Now the perturbations δn_2 and δn_3 must satisfy the same boundary conditions as n_2 and n_3 and moreover vanish for $t=0, \infty$. In view of this the following approximation[2] may be made,

$$\left.\frac{\partial(\delta n_i)}{\partial x}\right]_{x=a/2} = -\frac{\pi^2}{a^2}\left[\int_0^{a/2}\delta n_i dx\right]. \qquad (7)$$

Then one obtains from (1) and (2) two simultaneous linear ordinary differential equations for

$$\epsilon_2=\int_0^{a/2}\delta n_2 dx \quad \text{and} \quad \epsilon_1=\int_0^{a/2}\delta n_3 dx,$$

$$d\epsilon_1/dt=a_1\epsilon_1+b_1\epsilon_2+c_1, \qquad (8)$$

$$d\epsilon_2/dt=a_2\epsilon_1+b_2\epsilon_2+c_2. \qquad (9)$$

The coefficients a, b in (8) and (9) are dependent on the concentrations of gases "2" and "3" and the coefficients of diffusion D and D^*. The C_1 and C_2 terms are likewise dependent on these variables and proportional in addition to the pressure gradient of gas "1" evaluated at $x=a/2$. The result of the diffusion, initially, is that the mixture "2,3" diffusing into gas "1" has its concentration changed from λ, $[\lambda=n_2/(n_2+n_3)]$, by the amount

$$2\lambda(1-\lambda)\frac{D^*}{D^*+D}\left(\frac{\Delta D}{D}\right), \qquad (10)$$

where ΔD is the difference between the coefficients of diffusion of the mixture "3,1" and the mixture "1,2."

In the time $t=a^2/\pi^2 D$ the expression (10) changes by the factor $8/(e\pi^2-8)$, or approximately $\frac{1}{2}$.

It is interesting to apply this result to the diffusion of H_2 into air, which may be taken as N_2 (80 percent), O_2 (20 percent). The change in concentration of the diffusing air, assuming a difference of one part in 200 for the diffusion of N_2 and O_2 into H_2 would be of the order of 1/2000.

Thus the air mixture diffuses in this case effectively as a simple gas. However, when the gas "1" is not light, the change may be much greater as, if the H_2 should be replaced by some gas of large molecular weight and cross section, the change in the separation may be increased by a factor of 60 or 70.

An alternative method of separation of isotopes employing the action of a third gas would be to place the isotope mixture in a tube closed at both ends by porous plugs which would be impervious to the isotope mixture, but permit the passage of some other gas which could therefore be pumped through. The separation in this case would increase with the increase in the diffusion current.

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Note on Grüneisen's Constant for the Incompressible Metals

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Grüneisen's constant γ can be determined in terms of the thermal expansion, compressibility, and specific heat, as originally shown by Grüneisen. It can also be found from the compressibility and change of compressibility with pressure. Theoretically the two methods should give approximately the same result. This has proved to be the case experimentally, except for the more incompressible metals, where the discrepancies have been very great. Bridgman has now redetermined the change of compressibility of iron with pressure, obtaining a much smaller value than before, and as iron was used as a standard, this brings about a revision of other changes of compressibility with pressure, largest in proportion for the incompressible metals, whose volume change is about the same as for iron. It is shown that this revision is just enough to bring the two methods of finding γ into agreement, for practically all the metals.

If the frequencies of vibration of the normal modes of a crystal all vary as the inverse γ power of the volume, then it can be shown that there is a relation

$$\frac{(\text{thermal expansion})\times(\text{volume})}{(\text{compressibility})\times(C_V)}=\gamma. \qquad (1)$$

This relation is due to Grüneisen,[1] and γ is often called Grüneisen's constant. By means of the relation (1), experimental values of γ can be found, and for most simple solids they lie between

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[1] For discussion of this relation, see for instance J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill, 1939), Chapter XIII, Section 4.

1.5 and 2.5. In addition to (1), there is another quite different connection between γ and experiment. This arises from the fact that the natural frequencies can be computed from the elastic constants, in particular from the compressibility. The constant γ depends essentially on the change of frequency with volume, and hence on the change of compressibility with pressure. As a result of this, a value for γ can be computed from Bridgman's measurements of compressibility and its change with pressure. For many ionic crystals, and for the more compressible metals, the values computed in this way agree well with those found from Eq. (1), giving valuable verification of the theory, and a useful relation between experimental quantities, which could be used to find the thermal expansion from the change of compressibility with pressure, or vice versa. For the less compressible metals, however, the agreement is very poor, and to get better agreement, the change of compressibility with pressure should be considerably smaller (in the case of the least compressible metals several times smaller) than found by Bridgman.[2]

Bridgman[3] has now redetermined the change of compressibility of iron with pressure, obtaining a value only about a third as large as the previously measured value. This is important for all the other measurements, for iron is used as a standard, and the measurements on other elements give really the difference between the change of volume of the element in question and iron. For the compressible metals, and the ionic crystals, the change of compressibility with pressure is so much greater than that of iron that a change in the value for iron makes only a small correction in the result, but a number of the metals of the transition groups have changes of compressibility with pressure of the same order of magnitude as iron, and for these the new measurements make a very great difference. It is the purpose of this note to point out that Bridgman's new measurements for iron entirely remove the discrepancy between the two methods of determining γ for this element; and that if the old measurements of change of compressibility with pressure for other incompressible metals are corrected by using the new results for iron, they likewise fall into line, with one or two exceptions.

Bridgman's[4] experimental results are stated in the form

$$\Delta V/V_0 = -a_1 P + a_2 P^2, \tag{2}$$

where ΔV is the change in volume, V_0 the original volume, P the pressure, a_1 and a_2 constants at a given temperature. For iron, at 30°C, he found in 1923 $a_1 = 5.87 \times 10^{-7}$, $a_2 = 2.1 \times 10^{-12}$, where the pressure is expressed in kilograms per square centimeter. In the new paper, the change of lengths rather than that of volume is given, but when the change of volume is computed from it (taking account of the fact that in the term in P^2 we cannot simply multiply by 3, but must cube the length to find the volume), we find $a_1 = 5.83 \times 10^{-7}$, $a_2 = 0.80 \times 10^{-12}$. That is, the value of a_1 is decreased by 0.04×10^{-7}, and that of a_2 decreased by 1.30×10^{-12}. It is not hard to show that, to the accuracy with which the measurements are made, the measured values of a_1 and a_2 for other metals are to be corrected by subtracting equal amounts from them. In this way, we have obtained corrected values from the observed values of reference 4.

It is now easy to show[5] that γ can be found in terms of a_1 and a_2 by the equation

$$\gamma = a_2/a_1^2 - \tfrac{2}{3}. \tag{3}$$

In Table I we give values of a_1 and a_2 as originally found by Bridgman,[4] for most of the metals for which the most serious discrepancies existed, and the values of γ computed from them by Eq. (3); next we give revised values of a_1 and a_2, as described in the preceding paragraph, with

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[2] For comments on this, see N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford, 1936), Chapter I, Section 4. Comparisons of the two methods of determining γ are given in Slater, reference 1, Chapter XXIII, Section 4, for the alkali halides; and Chapter XXVII, Section 2, for metals.

[3] P. W. Bridgman, Phys. Rev. **57**, 235 (1940).

[4] P. W. Bridgman, Proc. Am. Acad. Arts and Sci. **58**, 165 (1923), for most of the metals mentioned in the present note.

[5] See Slater, reference 1, Chapter XIII, Section 1; and Chapter XIV, Section 4. In Chapter XIII, Eq. (1.1), (1.4), etc., neglect a_0, which represents the thermal change of volume. Then a_1, a_2 of the present paper become identical with the quantities defined in that chapter. In Eq. (4.6), Chapter XIV, it is shown that $\gamma = -\frac{2}{3} + P_2/P_1$. In Eq. (1.10), Chapter XIII, neglecting a_0, it is shown that $P_1 = 1/a_1$, $P_2 = a_2/a_1^3$. From these the result of Eq. (3) of the present paper follows at once. This result does not agree with Eq. (42) of Mott and Jones (reference 2) which in our present notation is $\gamma = a_2/a_1^2 - \frac{1}{6}$, or $\frac{1}{2}$ unit greater than our value. We believe Mott and Jones to be wrong, for they have incorrectly defined the compressibility as $-(1/V_0)(\partial V/\partial P)_T$, rather than $-(1/V)(\partial V/\partial P)_T$, and have thus lost a term coming from the change of V with volume, leading to the difference between the formulas.

TABLE I. *Original and revised values of a_1, a_2, and γ. Data for a_1 and a_2 are from Bridgman, reference 4. Values of γ by Grüneisen's method [$\gamma(Gr)$] are from the article by Grüneisen, "Zustand des festen Körpers," in Handbuch der Physik, Vol. X (Springer, 1926).*

METAL	$a_1\times10^7$ (OLD)	$a_2\times10^{12}$ (OLD)	γ (OLD)	$a_1\times10^7$ (REV.)	$a_2\times10^{12}$ (REV.)	γ (REV.)	γ (GR)
Fe	5.87	2.1	5.4	5.83	0.80	1.68	1.60
Co	5.39	2.1	6.6	5.35	0.8	2.1	1.87
Ni	5.29	2.1	6.9	5.25	0.8	2.2	1.88
Cu	7.19	2.6	4.4	7.15	1.3	1.9	1.96
Pd	5.19	2.1	7.1	5.15	0.8	2.4	2.23
Ag	9.87	4.4	3.8	9.83	3.1	2.5	2.40
W	2.93	1.5	17.	2.89	0.2	1.7	1.62
Pt	3.60	1.8	13.	3.56	0.5	3.3	2.54

a corresponding revised γ; finally we give values of γ computed by Grüneisen's relation, Eq. (1). It is plain from the table that the revision has completely removed the discrepancies between the old computed values of γ and Grüneisen's values of that quantity. The agreement between the revised γ's and Grüneisen's is within the experimental error of the a_2's, which are only known to a very rough approximation. We must remember in connection with this that an exact agreement is not required by the theory. It would be expected only if all natural frequencies of the solid varied in the same ratio with change of volume, and if the change of frequency with volume arose only from the change of compressibility, and not from a possible change in Poisson's ratio. Neither of these conditions is likely to be exactly fulfilled, so that the two methods of calculating γ may well differ by as much as the observed amounts.

For the more compressible metals, the revised values of a_2 lead to only a small change in γ, so that the agreement is not essentially changed from the values given in Table XXVII-2.[1] There are a few incompressible metals, however, for which there are outstanding discrepancies. For manganese, Bridgman[6] finds $a_1=7.91\times10^{-7}$, $a_2=5.3\times10^{-12}$; corrected values would be $a_1=7.87\times10^{-7}$, $a_2=4.0\times10^{-12}$, from which $\gamma=5.8$. Grüneisen's value is 2.42. Since this discrepancy is so much larger than for other metals, there is good reason to suspect that Bridgman's value of a_2 is considerably too large. This is perhaps explained by the fact that he states that it is very difficult to get manganese without small cracks, on account of a polymorphic transition; a cracked specimen would show an apparently high value of a_2. For molybdenum and tantalum, there are discrepancies in the opposite direction. Bridgman finds a_2 equal, respectively, to 1.2×10^{-12} and 0.25×10^{-12} for these metals. Making our correction of subtracting 1.3×10^{-12} would give negative values of a_2. This seems most implausible on general grounds, so that the observations for these two metals are certainly to be questioned. Finally for gold he used two samples, one giving $a_2=2.1\times10^{-12}$, the other 3.1×10^{-12}. These lead to $\gamma=1.8$ and 4.8, respectively, against Grüneisen's value of 3.03. Evidently the order of magnitude is right, but the discrepancies between the two observations are so great as to throw a good deal of doubt on the accuracy of the measurements. A remeasurement of these doubtful metals, if not of all the incompressible ones, would be very desirable. Since it appears as a result of the present note that Grüneisen's relation is really rather generally satisfied, it would be justified in future measurements to question any values of change of compressibility with pressure which disagree with it violently. For convenience, we may note that for most materials $\gamma+\frac{2}{3}$ is in the neighborhood of 2.5. Thus, from Eq. (3), we may expect that approximately

$$a_2=2.5a_1^2. \tag{4}$$

This relation should be expected to give the quadratic term in the volume change, in terms of the linear term, with an error of usually not over fifteen or twenty percent.

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[6] P. W. Bridgman, Proc. Am. Acad. Arts and Sci. **64**, 51 (1929).