemical atom in a crystal has its own special domain throughout which its influence is predominant as compared with that of any other atom. According to this conception the entire space occupied by the crystal can be regarded as portioned out among its constituent atoms, each atom having a cell allotted to it the boundaries of which consist of points at which the influence of some one or more neighbouring atoms is equal to that of the selected atom; thus no interstices are left between the cells. For the purpose of the present communication, the question of the shapes of these domains does not arise; the facts to which I am about to call attention are connected with the relative volumes thus definitely appropriated by the several atoms in a given compound, and not with the forms of the atomic domains. Evidence will, however, appear that as we pass from one compound to another partially similar to it, the shapes of the corresponding domains present a certain constancy of pattern, while differing in absolute magnitude.

The investigation of the structure of crystals by means of X-rays has afforded direct evidence of the soundness of the contention that the atom preserves its individuality after chemical combination with other atoms. This new method of analysis has indeed revealed the nature of the pattern of the point-system formed by atomic centres of the same kind in some simple cases; and it is important to notice that, when isomorphous substances of similar atomic composition are compared, close similarity of the pattern formed by the atomic centres of a given kind common to the compared bodies is associated with a marked difference of scale, viz. of actual dimensions. Thus the distances separating the sulphur atoms in potassium sulphate will not be the

same as those separating these atoms in caesium sulphate; corresponding dimensions of the two bodies, as is easily perceived, will be very approximately in the ratio of the cube roots of the respective molecular volumes. It is suggested that the same difference of scale characterizes the two systems of cells respectively produced by appropriate partitioning of the two isomorphous crystals into atomic domains as above indicated. And, if this is the case, these systems of cells will be extremely similar in form, indicating similar conditions of equilibrium, and the dimensions of an atomic domain of the one crystal will respectively bear to the corresponding dimensions of a similar domain of the other crystal approximately the ratio of the cube roots of the two molecular volumes.

With regard to the law of valency-volumes on which the work recorded in this communication is based: Experimental facts previously published have led to the conclusion that a certain relation subsists between the amounts of space appropriated by the several atoms in a given compound; the volumes of the cellular domains allotted as above described are found to be very approximately in the ratio of the integers which respectively express the fundamental chemical valencies of their contained atoms. In the cases of atoms which under different conditions possess different chemical valencies, a general study of the chemical behaviour and isomorphous relations of the atom is found to lead to the selection of one of its valency values as fundamental and giving the valency-volume for all its compounds of whatever nature, e. g. sulphur is taken to be fundamentally divalent, so that its atom appropriates a space equivalent to two units of valency-volume in all cases.

It is a familiar fact that in a strictly isomorphous series of substances of similar atomic composition, the atoms, the interchange of which produces one term from another, are of the same chemical valency; this is in agreement with the above law and the simple conception connected with it, taken in conjunction with the partial identity of composition pervading such a series. For if the same proportion of the total molecular volume is allotted to the common radicle or atom, as the case may be, in each of the two compared isomorphous assemblages, the two remaining volumes, which are respectively allotted to the interchangeable atoms or radicles, will also bear the same proportion to the respective molecular volumes; consequently the atoms or radicles respectively appropriating these remaining volumes will, in agreement with the above law, present the same fundamental valency or sum of fundamental valencies.

The dimensional similarities of crystals of allied substances to which I shall presently direct your attention, can be traced by comparing the ordinary axial ratios, but a recognition of these resemblances is much facilitated by the use of equivalence-parameters. These are obtained from the recorded axial ratios, or from some slight modification of them, by expressing the ratios in terms of a volume unit instead of making the parameter y unity. The crystal of each substance has its own volume unit, which is the space occupied in it by a monovalent atom, half that taken up by a divalent atom or one-third of that assigned to a trivalent atom, &c.; the alternative unit volumes thus reached will, in obedience to the law of valency-volumes, be practically identical in the same compound. The equivalence-parameters x, y, z , which correspond respectively to a, b, c or to three derivatives of a, b, c selected as hereafter appears, present the same ratios as the indices from which they are derived, and they are the three dimensions of a parallelepiped having the volume of the molecular unit of the given crystal expressed in terms of the unit volume assigned in it to a monovalent atom. Thus W , the total of the fundamental valencies of the atoms composing the molecular unit, gives the volume of the parallelepiped of which the edges are x, y, z respectively in terms of the unit volume referred to. This definition takes for granted the existence of the valency-volume law. The equivalence-parameters are calculated by means of formulae analogous to those employed for obtaining the 'topic axial ratios'. Thus

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

The relation between the x, y, z and the a, b, c of a crystal will clearly appear from the succeeding examples, and the advantages of the former notation over the latter in the cases cited will be sufficiently obvious.

The ordinary parameters derived for a given crystal from the directions of the principal faces are often tacitly assumed to express the ratios between the minimum translations of the crystal-structure. There is, however, no adequate evidence warranting this as a general proposition, and indeed some very familiar facts are opposed to any such assumption. A case in point is furnished by calcite. In consequence of the great variety of forms presented by this mineral, it would be virtually impossible, but for the existence of the very perfect cleavage, to select with certainty the set of rhombohedral faces which are to be regarded as fundamental. Such a condition of things clearly indicates that the

determination which of the structural planes of like points shall be face-directions does not necessarily depend on the nature of the unit of the atom arrangement; there is no reason to suppose that the disposition of the atoms differs in the different forms of calcite, and indeed the facts that the dimensional relations of all the forms are strictly compatible and the cleavages identical quite negative such a supposition. Fedorov's admirable system for obtaining uniformity in the method of measuring crystals has no application to the discovery of the fundamental space-lattice of the crystal-structure; for while the recorded parameters are data with which this space-lattice, which is based on the minimum translations, must be consistent, they do not give us its form. In simple cases we must look to the X-ray method of investigation to ascertain this if it is not deducible from the cleavages.

I make these remarks in connexion with the modification of the recorded indices which is resorted to in most of the examples that follow. My contention is that the modifications made, the multiplication of one or sometimes two of the parameters by some small integer, need no further justification. I may mention that in nearly every case I feel confident that no other simple modification than that suggested will lead to such remarkably close agreement between the equivalence-parameters of the compared crystals. It is not suggested that the modified parameters necessarily give the relative dimensions of the fundamental space-lattice; the object of the modification is to find for the crystal of the one compound a set of parameters compatible with the parameters of the crystal of the compound with which it is to be compared. The degree of correspondence reached is taken to indicate whether or no this object has been attained.

The theory finally reached by Sohncke that a crystal can be regarded as a combination of regular point-systems has received experimental support from the X-ray method of investigation, for this reveals an arrangement of the atomic centres to form a system of congruent interpenetrated space-lattices. It seems therefore unquestionable that isomorphous and other morphotropic resemblances between the crystals of allied compounds are traceable to some close approximation of pattern of the respective point-systems formed by the atomic centres. The X-ray results, as already remarked, do not indicate any equality of corresponding actual dimensions; comparable distances in the related crystals may be expected to bear approximately the ratio of the cube roots of the respective unit volumes.

An examination of the instances of atomic arrangement revealed by the application of X-rays shows that in some directions the centres of single atoms of the molecule and in others the centres of the atoms associated to form chemical radicles are together found in planes or strata equally spaced throughout the crystal and not containing other atomic centres. This naturally suggests that the cellular domains of the atoms thus distinguished form continuous or discontinuous tracts or strata also disposed at equal distances. Now, in testing the truth of the law by reference to the recorded axial ratios of related substances, it is found that in addition to the above simple conception regarding the similarity of the cells of corresponding atoms of isomorphous compounds of similar atomic composition, another ancillary to it, almost equally simple, is indicated by the facts. It is well known that compounds which are closely related chemically as a consequence of the presence in their molecules of the same or similarly constituted radicles, very commonly exhibit when crystallized a pronounced morphological resemblance; a close approximation is perceived between some of their respective axial ratios. This fact suggests the application to these cases of a conception similar to that just put forward with regard to isomorphous crystals, viz. that the corresponding radicles display the same geometrical form and are similarly arranged according to the same pattern in the respective assemblages of atoms containing them; and that the partial morphological resemblance found subsisting between two such assemblages is due to the presence in them both of continuous masses of similar pattern entirely composed of the radicles, these masses taking the shape of continuous uniformly constituted strata of the same mean thickness throughout, or of columns, the pattern and mean section of which are uniform. The similarly constituted strata or columns of domains of influence of the two assemblages thus produced will exhibit the relation just attributed to the similar strata of isomorphous crystals; corresponding atomic domains taken respectively in the portions of two related crystalline assemblages of similar composition and pattern will be extremely similar in form. And if V_1, V_2 be the respective molecular volumes, W_1, W_2 the respective sums of the fundamental valencies of the constituent atoms of the two related molecules, corresponding dimensions taken respectively in the similarly constituted portions of the two assemblages will bear approximately the ratio $\sqrt[3]{\frac{V_1}{W_1}} : \sqrt[3]{\frac{V_2}{W_2}}$. When similarly constituted strata of

almost identical pattern are present, it is manifest that the axial ratios of the planes of the strata taken in the two assemblages will be approximately equal, and thus that two of the three equivalence-parameters of the one assemblage will be approximately equal to two of the other. And it follows from this that the third equivalence-parameter of the one will bear to the corresponding third equivalence-parameter of the other approximately the ratio presented by the sums of the valency-volumes, viz. $W_1 : W_2$.

The following are a number of instances of close morphological resemblance in which the relation between the axial ratios of two allied substances is found to furnish evidence of the existence of the law of valency-volumes. In each case the molecules of the bodies compared contain a like chemical radicle, either identical or of similar constitution; and the dimensional relations observed, interpreted in the light of the law, indicate a stratification of the crystal structure, in both compounds, such that uniform similar layers or strata, evenly spaced, consisting solely of the radicles referred to, can be discriminated. These layers alternate with uniform layers, which can, however, be continuous or discontinuous, also similar to one another, consisting of the remaining constituents of the crystal. The pattern of the atomic arrangement in the two sets of layers of similar constitution, one in each crystal, is argued to be the same; a similar disposition of the atoms having similar relative dimensions, as measured in a single layer, being present in both sets. When the law of valency-volumes is postulated, the effect of this resemblance is to give two of the equivalence-parameters of the one crystal approximately equal to two parameters of the other crystal, while the remaining parameters, one of each crystal, are approximately in the ratio of the sums of the fundamental valencies of the constituent atoms of the respective molecules. The closeness of the approximation to this relation is very evident in the cases given.

Ex. 1. *Cupric sulphate (Hydrocyanite)*, CuSO_4 .

Rhombic, $a : b : c = 0.7968 : 1 : 0.5650$. $W = 12$.

$x : y : z = 2.8802 : 2.9872 : 1.6877$.

Magnesium sulphate monohydrate, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$.

Monoclinic, $a : b : c = 0.9147 : 1 : 1.7445$; $\beta = 91^\circ 7'$. $W_1 = 16$.

$a_1 : b_1 : c_1 = 2a : c : b = 1.8294 : 1.7445 : 1$; $\gamma_1 = \beta = 91^\circ 7'$.

$x_1 : y_1 : z_1 = 3.1812 : 2.9859 : 1.7116$.

Calculated $x_1 = \frac{W_1}{W} x = 3.17$.

Ex. 2. *Calcium sulphate (Anhydrite),* CaSO_4 .Rhombic, $a : b : c = 0.8932 : 1 : 1.0008$. $W = 12$.

$$\text{Since } b = c \text{ nearly, } a' : b' : c' = 0.8932 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{2}} = 1.2632 : 1 : 1.$$

$$x' : y' : z' = 2.6753 : 2.118 : 2.118.$$

Calcium sulphate dihydrate (Gypsum), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.Monoclinic, $a : b : c = 0.6895 : 1 : 0.4132$; $\beta = 98^\circ 58'$. $W_1 = 20$.

$$a_1 : b_1 : c_1 = \frac{b}{2} : a : c = 0.5 : 0.6895 : 0.4132 ; \alpha_1 = 98^\circ 58'.$$

$$x_1 : y_1 \sin \alpha_1 : z_1 = 2.6094 : 3.5544 : 2.1564.$$

$$\text{Calculated } y_1 \sin \alpha = \frac{W_1}{W} y' = 3.53.$$

Ex. 3. *Calcium sulphate (Anhydrite),* CaSO_4 .Rhombic, $a : b : c = 0.8932 : 1 : 1.0008$. $W = 12$.

$$x : y : z = 2.1228 : 2.3766 : 2.3785.$$

Manganese sulphate tetrahydrate, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$.Monoclinic, $a : b : c = 0.4321 : 1 : 0.5820$; $\beta = 90^\circ 53'$. $W_1 = 28$.

$$a_1 : b_1 : c_1 = \frac{2}{3} c : b : a = 0.3880 : 1 : 0.4321 ; \beta_1 = 90^\circ 53'.$$

$$x_1 : y_1 : z_1 = 2.1368 : 5.5072 : 2.3796.$$

$$\text{Calculated } y_1 = \frac{W_1}{W} y = 5.5454.$$

Ex. 4. *Calcium sulphate (Anhydrite),* CaSO_4 .Rhombic, $a : b : c = 0.8932 : 1 : 1.0008$. $W = 12$.

$$x : y : z = 2.1228 : 2.3766 : 2.3785.$$

Nickel sulphate hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.Tetragonal trapezohedral, $a : c = 1 : 1.9119$. $W_1 = 36$.

$$a' : c' = a : c \sqrt{2} = 1 : 2.7088.$$

$$a_1 : b_1 : c_1 = c' : a' : a' = 2.7088 : 1 : 1.$$

$$x_1 : y_1 : z_1 = 6.4085 : 2.37 : 2.37.$$

$$\text{Calculated } x_1 = \frac{W_1}{W} x = 6.368.$$

Ex. 5. *Cupric sulphate (Hydrocyanite),* CuSO_4 .Rhombic, $a : b : c = 0.7968 : 1 : 0.5650$. $W = 12$.

$$\text{Transforming axes } b \text{ and } c, a' : b' : c' = 0.7968 : 0.984 : 0.5743 ; a' = 91^\circ 5'.$$

$$x' : y' : z' = 2.3802 : 2.9394 : 1.7155.$$

Zinc sulphate hexahydrate, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$.Monoclinic, $a : b : c = 1.3847 : 1 : 1.6758$; $\beta = 98^\circ 12'$. $W_1 = 36$.

$$a_1 : b_1 : c_1 = 3 a : c : b = 4.1541 : 1.6758 : 1 ; \gamma_1 = 98^\circ 12'.$$

$$x_1 \sin \gamma_1 : y_1 : z_1 = 7.135 : 2.908 : 1.7352.$$

$$\text{Calculated } x_1 \sin \gamma_1 = \frac{W_1}{W} x' = 7.14.$$

Ex. 6. *Cupric sulphate (Hydrocyanite)*, CuSO_4 .Rhombic, 0.7968 : 1 : 0.5650. $W = 12$.Transforming axes b and c , $a' : b' : c' = 0.7968 : 0.984 : 0.5743$; $\alpha' = 91^\circ 5'$.Taking a group of three molecules as unit, $W' = 36$, and $x' : y' : z' = 3.493 : 4.24 : 2.474$.*Ferric sulphate enneahydrate (Coquimbite)*, $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.Rhombohedral, $a : c = 1 : 1.5613$. $W_1 = 70$.Written in rhombic form, $a : b : c = \frac{1}{\sqrt{3}} : 1 : 1.5613$. $a_1 : b_1 : c_1 = c : b : a = 1.5613 : 1 : \frac{1}{\sqrt{3}}$. $x_1 : y_1 : z_1 = 6.66 : 4.266 : 2.463$.Calculated $x_1 = \frac{W_1}{W'} x' = 6.675$.Ex. 7. *Calcium sulphate (Anhydrite)*, CaSO_4 .Rhombic, $a : b : c = 0.8932 : 1 : 1.0008$. $W = 12$.Transforming a and b axes, $a' : b' : c' = 0.8729 : 1.0236 : 1.0008$; $\gamma' = 91^\circ 29'$.Taking a group of three molecules as unit, $W' = 36$, and $x'' : y'' : z'' = 2.99 : 3.51 : 3.43$.*Lanthanum sulphate enneahydrate*, $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.Rhombohedral, $a : c = 1 : 0.7356$. $W_1 = 70$.Written in rhombic form, $a : b : c = 1 : \frac{1}{\sqrt{3}} : 0.7356$. $a_1 : b_1 : c_1 = a : 2b : 3c = 1 : \frac{2}{\sqrt{3}} : 2.2068$. $x_1 : y_1 : z_1 = 3.017 : 3.484 : 6.6586$.Calculated $z_1 = \frac{W_1}{W'} z'' = 6.67$.Ex. 8. *Cupric sulphate (Hydrocyanite)*, CuSO_4 .Rhombic, $a : b : c = 0.7968 : 1 : 0.5650$. $W = 12$.Transforming axes a and b , $a' : b' : c' = 0.8492 : 0.9407 : 0.5650$; $\gamma' = 94^\circ 8'$. $x' : y' : z' = 2.5368 : 2.810 : 1.6877$.*Cupric lead dihydroxy-sulphate (Linarite)*, $\text{CuPb}(\text{OH})_2\text{SO}_4$.Monoclinic, $a : b : c = 1.7161 : 1 : 0.8296$; $\beta = 102^\circ 37'$. $W_1 = 20$. $a_1 : b_1 : c_1 = 3c : a : b = 2.4888 : 1.7161 : 1$; $\gamma_1 = 102^\circ 37'$. $x_1 : y_1 \sin \gamma_1 : z_1 = 4.1978 : 2.8246 : 1.6867$.Calculated $x_1 = \frac{W_1}{W'} x' = 4.228$.

Ex. 9. *Cupric sulphate (Hydrocyanite),* CuSO_4 .Rhombic, $a : b : c = 0.7968 : 1 : 0.5650$. $W = 12$. $x : y : z = 2.3802 : 2.9872 : 1.6877$.*Tricupric dihydroxy-sulphate (Stelznerite),* $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$.Rhombic, $a : b : c = 0.4971 : 1 : 0.6881$. $W_1 = 28$. $a_1 : b_1 : c_1 = c : 2b : a = 0.6881 : 2 : 0.4971$. $x_1 : y_1 : z_1 = 2.3713 : 6.8925 : 1.7131$.Calculated $y_1 = \frac{W_1}{W} y = 6.97$.**Ex. 10.** *Cupric sulphate (Hydrocyanite),* CuSO_4 .Rhombic, $a : b : c = 0.7968 : 1 : 0.5650$. $W = 12$. $x : y : z = 2.3802 : 2.9872 : 1.6877$.*Tetracupric trihydroxy-sulphate monohydrate (Langite),* $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$.Rhombic, $a : b : c = 0.5347 : 1 : 0.6346$. $W_1 = 40$. $a_1 : b_1 : c_1 = \frac{a}{2} : \frac{b}{3} : c = 0.2673 : 0.3333 : 0.6346$. $x_1 : y_1 : z_1 = 2.3820 : 2.9699 : 5.654$.Calculated $z_1 = \frac{W_1}{W} z = 5.6259$.**Ex. 11.** *Lithium rubidium sulphate,* LiRbSO_4 .Hexagonal, $a : c = 1 : 1.6472$. $\underline{x} W = 12$.Written in rhombic form, $a : b : c = \sqrt{3} : 1 : 1.6472$. $x : y : z = 2.7959 : 1.6142 : 2.6589$.*Potassium hydrogen sulphate + Potassium iodate,* $\text{KHSO}_4 \cdot \text{KIO}_3$.Monoclinic, $a : b : c = 1.9288 : 1 : 1.0346$; $\beta = 93^\circ 14'$. $W_1 = 20$. $a_1 : b_1 : c_1 = c : b : \frac{a}{2} = 1.0346 : 1 : 0.9644$; $\beta_1 = 93^\circ 14'$. $x_1 : y_1 : z_1 = 2.812 : 2.718 : 2.62$.Calculated $y_1 = \frac{W_1}{W} y = 2.69$.**Ex. 12.** *Thallous sulphate,* Tl_2SO_4 .Rhombic, $a : b : c = 0.5555 : 1 : 0.7328$. $W = 12$. $x : y : z = 1.716 : 3.089 : 2.2637$.*Hydrazine sulphate,* $\text{H}_2\text{SO}_4 \cdot \text{N}_2\text{H}_4$. $a : b : c = 0.9012 : 1 : 0.6040$. $W_1 = 22$. $a_1 : b_1 : c_1 = b : 2a : 4c = 1 : 1.8024 : 2.4160$. $x_1 : y_1 : z_1 = 1.7159 : 3.0927 : 4.1456$.Calculated $z_1 = \frac{W_1}{W} z = 4.15$.

Ex. 13. *Potassium nitrate*, KNO_3 .Rhombic, $a : b : c = 0.5910 : 1 : 0.7011$. $W = 10$. $x : y : z = 1.708 : 2.89 : 2.026$.*Ammonium nitrate*, NH_4NO_3 .Rhombic, $a : b : c = 0.9092 : 1 : 1.0553$. $W_1 = 16$. $a_1 : b_1 : c_1 = \frac{c}{2} : a : b = 0.5276 : 0.9092 : 1$. $x_1 : y_1 : z_1 = 1.7 : 2.9267 : 3.219$.Calculated $z_1 = \frac{W_1}{W} z = 3.2416$.Ex. 14. *Rubidium hexachloro-antimonate*, RbSbCl_6 .Rhombic, $a : b : c = 0.6719 : 1 : 0.8136$. $W = 9$. $x : y : z = 1.7093 : 2.544 : 2.0697$.*Potassium hexafluoro-arsenate hemihydrate*, $\text{KAsF}_6 \cdot \frac{1}{2} \text{H}_2\text{O}$.Rhombic, $a : b : c = 0.8401 : 1 : 2.5172$. $W_1 = 11$. $a_1 : b_1 : c_1 = a : b : \frac{c}{3} = 0.8401 : 1 : 0.8391$. $x_1 : y_1 : z_1 = 2.0993 : 2.5 : 2.0968$.Calculated $x_1 = \frac{W_1}{W} x = 2.0891$.

Attention is specially directed to the case of potassium nitrate and ammonium nitrate, because this forms an exception to the rule that compounds related as these are display isomorphism. It is suggested that in the ordinary cases, in which isomorphism is presented, the resemblance of the two crystal-structures is of the same nature as that just indicated for the two compounds referred to; that the arrangement in both is such that they can be regarded as stratified in the manner described. The isomorphism displayed is ascribed to the predominant influence of the strata composed of the important radicles; this, it is suggested, causes in both crystals planes of atom-centres which are the important planes in these strata, to be selected as face-directions, subject only to such modification as is demanded by the law of rational indices. According to this view, the structural arrangement of the remaining portions, which are unlike in the two crystals, has some considerable compatibility with that of the predominating strata, and, in consequence of this compatibility, has no influence in determining crystal face-directions beyond a slight modifying effect on the parameters.