

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

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ACCURATE knowledge of the compressibility of solids was first due in a large measure to the investigations of T. W. Richards, who showed that the pressure-volume curves for sodium and potassium approximate in form to rectangular hyperbolae,² that the compressibilities of the free alkali metals are nearly proportional to the atomic volumes, and that the atoms can be treated as filling the available space. Richards then endeavoured to calculate the relative volumes of the combined elements in the alkali halides, assuming that the large contraction which takes place on forming the compound was due to an internal pressure which affected equally the alkali metal and the halogen. The values obtained in this special case agree with those obtained in other ways, but Richards pointed out that his proposed method was not of general application; consideration of a wider range of compounds showed that the partial volumes of the elements in combination could not be derived solely by the operation of a common internal pressure, but must be influenced also by factors

¹ Communicated by permission of the Director. Previous papers of this series in *Min. Mag.*, 1927, vol. 21, p. 277; 1928, vol. 21, p. 480.

² T. W. Richards, *Journ. Amer. Chem. Soc.*, 1923, vol. 45, pp. 422-437. Additional data for the compressibilities have been made available in the observations of Adams, Johnson and Williamson, Bridgeman, and Slater. The data were studied extensively by Richards in a series of papers of which a brief account is given in *Trans. Faraday Soc.*, 1928, vol. 24, pp. 53-164, 165-179. A fuller account will be found in *Journ. de Chimie Physique*, February, 1928, vol. 25, pp. 83-119. News of the death of this distinguished investigator was received only a few weeks after the latter summary appeared ('*Nature*', May 5, 1928). In his later work Richards developed the formula $pv = k$ into relationships of the type $(p+II)(v-b) = k$, but for the present purpose the simpler formula affords an extensive agreement with the data, and will be used as a first approximation to the real form of the pressure-volume curve.

affecting each element independently: for example, by the state of chemical combination.

In the earlier sections of the present paper the volume-relations of the salts derived from certain eutropic series of elements were shown to be consistent with the assumption that when the atoms in a eutropic series are combined with a given radicle, their volumes are related by a common factor to the corresponding volumes in the free state or when combined with another radicle. This at once suggests a further analogy with the behaviour of a perfect gas under varying temperature and pressure, and it has therefore seemed of interest to examine upon what conditions the volume-relations can be reconciled with the known data for the compressibility of the elements. It will be shown that pressure-volume relations of the type $pv = k$, already proved experimentally by Richards for the free alkali metals, can be used also to calculate the volumes and compressibilities of the alkali halides, by adopting a different value of k for the eutropic series of elements in the combined state. The combined elements behave to a close approximation as regions of a perfect gas which together completely fill the crystal lattice, without interstitial spaces.

Relevant formulae.—The properties of the equation $pv = k$ are, of course, well known. The curves form a family of rectangular hyperbolae, the compressibility being given by $\beta = 1/v \cdot dv/dp = -1/p$. The compressibility is thus independent of k , i. e. it is the same for all the hyperbolae at a given pressure. The corresponding internal pressure for an element can therefore be assigned at once as approximately the reciprocal of the compressibility. For a gram atom, $K = pV = -V/\beta$, where V is the atomic volume; thus the compressibilities of substances with K in common are proportional to the atomic volumes, as was shown experimentally by Richards for the eutropic alkali metals.

Direct compression of the alkali metals.—For $pv = k$, $\log p + \log v = \log k$. If the 'internal pressure' of an element is given by $-1/\beta$ (above) this value must be added to the external pressure applied. Bridgeman's data are quoted in the table below. For the first 1,000 megabars, for sodium, $\beta = -15.0 \times 10^{-6}$ per megabar; for potassium, $\beta = -33.0 \times 10^{-6}$. The corresponding pressures ($-1/\beta$) are 66.65 and 30.31 thousand megabars. These have been added to the external pressures applied, which ranged from 0 to 12,000 megabars.

Sodium (30° C.). ¹			Potassium (45° C.). ¹		
<i>p.</i>	<i>v.</i>	log <i>p</i> + log <i>v.</i>	<i>p.</i>	<i>v.</i>	log <i>p</i> + log <i>v.</i>
66	1.0000	1.8238	30	1.0000	1.4816
68	0.9701	1.8234	32	0.9385	1.4817
70	0.9430	1.8236	34	0.8905	1.4850
72	0.9181	1.8241	36	0.8496	1.4892
74	0.8950	1.8248	38	0.8123	1.4930
76	0.8737	1.8259	40	0.7778	1.4964
78	0.8535	1.8269	42	0.7456	1.4989

The total in the last columns at first diminishes and then steadily increases. Closer constancy is obtained over the higher pressures if somewhat higher internal pressures are assigned to the metals, so that the values become those given in the following table :

Sodium (30° C.).			Potassium (45° C.).		
<i>p.</i>	<i>v.</i>	log <i>p</i> + log <i>v.</i>	<i>p.</i>	<i>v.</i>	log <i>p</i> + log <i>v.</i>
74	1.0000	1.8692	37	1.0000	1.5682
79	0.9303	1.8663	42	0.8694	1.5620
81	0.9063	1.8658	44	0.8305	1.5627
83	0.8841	1.8656	46	0.7947	1.5630
86	0.8535	1.8657	49	0.7456	1.5627

Over the latter half of the range of applied pressure the agreement is now almost perfect. As the pressure falls to atmospheric, the volume increases slightly above that required by $pv = k$, but the extent of this deviation is remarkably small, being of the order of 1 % of the volume. The internal pressures are, for sodium, 74,000 megabars; for potassium, 37,000 megabars. For a gram atom, for sodium, $K = 1.70 \times 10^6$; for potassium, $K = 1.76 \times 10^6$.

Relation of compressibility to atomic volume in eutropic series.—The degree of constancy of K in each series may be seen from the following values :

Element.	Atomic volume.	Compressibility per megabar ($\times -10^6$).	$K = -V/\beta$ ($\times 10^{-6}$).
Cs	70.5	61	1.18
Rb	55.9	40	1.40
K	45.4	31.7	1.43
Na	23.7	15.6	1.52
Li	13.0	9.0	1.44
K	45.8	(27.0)	1.70
Na	23.7	(13.5)	1.76
Ag	10.23	0.97	10.5
Cu	7.08	0.75	9.4
Sr	36.0	8.35	4.31
Ca	25.9	5.84	4.44
Cd	12.98	2.24	5.8
Zn	9.02	1.74	5.18

¹ P. W. Bridgeman, Proc. Amer. Acad., 1923, vol. 58, pp. 165-242.

The two additional values for sodium and potassium are those derived above from the data at higher pressures; they indicate that the curves for the two elements approach tangentially to the same hyperbola, with which they appear to coincide under high pressure.

For the other alkali metals the values for K , though somewhat lower than the preceding because they were obtained by using the compressibilities at atmospheric pressure, point to a similar relation: the pressure-volume curves coincide very closely with one hyperbola for which $pV = 1.7$. The same is true in the other eutropic groups, though the values for K differ widely. The constancy of K offers a definition of eutropy which is alternative to that based upon the rule of proportional differences (Part I, p. 279).

In this connexion it may be of interest to consider for a moment the properties of the various substances in one of the large isostructural groups. As an example, there is in Ewald's 'Strukturbericht'¹ a very full list of substances that crystallize in the face-centred cubic lattice. Structurally, from the standpoint of X-ray research, the space-lattice is the same in all cases, so that they form an isostructural or 'homotaxial' group. But it will be seen from the following table that, when classified according to the values of K , they fall into sub-groups which correspond with the eutropic series, though in some cases only one member of a series may be represented.

Type A 1.—

Element	...	Cu.	Ag.	Au.	Ca.	Al.	Pb.
K	...	9.4	10.5	17.3	4.4	7.3	7.62
Element	...	Co.	Ni.	Rh.	Pd.	Ir.	Pt.
K	...	20.4	20.2	35.8	27.4	50.8	40.3

Rate of change of compressibility.—For $pv = k$, the rate of change of β is given by $d\beta/dp = -d/dp(1/p) = \beta^2$. The change is not very easily measurable. Even for sodium and potassium the changes in β per 1,000 megabars are only 6 and 34 units in the third significant figure. Values taken directly from the observed pv curves (see below) show that at high pressures the second differential, like the compressibility, is in agreement with the value required by the simple formula, i. e. the pv curve really coincides with the ideal hyperbola; but at low pressures the upward trend of the observed curve, already noted, is most clearly evidenced in the difference between the observed values for $d\beta/dp$ and those calculated (β^2) for the tangent hyperbola.

¹ Zeits. Krist., 1927, vol. 65, appendix, p. 14.

Rate of change of compressibility for Na and K.

	$\beta \times 10^6$ (observed).	$d\beta/dp \times 10^9$ (observed).	$\beta^2 \times 10^9$
Na at 10,000 megabars ...	11.4	0.2	0.13
K „ „ „ „ ...	21.7	0.6	0.47
Na at atmosphere ...	15.3	0.6	0.24
K „ „ „ „ ...	33.0	3.4	1.09

The metals behave as though they contained small amounts of included gas, which become negligible at higher pressures; but the volume to be assigned, about 1 %, seems higher than could be due to such a cause, and it is probable that the effect is a true property of the crystal, possibly related to the heat movements of the atoms, which still have an appreciable amplitude.¹

The existence of a general, possibly single-valued, relation between the compressibility of the elements and the rate of change of compressibility with pressure has been suggested by Adams.² For $pv = k$, $d\beta/dp = \beta^2$, a relation independent of the nature of the element. Adams plotted the difference $\Delta\beta$ due to a change in pressure of 10,000 megabars; in this case $\Delta\beta = \Delta p/p_0(p_0 + \Delta p) = \Delta p\beta_0/(1/\beta_0 + \Delta p)$, a relation also independent of the nature of the element. As Adams remarks, the uncertainty of the data prevents a rigorous comparison; the values of $\Delta\beta$ for the less compressible elements are still of the right order, but they are larger than is required by theory, probably owing to the same cause as the corresponding anomaly for the alkali metals near atmospheric pressures.

Calculation of compressibility for the alkali halides.—At first it appears surprising that, while the compressibility of metallic potassium is -33×10^{-6} , that of potassium chloride is only -5.6×10^{-6} . It is true that the volume calculated for the metals in these salts is only about half that in the free state; but if the metals are compressed along their hyperbola to about half their volume, as Richards at first suggested, their compressibility is only reduced to about half its initial value, and is still much too high. It will be shown, however, that a simultaneous solution for both volumes and compressibilities can be obtained if the whole group of metals is removed to another hyperbola, i. e. if the effects of chemical combination and of removal to another space-lattice are comprised in an alteration of the con-

¹ R. W. James and Elsie M. Firth, Proc. Roy. Soc. London, Ser. A, 1927, vol. 117, pp. 62–87.

² L. H. Adams, Journ. Washington Acad. Sci., 1927, vol. 17, pp. 529–533.

stant K , the volumes being diminished proportionally in accordance with the rule of proportional differences. If v_1 is the new value of V and K_1 the corresponding new value of K , the compressibility of the metal is given by $\beta_1 = -v_1/K_1$. The compressibility for the halogen can then be calculated from the observed compressibility of the salt. For an arbitrary new value of K for the metals, the compressibilities that must be assigned to the halogens are usually quite improbable, being often negative; but the following table will show that for the special value $K_1 = 4.0$ for the metals, a consistent set of values is obtained for the compressibilities of the halogens in the alkali halides, these in their turn being subject to a relation, $pv = K_2$, where K_2 is a constant for the eutropic series F, Cl, &c.

*Partial volumes and compressibilities in the alkali halides.*¹

Salt.	Partial volumes.		$\beta_1 = -v_1/K_1$		β_2 (Halogen).	
	Metal.	Halogen.	(Metal). $(K_1 = 41 \times 10^6)$ $\times -10^6$.	Observed. $\times -10^6$.	Calculated. $\times -10^6$.	K_2 (Halogen). $\times 10^{-6}$.
LiF	6.2	5.1	1.55	1.53	1.5	3.4
LiCl	7.7	12.7	1.92	3.41	4.3	2.95
LiBr	8.6	16.3	2.15	4.31	5.4	3.02
NaCl	14.0	12.7	3.50	4.20	5.0	2.54
NaBr	15.7	16.3	3.92	5.08	6.2	2.63
KF	18.16	4.6	4.54	3.31	—	—
KCl	24.6	12.5	6.15	5.63	4.6	2.72
KBr	26.0	17.0	6.50	6.70	7.0	2.42
KI	28.1	24.5	7.02	8.54	10.3	2.38
RbBr	32.0	17.0	8.00	7.94	7.8	2.18
RbI	34.6	24.5	8.65	9.58	10.89	2.25

The first column shows those halides for which data are available. Columns 2 and 3 give the partial volumes calculated by the rule of proportional differences (Part I of the present paper). According to the theory just outlined, the compressibilities of the metals should be calculable from the volumes by the relation $\beta_1 = -v_1/K_1$. The most satisfactory value of K_1 for the metals in these salts is found by trial to be 4.0,² and the resulting compressibilities are shown in column 4. The observed compressibility of the crystal (column 5) will be the mean (weighted for the relative volumes concerned) of those for the metal and the halogen. The values required for the compressibilities of the combined halogens can thus be calculated and are those shown

¹ J. C. Slater, *Physical Review*, 1924, vol. 23, pp. 488–500.

² Both 3.5 and 4.5 lead to less satisfactory results for the halogens.

in column 6. These in their turn should be related to the partial volumes of the halogens (column 3), so that $-v_2/\beta_2 = K_2$; for the halogens are, like the metals, a eutropic group of elements. Column 7 contains the values of K_2 ; in view of the wide range of the data the constancy appears satisfactory; a small diminution in K_2 is probably the result of the anomalous increment in the volume-differences (Part I, p. 282), for the volumes are not perfectly additive in this very wide isomorphous series. An irregular value for potassium fluoride is almost certainly due to a special cause, possibly a slight error in the reported data.

A very interesting confirmation of the compressibilities here assigned to the alkali metals (in the halides) is the estimate given by L. H. Adams and E. D. Williamson,¹ who find by direct computation that the compressibility of K_2O and Na_2O in certain minerals must be about 6.0×10^{-6} . The volumes here assigned to the metals in the halides do not greatly differ from those in the minerals in question (mica,² &c.), being in both cases about half those in the free state; it is therefore permissible to compare this value—a rough average—with the figures 6.5 and 3.5 for potassium and sodium in the foregoing table.

¹ L. H. Adams and E. D. Williamson, *Journ. Franklin Inst.*, 1923, vol. 195, p. 494.

² A. F. Hallimond, *Min. Mag.*, 1927, vol. 21, p. 204.
