

*Characteristic Frequency and Atomic Number.*

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## PART I.—ATOMIC FREQUENCY AND ATOMIC NUMBER.

§ 1. *Characteristic Atomic Frequency.*

Recent work on the specific heat of chemical elements in the solid state has led to important conclusions with regard to the values of the atomic heat at constant volume. The curves showing the variation of atomic heat with temperature are all of the same form, and any given curve can be transformed into any other merely by altering the scale on which the temperature is plotted. This implies that the atomic heat  $C_v$  is a function of the temperature  $T$ , dependent on a single parameter, the function being the same for different elements. Thus

$$C_v = F(\Theta/T),$$

where  $\Theta$  is a certain temperature characteristic of the element in question. According to the quantum theory  $\Theta = \beta\nu = h\nu/k$ , where

$\nu$  is the characteristic atomic frequency,

$h$  is Planck's constant,  $6.558 \times 10^{-27}$ ,

$k$  is the gas constant for a single molecule,  $1.372 \times 10^{-16}$ .

The work of Moseley\* has shown that the frequency of the X-radiation from an element depends upon the atomic number, that is the number which determines the position of the element in the periodic classification, and is probably equal to the number of positive unit charges in the core of the atom. Isotopic elements, which occupy the same place in the periodic table, have the same atomic number, and chemically are inseparable. They must therefore have the same chemical constant or chemical affinity. But the affinity may be expressed in terms of the atomic heat at constant pressure  $C_p$ . Hence  $C_p$  must be the same for isotopes. But  $C_v$  is a function of the frequency. It is, then, probably fair to assume with Lindemann† that the atomic frequencies are identical for isotopic elements. This leads to the conclusion that the characteristic frequency is a function of the atomic number, and is independent of the atomic weight. It is the

\* Moseley, 'Phil. Mag.', vol. 26, p. 1024 (1913); vol. 27, p. 703 (1914).

† Lindemann, 'Nature', vol. 95, p. 7 (1915).

object of Part I of the present paper to show from the observed values that a simple relation holds between the atomic frequency  $\nu$  and the atomic number  $N$ .

### § 2. *The Relation between $N$ and $\nu$ .*

Determinations of the characteristic temperature, or of the atomic frequency, from the observed values of the specific heats, have been made by Nernst and Lindemann, E. H. Griffiths\* and E. Griffiths,† and at very low temperatures by Keesom and Onnes,‡ Some further results have been collected for a number of elements in a paper by C. E. Blom,§ but to these smaller value must be attached.

Examination of the graph obtained by plotting  $\log \nu$  against  $\log N$  suggested that, for certain sets of elements, the product  $N\nu$  had a constant value. Further investigation showed that the value of the product in some cases was a simple multiple of the value in other cases. Thus, the value of  $N\nu \times 10^{-12}$  for Ag is 211.0, for Fe 209.0. For Al the value is 107.5, which is nearly one-half the former number. For Pt we find 413.4, and for Ir 415.8, numbers which are nearly double those for Ag or Fe. Finally it was found that, in almost every case examined, the value of  $N\nu$  could be expressed with an accuracy of 4 or 5 per cent. as a simple multiple of a certain definite frequency. This is illustrated in Table I, which contains the results for those metals for which the atomic frequency has been determined with the greatest accuracy. All metals are included for which low temperature measurements are available, with the exception of sodium. The product of the atomic number and the atomic frequency can be expressed in the form

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

where  $n$  is an integer, which may be termed the *frequency number*, and  $\nu_A$  is a definite frequency, for which the weighted mean value is  $21.3 \times 10^{12}$  sec.<sup>-1</sup>. The variations in the values of  $\nu_A$  recorded in the Table are not greater than can be accounted for by experimental errors in the determination of the frequency  $\nu$ .

Commenting on the want of concordance in the values found by Nernst for the atomic heat of lead, Messrs. Griffiths remark: "Lead, from our own experience, appears to be a metal with which it is difficult to obtain concordant results."

\* Nernst, 'Vorträge über die Kinetische Theorie der Materie,' 1914, p. 77.

† E. H. Griffiths and E. Griffiths, 'Phil. Trans.,' A, vol. 214, p. 319 (1914).

‡ Keesom and Onnes, 'K. Akad. Amsterdam Proc.,' vol. 18, p. 1247 (1916).

§ C. E. Blom, 'Ann. d. Phys.,' vol. 42, p. 1397 (1913).

Table I.

Element.	N.	$N\nu \times 10^{-12}$ .			
		Nernst.	Griffiths.	Keesom-Onnes.	Mean.
Al .....	13	$5 \times 21 \cdot 6$	$5 \times 21 \cdot 4$		$5 \times 21 \cdot 5$
Fe .....	26		$10 \times 20 \cdot 9$		$10 \times 20 \cdot 9$
Cu .....	29	$9 \times 21 \cdot 3$	$9 \times 21 \cdot 9$	$9 \times 21 \cdot 2$	$9 \times 21 \cdot 3$
Zn .....	30	$7 \times 20 \cdot 6$	$7 \times 20 \cdot 6$		$7 \times 20 \cdot 6$
Ag .....	47	$10 \times 21 \cdot 2$	$10 \times 21 \cdot 1$		$10 \times 21 \cdot 1$
Cd .....	48		$8 \times 21 \cdot 1$		$8 \times 21 \cdot 1$
Hg .....	80	$8 \times 20 \cdot 2$			$8 \times 20 \cdot 2$
Pb .....	82	$7 \times 22 \cdot 2$	$7 \times 22 \cdot 5$	$7 \times 21 \cdot 6$	$7 \times 22 \cdot 0$
Weighted mean .....		21·1	21·3	21·4	21·3

In discussing the experimental values recorded in the Table, attention must be directed to the temperature at which the observations have been made. There are several reasons why determinations at low temperatures are to be preferred. In the first place, the difference between  $C_p$  and  $C_v$  becomes negligible at such temperatures. Again: "It is at very low temperatures that the assumption made by Debye, namely, that the vibrations whose frequency is greater than  $\nu$  are negligible, can best be justified, since at such temperatures the slow heat vibrations would be the most important" (Griffiths). Thirdly, at such temperatures the formula of Debye simplifies to the form  $C_v = \text{const.} (T/\Theta)^3$ , which is probably the correct type at low temperatures, and must be approximated to by any formula that is to give an accurate representation of the variation of specific heat with temperature.

Accordingly greater weight has been attached to the determinations of Keesom and Onnes, who determined the specific heat of copper between  $14^\circ$  and  $90^\circ$  K, and that of lead between  $14^\circ$  and  $80^\circ$  K, taking special precautions as to the temperature measurements and the purity of the material employed. It is to be noticed that the value of  $\nu_\Lambda$  for lead from these observations is much nearer to the mean value than the results obtained by the earlier investigators.\*

Messrs. Griffiths give two sets of values for  $\Theta$  or  $\beta\nu$ . In the first set the values are chosen so as to give agreement with Debye's formula over the lowest portion of the temperature range considered. In the second set  $\beta\nu$  is chosen

\* The results of Keesom and Onnes for lead have been confirmed by Eucken and Schwerts in a series of experiments for which great accuracy is claimed. The latest determinations in Nernst's laboratory give for aluminium  $N\nu = 5 \times 21 \cdot 0 \times 10^{12}$ , and for copper  $9 \times 21 \cdot 1 \times 10^{12}$ , showing even better agreement than the earlier figures. Schwerts, 'Phys. Rev.,' vol. 8, p. 117 (1916).

so as to give coincidence at about  $125^{\circ}$  K, with the result that, in general, a slightly smaller value of  $\nu$  is obtained. In Table I the values for  $\nu$  are those belonging to the first set.

These experimenters also investigated  $\nu$  for sodium, which appears to be somewhat exceptional in its thermal behaviour, and for that reason has not been included in the Table. At low temperatures they found  $\beta\nu = 180$ , whilst at  $125^{\circ}$  K the value is considerably lower,  $\beta\nu = 152$ . Taking the low temperature value,  $\nu = 3.77 \times 10^{12}$ , and  $N\nu = 2 \times 20.71 \times 10^{12}$ , a result which is in good agreement with those recorded in the Table.

Nernst has published determinations of the atomic frequency for two non-metals, carbon (in the form of diamond) and iodine, and it is interesting to find that they fall into line with the metallic elements. For C we find  $N\nu = 12 \times 20 \times 10^{12}$ , and for I,  $N\nu = 5 \times 21.6 \times 10^{12}$ .

Similar results were obtained for nearly all the elements contained in the list given by Blom. Table II gives the figures for these elements with the exception of Li\* and P†. The value of  $N\nu \times 10^{-12}$  is in brackets in those cases in which the atomic frequency is stated by Blom to be less reliable. Even in these cases it will be noticed that  $\nu_A$  has practically the same value as was found to hold when accurate determinations of  $\nu$  were available.

Table II.

Element.	N.	$N\nu \times 10^{-12}$ .	Element.	N.	$N\nu \times 10^{-12}$ .
Be .....	4	$4 \times 20.3$	Ni .....	28	$11 \times 20.4$
B .....	5	$6 \times 20.3$	Mo .....	42	$(12 \times 21.0)$
Mg .....	12	$4 \times 20.1$	Pd .....	46	$(11 \times 20.9)$
Si .....	14	$9 \times 20.2$	Su .....	50	$(9 \times 21.1)$
K .....	19	$(2 \times 20.0)$	Sb .....	51	$12 \times 21.2$
Ti .....	22	$11 \times 21.0$	Ir .....	77	$20 \times 20.8$
Cr .....	24	$11 \times 21.4$	Pt .....	78	$(20 \times 20.7)$
Mn .....	25	$8 \times 21.6$	Au .....	79	$(16 \times 20.7)$
Fe .....	26	$10 \times 21.8$	Bi .....	83	$(12 \times 22.1)$
Co .....	27	$10 \times 20.8$			

The weighted mean value found from the results of Table II is  $\nu_A = 20.85 \times 10^{12}$ .

It will be noticed that the mean value for  $\nu_A$  found from Table II,  $20.85 \times 10^{12}$ , is somewhat smaller than the mean value found from Table I,  $21.3 \times 10^{12}$ . This may arise from the fact that the values of  $\nu$  given by Blom

\* For Li Blom gives  $\nu = 8.3 \times 10^{12}$ , which would make  $N\nu = 24.9 \times 10^{12}$ . This suggests that  $n = 1$  in this case. Determinations of the specific heat at low temperatures are much to be desired.

† For red phosphorus Blom's value is  $\nu = 6.3 \times 10^{12}$ . This non-metallic element is exceptional; we may write  $N\nu$  in the form  $4\frac{1}{2} \times 21.0 \times 10^{12}$ .

are derived from observations of the specific heat at higher temperatures, a procedure which, as we have noticed already, usually gives a smaller value for the frequency.

### § 3. *Application of the Theory of Probability.*

In view of the unexpected character of these results it is desirable to have some check upon them in order to be reasonably sure that the agreement between the values of  $\nu_A$  is not accidental. Such a check is provided by the theory of probability. The case is similar to that discussed by Strutt\* in a paper on the tendency of the atomic weights to approximate to whole numbers. Individual values of  $N\nu$  cannot deviate by more than a fixed amount  $y (= \frac{1}{2}\nu_A)$  from the nearest integral multiple of  $\nu_A$ . "What we require is the probability that after a given number ( $i$ ) of 'trials' the sum of the results should not exceed a certain given amount  $x$ ; the result of each trial lying between 0 and  $y$ , and any value between these limits being equally likely." A formula for the probability has been given by Laplace.†

$$\frac{1}{i!} \left\{ \left(\frac{x}{y}\right)^i - i\left(\frac{x}{y}-1\right)^i + \frac{i(i-1)}{1 \cdot 2}\left(\frac{x}{y}-2\right)^i - \dots \right\}.$$

The series is to be continued only so long as the quantities raised to the power  $i$  are positive.

Applying this formula to the results of Table I, taking  $y = \frac{1}{2} \times 21.3$  and for  $x$  the sum of the differences between the observed and the calculated values of  $N\nu \times 10^{-12}$ , the approximate value of the probability is found to be:—

$$\text{Results of Nernst, } \frac{1}{9},$$

$$\text{Results of Griffiths, } \frac{1}{11},$$

$$\text{Mean results, } \frac{1}{26}.$$

That is, there is one chance in 26 that the mean values of  $N\nu \times 10^{-12}$  should approximate so closely to integral multiples of the number 21.3 by accident.

The application of the formula to the results of Table II gives for the probability approximately  $\frac{1}{31}$ . Consequently when the results of both Tables are taken into consideration there is but a small chance that the assumed regularity may be accidental.

### § 4. *The Formula of Debye.*

In the theory of Debye‡ the characteristic frequency is a maximum frequency which limits abruptly the range of vibrations forming the

\* Strutt, 'Phil. Mag.,' vol. 1, p. 311 (1901).

† 'Théorie Analytique des Probabilités,' p. 259.

‡ Debye, 'Ann. d. Phys.,' vol. 39, p. 789 (1912).

"spectrum" of the solid. Its value in terms of the elastic constants is given by the formula

$$\nu = \left( \frac{3N'}{\sqrt{F}} \right)^{1/3},$$

where  $N'$  is the number of atoms in volume  $V$ , and

$$F = \frac{4\pi}{3} \rho^{3/2} K^{3/2} \left[ 2 \left( \frac{2(1+\sigma)}{3(1-2\sigma)} \right)^{3/2} + \left( \frac{1+\sigma}{3(1-2\sigma)} \right)^{3/2} \right],$$

$\rho$  being the density,  $K$  the compressibility, and  $\sigma$  Poisson's ratio. When the mass of the solid considered is equal to the atomic weight,  $V$  becomes the atomic volume, and  $N'$  Avogadro's constant.\* It should be noticed that this formula for the frequency contains no undetermined constant; all the quantities involved can be measured experimentally. Table IX of Debye's paper gives the value of the characteristic temperature found from the elastic constants for 12 metals, and these results have been employed in the calculation of  $\nu$  and of  $N\nu$  in the following Table (III). It will be seen that in each case the product  $N\nu$  can be expressed in the form  $n\nu_A$  :—

Table III.—Atomic Frequency by Debye's Formula.

Element.	N.	$\nu \times 10^{-12}$ .	$N\nu \times 10^{-12}$ .
Al .....	13	8.26	$5 \times 21.5$
Fe .....	26	9.67	$12 \times 20.9$
Ni .....	28	9.01	$12 \times 21.0$
Cu .....	29	6.81	$9 \times 21.7$
Pd .....	46	4.22	$9 \times 21.6$
Ag .....	47	4.39	$10 \times 20.6$
Cd .....	48	3.48	$8 \times 20.9$
Sn .....	50	3.83	$9 \times 21.3$
Pt .....	78	4.68	$18 \times 20.3$
Au .....	79	3.44	$13 \times 20.9$
Pb .....	82	1.49	$6 \times 21.4$
Bi .....	83	2.30	$9 \times 21.2$

Mean value of  $N\nu = 21.02 \times 10^{12}$ .

Calculation of the probability in this case shows that there is only one chance in 45 that the product  $N\nu$  should by accident approach so nearly to integral multiples of a single fundamental frequency,  $\nu_A$ . Considering the difficulties in the determination of the elastic constants, and the uncertainty attaching to the temperature at which the measurements should be made, this is a striking result.

\* Debye assumes  $N' = 5.66 \times 10^{23}$ ; Millikan's value,  $N' = 6.062 \times 10^{23}$ , would increase the values of  $\nu$  by rather more than 2 per cent.

A comparison of the values of the frequency number,  $n$ , obtained by the use of Debye's formula, with those obtained from the specific heat, reveals the unexpected result that in several cases the integers are not the same. This difference in the values of  $n$  no doubt arises from variations in the physical conditions of the substance under examination. The temperature at which the determinations are made must be taken into consideration. It is well known that in the case of certain elements various physical modifications exist consequent upon structural changes in the solid.

#### § 5. *Choice of the Atomic Numbers.*

In the foregoing work the atomic numbers employed have been those given by Moseley. It has been suggested by Rydberg that two unknown elements should be included in the Periodic Table between hydrogen and lithium, so that lithium would have an atomic number 5 instead of 3. For all the elements later in the Table, Rydberg's ordinals are greater by 2 units than Moseley's numbers. It is found that the relation  $N\nu = n\nu_A$  fits the results of observation more closely when Moseley's numbers are used for  $N$ . This is clearly shown by calculating the probability for the two sets of numbers. Taking the observations of Nernst, the probability given by Rydberg's ordinals is  $1/1.3$  instead of  $1/9$ . For the observations of Griffiths, the probability given by Rydberg's ordinals is  $1/1.5$  instead of  $1/11$ . When Debye's formula for the characteristic frequency is employed, the probability is  $1/5.4$  for Rydberg's ordinals, but  $1/45$  for Moseley's numbers. These results may be regarded as evidence strongly in favour of the atomic numbers proposed by Moseley.\*

#### § 6. *The Physical Significance of the Relation $N\nu = n\nu_A$ .*

The results so far obtained may be summarised in the equation  $N\nu = n\nu_A$ . Thus for each element the characteristic frequency (or frequencies) may be expressed in terms of a single fundamental frequency,†  $\nu_A$ , by employing two integers  $N$  and  $n$ . The integer  $N$  denotes Moseley's atomic number; the physical significance of  $n$  is not as yet clear, but it may be suggested that it is related to the number of (valency) electrons which determine the crystalline structure of the solids. A possible interpretation may be given to the empirical relation by the Quantum Theory. Multiply each side of the equation by Planck's constant,  $h$ , which denotes the quantum of action. Then

$$Nh\nu = nh\nu_A.$$

\* The same conclusion was arrived at, in a different way, by van den Broek, 'Phil. Mag.', vol. 28, p. 630 (1914).

† It is possible that, in some cases, instead of the value  $\nu_A = 21.3 \times 10^{12}$ , it may be necessary to take a simple submultiple, such as  $\frac{1}{2}$ , of this quantity.

Considering an atom of any element,  $h\nu$  represents one quantum of energy corresponding to the critical temperature  $\Theta$ . The left-hand side of the equation accordingly represents the amount of energy for as many quanta as there are positive charges in the core of the atom. The right-hand side may be regarded as the energy corresponding to an integral multiple of a certain fundamental quantum,  $h\nu_A$ . It is necessary to emphasise the fact that this does not imply the actual existence of "atoms of energy." We are here concerned with the characteristic frequency, that is, with a certain limiting condition affecting each element in the solid state, and the occurrence of the quantity  $h\nu_A$  implies only that there is a certain limiting amount of energy involved, which is the same for various elements.

According to the theories of Debye and of Born and Kármán, the vibrations of the atoms in a solid form a continuous spectrum, limited by a definite boundary on the side of the shorter wave-lengths. It is this limiting frequency which is taken as the characteristic atomic frequency. It is not unreasonable to suppose that this frequency may be subject to a condition similar to that expressed by Einstein's relation,  $Vc = h(\nu - \nu_0)$ , which has been proved true by the experiments of Richardson and Compton, Hughes and Millikan, for the photoelectric effect. It has, in fact, been proved by several investigators that the relation  $Vc = h\nu$  accurately defines the boundary on the side of the shorter wave-lengths of the spectrum of X-radiation. In the equation  $Nh\nu = nh\nu_A$  we may substitute  $Vc$  for  $h\nu$ , and  $V_Ac$  for  $h\nu_A$ , where  $V$  and  $V_A$  denote potentials at present undefined, and  $e$  is the charge on an electron. Then  $NeV = neV_A$ , or  $NeV - neV_A = 0$ . But  $Ne$  is  $E$ , the charge on the nucleus of the atom, and  $-ne$  is the charge carried by  $n$  electrons. If we may identify  $V$  with the potential of the nucleus, and  $V_A$  (equal to about  $\frac{1}{12}$  volt) with the potential of a ring of electrons (or of the valency electrons), the relation expresses the fact that the energy of the atomic system is zero, or perhaps a minimum, in the condition corresponding to the limiting frequency. This involves the supposition that in the limiting condition the potential of the electrons in question assumes a constant value (or perhaps a multiple of some constant value, since  $n$  may be  $p \times q$ , where  $p$  and  $q$  are integers).

The relation may also be written in the form  $EV = nA$ , where  $A$  is constant. This may be interpreted as expressing the fact that in the limiting condition the energy of the nucleus is an integral multiple of a certain quantity of energy  $A$ .



## PART II.—ELECTRONIC FREQUENCY AND ATOMIC NUMBER.

§ 7. *Electronic Frequencies.*

A relation similar to that already discussed appears to hold for certain electronic frequencies. When, however, the vibration of an electron is in question, it is necessary to replace the atomic constant  $\nu_A$  ( $21.3 \times 10^{12}$  sec.<sup>-1</sup>) by the fundamental electronic frequency,  $\nu_E = 3.289 \times 10^{15}$  sec.<sup>-1</sup>, which is Rydberg's constant in spectral series, usually expressed as the wave number 109679.22. (Curtis). The relation then takes the form

$$N\nu = n\nu_E, \quad \text{or} \quad N\nu = (n + \frac{1}{2})\nu_E.$$

In these cases, as in dealing with the characteristic atomic frequency,  $\nu$  refers to some limiting frequency or to a frequency associated with a maximum value of some variable quantity.

§ 8. *The Maximum of the Photoelectric Effect.*

Pohl and Pringsheim\* have determined the value of the wave-length corresponding to the maximum of the "selective" photoelectric effect with an accuracy of about 2 or 3 per cent. Their results have been employed in the construction of Table IV, which gives the values of  $\nu$  and of  $N\nu$  for the four alkali metals examined.

Table IV.

Element.	N.	$\lambda$ in $\mu\mu$ .	$\nu \times 10^{-14}$ .	$N\nu \times 10^{-15}$ .
Li .....	3	280	10.71	$1 \times 3.21$
Na .....	11	340	8.82	$3 \times 3.23_5$
K .....	19	435	6.90	$4 \times 3.27_5$
Rb .....	37	480	6.25	$7 \times 3.30$

The figures in the last column of the Table show that  $N\nu$  may be expressed in the form  $n\nu_E$ , where  $n$  is a simple integer and  $\nu_E$  is very nearly constant. The mean value of  $\nu_E$  for these four elements is  $3.255 \times 10^{15}$  sec.<sup>-1</sup>, which is so near the Rydberg value  $3.289 \times 10^{15}$  sec.<sup>-1</sup> that there can be little doubt as to the identity of the two numbers.

A maximum photoelectric activity has been recorded for the four elements, magnesium, aluminium, calcium, and barium, which do not show a true "selective" effect. It is possible that the corresponding frequency and the atomic number are related in a similar way in these cases also, but the results are not decisive.

\* 'Die Lichtelektrischen Erscheinungen' (Vieweg, 1914).

§ 9. The Limiting Frequency of the Photoelectric Effect.

The emission of electrons under the influence of light takes place only when the frequency of the exciting light exceeds a certain limiting frequency,  $\nu_0$ . Richardson and Compton\* have determined this limit both from the maximum energy of the electrons emitted, and also from their mean energy. The results have been employed in the construction of Table V.

Table V.

Element.	N.	$N\nu_0 \times 10^{-15}$ .	
		Maximum energy.	Mean energy.
Na .....	11	$2 \times 2 \cdot 83$	$2 \times 2 \cdot 86$
Al .....	13	$3 \times 2 \cdot 73$	$3 \times 3 \cdot 16$
Mg .....	12	$3 \times 3 \cdot 14$	$3 \times 3 \cdot 20$
Zn .....	30	$8 \times 3 \cdot 00$	$8 \times 3 \cdot 15$
Sn .....	50	$13 \times 3 \cdot 19$	$13 \times 3 \cdot 42$
Bi .....	83	$23 \times 3 \cdot 28$	$23 \times 3 \cdot 21$
Cu .....	29	$9 \times 3 \cdot 22$	$9 \times 3 \cdot 13$
Pt .....	78	$25 \times 3 \cdot 24$	$25 \times 3 \cdot 21$

With the exception of the values for sodium and one value for aluminium, the results are in fair agreement with the relation  $N\nu_0 = n\nu_E$ .

§ 10. Ionisation Potentials.

The minimum potential required for the ionisation of a gas is probably connected with  $\nu_0$ , the least frequency of radiation which can ionise the gas photoelectrically.†

Einstein's equation is

$$eV_0 = h\nu_0,$$

where  $V_0$  denotes the ionisation potential. If then  $\nu_0$  is subject to the relation  $N\nu_0 = n\nu_E$ , we should expect to find  $NV_0 = nV_E$ , where  $V_E$  denotes a constant potential determined by  $eV_E = h\nu_E$ . From this relation the value of  $V_E$  is found to be 13.5 volts. This is the value in Bohr's theory for the ionising potential in the case of (atomic) hydrogen. For, according to this theory, the work done in moving the electron from its orbit to a position of rest at infinity is  $W = 2\pi^2me^4/h^2$  and  $\nu_E = 2\pi^2me^4/h^3$ . Hence  $W$ , which is  $eV_E$ , is equal to  $h\nu_E$ .

The value of the ionisation potential for (molecular) hydrogen determined

\* Richardson and Compton, 'Phil. Mag.,' vol. 24, p. 575 (1912); vol. 26, p. 549 (1914).

† Einstein, 'Ann. d. Phys.,' vol. 17, p. 132 (1905); Richardson, 'Phil. Mag.,' vol. 24, p. 570 (1912); K. T. Compton, 'Phys. Rev.,' vol. 8, pp. 386, 412 (1916).

experimentally is of the right order of magnitude, but is only 11 volts instead of 13·5 volts.

The following Table (VI) gives the value of the ionisation potential,  $V_0$ , and of the product  $NV_0$ , in all cases where direct experimental determinations have been carried out.\* The results in the last column of the Table show that, with the exception of hydrogen and oxygen, there is remarkable agreement with the relation  $NV_0 = nV_E$ .

Table VI.

Element.	N.	$V_0$ (volts).	$NV_0$ .
Hydrogen .....	1	11·0	$1 \times 11 \cdot 0$
Helium .....	2	20·5	$3 \times 13 \cdot 7$
Nitrogen .....	7	7·5	$4 \times 13 \cdot 1$
Oxygen .....	8	9·0	$5 \times 14 \cdot 4$
Neon .....	10	16·0	$12 \times 13 \cdot 3$
Argon .....	18	12·0	$16 \times 13 \cdot 5$
Mercury .....	80	4·9	$30 \times 13 \cdot 1$

In the case of mercury ionisation of a second type also occurs for a potential of 10 volts,† which is almost exactly double the value recorded in the Table, so that the corresponding frequency number,  $n$ , would be 60.

### § 11. Thermionic Potentials.

Intimately connected with the potentials here discussed are the potentials observed in dealing with the emission of electrons from glowing solids and the contact potentials between different metals. In these cases the results obtained depend to such an extent on surface conditions and the presence of gaseous films, that as yet it is hardly possible to assign to the various elements reliable values that shall be characteristic of the elements themselves. The work that an electron would have to do to escape from the substance may be measured by the equivalent potential difference,  $\phi$ . The values quoted in Table VII for  $\phi$ , the "electron affinity" of the elements in volts, are derived from thermionic measurements,‡ and for the reason stated must be received with some reserve. It is, however, interesting to find that the values of  $N\phi$  approximate fairly closely to multiples of 13·5 volts.

\* Franck and Hertz, 'Verh. Deutsch. Phys. Gesell.,' vol. 15, p. 34 (1913); vol. 16, pp. 457, 512 (1914); McLennan and Henderson, 'Roy. Soc. Proc.,' A, vol. 91, p. 485 (1915); Goucher, 'Phys. Rev.,' vol. 8, p. 561 (1916); Bazzoni, 'Phil. Mag.,' vol. 32, p. 566 (1916).

† Tate, 'Phys. Rev.,' vol. 7, p. 686 (1916).

‡ O. W. Richardson, 'The Emission of Electricity from Hot Bodies,' pp. 69-79 164-178 (1916); Langmuir, 'American Electrochemical Society,' pp. 341-396 (1916).

Table VII.

Element.	N.	$\phi$ (volts).	Authority.	$N\phi$ .
Carbon .....	6	4.14	Langmuir	$2 \times 12.4$
		4.51	Deininger	$2 \times 13.5$
Calcium .....	20	3.04	Horton	$5 \times 12.2$
Titanium .....	22	2.4*	Langmuir	$4 \times 13.2$
Iron .....	26	3.2*	Langmuir	$6 \times 13.9$
Nickel .....	28	2.9	Schlichter	$6 \times 13.5$
Molybdenum .....	42	4.31	Langmuir	$14 \times 13.0$
Tantalum .....	73	4.31	Langmuir	$23 \times 13.7$
Tungsten .....	74	4.52	Langmuir	$25 \times 13.4$
Platinum .....	78	5.02	Deininger	$30 \times 13.1$
		5.1	Horton	$30 \times 13.3$
Thorium .....	90	3.36	Langmuir	$22 \times 13.7$

\* Preliminary measurements by Dr. Dushman.

§ 12. Conclusion.

The empirical relations discussed in Part II may be summarised in the formula

$$N\nu = n\nu_E.$$

On multiplying each side of this equation by  $h$ , we obtain

$$Nh\nu = nh\nu_E,$$

or, by using the quantum relation  $h\nu = eV$ ,

$$NeV = neV_E.$$

But  $Ne$  is equal to the charge,  $E$ , on the atomic nucleus. Hence

$$EV - neV_E = 0.$$

This suggests that in the limiting conditions which arise in all the physical phenomena under discussion, we have to deal with a minimum value of the energy of a system comprising the nucleus and a certain number of electrons.