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THE COMPRESSIBILITY OF SOLID NOBLE GASES AND THE ALKALI METALS AT 0°K

ARISTID V. GROSSE
Research Institute of Temple University, Philadelphia, Pa.

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Abstract—The compressibilities of the solid noble gases at 0°K (and 0 pressure) were calculated from their experimental and theoretical compressions ($\Delta V/V_0$). They are compared with the experimental values of the compressibilities of the alkali metals, also at 0°K. The compressibilities of the noble gases follow an unusual pattern, different from all other families in the Periodic System, the latter being essentially proportional to the atomic volume and therefore the atomic number of the element. Solid helium is by far the most compressible element, to be followed by solid neon; on the other hand Kr, Xe and Em are *substantially less compressible* than the alkali metal directly following them. Finally, Ar has practically the same compressibility as K (see Fig. 1).

RICHARDS⁽¹⁾ determined the compressibility of many elements and first pointed out that compressibility is a strongly periodic function of their atomic weight (or number). It was, however, BRIDGMAN who made the greatest experimental contributions in this field and who measured the compressibilities of over 50 elements. In his book *The Physics of High Pressure*,⁽²⁾ which is now a classic, he discusses the wide range of compressibilities of the elements from diamond to cesium. He states⁽³⁾: "The most important gap in the results is in the compressibilities of the rare gases, none of which are known in solid form. The direct experimental determination of these would be difficult, because of the necessity for making the measurements at low temperatures; we have seen, however, that measurements of gaseous H₂ and He enable lower limits to be set to the compressibilities of the corresponding solids, and that the probable compressibilities are very high, in fact much higher than that of any of the elements shown in the figure*. *It seems almost certain that the positions of greatest compressibility in the completed diagram will be occupied by the solid rare gases, instead of the alkali metals as at present.*"

He says further⁽⁴⁾: "The great range of numerical values of compressibility is striking, the range of C to Cs being by a factor of 240; the variation would be much greater if the compressibility of the solidified rare gases were known." BRIDGMAN has shown⁽⁵⁾ that by plotting compressibility in a group of elements of the periodic

* The figure is the one showing the RICHARDS relationship between the compressibility of the elements plotted vs. their atomic number (similar to our Fig. 1).

⁽¹⁾ T. W. RICHARDS, *J. Amer. Chem. Soc.* **34**, 971 (1912); **37**, 1643 (1915); **46**, 1419 (1924); **48**, 3063 (1926); **50**, 3290, 3304 (1928).

⁽²⁾ P. W. BRIDGMAN, *The Physics of High Pressure* (1st. Ed) Bell, London (1931); reprinted (1949).

⁽³⁾ P. W. BRIDGMAN, *The Physics of High Pressure* (1st. Ed) p. 165, Bell, London (1931); reprinted (1949).

⁽⁴⁾ P. W. BRIDGMAN, *The Physics of High Pressure* (1st. Ed) p. 166, Bell, London (1931); reprinted (1949).

⁽⁵⁾ P. W. BRIDGMAN, *The Physics of High Pressure* (1st. Ed) p. 167, Bell, London (1931); reprinted (1949).

system vs. their atomic volume (or some power of it) a steady linear increase is observed, for example, in the sequence: Li, Na, K, Rb and Cs or Be, Mg, Ca, Sr, Ba and Ra. He therefore concluded that⁽⁶⁾: "If one may reason by analogy with alkali metals, solid xenon would be expected to be the most compressible solid element."

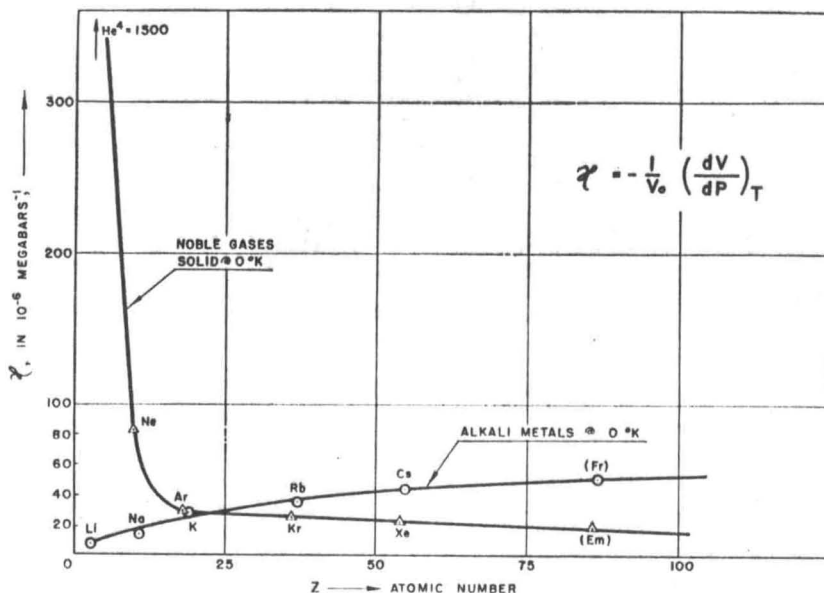


FIG. 1.—Compressibilities, κ , at 0°K (and 0 pressure) of solid noble gases and alkali metals.

It is only now, a third of a century later, that RICHARDS' diagram can be completed. The result is unexpected and, we believe, interesting and proves BRIDGMAN to be half right. The compressibilities of the solid noble gases and the alkali metals, both at 0°K , are plotted in Fig. 1 against their atomic numbers and in Fig. 2 against their respective atomic volumes also at 0°K . It is obvious from these figures that the noble gases behave in a remarkably different manner from all other families or groups of elements. We see that helium is the most compressible solid element known; neon is less so but still substantially more compressible than the alkali metals cesium and francium, the first being according to BRIDGMAN'S early measurement the most compressible element known. Argon is as compressible as potassium, but the higher noble gases, krypton, xenon and emanation, have definitely *smaller* compressibilities than the alkali metals immediately following them in the Periodic System.

Following BRIDGMAN'S procedure, we plot in Fig. 2 the compressibility of an element as a function of its atomic volume. In contrast to the alkalis, alkaline earth metals and other groups of the Periodic System, the noble gases again behave quite differently; krypton and its lower homologues have, for the same atomic volume *higher* compressibilities, while xenon and its higher homologues (including eka-emanation or element 118) are much *less* compressible.

⁽⁶⁾ P. W. BRIDGMAN, *The Physics of High Pressure*, (1st. Ed) p. 115, Bell, London (1931); reprinted (1949).

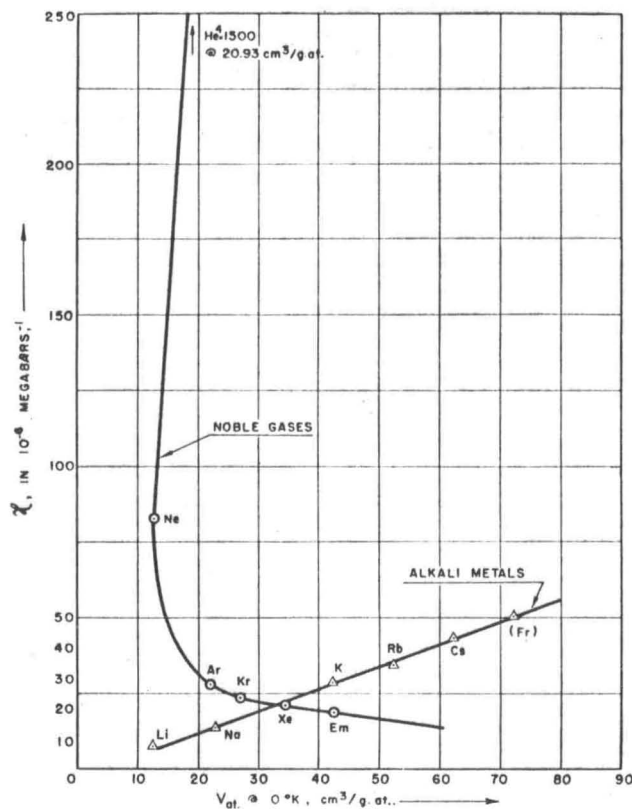


FIG. 2.—Compressibilities of solid noble gases and alkali metals, both at 0°K (and 0 pressure) vs. atomic volume at 0°K.

EXPERIMENTAL AND THEORETICAL INVESTIGATIONS

The above comparison is the result of numerous recent experimental and theoretical studies, primarily by physicists, of the compressibilities of the solid noble gases and also the alkali metals at 0°K.

While the compressibility of solid xenon has not yet been measured, STEWART⁽⁷⁾ determined the compressibility, in the pressure range of 0 to 4000 kg/cm², of neon at 4°K, of krypton at 77°K and of argon at 65 and 77°K.

SWENSON⁽⁸⁾ measured the compressibility of all five alkali metals at 4.2°K in the pressure range of 0 to 10,000 atmospheres. Together with BRIDGMAN'S data⁽⁹⁾ at room temperature, covering the range up to 100,000 atms, a complete picture of the alkali metal compressibilities is now available.

Although, in contrast to the alkali metals, the experimental data on the noble gases are far from complete, the theoretical understanding of their properties at absolute zero is much further advanced; in fact, we have here the simplest case, a

⁽⁷⁾ J. W. STEWART, *Phys. Rev.* **97**, 578-582 (1955).

⁽⁸⁾ C. A. SWENSON, *Phys. Rev.* **99**, 423-430 (1955).

⁽⁹⁾ P. W. BRIDGMAN, *The Physics of High Pressure*, (1st. Ed) p. 162, Bell, London (1931); reprinted (1949).

known geometrical array of individual atoms—all noble gases (except the special case of He) crystallize in the face centered cubic lattice (space group O_h^5 or $Fm3m$)—with weak van der Waals forces holding the lattice together. The equation of state of frozen Ne, Ar, Kr and Xe was developed already twenty years ago by KANE.⁽¹⁰⁾ Recently, the quantum mechanical variational method was applied to an Einstein model of a solid and the equation of state of the same solid gases developed by

TABLE 1.—SELECTED VALUES OF THE ATOMIC CONSTANTS OF THE SOLID NOBLE GASES, ALL AT 0°K

Metal	D_0 , °K. (g/cm ³)	Lit.	At.wt. ¹² C = 12.0000	$V_{at}^{0°K}$. (cm ³ /g atom)	v_0 (Å ³ /atom)	a_0 (Å)	d_0 (Å)	Crystal System	Atoms/ cell	Space Group
Ne	1.544	13	20.183	13.07	21.70	4.427	3.131	f.c.c.	4	O_h^5
Ar	1.827	13	39.948	21.86	36.29	5.255	3.716	f.c.c.	4	O_h^5
Kr	3.093	14	83.80	27.09	44.96	5.645	3.991	f.c.c.	4	O_h^5
Xe	3.783	15	131.30	34.71	57.60	6.131	4.335	f.c.c.	4	O_h^5
Em	(5.25)		222.0	(42.3)	(70.2)	(6.50)	(4.63)	(f.c.c.)	(4)	(O_h^5)

TABLE 2.—BERNARDES⁽¹¹⁾ SELECTION OF NOBLE GAS CONSTANTS

Metal	$V_{at}^{(0)}$ 0°K (cm ³ /g atom)	Heat of Sublimation
		at 0°K (cal/g atom)
Ne	13.1	420
Ar	22.6	1852
Kr	27.5	2630
Xe	35.1	3824

BERNARDES.⁽¹¹⁾ The change of volume with pressure and the compressibility follow directly from the two-body potential parameters (σ and ϵ), which are selected to give the best fit with the experimental atomic volume and heat of sublimation, both at 0°K (see Tables 1 and 2). The theoretical deviation of quantum mechanical laws of corresponding states from classical behaviour for the various properties, including compressibility, of the solid noble gases at 0°K was also determined recently by BERNARDES.⁽¹²⁾

The most precise lattice parameters of solid neon and argon at 4.2°K were determined by neutron diffraction by HENSHAW⁽¹³⁾ and those of krypton⁽¹⁴⁾ and xenon⁽¹⁵⁾ by SMITH from X-ray data at 20° to 120°K.

The values selected by us are correlated in Table 1. It should be clarified here that the inorganic chemist is used to compare atomic volumes, V_{at} , in cm³/g atom, defined as at. wt./density, D , in g/cm³, while the crystallographer uses the dimensions and angles of a unit cell. The physicist thinks of the same properties in units of

⁽¹⁰⁾ G. KANE, *Phys. Rev.*, **7**, 603–613 (1939); see also J. O. HIRSCHFELDER, C. I. CURTIS and R. B. BIRD, *Molecular Theory of Gases and Liquids*, pp. 1035–1044. J. Wiley, New York (1954).

⁽¹¹⁾ N. BERNARDES, *Phys. Rev.* **112**, 1534–39 (1958).

⁽¹²⁾ N. BERNARDES, *Phys. Rev.* **120**, 807–813 (1960).

⁽¹³⁾ D. G. HENSHAW, *Phys. Rev.* **111**, 1470–1475 (1958).

⁽¹⁴⁾ B. F. FIGGINS and B. L. SMITH, *Phil. Mag.* [8] **5**, 186–8 (1960).

⁽¹⁵⁾ A. J. EATWELL and B. L. SMITH, *Phil. Mag.* [8] **6**, 461–3 (1961).

specific atomic volume or volume per atom, v_0 , (in cubic Ångstroms, Å³) and distance between nearest neighbours d_0 (in Å).

For a face centred cubic lattice, with the length of a unit cell = a_0 and 4 atoms/cell, the relationship between a_0 , d_0 and v_0 is as follows:

$$v_0 = \frac{1}{4} \cdot a_0^3 \quad \text{and} \quad d_0^3 = (\sqrt{2}) \cdot v_0$$

and

$$a_0 = 1.4142 \cdot d_0 \quad \text{or} \quad d_0 = 0.70711 \cdot a_0 = 1.1224 \cdot v_0^{\frac{1}{3}}$$

For a hexagonal close packed lattice d_0 also equals $1.1224 \cdot v_0^{\frac{1}{3}}$. Furthermore, if $N_{\text{Avog.}}$ is Avogadro's number, = 60.225×10^{22} atoms per g. atom,

$$V_{\text{at.}} = N_{\text{Avog.}} \cdot v_0 = \frac{\text{at. wt.}}{D_0}$$

Throughout this paper we understand, by the compressibility κ , the isothermal compressibility proper, defined as⁽¹⁶⁾

$$-\frac{1}{v_0} \left(\frac{dv}{dp} \right)_T$$

and *not* the instantaneous compressibility

$$-\frac{1}{v} \left(\frac{dv}{dp} \right)_T$$

which has a greater tendency to increase at high pressure, because the factor $1/v$ increases with pressure, while $1/v_0$ is, of course, constant. We express κ in c.g.s. units, i.e., in megabars⁻¹, and not in (kg/cm²)⁻¹, as has been BRIDGMAN's preference, nor in atmospheres. The procedure adopted has the advantage that the data can be easily converted to other c.g.s.-units. The conversion factors used were:

$$1 \text{ atm} = 1.01325 \times 10^6 \text{ dynes/cm}^2 \text{ (or megabar}^{-1}\text{)}$$

$$1 \text{ kg/cm}^2 = 0.980665 \times 10^6 \text{ dynes/cm}^2 \text{ (or megabar}^{-1}\text{)}$$

The data of Table 1 for Ne and Ar are based on HENSHAW's⁽¹³⁾ a_0 values obtained by neutron diffraction at 4.2°K. A slight correction was applied (same as in the case of Kr and Xe) to extrapolate his values to 0°K. The data for Kr and Xe are based on SMITH's^(14,15) values of the density in the range of 20° to 120°K, obtained by X-ray diffraction. From the known coefficients of expansion, α , in that range, and the fact that $\alpha = 0$ at 0°K, extrapolations were made to 0°K. The data for emanation were estimated by us on the basis, originally developed by F. PANETH, that the differences in atomic volume of elements from period to period in the last periods of the Periodic System are practically constant.

Our values in Table 1 are close to the earlier ones, given in Table 2 and used by BERNARDES⁽¹¹⁾ in developing the theory of solid noble gases at 0°K.

BERNARDES'^(11,12) theoretical calculations of the change of volume, v/v_0 , with pressure check STEWART's⁽⁷⁾ experimental data on Ne at 4.2°K and his extrapolated data on Ar at 65° and 77°K and on krypton at 77°K.

⁽¹⁶⁾ P. W. BRIDGMAN, *The Physics of High Pressure* (1st. Ed) p. 169, Bell, London (1931); reprinted (1949).

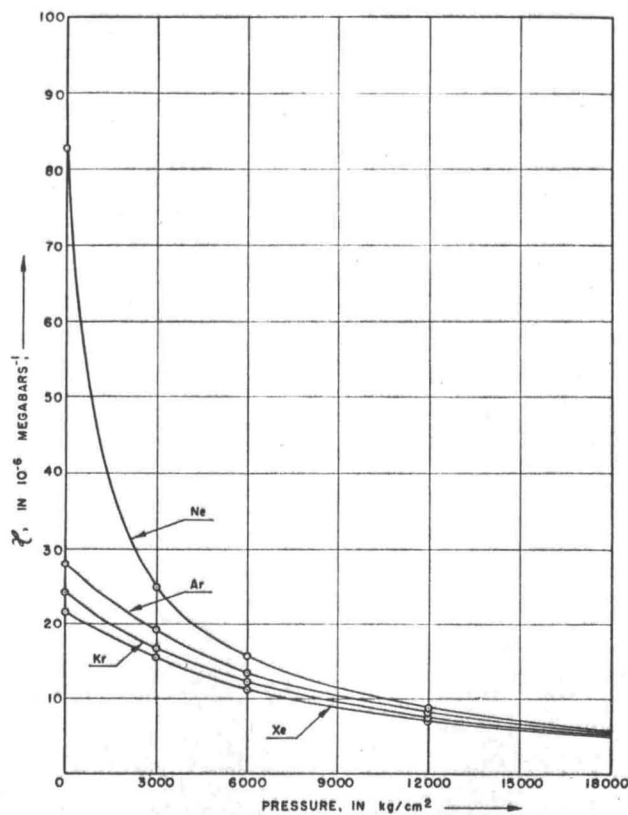
TABLE 3.— κ , AT 0°K, IN 10^{-6} MEGABARS, $^{-1}$ OF SOLID NOBLE GASES

Pressure (kg/cm ²)	Ne	Ar	Kr	Xe
0	83	28	24	21.5
3,000	24.9	19.4	16.6	15.8
6,000	15.8	12.2	13.4	11.1
12,000	8.7	8.1	7.7	7.2
18,000	5.7	5.4	5.1	4.6

In view of the excellent agreement generally between theory and experiment for the solid and also liquid and gaseous states and in view of the theoretical simplicity of this particular case (i.e., monatomic solid, van der Waals forces, Mie-Lennard-Jones potential, energy of solid and atomic distances well known) we have no hesitation in accepting his calculated values of v/v_0 .

Thus, BERNARDES⁽¹²⁾ functions of v/v_0 vs. pressure were differentiated to obtain κ at various pressures and the values obtained are given in Table 3 and plotted, as shown, in Fig. 3.

It should be noted only that STEWART'S experimental κ -value for neon at 4.2°K was corrected to 0°K, because the reduced temperature of neon is still significant at

FIG. 3.—Compressibility, $\kappa = 1/V_0(dV/dP)$ of solid noble gases at 0°K.

4.2°K, in contrast for example to the alkali metals where the values for 4.2°K equal those at 0°K.

SWENSON'S⁽⁸⁾ data on κ of the alkali metals at 0 and 77°K are correlated in Table 4, together with the atomic volumes at 0°K. The data for francium were estimated by the PANETH procedure.

In one respect the noble gases follow the behaviour of all other elements; their κ also decrease rapidly with pressure as Table 3 shows. For a comparison, one may compare SWENSON'S data at 0°K and 0 pressure (see Table 4) with the following: κ of Li has decreased from 7.7×10^{-6} to 4.2×10^{-6} and that of cesium from 43.5×10^{-6} to

TABLE 4.— κ , IN 10^{-6} MEGABARS⁻¹, ATOMIC VOLUMES OF SOLID ALKALI METALS⁽⁸⁾
(AT 0°K AND 77°K AND AT 0 PRESSURE), AND ATOMIC WEIGHTS

Temperature	Li	Na	K	Rb	Cs	Fr
at 0°K	7.7	13.7	28.4	34.3	43.5	(50.6)
at 77°K	8.7	15.4	29.2	38.3	48.6	—
atomic vol @ 0°K						
cm ³ /g.atom	12.40	22.80	42.50	52.50	62.30	(72.50)
at.wt.	6.939	22.9898	39.102	85.47	132.905	(224)

15.9×10^{-6} megabar⁻¹ at 0°K and 10,000 kg/cm² pressure. It is expected that at the extreme range of BRIDGMAN'S pressure measurements, i.e., at 100,000 kg/cm², the differences in κ between the solid noble gases and alkali metals will become less and less significant.

THE CASE OF HELIUM

Helium, the lightest noble gas, is a special case. At atmospheric pressure it remains a liquid even at 0°K. It is a quantum liquid and the quantum effects are large so that the theory which works well for the heavier noble gases⁽¹²⁾ does not apply to helium.

However, liquid helium can be solidified under pressures of the order of 100 atms. The isotope ⁴He was first solidified by KEESOM⁽¹⁷⁾ in a historical experiment at Leiden on June 25, 1926. In its appearance, it is a transparent colourless mass, crystalline because of its sharp melting point.

Its compressibility has been measured by SIMON⁽¹⁸⁾ and equals approximately 1500×10^{-6} megabars⁻¹ at 3.7°K and 115 atm pressure. It is thus the most compressible of the noble gases and of all elements; it lies on the scale of Figs. 1 and 2 about $20 \times$ higher than the point for neon. Certainly BRIDGMAN'S prediction has been fulfilled in this case!

³He, the isotope of mass 3, has been solidified about a decade ago;⁽¹⁹⁾ at 0°K its melting pressure is about 26.8 atm. One would expect, in view of quantum effects, substantial differences between the two isotopes in atomic volume, compressibility and other properties. Its compressibility has not yet been measured, but one would

⁽¹⁷⁾ W. H. KEESOM, Commun. Leiden No. 184b; *Proc. Roy. Acad. Amsterdam* **29**, 1136 (1926); see also KEESOM'S book *Helium*, Elsevier, Amsterdam (1942).

⁽¹⁸⁾ R. KAISCHEN and F. SIMON, *Nature* **133**, 460 (1934).

⁽¹⁹⁾ D. W. OSBORNE, B. M. ABRAHAM and B. WEINSTOCK, *Phys. Rev.* **82**, 263 (1951) **85**, 158 (1952).

expect it to be even greater than of ^4He , if the same isotopic relations exist as between protium and deuterium (κ of $^1\text{H} = 480 \times 10^{-6}$ megabars vs. $D = 300 \times 10^{-6}$!). The liquid atomic volumes of ^3He and ^4He , under their respective saturated vapour-pressure, at 1.2° and 1.6°K are known⁽²⁰⁾ and are as follows:

		^3He	^4He
Atomic volume, ($\text{cm}^3/\text{g atom}$) . . .	(\bar{v})		
	1.2°K	37.11	27.515
	1.6°K	37.77	27.504

Thus, the atomic volume of ^3He is by a factor of $1\frac{1}{3}$ greater than ^4He , an exceptional situation for isotopes. In solid form both ^3He and ^4He exist each in a body centered cubic (space group $-O_h^9$ or $I m\bar{3}m$, 2 atoms/cell, $d_0 = 1.0911 \cdot v_0^{\frac{1}{3}}$) and hexagonal close packed (D_6^4h or $C6/mmc$, 2 atoms/cell, $d_0 = 1.1224 \cdot v_0^{\frac{1}{3}}$) lattice and their atomic volumes and cell dimensions have been accurately measured.⁽²¹⁻²⁴⁾ They are correlated in Table 5.

TABLE 5.—PROPERTIES⁽²¹⁻²⁴⁾ OF SOLID ^3He AND ^4He

	^3He	^4He
Atomic volume of b.c.c., ($\text{cm}^3/\text{g atom}$)	20.060	20.928
Atomic volume of h.c.p., ($\text{cm}^3/\text{g atom}$)	20.060	20.737
Density, (g/cm^3)	} 0.1504	0.1913
{ b.c.c.		0.1930
{ h.c.p.	0°	1.73°
Conditions for above	98.5	29.01
{ °K		
{ atm.		
a_0 of b.c.c., (Å)	4.054	4.111
a_0 of h.c.p., (Å)	3.612	3.655
c_0 of h.c.p., (Å)	5.898	5.954
c_0/a_0	1.633	1.629
Atomic weight ($^{12}\text{C} = 12.0000$)	3.01596	4.00259

Table 5 shows that both isotopes of solid helium have, in contrast to all other groups of the Periodic System, a substantially higher atomic volume (i.e., 20 and 21 $\text{cm}^3/\text{g atom}$) than their next homologue—neon (13.07 $\text{cm}^3/\text{g atom}$, see Table 1). It is this fact which is responsible for the "retrograde" or upper part of the curve of the solid noble gases in Fig. 2.

In conclusion, a few remarks regarding the reason for this singular behaviour of the noble gas family when compared to the families of *metals* in the Periodic System. First of all, there is a big difference in the nature of forces holding the atoms together in the lattice; in the case of noble gases—weak van der Waals forces, as against much stronger metallic bonding (see Table 6).

However, in both cases, the distances between atoms and the forces or energies holding them together describe the behavior of the solid; these are determined by the atomic volume (or v_0 , or a_0 and d_0) and the heat of sublimation of the solid at 0°K . The latter gives directly the energy required to separate the lattice atoms from each other and convert it to a gas.

⁽²⁰⁾ See K. R. ATKINS, *Liquid Helium*, Cambridge Univ. Press (1959).

⁽²¹⁾ A. F. SCHUCH and R. L. MILLS, *Advan. Cryogenic Eng.* **7**, 311 (1960).

⁽²²⁾ E. R. GRILLY and R. L. MILLS, *Ann. Phys.* **8**, 1 (1956).

⁽²³⁾ A. F. SCHUCH and R. L. MILLS, *Phys. Rev. (Letters)* **8**, 469 (1962).

⁽²⁴⁾ J. DONOHUE, *J. Amer. Chem. Soc.* **85**, 1238-40 (1963).

Now the atomic volume of an element increases in all families with its atomic weight or number. In a family or group of metals, the heat of sublimation (or in the absence of precise data, the heat of vaporization at the N.B.P., which runs parallel to it) *decreases*, with a few exceptions, with the atomic number; Table 6 demonstrates this fact for the I, II, III and IV group of metals (including the half metals: Si, B and C). Therefore, the combination of these two factors in metals, namely, *increase* in volume per atom and *decrease* of binding energy per atom, accounts for the compression of the metals with increasing atomic weight. Furthermore, the single

TABLE 6.—EXPERIMENTAL HEATS OF VAPORIZATION OF METALS* AT THEIR N.B.P.

Group I	Group II	Group III	Group IV	Experimental heats of sublimation of solid noble gases at 0°K, (cal/g.atom)
Li 32,190	Be 70,400	B 128,800	Ge 210,000	He 25
Na 21,280	Mg 34,470(!)	Al 70,200	Si 90,000	Ne 450 ± 10
K 18,530	Ca 36,740	Ga 61,200	Ge 79,900	Ar 1850 ± 12
Rb 16,540	Sr 33,610(!)	In 54,100	Sn 69,400	Kr 2590 ± 50
Cs 15,750	Ba 35,670	Tl 38,740	Pb 42,880	Xe 3830 ± 50
Fr (15,200) ↓	Ra (27,400) ↓			Em (4700) ↑

NOTE: Arrow indicates direction of decrease.

* The metal data were taken from D. R. STULL and G. C. SINKE's, *Thermodynamic Properties of the Elements*, Advances in Chemistry Series, No. 18, Amer. Chem. Soc. Washington, D.C. (1956), and LEO BREWER's chapter in Vol. 19B, Div. IV, Manhattan Project Tech. Sc. of National Nuclear Energy Series, McGraw-Hill, New York (1950). For noble gas data: see reference (11).

valence electron of the alkali metals, on its large satellite orbit, is responsible for the larger atomic volume of the alkali metals vis a vis the II, III or IV group metals with their successively smaller orbitals; this fact coupled with their smaller binding energy (see Table 6) explains the much greater compressibility of the alkali versus the alkaline earth metals. The latter have again greater compressibilities than the transition metals with their many metallic valence electrons.

In the case of the noble gases, however (see also Table 6) the energy required to separate the noble gas atoms in the solid lattice *increases together* with their atomic volume (see Table 1), with the overall effect that the compressibility decreases as shown in Figs. 1 and 2 or in Table 3. The hard core of the xenon atom, with its complete valence shell, is much less compressible than the cesium atom. The helium isotopes, with their solid atomic volume of 20 cm³, are even more exceptional, because they are about three times "puffed up" over and above the atomic volume of 6 cm³, expected for He from the volumes of the other noble gases and the usual *decrease* in volume with atomic number observed in all other families of elements. This fact coupled with the extremely small energy of the lattice of about 25 cal/g atom (see Table 6) explains how small pressures compress this element more than any other!