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XLV. Atomic Frequency and Atomic Number.—Frequency Formule with Empirical Constants. By H. STANLEY ALLEN, M.A., D.Sc., University of London, King's College.*

§ 1. *Introduction.*

A RELATION between the characteristic frequency of an element in the solid state and the atomic number is to be expected on theoretical grounds. In a paper communicated to the Royal Society the author has sought to establish such a relation, and it will be convenient to summarize briefly the conclusions already reached.

1. If N denote Moseley's atomic number for an element and ν the characteristic frequency deduced from determinations of the specific heat in the solid state, simple relations are found to hold between the values of the product $N\nu$ for different elements.
2. For 26 metals it is found that the product can be expressed in the form

$$N\nu = n\nu_A,$$

where n is a whole number and ν_A a constant having the value 21.3×10^{12} sec.⁻¹ (approximately).

3. The same rule is obeyed in the case of certain non-metallic elements.
4. Similar results are found when the characteristic frequency is calculated from the elastic constants of the solid by Debye's formula. The value of the "frequency number," n , thus obtained is not in all cases the same as that deduced from the specific heat.
5. Application of the theory of probability shows that there is but a small chance of the product approaching so nearly to integral multiples of a constant frequency by a mere accident.
6. It is found that the atomic numbers of Moseley give better agreement with the proposed relation than do the atomic ordinals of Rydberg.
7. The empirical results have been discussed from the standpoint of the Quantum Theory, and it may be suggested that the integer n is related to the number of electrons concerned in determining the crystalline space-lattice of the element in the solid state.

In the present communication an attempt is made to extend these results by considering other methods of determining the characteristic frequency.

* Communicated by the Author.

§ 2. Frequency Formulæ with Empirical Constants.

Various formulæ have been suggested for the purpose of expressing the atomic frequency in terms of other physical properties. Several of these have been discussed and compared in a paper by Blom *. They are based on grounds partly theoretical, partly empirical, but are all variants of the expression for the frequency in simple harmonic motion

$$v = \frac{1}{2\pi} \sqrt{\frac{D}{A}},$$

where A is the atomic mass, and D is the restoring force for unit displacement from the equilibrium position.

It has been overlooked by later writers that the first formula of this kind was given by Sutherland †, who claimed that he had found simple relations between the *periods* of vibration of elements at the melting point for several chemical families. His reasoning may be summarized as follows:—When a molecule, mass M, and specific heat (mean) *c*, is heated from rest at absolute zero to its melting-point T_s , it receives heat McT_s , which is taken to be proportional to its mean kinetic energy $\frac{1}{2}Mv^2$. Thus *v* is proportional to $\sqrt{(McT_s/M)}$. The length or amplitude of the vibration is assumed to be equal to (or proportional to) $\alpha T_s (M/\rho)^{\frac{1}{3}}$, where α is the mean coefficient of linear expansion and ρ is the density. Hence the periodic time is proportional to

$$\alpha T_s (M/\rho)^{\frac{1}{3}} / \sqrt{(McT_s/M)}.$$

Now it is a characteristic feature of Sutherland's theory of the process of fusion, that melting occurs when the space between the molecules attains a certain value relatively to the size of the molecules. Thus αT_s is constant, a relation that has been verified by Grüneisen ‡ for monatomic elements. Again, according to the law of Dulong and Petit, Mc is constant. Hence the periodic time is proportional to

$$(M/\rho)^{\frac{1}{3}} / \sqrt{(T_s/M)}.$$

Putting $M/\rho = V$, the molecular (or atomic) volume, the frequency is proportional to

$$\sqrt{\left(\frac{T_s}{MV^{\frac{1}{3}}}\right)}.$$

* Blom, *Ann. d. Physik*, vol. xlii. p. 1402 (1913).

† Sutherland, *Phil. Mag.* vol. xxx. p. 318 (1890); vol. xxxii. p. 524 (1891).

‡ Grüneisen, *Ann. d. Physik*, vol. xxxix. p. 257 (1912).

This is exactly the relation obtained later by Lindemann* for the atomic frequency at the melting-point. For an element of atomic weight A the relation may be written

$$\nu = k \sqrt{\left(\frac{T_m}{AV^{\frac{2}{3}}}\right)} = \frac{k}{V^{\frac{1}{3}}} \sqrt{\left(\frac{T_m}{A}\right)}.$$

The value of the multiplying constant k , which is found empirically, was given by Lindemann as 2.06×10^{12} .

The same formula was afterwards employed by Nernst for the calculation of the characteristic frequency, using for k the value 3.08×10^{12} , which is almost exactly half as large again as the factor employed by Lindemann for the frequency at the melting-point.

§ 3. Results obtained by using Lindemann's Formula.

With Nernst's value for the constant and with experimental data from the Smithsonian Physical Tables (1914), the atomic frequency, ν , and the product, $N\nu$, have been calculated for a large number of elements. For our present purpose Lindemann's formula has an important advantage in the fact that the melting-point in many cases is known accurately, whilst the value of $V^{\frac{2}{3}}$, the only quantity in the formula varying with temperature, does not differ greatly for most of the elements.

For a test of the formula we select seven of the metals for which results derived from the specific heats have been given in the former paper. For these metals the data required in Lindemann's formula are known with considerable accuracy. The results are collected for comparison in the following Table.

TABLE I.

Element.	N.	$N\nu \times 10^{-12}$.	
		Specific Heat.	Lindemann.
Al	13	107.5 = 5×21.5	108.2 = 5×21.6
Fe	26	209.0 = 10×20.9	236.8 = 11×21.5
Cu	29	191.7 = 9×21.3	214.5 = 10×21.4
Zn	30	144.2 = 7×20.6	143.6 = 7×20.5
Ag	47	211.0 = 10×21.1	225.2 = 11×20.5
Cd	48	163.8 = 8×21.1	144.5 = 7×20.6
Pb	82	154.0 = 7×22.0	163.2 = 8×20.4

Mean value of ν_A from Lindemann's formula = 20.9×10^{12} sec.⁻¹.

* Lindemann, *Phys. Zeitschr.* vol. xi. p. 609 (1910).

An examination of the figures in the last column of the table shows a maximum divergence of about 3 per cent. from the mean value of ν_A . This is too large to be accounted for by uncertainty as to the experimental data (T_s , A , V) used in the calculation of the frequency, so that we are forced to conclude either that Lindemann's formula is not exact*, or that the proposed relation $N\nu = n\nu_A$ is only an approximation.

A comparison of the two columns of integers in bold type reveals the unexpected result that the integer required for the frequency determined from the specific heat is not in all cases the same as the integer required in connexion with Lindemann's formula. For Al and Zn the same integer appears in both columns of the table; in the other cases there is a difference of one unit between the figures in the two columns. There does not appear to be any obvious regularity in the relative position of the larger unit.

This surprising result at first produced some degree of scepticism as to the trustworthiness of the relation in question, but similar results have been found in such a large number of different cases that it is almost impossible to doubt the general accuracy of the relation.

The atomic frequency has been calculated by means of Lindemann's formula for all elements for which data are available. The results are given in the following Tables. Where the data are uncertain the frequency is in brackets. In such cases the value of $N\nu$ is to be regarded merely as giving the most probable value of the integer n , which may be called the *frequency number*.

An examination of the figures in the column headed $N\nu \times 10^{-12}$ makes it difficult to escape the conclusion that the product $N\nu$ may be expressed as an integral multiple of a constant frequency of about 21×10^{12} sec.⁻¹ It is true that little weight can be attached to those cases where the product has a large value, for then it is always possible to choose the integer to give a suitable value for ν_A ; but even if we exclude all elements for which the frequency number is greater than 10, sufficient instances remain to make our conclusion secure that the coincidences cannot be accidental.

At the same time we must admit that for 14 elements not

* A conclusion reached from theoretical considerations by Grüneisen, *Ann. d. Physik*, vol. xxxix. p. 298 (1912). The same result would follow from Sutherland's argument if αT_s were constant only for similar elements.

in Table II. the results given by Lindemann's formula are not in agreement with the proposed relation. Various suggestions might be made to account for these discrepancies.

TABLE II.

Atomic Frequency by Lindemann's Formula.

Element.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.	Element.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
B.....	5	(28.1)	7×20.1	Rh	45	7.01	15×21.1
C.....	6	(36.4)	10×21.8	Pd	46	6.16	14×20.2
O	8	2.54	1×20.3	Ag	47	4.792	11×20.48
Al	13	8.33	5×21.7	Cd	48	3.01	7×20.6
Si	14	10.5	7×21.0	Sn	50	2.50	6×20.9
Ca	20	4.28	4×21.4	Sb	51	3.22	8×20.5
Sc	21	(6.84)	7×20.5	Te	52	(2.69)	7×20.0
Ti	22	9.17	10×20.2	Cs	55	1.12	3×20.6
V	23	9.26	10×21.3	Ba	56	2.66	7×21.3
Cr	24	(9.23)	11×20.2	La	57	3.04	8×21.7
Mn.....	25	8.35	10×20.9	Ce	58	2.86	8×20.7
Fe	26	9.11	11×21.5	Pr	59	3.24	9×21.2
Co	27	8.87	11×21.8	Nd	60	3.11	9×20.8
Ni	28	8.86	12×20.7	Sa	62	3.76	11×21.2
Cu	29	7.397	10×21.45	Ta	73	5.72	20×20.9
Zn	30	4.79	7×20.5	W	74	(6.06)	22×20.4
Ga	31	2.82	4×21.8	Os	76	5.96	22×20.6
Ge	32	(5.23)	8×20.9	Ir	77	5.47	20×21.1
Se	34	(2.94)	5×20.0	Pt	78	4.75	18×20.6
Sr	38	(3.44)	6×21.8	Au	79	3.69	14×20.8
Yt	39	(4.07)	8×21.7	Tl	81	2.00	8×20.3
Zr	40	(4.63)	9×20.6	Pb	82	1.99	8×20.4
Ob	41	(6.73)	13×21.2	Bi	83	1.80	7×21.3
Mo.....	42	7.57	15×21.2	Th	90	(3.06)	13×21.2
Ru	44	6.99	15×20.5	U	92	(4.67)	20×21.4

In the first place it has been assumed in the application of Lindemann's formula that the solid is monatomic. If the molecule contains several atoms the result must necessarily be modified, and it would obviously be possible by properly choosing the number of atoms to be assigned to the molecule to obtain agreement with the proposed relation. In the present state of our knowledge of the constitution of the solids in question little would be gained from such a procedure, and to the writer it appears better to adopt, tentatively at least, a suggestion made in the earlier paper, and admit that in certain cases simple submultiples of the fundamental frequency, ν_A , may occur. This has been done in the following Table (III.) in which fractions $\frac{1}{2}$, $\frac{1}{3}$, or $\frac{2}{3}$ have been introduced into the frequency number to secure agreement between the values of ν_A . It is significant that the table includes four alkali metals, which are peculiar in their large atomic volume, and three or four elements which are known to exist in allotropic modifications.

TABLE III.
Elements with Fractional Values for n .

Element.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
Li	3	10.65	$1\frac{1}{2} \times 21.3$
Be	4	23.63	$4\frac{1}{2} \times 21.0$
Na	11	4.31	$2\frac{1}{2} \times 21.0$
Mg	12	7.88	$4\frac{1}{2} \times 21.0$
P (red)	15	6.72	5×20.2
(yellow)	3.83	$2\frac{3}{4} \times 20.9$
S (rhombic)	16	4.30	$3\frac{1}{4} \times 21.1$
(monoclinic)	4.24	$3\frac{1}{4} \times 20.9$
K	19	2.53	$2\frac{1}{4} \times 21.4$
As	33	4.20	$6\frac{1}{3} \times 21.3$
Rb	37	1.54	$2\frac{3}{4} \times 20.7$
In	49	2.37	$5\frac{1}{2} \times 21.1$
I	53	1.82	$4\frac{1}{3} \times 21.5$
Hg	80	1.38	$5\frac{1}{4} \times 21.0$

It should be noted that the product $N\nu$ is the same for beryllium as it is for magnesium, and practically the same for sodium as it is for potassium.

The data for hydrogen and nitrogen are not known very accurately, but it may be mentioned that ν for hydrogen (4.88×10^{12}) is approximately $\frac{1}{4}\nu_A$, whilst for nitrogen ($N=7$, $\nu=2.5 \times 10^{12}$) the product $N\nu$ is approximately $\frac{2}{3}\nu_A$.

§ 4. *The Formula of Einstein.*

Einstein* has put forward an equation for the atomic frequency depending upon the elastic properties of the solid. He takes the restoring force proportional to the distance between two molecules and to the bulk modulus of elasticity.

Thus $D = \text{const.} \cdot V^{\frac{1}{3}} K^{-1}$, where K is the compressibility, and therefore

$$\nu = k \sqrt{\left(\frac{V^{\frac{1}{3}}}{KA}\right)}.$$

The constant k was evaluated by Einstein on certain assumptions as to the arrangement and interaction of the molecules, and found to be 2.8×10^7 , but the empirical value 3.3×10^7 is found to give more satisfactory agreement with the frequency determined from the specific heat. The values of the frequency calculated by Blom with the use of the latter constant have been employed for the determination of $N\nu \times 10^{-12}$. The results are given in Table IV., and an inspection of the column headed "Einstein" shows that the product can be expressed in the form $n\nu_A$, where n is an integer in 23 cases, and differs from an integer by $\frac{1}{2}$ in 4 cases.

* Einstein, *Ann. d. Physik*, vol. xxxiv. p. 170 (1911).

TABLE IV.

Element.	N.	VALUES OF $N_p \times 10^{-12}$ *						5. Debye.
		Specific Heat.	1. Einstein.	2. Lindemann.	3. Alterthun.	4. Grüneisen.	5. Debye.	
Li	3	$1\frac{1}{2} \times 19.9^a$	1×19.2	$1\frac{1}{2} \times 21.3$	$1\frac{1}{2} \times 22.1$	
Be	4	4×20.3	$4\frac{1}{2} \times 21.0$	
B	5	6×20.3	10×21.8	20×21.0	
C	6	12×20	$3 \times 23.4?$	11×20.8	
N	7	1×20.3	
O	8	
F	9	
Ne	10	
Na	11	2×20.7	$1\frac{1}{2} \times 21.3$	$2\frac{1}{2} \times 21.0$	2×19.8	
Mg	12	4×20.1	$3\frac{1}{2} \times 20.9$	$4\frac{1}{2} \times 21.0$	4×21.3	4×20.7	
Al	13	5×21.6	5×20.5	5×21.65	5×19.7	5×20.0	5×21.5	
Si	14	9×20.2	10×20.6	7×21.0	9×19.7	$7 \times 22?$	
P	15	$\left. \begin{array}{l} 2\frac{3}{4} \times 20.9 \\ 5 \times 20.2 \end{array} \right\}$	1×21.0	
S	16	$\left. \begin{array}{l} 3\frac{1}{2} \times 21.1 \\ 3\frac{1}{2} \times 20.9 \end{array} \right\}$	
Cl	17	
A	18	$1\frac{1}{2} \times 21.3$	
K	19	2×20.0	$1\frac{1}{2} \times 21.5$	$2\frac{1}{2} \times 21.4$	2×20.0	
Ca	20	4×21.4	
Sc	21	7×20.5	
Ti	22	11×21.0	10×20.2	
V	23	10×21.3	
Cr	24	11×21.4	8×20.4	11×20.2	
Mn	25	8×21.6	8×20.6	10×20.9	
Fe	26	10×21.8	9×22.0	11×21.5	
Co	27	10×20.8	11×21.8	
Ni	28	11×20.4	11×20.1	12×20.7	
Cu	29	9×21.3	9×21.3	10×21.45	
Zn	30	7×20.6	7×19.7	7×20.5	11×21.0	11×20.1	12×20.9	
Ga	31	4×21.8	11×20.4	
Ge	32	8×20.9	12×20.6	9×21.5	12×21.0	
As	33	$6\frac{1}{2} \times 21.3$	7×20.5	9×21.7	

Se
Br
Kr
Rb
Sr
Yt
Zr
Cb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
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Cs
Ba
La
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a. Determinations of the specific heat of lithium at low temperatures are much to be desired.

b. The larger value is for very low temperatures.

* The columns are numbered to correspond with Blom's paper.

§ 5. *The Formula of Alterthun.*

A formula for the atomic frequency involving the coefficient of linear expansion, α , has been proposed by Alterthun*. For a number of elements the product αT_0 is found to be approximately constant. If, then, for T_0 in Lindemann's formula we substitute the reciprocal of the coefficient of expansion, we find

$$\nu = k\sqrt{(1/A\alpha V^{\frac{2}{3}})}.$$

The constant is taken as 4.2×10^{11} .

The frequencies calculated by Blom by means of this formula have been used in the preparation of the corresponding column in Table IV. As might have been anticipated from the fact that the coefficient of expansion at ordinary temperatures has been employed in the calculation, the agreement here is only moderately good.

§ 6. *The Formula of Grüneisen.*

On the basis of his theory of the solid state Grüneisen † has obtained a relation between the coefficient of expansion, the compressibility, and the specific heat of a substance. The relation, however, involves a coefficient which, according to Grüneisen, is approximately but not strictly constant for different elements. By using this relation in connexion with Einstein's formula an equation for the atomic frequency is found, which may be written

$$\nu = 2.9_2 \times 10^{11} \sqrt{(C_v/3\alpha V^{\frac{2}{3}})},$$

where C_v is the specific heat expressed in gram calories per degree. Taking the values of the frequency given in Table V. of Grüneisen's paper, the values of $N\nu \times 10^{-12}$ have been calculated and are recorded in Table IV. It should be mentioned that the value given for the frequency of silicon is regarded as open to question. The majority of these results show good agreement with the proposed relation.

For the sake of completeness the results obtained from the specific heat and by the formula of Debye have been included in the Table. It must be remembered that the fractional values in the Table are in all cases provisional.

§ 7. *Comparison of Frequency Formulae.*

A comparison of the frequency numbers given in Table IV. for a specified element shows that in many cases the numbers differ according to the formula employed. When allowance

* Alterthun, *Deutsch. Phys. Gesell. Verh.* vol. xv, pp. 25, 65 (1913).

† Grüneisen, *Ann. d. Physik*, vol. xxxix, p. 257 (1912).

has been made for want of accuracy in the formula or in the experimental data, it still appears probable that the same element may have different frequency numbers according to the physical conditions and the particular modification of the solid state that is under examination.

It has usually been assumed that the various frequency formulæ are equivalent to one another.

Thus, if the formulæ of Einstein and of Lindemann give the same frequency,

$$k_E \sqrt{(V^3/KA)} = k_L \sqrt{(T_s/AV^3)},$$

and therefore V/KT_s should be constant for different elements. The experimental values, however, are in agreement with this conclusion only in particular cases*. A reason for this may now be assigned. Instead of identifying the frequencies given by the two formulæ, we must put

$$N\nu_E = n_E\nu_A \quad \text{and} \quad N\nu_L = n_L\nu_A,$$

where the subscript E or L refers to the author of the formula employed.

Hence

$$\frac{\nu_E}{\nu_L} = \frac{n_E}{n_L},$$

from which it follows that $\frac{n_L^2 V}{n_E^2 K T_s}$ must be constant for different elements. It is only in those cases in which $n_L = n_E$ that the simpler expression can legitimately be employed.

§ 8. Conclusion.

The frequency formulæ here considered, unlike the formula of Debye discussed in a former paper, have an undetermined constant, the value of which must be found experimentally. The formulæ themselves are to some extent empirical, and it cannot be said with certainty that they are applicable to all elements without modification. It is, therefore, the more remarkable that for the majority of elements the frequency calculated by these formulæ conforms to the relation $N\nu = n\nu_A$. It appears from the results that, for a particular element, the frequency number, n , is conditioned by the physical state of the solid. Broadly speaking, the number n varies in a periodic way with the atomic number, but the discussion of the dependence of the value of n on the place in the Periodic Table is deferred till it can be dealt with more completely.

* Einstein, *Ann. d. Physik*, vol. xxxv. p. 679 (1911); Grüneisen, *Ann. d. Physik*, vol. xxxix, p. 300 (1912); Richards, *Journ. Am. Chem. Soc.* vol. xxxvii. p. 1643 (1915).