On the atomic volume relations in certain isomorphous series.

By A. F. HALLIMOND, M.A., F.G.S.

Assistant Curator, Museum of Practical Geology, London.[1]

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CONSIDERABLE interest attaches to the estimation of the volume occupied by the several atoms in a crystalline compound. For the complete molecule a volume can at once be calculated from the density and the chemical composition, but the further subdivision of this space into domains belonging to the constituent atoms or groups can only be made by methods that are limited and frequently very indirect. In general, the volume is not additive, and it seems clear that the same atom may occupy very different volumes in its different compounds; indeed, it is only within the limits of a truly isomorphous series that the volume can be treated as an additive property. But even in this case it is not possible directly to calculate volumes for the constituents of the molecule if the chemical formulae are of the same type throughout; when, however, the formulae differ in type a solution may be possible. In this way approximate values have been obtained for the volumes of the several component oxides of the mica group,[2] and it seemed desirable

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[1] Communicated by permission of the Director.
[2] A. F. Hallimond, Min. Mag., 1927, vol. 21, pp. 195-204.

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to examine some of the better known isomorphous series in order to see how far the conclusions to be drawn from the latter would correspond with those based on the poorer data available for the micas. By far the best available series are those containing the alkali metals, for many of which data of the highest accuracy have been supplied in the extensive researches of Tutton and other workers. In these salts the formulae are strictly analogous, so that the direct method which served for the micas is not available ; some other hypothesis must form a basis for calculating the atomic volumes, and the present paper contains a discussion of the data from this standpoint. The several isomorphous salt-series formed by the eutropic metals potassium, rubidium, and caesium are characterized by an approximate constancy in the ratio between the volume-differences produced by interchange of the metals. Further, the volumes of the free metals yield the same ratio, so that the metals themselves apparently constitute an isomorphous series quite analogous with the sulphates, selenates, and other salts. The differences vary in size in the different series ; a direct additive relation does not hold good throughout, but the volume of the combined metal appears to be derived from that of the free metal by a factor common to each salt-series. In this way volumes can be calculated for the metal and acid radicle in each salt. A similar constant ratio holds good for the chlorides, bromides, and iodides ; in the absence of a solid isomorphous series for the free halogens a set of comparable volumes can be obtained from the partial volumes calculated for the alkali halides ; .these agree with the values obtained by Richards from the compressibility, and are nearly proportional to those given by Kopp's method of comparing the volume of the liquids at the boiling-point. By the use of these and similar data estimates can be obtained for the volume of the atoms and radicles in numerous compounds of the alkali metals and the halogens, and these estimates agree well with the approximate values generally accepted.

A. *Isomorphous series derived from the eutropic metals K, Rb, Cs.*

Some of the most accurately known data for the alkali salts are collected in Table I. The first three columns contain the molecular volumes of the salts ; the next two columns give the values for the differences produced by the eutropic replacement of K by Rb and by Cs, and the fifth column shows the ratio between these differences. Although the data exhibit a wide variety in molecular volume, in composition, and

in the magnitude of the differences, yet the ratio remains very closely constant throughout, and has the same value even in the case of the free metals, though these have a greater volume than the whole of the sulphate molecule.

Table I. *Molecular volumes of isomorphous salts of K, Rb, Cs.*

	K.	Rb.	Cs.	Rb–K.	Cs–K.	$\dfrac{\text{Cs–K}}{\text{Rb–K}}$.
Free metal M_2 [1] ...	90·8	111·8	141·0	21·0	50·2	2·39
Sulphate [2]	64·91	73·34	84·58	8·43	19·67	2·34
Selenate [2]	71·67	79·94	91·09	8·27	19·42	2·35
Double Sulphate (Zn) [2]	196·16	205·58	217·97	9·42	21·81	2·32
Double Selenate (Zn) [2]	208·80	218·35	230·77	9·55	21·97	2·30
Perchlorate [3]	54·91	61·33	70·05	6·42	15·14	2·36
Permanganate [4] ...	58·53	63·23	70·01	4·70	11·48	2·44
$C_6H_4.COOH.COOM$ [4] ...	124·8	129·6	136·7	4·8	11·9	2·48
Metaperiodate [4] ...	63·7	70·6	—	6·9	—	—
Bichromate [4]	110·2	123·9	—	13·7	—	—

This constancy of the difference-ratio would seem to afford an exact numerical significance for the special term *eutropic*; thus in any isomorphous series derived from a given eutropic group of metals, it appears that the differences in molecular volume along the series stand in a constant ratio which is characteristic of the metals but is the same in all the series, and so is independent of the nature of the acid radicle. This relation is strictly confined to the eutropic elements,[5] and is not fulfilled by the salts of ammonium or thallium.

Calculation of atomic volumes.—Since the differences in all the isomorphous series of Table I stand in the same constant ratio, it follows that the volumes $V_1, V'_1, V''_1 \ldots$ of the salts [6] in any one series may be related to those in another series $V_2, V'_2, V''_2 \ldots$ by equations of the following type :

$$V_1 = aV_2 + C$$
$$V'_1 = aV'_2 + C$$
$$V''_1 = aV''_2 + C.$$

[1] See Landolt-Börnstein, Physikalisch-chemische Tabellen, 1920 edition.

[2] A. E. H. Tutton; see P. Groth, Chem. Kryst., vol. 2, pp. 323, 326, 490.

[3] A. E. H. Tutton, Proc. Roy. Soc. London, Ser. A, 1926, vol. 111, pp. 462–491. [Min. Abstr., vol. 3, p. 161.]

[4] Values taken from P. Groth, loc. cit.

[5] A. E. H. Tutton, Crystalline structure and chemical constitution, 1910, p. 125.

[6] The series in Table I relate to three metals only, but if more than three eutropic metals were available the relation would probably extend to them also.

For, by subtracting these equations in pairs, $V'_1 - V_1 = a(V'_2 - V_2)$ and $V''_1 - V_1 = a(V''_2 - V_2)$. Then, on dividing,

$$\frac{V' - V_1}{V''_1 - V_1} = \frac{V'_2 - V_2}{V''_2 - V_2},$$

this being the relation observed in the last column of Table I. C is a volume, constant for each isomorphous series, i. e. for each acid radicle, but independent of the metal. a is a factor, also constant, for the isomorphous series and independent of the metal; it is the ratio between any difference in the isomorphous series $V_1 \ldots$ and the corresponding difference in the other isomorphous series $V_2 \ldots$.

Now the metals themselves form one of these series (Table I); the volumes of the free metals may therefore be chosen as $V_2, V'_2, V''_2 \ldots$. Each of the three equations given above then assumes the form

$$V(\text{salt}) = aV(\text{metal}) + C.$$

Expressed in words, this implies that the volume of any salt in a given isomorphous (eutropic) series is the sum of a variable volume, which is a times the volume of the metal in the free state (if the free metals are isomorphous), and a constant volume C depending solely on the nature of the acid radicle. Reasons will be given below for supposing that the atoms in these crystals can be treated as relatively incompressible, but plastic, units completely filling the available space in the crystal; the above partial volumes will therefore be termed the partial volumes of the metal and acid radicle (or other residue) in the crystal. Values for these quantities are readily calculated from the data in Table I, and have been summarized in Table II. The results are derived from the average of

Table II.   *Calculated volumes of metal and acid radicle in salts of K, Rb, Cs.*

	Metal (K).	Radicle.	Metal (Rb).	Radicle.	Metal (Cs).	Radicle.	Mean Radicle.
Sulphate	36·0	28·91	44·4	28·94	56·0	28·58	28·8
Selenate	35·5	36·17	43·7	36·24	55·1	35·99	36·1
Double Sulphate (Zn)	40·2	155·96	49·5	156·08	62·4	155·57	155·9
Double Selenate (Zn)	40·5	168·30	49·9	168·45	63·0	167·77	168·2
Perchlorate	27·6	27·31	34·0	27·33	42·8	27·25	27·3
Permanganate ...	20·8	37·7	25·6	37·6	32·3	37·7	37·7
$C_6H_4.COOH.COOM$	21·5	103·3	26·5	103·1	33·4	103·3	103·2
Metaperiodate ...	29·8	33·9	36·7	33·9	—	—	—
Bichromate	59·3	50·9	72·9	50·9	—	—	—

the ratios given by Rb–K and Cs–K. The calculation can also be made on any pair of salts for which isomorphism has been fully proved on

crystallographic grounds, and two examples of this class are included in Tables I and II.

B. *Series containing sodium and lithium.*

These salts are very rarely isomorphous with those of potassium, but several isomorphous pairs are available for sodium and lithium, and partial volumes can be calculated from the free metals by the method already used for potassium and rubidium. The values are given in Table III.

Table III.   *Molecular volumes of isomorphous salts of Li, Na.*

Type.	Li.	Na.	Diff.	Calculated volumes. Li.	Na.	Radicle.
Metal [1]	13·0	23·7	10·7	—	—	—
LiCl [2]	20·39	26·72	6·33	7·69	14·02	12·7
LiBr [2]	24·90	31·97	7·07	8·59	15·66	16·3
LiI [2]	32·75	40·72	7·97	9·69	17·66	23·1
Li_3PO_4 [2] ...	48·1	64·7	16·6	20·15	36·75	27·95
$Li_2S_2O_6.2H_2O$ [2] ...	97·5	110·7	13·2	16·04	29·24	81·5
LiF [2]	11·3	16·4	5·1	6·2	11·3	5·1
Li_2O [3]	16·6	27·6	11·0	13·3	24·4	3·3
Li_2S [4]	27·9	41·95	14·05	17·07	31·12	10·8

C. *Isomorphous series derived from the halogens Cl, Br, I.*

Next to the alkali metals, these elements probably afford the best example of eutropic isomorphism. Data for a number of isomorphous series are collected in Table IV. Here the ratio (I–Cl)/(Br–Cl) is

Table IV.   *Molecular volumes of isomorphous salts of Cl, Br, I.*

	Cl.	Br.	I.	Br–Cl.	I–Cl.	$\frac{I-Cl}{Br-Cl}$
K [2]	37·11	42·90	52·57	5·79	15·46	2·67
Rb	42·80	48·90	59·07	6·10	16·27	2·67
Cs	41·80	47·40	56·85	5·60	15·05	2·69
Li	20·39	24·90	32·75	4·51	12·36	2·74
Na	26·72	31·97	40·72	5·25	14·00	2·67
$Ba(X_2)$ [5]	54·1	62·2	76·0	8·1	21·9	2·70
$Ca(X_2)$ [5]	51·6	59·6	74·3	8·0	22·7	2·84

[1] See Landolt-Börnstein, Physikalisch-chemische Tabellen, 1920 edition.
[2] Values taken from P. Groth, loc. cit.
[3] J. W. Mellor, Treatise on inorganic chemistry.
[4] Values obtained from X-ray measurements, A. Claassen, Recueil Trav. Chim. Pays-Bas, 1925, vol. 44, pp. 790–794. [Min. Abstr., vol. 3, p. 245.]
[5] Landolt-Börnstein, loc. cit. No crystal measurements available.

constant in exactly the same way as the ratio $(Cs–K)/(Rb–K)$ in
Table I. The volumes will therefore be given by expressions of the type
$V(\text{salt}) = a'V(\text{halogen}) + C'$, where a' and C' depend only on the
metal, and $V(\text{halogen})$ is the volume the free halogen would have in an
isomorphous series. The solid series is not known, but estimates of the
relative volumes can be obtained from the salts of the alkali metals.
These require more detailed discussion, for the values tabulated by
Groth (Table Va) show a small but definite increment in the differences
along the series.

Table Va.   Molecular volumes of alkali halides.[1]

		Cl.	Diff. (Br–Cl).	Br.	Diff. (I–Br).	I.
K ...	...	37·11	5·79	42·90	9·67	52·57
(Rb–K)	...	5·69	—	6·00	—	6·50
Rb ...	...	42·80	6·10	48·90	10·17	59·07
Li ...	...	20·39	4·51	24·90	7·85	32·75
(Na–Li)	...	6·33	—	7·07	—	8·00
Na ...	...	26·72	5·25	31·97	8·75	40·72

It is evident that the formulae given do not hold good absolutely in
these series; the ' constants ' are apparently undergoing a progressive
change. But this change could be eliminated if the data were observed
under suitably graduated conditions of temperature and pressure; it
would seem, therefore, that in this rather extreme case the ' corre-
sponding states ' should be defined even more closely than is done by
taking the volumes of isomorphous salts at normal temperature and
pressure.

So great an increment in the differences is exceptional; only a rela-
tively small change occurs on the substitution of K, Rb, Cs, and of S, Se
in the sulphates and selenates (Table I). It would seem, therefore, to be
associated rather with the marked gradation of properties in chlorine,
bromine, and iodine than with any peculiarity in the alkali metals;
comparable conditions will therefore most probably be obtained by taking
the volumes of the chlorides, bromides, and iodides under conditions of
progressively greater compression chosen so as to eliminate the increase
in the differences. This requires that the bromides of K, Rb should be
compressed in the ratio of $6·00/5·69$ and the iodides in the ratio
$6·5/5·69$. The result of this correction is shown in Table Vb. The
differences are now substantially equal and the usual method of calcula-

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[1] See P. Groth, Chemische Krystallographie, 1906, vol. 1, pp. 165, 166.

tion can be applied, yielding the partial volumes given in Table V c. A similar correction is required for the corresponding salts of sodium and lithium (also given in Table V), which then yield an independent estimate for the relative volumes of the halogens.

Table V b.   Molecular volumes of alkali halides after compression of bromides and iodides.

			Cl.	Diff. (Br–Cl).	Br.	Diff. (I–Br).	I.
K	...	...	37·11	3·54	40·65	5·35	46·00
(Rb–K)		...	5·69	—	5·75	—	5·70
Rb	...	...	42·80	3·60	46·40	5·30	51·70
Li	...	...	20·39	1·91	22·30	3·63	25·93
(Na–Li)		...	6·33	—	6·31	—	6·30
Na	...	...	26·72	1·89	28·61	3·62	32·23

Table V c.   Partial volumes in alkali halides (after compression).

			Metal.	Cl.	Br.	I.
K	...	...	24·65	12·46	16·00	21·35
Rb	...	...	30·35	—	—	—
Li	...	...	7·69	12·70	14·61	18·24
Na	...	...	14·02	—	—	—

This method of correction is, of course, only approximate, the general result being to minimize the increment in volume along the halogen series, but it may be of interest to compare various estimates for the relative volume of the halogens.

Relative volumes of the halogens.

			In Halides.			Elements.
			Richards.[1] Mean N. T. P.	A. F. H. Mean N. T. P.	Mean corr.	Observed values at boiling-point.[2]
Cl ...	...		13·3	12·4	12·6	21·7
Br ...	...		17·1	16·6	15·3	27·0
I ...	...		—	23·8	19·8	37·0

The apparent expansion of the bromides and iodides renders it difficult to employ the equations given at the beginning of this section to calculate partial volumes for the halogens in these salts. It would seem necessary in each case first to apply a correction for the change in pressure along the series ; this unfortunately has a rather pronounced effect on the differences, so that the accuracy of the estimate of the size of the halogen

[1] T. W. Richards, Journ. Amer. Chem. Soc., 1923, vol. 45, pp. 422–437.

[2] See J. W. Mellor, Treatise on inorganic chemistry, 1922, vol. 2, pp. 50 and 66.

is adversely affected ; only a rough estimate could be obtained by using the average values for the elements in the above table, and it seems better, when possible, to rely on the indirect estimate obtained by difference after calculating the volume occupied by the metal in the manner given for the alkalis.

General considerations.

The data here examined seem to indicate the operation of two general principles : first, that *in any two isomorphous salt-series formed from the same group of eutropic elements the volume of an element in one series bears to its volume in the other series a ratio which is the same for all members of the group,* and, second, *the eutropic replacement of one element by another of different volume does not alter the volume of the rest of the molecule.* It is very difficult to reconcile the close accuracy of these additive relations with the conception of the crystal as a structure of hard spheres ; for there is no indication of a ' co-volume ' which should represent the interstitial spaces. On the other hand, simple additive relations of this type would be entirely consistent with a structure built up of atoms which behave as if plastic and perfectly deformable under the stress of neighbouring atoms, but have only the small degree of compressibility common to the solid state. This mode of treatment, though perhaps somewhat at variance with the usual method of treating the atoms as hard spheres with interspaces, possesses certain advantages in dealing with other properties of crystals. For example, topic axes in an isomorphous group may vary in an apparently arbitrary manner while the volume is additive in accordance with the law of Retgers. This would imply that deformation of the lattice in two directions must always be compensated by an adjustment of the third axis, a result which lends itself to numerical treatment in accordance with the idea of a plastic atom. These considerations, though of a general character, seem to lend a measure of support to the view that the space-lattice might be treated as an aggregate of plastic atoms, of which the volume is relatively fixed ; the volume of the atom itself being subject to variation with temperature and pressure, and also to discontinuous changes corresponding with the state of chemical combination.