Note on a connexion between the molecular volume and chemical composition of some crystallographically similar minerals.

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THE molecular volumes of the members of an isomorphous group of minerals in general show an approach to equality. In other words, minerals having an analogous chemical composition show not only closely related crystalline forms, but have also approximately equal molecular volumes. Many years ago J. D. Dana [1] endeavoured to show that a simple relationship as regards molecular volume also subsisted in the case of various minerals which were closely related crystallographically, although unlike chemically. He concluded that in these cases the similarity in form depended solely on the relationship in molecular volume, and had nothing whatever to do with the chemical composition.

In the case of many of these minerals, however (more particularly those showing the closest crystallographic similarity), it is possible to discover a chemical relationship, although it is not one of so intimate a nature as that which connects the members of the ordinary isomorphous groups. This relationship depends on the fact that the chemical formulae of the minerals showing close crystallographic similarity and approximately equal molecular volumes are of the same form and contain approximately the same number of atoms, although they may not represent salts of the same acid or salts of metals having the same valencies. As examples of 'isomorphous' minerals of this kind we have the often-cited case of

$$\text{Calcite, } CaCO_3, \qquad (V = 37)^2,$$
$$\text{Sodium nitrate, } NaNO_3, (V = 40),$$

and of the felspars

$$\text{Albite, } NaAlSi_3O_8, \qquad (V = 100),$$
$$\text{Anorthite, } CaAlAlSi_2O_8, (V = 100).$$

[1] Amer. Journ. Sci., 1850, ser. 2, vol. ix, p. 220.
[2] $V =$ molecular volume, i. e. molecular weight divided by the density.

THE HAMLINITE-BEUDANTITE-JAROSITE GROUP.

In a previous note in this Magazine (1900, vol. xii, p. 253) the above kind of chemical relationship was shown to subsist in the case of the crystallographically similar minerals hamlinite, florencite, plumbogummite, svanbergite, and beudantite, and it was suggested that these minerals formed a natural group. Of this group the three first minerals are phosphates, and the last two double phosphates and sulphates. The group may be made more complete by the addition of five minerals which are wholly sulphates, viz. alunite, jarosite, utahite, and the two new minerals, recently described by Hillebrand and Penfield, natrojarosite and plumbojarosite[1].

In the following table are exhibited the chemical and crystallographic relations of this group of rhombohedral minerals[2]. The molecular volumes given in the last column show an approximation to equality, so that the group behaves in this respect like the more ordinary isomorphous groups.

	Formula.	rr'.		δ.	V.
Hamlinite	$AlPO_4 . SrHPO_4 . Al_2(OH)_6$	87°	2'	1·1353	142
Florencite	$AlPO_4 . CePO_4 . Al_2(OH)_6$	88	56	1·1901	143
Svanbergite[3]	$AlPO_4 . SrSO_4 . Al_2(OH)_6$	89	25	1·2063	140
Beudantite	$Fe'''PO_4 . PbSO_4 . Fe_2(OH)_6$	88	42	1·1842	155
Alunite	$AlSO_4KSO_4 . Al_2(OH)_6$	90	50	1·2520	150
Jarosite	$Fe'''SO_4KSO_4 . Fe_2(OH)_6$	90	45	1·2492	154
Natrojarosite	$Fe'''SO_4NaSO_4 . Fe_2(OH)_6$	85	54	1·1088	154
Plumbojarosite	$Fe'''SO_4Pb_{\frac{1}{2}}SO_4 . Fe_2(OH)_6$	89	42	1·2156	154
Utahite[4]	$Fe'''OHSO_4 . Fe'''OHSO_4 . Fe_2(OH)_6$	84	9	1·0576	—

Plumbojarosite, it must be confessed, stands a little out of the picture. The isomorphism of Pb and K_2 is certainly very unusual: it is considered by Penfield to be conditioned by the controlling influence or *mass effect* of the other constituents in the complex molecule. Whether 'mass effect' is to be appealed to or not as the cause of the close crystallographic relationship of the other members of the group, it is evident that in these minerals of complex chemical composition such a grouping

[1] Amer. Journ. Sci., 1902, ser. 4, vol. xiv, p. 211; and Zeits. Kryst. Min., 1902, vol. xxxvi, p. 545.

[2] Plumbogummite is left out of account owing to the lack of crystallographic data.

[3] The presence of strontia with lime in the mineral from Horrsjöberg has been determined by testing in the same way as in the case of the Westanå mineral (see previous paper, l.c., p. 252).

[4] A. Arzruni and K. Thaddéeff, Zeits. Kryst. Min., 1899, vol. xxxi, pp. 234, 244.

as $CePO_4$ can be replaced by $SrSO_4$, and $AlPO_4CePO_4$ by $AlSO_4KSO_4$, &c., without materially affecting the crystalline form. The formulae are written as above in order to make clear this chemical relationship. If doubled in order to show the isomorphism of K_2 and Pb, and written on the same plan as that adopted by Penfield, with hamlinite regarded as a pyrophosphate, they are as follows:—

Hamlinite	. .	$[SrOH]_2[Al(OH)_2]_6[P_2O_7]_2$
Florencite	. . .	$Ce_2[Al(OH)_2]_6[PO_4]_4$
Svanbergite	. . .	$Sr_2[Al(OH)_2]_6[PO_4]_2[SO_4]_2$
Beudantite	. . .	$Pb_2[Fe(OH)_2]_6[PO_4]_2[SO_4]_2$
Alunite	. . .	$K_2[Al(OH)_2]_6[SO_4]_4$
Jarosite .	. . .	$K_2[Fe(OH)_2]_6[SO_4]_4$
Natrojarosite .	. .	$Na_2[Fe(OH)_2]_6[SO_4]_4$
Plumbojarosite	. .	$Pb[Fe(OH)_2]_6[SO_4]_4$
Utahite .	. .	$[Fe(OH)_2]_2[Fe(OH)_2]_6[SO_4]_4$

As further examples of similar relations connecting crystalline form, molecular volumes, and chemical composition may be mentioned the following groups of minerals.

	Formula.	System.	Elements.	V.
{ Monazite	$CePO_4$	Monoclinic	$0.9693:1:0.9256; \beta=76° 20'$	47
{ Crocoite	$PbCrO_4$	,,	$0.9603:1:0.9159; \beta=77° 33'$	54
{ Gypsum	$CaSO_4.2H_2O$	,,	$0.6899:1:0.4124; \beta=80° 42'$	74
{ Brushite	$HCaPO_4.2H_2O$	,,	$0.6221:1:0.3415; \beta=84° 45'$	78
{ Fergusonite	$YNbO_4$	Tetragonal (pyr. hemih.)	$1:1.4643$	47
{ Scheelite	$CaWO_4$	,,	$1:1.5356$	48
{ Chrysoberyl	$BeAlAlO_4$	Orthorhombic	$0.4700:1:0.5800$	36
{ Olivine	$MgMgSiO_4$	,,	$0.4657:1:0.5865$	44
{ Andalusite	Al_2SiO_5	,,	$0.9861:1:0.7024$	51
{ Olivenite	$Cu_2(OH)AsO_4$	,,	$0.9396:1:0.6726$	64
{ Diopside	$CaMgSi_2O_6$	Monoclinic	$1.0921:1:0.5893; \beta=74° 10'$	66
{ Spodumene	$LiAlSi_2O_6$	,,	$1.1238:1:0.6355; \beta=69° 40'$	60
{ Perofskite	$CaTiO_3$	Cubic	——	34
{ Bixbyite	$FeMnO_3$	,,	——	32
{ Geikielite	$MgTiO_3$	Rhombohedral	$1:1.370$ [1]	30
{ Ilmenite	$FeTiO_3$	,,	$1:1.3846$	32
{ Hematite	$FeFeO_3$	,,	$1:1.3656$	30

[1] P. von Sustschinsky, Zeits. Kryst. Min., 1902, vol. xxxvii, p. 57; abstract this vol., p. 307.

In the preceding examples the chemical relationship of the minerals in each group is made evident by taking the ordinary formulae, and the molecular volumes which show an approximate equality are calculated from these formulae.

There are cases, however, of groups of two or more minerals which are very closely related crystallographically, but have molecular volumes far from equal when these are calculated from the ordinary formulae: these formulae, moreover, show no obvious relationships. In many of these cases it is found, in accordance with the principle which seems to hold good in the case of the preceding examples, that if in each group suitable multiples of the ordinary formulae of the minerals be taken so that the molecular volumes calculated from them are approximately equal, then these new formulae exhibit a similarity in form with approximately the same number of atoms.

This principle may supply a means in some cases of determining the simplest formulae of polymeric minerals, as in the following example of rutile, brookite, and anatase.

Formulae of Rutile, Brookite, and Anatase.

In the case of *rutile*, as an aid in the determination of its simplest chemical formula, we have its close crystallographic similarity with zircon.

For these two minerals the molecular volumes are:—

$$\text{Rutile (TiO}_2\text{)},\quad V = \frac{80}{4\cdot2} = 19.$$

$$\text{Zircon (ZrSiO}_4\text{)},\ V = \frac{182}{4\cdot7} = 39.$$

In order to bring these molecular volumes into approximate equality, that of rutile must be multiplied by 2.

The simplest formula, therefore, for rutile is Ti_2O_4 or $TiTiO_4$, which brings it into correspondence with that of zircon, $ZrSiO_4$.

In the case of *brookite*, its close crystallographic similarity with tantalite serves to suggest its formula.

The molecular volumes are:—

$$\text{Brookite (TiO}_2\text{)},\qquad V = \frac{80}{4\cdot084}{}^{[1]} = 19\cdot6.$$

$$\text{Tantalite (FeTa}_2O_6\text{)},\ V = \frac{439}{8\cdot200}{}^{[2]} = 62\cdot32.$$

[1] Penfield's determination for brookite from Magnet Cove, Arkansas. Amer. Journ. Sci., 1886, ser. 3, vol. xxxi, p. 387.

[2] Headden's determination for tantalite from S. Dakota. Amer. Journ. Sci., 1891, ser. 3, vol. xli, p. 98.

Here the molecular volume of brookite must be multiplied by 3, and the simplest formula for brookite is therefore Ti_3O_6 or $TiTi_2O_6$, to correspond with that of tantalite, $FeTa_2O_6$.

That these formulae, however, both of brookite and of tantalite, may have to be doubled is suggested by the well-known crystallographic relationship of these minerals with wolframite (hübnerite).

Thus for these three minerals the molecular volumes calculated from the simplest formulae are as follows :—

Brookite (TiO_2), $V = 19.6$.

Tantalite ($FeTa_2O_6$), $V = 62.32$.

Hübnerite ($MnWO_4$), $V = \dfrac{302.4}{7.177} = 42.133$.[1]

In order to bring these molecular volumes into approximate equality, the simple formulae of the three minerals must be multiplied by 6, 2, and 3 respectively, when the chemical relationship becomes at once apparent.

The molecular volumes and topic axes of the three minerals are then as follows :—

	V	χ	ψ	ω
Brookite ($Ti_3Ti_3O_{12}$),	117.54	4.450	5.288	4.994
Tantalite ($Fe_2Ta_4O_{12}$),	124.64	4.581	5.530	4.920
Hübnerite ($Mn_3W_3O_{12}$),	126.40	4.647	5.599	4.859.

In the case of *anatase* (TiO_2, $V = 20$), its close crystallographic similarity with calomel (Hg_2Cl_2, $V = 72$) and matlockite (Pb_2Cl_2O, $V = 70$) suggests that Ti_4O_8 ($V = 80$) is the most probable formula, although here the dissimilarity between the chemical compounds renders the evidence less convincing than in the case of rutile and brookite.

The most probable simplest chemical formulae therefore for the three modifications of titanic acid are:—

Rutile   .   .   . Ti_2O_4.

Anatase .   .   . Ti_4O_8.

Brookite .   .   . Ti_6O_{12}.

This result is the same as that to which Schrauf[2] was led from the consideration of atomic groupings in accordance with the crystallographic symmetry.

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[1] Hillebrand's determination for hübnerite from Ouray Co., Colorado.   Amer. Journ. Sci., 1884, ser. 3, vol. xxvii, p. 357.

[2] Zeits. Kryst. Min., 1884, vol. ix, p 483.

The chemical and crystallographic relations and the molecular volumes of the above and other similar groups of minerals are exhibited in the following table :—

	Formula.	System.	Elements.	V.
Zircon	$ZrSiO_4$	Tetragonal	$1 : 0.6404$	39
Rutile	$TiTiO_4$	,,	$1 : 0.6442$	38
Sellaite	$MgMgF_4$	,,	$1 : 0.6596$	41
Xenotime	YPO_4	,,	$1 : 0.6187$	41
Brookite	$Ti_2Ti_4O_{12}$	Orthorhombic	$0.8416 : 1 : 0.9444$	118
Tantalite	$Fe_2Ta_4O_{12}$	,,	$0.8285 : 1 : 0.8898$	125
Hübnerite	$Mn_2MnW_3O_{12}$ Monoclinic		$0.8300 : 1 : 0.8678 ; \ \beta = 89° 22'$	126
Celestite	$SrSO_4$	Orthorhombic	$0.7789 : 1 : 1.2800$	47
Marcasite	$FeFeS_4$	,,	$0.7662 : 1 : 1.2342$	50
Copper-pyrites	$Cu_2Fe_2S_4$	Tetragonal	$1 : 0.9853$	88
Stannite	Cu_2FeSnS_4	,,	$1 : 0.9827$	95
Calcite	$Ca_2C_2O_6$	Rhombohedral	$1 : 0.8543$	74
Nordenskiöldine	$CaSnB_2O_6$	,,	$1 : 0.8221$	65
Calomel	Hg_2Cl_2	Tetragonal	$1 : 1.7229$	72
Matlockite	Pb_2Cl_2O	,,	$1 : 1.7627$	70
Anatase	Ti_4O_8	,,	$1 : 1.7771$	80

The principle enunciated in the present note of the approximate equality of molecular volumes corresponding to similarity in form of the chemical formulae in the case of minerals showing close crystallographic relations, although holding good for a large number of cases, is not of general application to compounds of any elements whatever. Thus the well-known homoeomorphous minerals zincite (ZnO), greenockite (CdS), and iodyrite (AgI), although having equal number of atoms in the molecule and showing the closest possible crystallographic relationship, have molecular volumes of 15, 30, and 40 respectively, which are certainly not equal, although, it may be pointed out, nearly in the simple ratio of $1 : 2 : 3$. Further, the principle is not always a reversible one, for minerals having approximately equal molecular volumes and formulae similar in form may show no crystallographic similarity; e. g. neither scorodite, $FeAsO_4 \cdot 2H_2O$ ($V = 72$), and gypsum, $CaSO_4 \cdot 2H_2O$ ($V = 74$), nor pucherite, $BiVO_4$ ($V = 53$), and celestite, $SrSO_4$ ($V = 47$), show any close similarity in crystalline forms.

It would seem that, just as in an ordinary isomorphous group there are *single* elements which may be termed crystallographically equivalent, so in the case of the crystallographically similar minerals discussed in the

present note there are *groups* of elements which are crystallographically equivalent. Thus, as regards their influence on molecular volume and the determination of crystalline form, it would appear from the preceding examples that

CaC	is equivalent to	NaN
NaSi	,,	CaAl
CeP	,,	PbCr
YNb	,,	CaW
Al_2Si	,,	Cu_2As
$BeAl_2$	,,	$SiMg_2$, &c.

In many cases, however, especially where the chemical molecule is a very complex one, the equivalence of certain groups may be only approximate, and the fact that they can replace each other in such complex minerals without appreciably affecting the crystalline form may depend to some extent on the 'mass effect' of the other constituents of the molecule, as suggested by Penfield.