The Compressibility of Solid Elements as Expressed in Terms of their Melting Points and Atomic Volumes

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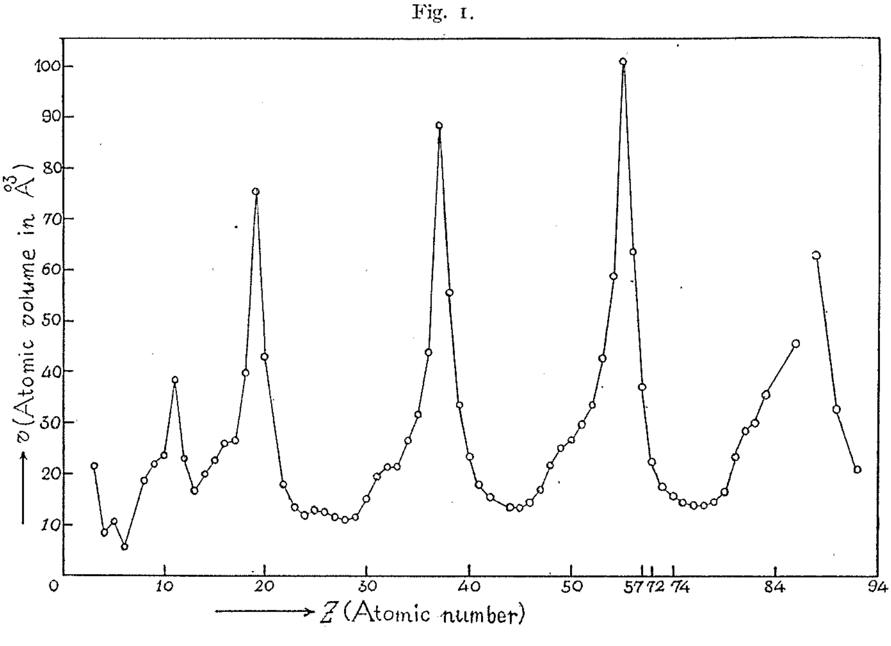
Abstract

The compressibility of solid elements is found to be expressed approximately in terms of their melting points, atomic volumes and atomic numbers by an empirical formula, which is more reasonable than that proposed by Richards.

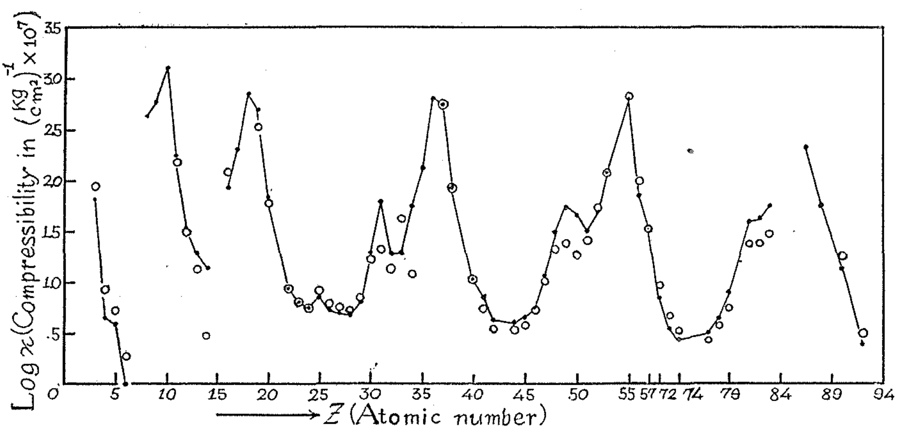
The compressibility of solid elements is a strongly periodic function of the atomic number, as was first pointed out by Richards. Besides the compressibility, the atomic volume of solid elements is also very clearly periodic with respect to the atomic number, as is seen in Fig. 1. In this and in the following three figures, all the rare earth elements other than lanthanum are omitted, so as to be in accord

Fig. 1.



with the periodic table of the elements; and the element hafnium of the atomic number 72 is arranged next to lanthanum whose atomic number is 57, As is seen in Fig. 1, the periodicity in the atomic volume is especially regular with the elements having the atomic numbers higher than 19, which belong to the long periods in the periodic table. The compressibilities of solid elements, which are measured at room temperature, are represented by small circles in Fig. 2. In this figure the logarithm to the base 10 of the compressibility is plotted, in order to get a manageable scale, against atomic number. The periodic change of the compressibility with atomic number

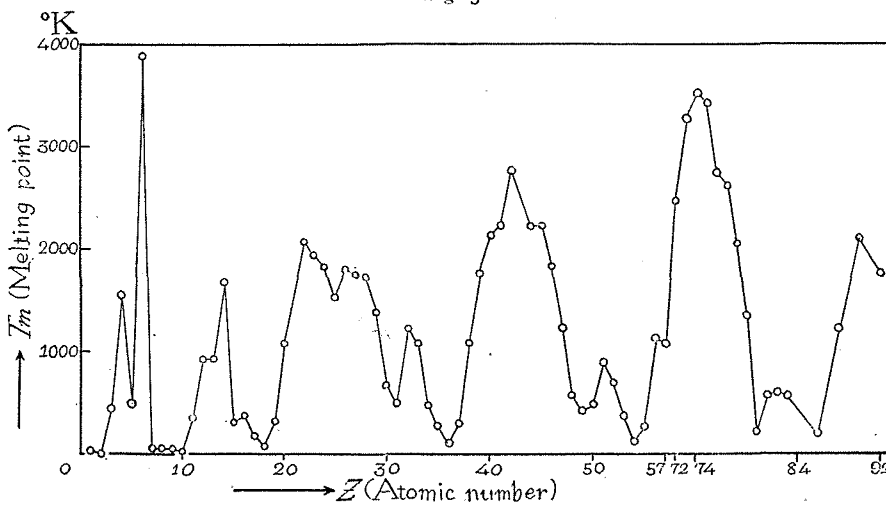
Fig. 2.



is also well revealed especially with the elements in the long periods; and it runs similarly in main features with atomic volume, by taking maxima at the positions of the alkali-metals and minima at the intermediate positions. However, this similarity is not perfect; and the general tendency of the compressibility to decrease in its value at the positions about its minima with increase of atomic number does not accord with the increase of the atomic volume about the positions of its minima with increase of atomic number. This shows that the compressibility of the solid elements can not be represented as a function of the atomic volume alone.

Besides the atomic volume, the melting point of the elements is also related to the compressibility, because the hardness is generally higher for an element whose melting point is higher. Fig. 3 shows the relation between the melting point and the atomic number of the elements. A general periodicity is also detected in this case. Alkali-

Fig. 3.



metals occupy the positions next to the minima which are occupied by rare gases, and the intermediate elements lie at the positions about the maxima, Moreover, the maxima of the melting points increase generally with atomic number. Taking this fact into consideration, the writers assumed that the compressibility $\varkappa$ is directly proportional to a certain power n of the atomic volume v and is inversely proportional to the melting point T_m, expressed in absolute scale. In order to get the value of n, $\varkappa T_m$, the products of the observed values of $\varkappa$ and T_m for the elements, were compared with their observed values of v, by plotting the logarithms of $\varkappa T_m$ and v in a graph; and from an approximately linear relation between the values of these logarithms the value of n was found to be about 1.5. The proportionality thus found between $\varkappa T_m$ and $v^{1.5}$ is only an approximation; and a small systematic increase of tbe value of $v^{1.5}/\varkappa T_m$ with increase of the atomic number Z was clearly detected. Thus $v^{1.5}/\varkappa T_m$ was assumed to be proportional to $a(1+\beta Z)$, and the values of a and β were obtained by plotting the values $v^{1.5}/\varkappa T_m$ and Z in a graph.

The observed values of v, T_m, $\varkappa$ and $\log \varkappa$ for the elements are tabulated in Tables I_a and I_b. The values of the melting point T_m were taken from Landolt-Boernstein's "Physikalisch-chemische Tabellen" and others. The values of the atomic volume v expressed in the unit of $Å^3$ per atom were taken mostly from Masing's "Handbuch der Metallphysik" (Bd. I, p. 43–62) for the elements whose atomic volumes were determined from their crystal structures; and for some other

Table I a.

Element	Atomic number Z	Atomic volume v in $Å^3$	Melting point T_m in °K	Compressibility $\varkappa_{obs.}$ in $\left(\frac{kg}{cm^2}\right)^{-1} \times 10^7$	$\varkappa_{calc.}$	$\log \varkappa_{calc.}$	$\log \varkappa_{obs.}$
H	1	37.3	15	—	—	—	—
He	2	3.5	1	—	—	—	—
Li	3	20.7	453	87.0	65.7	1.818	1.94
Be	4	8.2	1551	8.6	4.67	.669	.934
B	5	10.3	2573	5.5	3.96	.598	.740
C (graphite)	6	8.9	3870	1.8	.98	$\bar{1}.991$	.255
N	7	46.2	62	—	—	—	—
O	8	18.4	55	—	421	2.624	—
F	9	22.0	50	—	594	2.774	—
Ne	10	23.1	24	—	1313	3.118	—
Na	11	38.1	371	156	178.7	2.252	2.193
Mg	12	23.0	923	29.5	33.1	1.520	1.47
Al	13	16.5	931	13.4	19.5	1.29	1.127
Si	14	20.0	1693	3.1	14.25	1.154	.491
S	16	26	390	129	88.4	1.946	2.111
Cl	17	26.6	172	—	204	2.310	—
A	18	39.8	83	—	750	2.875	—
K	19	75.8	337	357	499	2.698	2.553
Ca	20	43	1078	57	64.9	1.812	1.756
Ti	22	17.7	2073	8.0	8.55	.932	.903
V	23	13.7	1953	6.1	6.14	.788	.785
Cr	24	11.9	1823	5.2	5.28	.723	.716
Mn	25	13.3	1518	7.9	7.4	.869	.898
Fe	26	12.2	1803	5.9	5.47	.738	.771
Co	27	11.2	1763	5.4	4.86	.687	.732
Ni	28	10.9	1725	5.3	4.65	.667	.724
Cu	29	11.8	1356	7.2	6.62	.821	.857
Zn	30	15.0	693	16.9	18.2	1.26	1.228
Ga	31	19.6	303	20	62.2	1.794	1.301
Ge	32	21.9	1231	13.8	17.8	1.25	1.14
As	33	21.7	1090	44	19.5	1.29	1.643
Se	34	26.9	493	11.8	59.2	1.772	1.072
Br	35	31.7	267	—	138	2.14	—
Kr	36	43.7	104	—	660	2.820	—
Rb	37	88.7	312	520	543	2.735	2.716

Table I b.

Element	Atomic number Z	Atomic volume v in $Å^3$	Melting point T_m in °K	Compressibility $\varkappa_{obs.}$ in $\left(\frac{kg}{cm^2}\right)^{-1} \times 10^7$	$\varkappa_{calc.}$	$\log \varkappa_{calc.}$	$\log \varkappa_{obs.}$
Sr	38	56	1073	82	78.3	1.894	1.914
Y	39	33.7	1763	—	—	—	—
Zr	40	23.4	2133	11	10.4	1.017	1.041
Nb	41	18.0	2223	5.7	6.67	.824	.756
Mo	42	15.5	2773	3.6	4.23	.626	.556
Ru	44	13.4	2223	3.4	4.15	.618	.531
Rh	45	13.6	2243	3.7	4.19	.622	.568
Pd	46	14.5	1823	5.3	5.6	.748	.724
Ag	47	17.0	1233	9.9	10.4	1.017	.996
Cd	48	21.4	594	22.5	30.2	1.48	1.343
In	49	25.1	427	25.0	52.8	1.723	1.398
Sn	50	27.0	505	18.8	49.0	1.69	1.274
Sb	51	29.7	903	27.0	31.6	1.50	1.431
Te	52	33.7	723	50.8	47.1	1.673	1.706
I	53	42.5	387	127	123.5	2.092	2.104
Xe	54	59.0	133	—	585	2.767	—
Cs	55	100.7	302	700	638	2.805	2.845
Ba	56	63.1	1123	102	75.3	1.877	2.009
La	57	37.0	1083	35	34.8	1.542	1.544
Hf	72	22.5	2480	9.0	7.16	.855	.954
Ta	73	17.7	3303	4.8	3.68	.566	.681
W	74	15.8	3543	3.2	2.87	.458	.505
Re	75	14.8	3440	—	—	—	—
Os	76	14.0	2773	—	—	—	—
Ir	77	14.0	2623	2.7	3.17	.501	.431
Pt	78	14.9	2048	3.6	4.42	.645	.556
Au	79	16.9	1336	5.8	8.09	.908	.763
Hg	80	23.2	234	37	—	—	—
Tl	81	28.5	573	22.8	40.7	1.610	1.358
Pb	82	30.0	600	23.7	41.4	1.617	1.375
Bi	83	35.2	545	29.2	57.7	1.761	1.465
Rn	86	45.6	202	—	224	2.350	—
Ra	88	62.3	1233	—	57.7	1.761	—
Th	90	32.8	2113	18.2	14.0	1.146	1.26
U	92	20.1	1773	9.7	8.34	.921	.987

elements they were calculated from the values of the densities and the molecular weights. As the compressibility of the solid elements which is measured at room temperature changes with pressure, its limitting value at zero pressure is adopted, and the values expressed in the unit of $\left(\frac{Kg}{cm^2}\right)^{-1}\times 10^7$ are tabulated in Tables I_a and II_b. These are taken from Bridgman's "The Physics of High Pressure". By taking the units of v and the compressibility $\varkappa$ as above, the empirical formula obtained for the relation between $\varkappa$, v, T_m and Z became

$$\varkappa=\frac{v^{1.5}}{0.003(1+0.0175Z)T_m}$$

The values of $\varkappa$ and $\log\varkappa$ which are calculated by this formula from the values of v, T_m and Z are tabulated in the 6^{th} and 7^{th} columns of the tables, and the values of $\log\varkappa$ for the observed values of $\varkappa$ are given in the last column of the tables. The values of $\log\varkappa$ thus calculated are represented by the dots in Fig. 2, where the successive dots are connected by the straight lines. When the positions of dots are compared with those of small circles representing the observed values of $\log\varkappa$ in Fig. 2, we see that the agreement between the observation and the calculation is, in main features, rather satisfactory for this kind of phenomenon, because the compressibility changes with temperature and pressure and is accompanied by a considerable amount of errors in its measurement. The unsatisfactory agreement is met within the elements belonging to the short periods in the periodic table, in the Ga ($Z=31$), Ge($Z=32$), As($Z=33$), Se($Z=34$) sequence, in the Cd($Z=48$), In($Z=49$), Sn($Z=50$) sequence, and in the Tl($Z=81$), Pb($Z=82$), Bi($Z=83$) sequence.

There is no direct measurement reported on the compressibilities of rare gases, but they are supposed by Bridgman[1] to be much higher than those of other elements. This suggestion is in accord with the present results. The compressibilities calculated by the present formula for Ne, A and Kr occupy the maximum positions as is seen in Fig. 2, and they are higher than those of corresponding alkali-metals which take the maximum positions among the measured values. For Xe, its calculated compressibility is almost the same as that observed for the following element Cs.

Prior to the present writers, a similar empirical formula representing the compressibility in terms of the atomic volume, melting point

1. Bridgman: The Physics of High Pressure, p. 165 (1931).

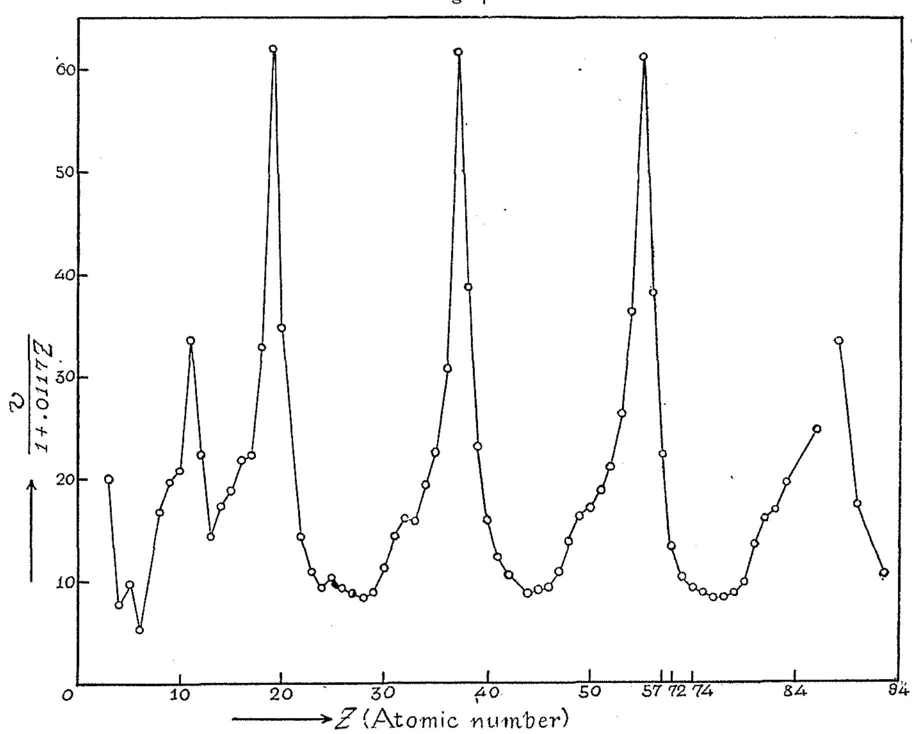
and the specific gravity of the element had been proposed by Richards[1]. His formula is as follows

$$x = 0.00021 \frac{A}{S^{0.25}(T_m - 50)},$$

where A is the atomic volume, and S is the specific gravity. Richards' formula can represent the observed values of the compressibilities equally well as that proposed by the writers; but the applicability of his formula is limitted for the elements whose melting point is higher than 50°K. With the formula proposed by the writers this defect is removed, and it can be applied generally for all the elements.

It has already been stated that the periodicity in the atomic volume is especially regular with the elements which belong to the long periods in the periodic table. However, this regularity is not entirely perfect; and we can detect, in Fig. 1, a systematic and linear increase in the value of the atomic volume with increase of the atomic number. This linear increase of the atomic volume was found to be well

Fig. 4.



1. Sachs: Mechanische Technologie der Metalle, p. 226 (1925).

systematized by adopting, instead of the actual atomic volume v, the reduced atomic volume v_r, which is connected with v by the relation

$$v_r = \frac{v}{1+0.0117Z}$$

where Z represents the atomic number as before. The relation between v_r and Z is plotted in Fig. 4, and an almost perfect periodicity of the reduced atomic volume in the long periods is obtained in this figure: the corresponding elements in different periods take almost the same reduced atomic volume.

In the case of compressibility the value of $\varkappa T_m$ was found to be proportional to $v^{1.5}/(1+0.0175Z)$. If we use the reduced atomic volume v_r instead of v, we have

$$v_r^{1.5} = \frac{v^{1.5}}{(1+0.0117Z)^{1.5}} \doteqdot \frac{v^{1.5}}{1+0.0175Z}.$$

and consequently the empirical formula representing the compressibility becomes more simple, as

$$\varkappa = \frac{v_r^{1.5}}{0.003T_m}.$$