On the atomic volume relations in certain isomorphous series. II.

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THE isomorphous replacement of one element by another, in a pair of crystalline salts, is usually accompanied by a substantial change in the molecular volume. This progression is exceptionally well illustrated in the 'eutropic' elements K, Rb, Cs, and Cl, Br, I, which formed the subject of the first part of this paper.[2] It was there shown that the differences produced by interchanging these elements stood in the same ratio in all the salt-series, though the size of the differences varied with the acid radicle. The object of the present note is to draw attention to the existence of similarly constant (though different) ratios for the salts of O, S, Se, Te, and for the salts of Ca, Sr, Ba. The spacings in these compounds have recently been obtained by X-ray determinations, in many cases due to V. M. Goldschmidt and his co-workers, so that it is possible to verify the rule of proportional differences in these series, although the results do not possess an accuracy so high as that of densities measured by the pyknometer. The molecular volumes given in the following tables are calculated from the dimensions of the unit cell, as indicated by Wyckoff,[3] the real volumes being divided by 1.65×10^{-24} in order to reduce them to the ordinary chemical notation ($V = M/d$).

Table VI contains data for the oxides, &c., of the calcium metals. These form an unusually complete group which will be discussed before the general tables VII and VIII, which contain other salts of the two series.

The figures in the last column indicate a nearly constant ratio between the differences due to the interchange of the metals; the values in the lower lines show that a similar constancy holds good for the acidic elements, and is equally valid for oxygen, the fourth member of the group.

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[1] Communicated by permission of the Director.
[2] A. F. Hallimond, Min. Mag., 1927, vol. 21, pp. 277–284 (Tables I–V).
[3] R. W. G. Wyckoff, The structure of crystals, 1924, p. 203.

The differences themselves show a progressive increase as the size of the unit cell increases.

Table VI.   Molecular volumes of compounds of Ca, Sr, Ba, with O, S, Se, Te (sodium chloride structure).[1]

Type.		Ca.	Sr.	Ba.	Sr–Ca.	Ba–Ca.	$\dfrac{\text{Ba–Ca}}{\text{Sr–Ca}}$
CaO	...	16·76	20·64	25·64	3·88	8·88	2·29
CaS	...	27·85	32·85	39·10	5·00	11·25	2·25
CaSe	...	31·30	36·54	43·03	5·24	11·73	2·24
CaTe	...	38·65	44·50	51·63	5·85	12·98	2·22
Se–S	...	3·45	3·69	3·93			
Te–S	...	10·80	11·65	12·53			
$\dfrac{\text{Te–S}}{\text{Se–S}}$	...	3·13	3·16	3·19			
S–O	...	11·09	12·21	13·46			
Te–O	...	21·89	23·86	25·99			
$\dfrac{\text{Te–O}}{\text{S–O}}$	...	1·97	1·95	1·93			

A few other isomorphous series are available for these elements, and these are given in Tables VII and VIII.

Table VII.   Molecular volumes of isomorphous salts of Ca, Sr, Ba.

Type.			Ca.	Sr.	Ba.	Sr–Ca.	Ba–Ca.	$\dfrac{\text{Ba–Ca}}{\text{Sr–Ca}}$
Free Metal [2]	...	...	25·9	36·0	[48·6]	10·1	[22·7]	—
CaF$_2$ [3]	...	...	24·55	29·3	35·85	4·75	11·30	2·38
CaTiO$_3$ [4]	...	...	34·6	36·5	37·9	1·9	3·3	(1·7)
							Ba–Sr.	
SrSO$_4$ [5]	...	...	—	46·18	51·96	—	5·78	—
SrCO$_3$ [5]	...	...	—	39·87	45·82	—	5·95	—
Sr(NO$_3$)$_2$ [6]	...	...	—	71·0	80·4	—	9·4	—
CaSiO$_3$ [5]	...	...	40·11	44·91	—	4·80	—	—
CaC$_2$ [7]	...	...	28·9	35·0	43·0	6·1	14·1	2·31

[1] V. M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente, VIII. Skrifter Norske Vidensk.-Akad. I. Mat.-nat. Kl. Oslo, 1927, no. 8 (for 1926), p. 20. [Min. Abstr., vol. 3, p. 326.]

[2] J. W. Mellor, Treatise on Inorganic Chemistry, 1923, vol. 3, p. 631.

[3] V. M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente, VIII. 1927, p. 56.

[4] V. M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente, VII. 1926, p. 79. Retaining the earlier (comparable) value for CaTiO$_3$.

[5] P. Eskola, Amer. Journ. Sci., 1922, ser. 5, vol. 4, p. 370.

[6] P. Groth, Chemische Krystallographie, 1908, vol. 2, p. 104.

[7] J. W. Mellor, Treatise on Inorganic Chemistry, 1924, vol. 5, p. 860.

Table VIII.　Molecular volumes of isomorphous salts of O, S, Se, Te.[1]

Type.	O.	S.	Se.	Te.	Se–S.	Te–S.	$\frac{\text{Te–S}}{\text{Se–S}}$.
Zinc-blende structure :							
BeS ...	—	17·34	20·45	26·82	3·11	9·48	3·05
ZnS ...	—	24·08	27·50	34·20	3·42	10·12	2·96
CdS ...	—	29·91	33·40	40·90	3·49	10·99	3·15
HgS ...	—	30·05	33·85	40·39	3·80	10·34	2·72
Sodium chloride structure (see also Table I) :							
MgO ...	11·28	21·16	24·55	—	3·39		
CdO ...	15·63	—	—	—			
PbS ..	—	31·30	34·99	40·45	3·69	9·15	2·48
MnO ...	13·22	21·05	24·55	—	3·50		
Cadmium iodide structure :							
TiS₂ ...	—	34·45	39·14	48·6	4·69	14·15	3·02

Partial volumes can be calculated by applying the rule of proportional differences to the metals and salts in Tables VI and VII, in the manner already used for the alkali compounds. The values for the free metals are not yet accurately established and isomorphism has not been fully proved. The value for barium has been calculated proportionately and is given for the purpose of comparison with the salts ; the only recorded volume, 36·16, appears improbable, for it is nearly identical with the volume of metallic strontium. Using the values for Ca and Sr, the resulting volumes are shown in Table VII a ; the remainders, representing the volumes of the negative elements or groups, correspond fairly closely with the values deduced for the same constituents in the alkali salts (Part I).

Table VII a.　Calculated volumes of elements in salts of Ca, &c.

Type.	Ca.	Sr.	Ba.	Radicle.
CaF₂	12·2	16·9	22·8	12·5
CaTiO₃	3·8	5·2	7·0	31·0
SrSO₄	—	16·5	22·3	29·7
SrCO₃	—	17·0	23·0	19·8
Sr(NO₃)₂	—	26·9	36·2	44·2
CaO	10·1	14·1	19·0	6·5
CaS	12·8	17·8	24·1	15·0
CaSe	13·4	18·6	25·1	17·0
CaTe	14·8	20·6	27·8	23·9
CaSiO₃	12·3	17·1	—	27·8
CaC₂	16·1	22·4	30·2	12·8

[1] See V. M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente, VIII. 1927, pp. 144, 146, 147.

The volumes for O, S, Se, Te, correspond closely with those of spheres having J. A. Wasastjerna's radii O $= 1.32$ Å., &c.; the metals are larger than those of Goldschmidt, since their volume includes that which would be assigned to interstitial spaces in a structure of hard spheres.

Relation to the law of constant atomic radii:—Data including those quoted in Tables VI and VIII have been discussed by V. M. Goldschmidt[1] from the standpoint of Bragg's law of constant atomic radii. From an extensive series of X-ray measurements, Goldschmidt[2] obtains the radii of the chemical elements by difference, starting with the assumption that the radius of oxygen is 1.32 Å., a figure derived by J. A. Wasastjerna from considerations relative to the refractive power of certain compounds. The radii are, in fact, not strictly additive, and it is of interest to compare the extent to which the molecular volumes deviate from the ideal conditions represented on the one hand by a law of constant atomic radii, and on the other by one of constant atomic volumes. If the volume of each atom remains the same throughout a series of isomorphous compounds, the differences produced by substituting an element of volume V_1 for one of volume V_2 should be constant, no matter what may be the size of the unit cell. With constant radii, on the other hand, the volume of the unit cell in the sodium chloride lattice is $8a^3$ where $a = r_1 + r_2$, the radii of the two atoms. If an atom of radius $r_2 + \delta$ is substituted for r_2, the volume of the cell is increased to $8(a + \delta)^3$; if δ is small this is approximately $8(a^3 + 3\delta a^2)$, i. e. the difference in the volume is $24\delta a^2$. The volume-difference in this case varies with the size of the cell, so that in cells with volumes V_1 and V_2 the ratio of the differences (d_1 and d_2) produced by a given substitution should be approximately $d_1/d_2 = a_1^2/a_2^2 = (V_1/V_2)^{\frac{2}{3}}$. In the following table the second column shows the difference produced by substituting one element for another in a small cell; the third column, the difference produced by the same substitution in a larger cell. Column 4 shows the ratio of these differences, and column 5 the ratio required by a law of constant radii.

The difference increases with the cell-size, but the increment never attains the proportion required for constant radii. The ratio d_2/d_1 varies from near unity up to $(V_2/V_1)^{\frac{1}{2}}$ (last column), and this would seem to represent the limit of the anomaly. Considered from the standpoint of a law of constant radii, the cells must be supposed to exhibit an

[1] V. M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente, VIII. 1927, p. 57, &c.
[2] V. M. Goldschmidt, op. cit., No. VII, p. 15.

Table IX.   Effect of substitution in cells of varying size.

Substitution.	Difference produced by substitution in compounds with:		$\dfrac{d_2}{a_1}$.	$\left(\dfrac{V_2}{V_1}\right)^{\frac{2}{3}}$.	$\left(\dfrac{V_2}{V_1}\right)^{\frac{1}{2}}$.
Sodium chloride lattice :	Cl.	I.			
Rb–K	5·69	6·50	1·14	1·24	1·18
Na–Li	6·33	8·00	1·26	1·34	1·25
	O.	Te.			
Sr–Ca	3·88	5·85	1·51	1·73	1·51
Ba–Sr	5·00	7·13	1·43	1·64	1·45
	Mg.	Ba.			
Se–S	3·39	3·93	1·16	1·47	1·33
S–O	9·88	13·46	1·36	1·60	1 42
	S.	Te.			
Sr–Ca	5·00	5·85	1·17	1·23	1·17
	Ca.	Ba.			
Se–S	3·45	3·93	1·14	1·24	1·18
Zinc-blende lattice :	S.	Te.			
Cd–Zn	5·83	6·70	1·15	1·24	1·18
	Be.	Cd.			
Se–S	3·11	3·49	1·12	1·42	1·30

anomalous expansion as the atoms become more closely spaced. From the standpoint of a law of constant volumes, on the other hand, the deviation would be regarded as a contraction of the smaller cells, in a manner which suggests that close-spaced compounds like the oxides are subject to a somewhat greater relative pressure than, say, the tellurides.

The present series offers an extreme example of isomorphism between compounds differing in molecular volume, and of the anomalous increment in the differences. Very frequently, as in the alkali sulphates, the differences are closely the same for all sizes of cell, and the volumes can be represented as strictly additive. Moreover, according to the law of Retgers, the molecular volume is additive in a series of isomorphous mixtures. If, as is generally supposed, the relation between neighbouring atoms in a mixed crystal of the present type is of the same nature irrespective of the chemical molecules to which they may belong, it is perhaps more consistent to extend the law of additive volumes to the constituent atoms, treating the above results as minor deviations from the well-established rule, rather than to regard both and those for all other crystals as deviations from a law of constant radii.