



LIII. Molecular frequency and molecular number.—Part III. Inorganic compounds. Lindemann's Formula

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LIII. *Molecular Frequency and Molecular Number.*—Part III.
Inorganic Compounds. Lindemann's Formula. By H.
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IN the present communication are given the values of the characteristic molecular frequency, ν , calculated by Lindemann's formula for those inorganic compounds for which data are available. The formula in question may be written

$$\nu = k \sqrt{\left(\frac{T_s}{MV^{\frac{2}{3}}}\right)},$$

where T_s is the absolute temperature of the melting-point, M is the molecular weight, and V the molecular volume. The coefficient k has been assumed constant, and Nernst's empirical value, 3.08×10^{12} , has been employed.

For each compound is tabulated the value of the molecular number, N , and of the product $N\nu \times 10^{-12}$. In the majority of cases it has been found possible to express $N\nu$ either in the form $n\nu_A$ or in the form $(n + \frac{1}{2})\nu_A$, where n is an integer and ν_A is a constant frequency having a value about 21×10^{12} sec.⁻¹. In the few exceptional cases where neither of the above forms is applicable the product has been expressed as $(n + \frac{1}{4})\nu_A$ or $(n + \frac{3}{4})\nu_A$, but no special significance is at present attached to such results. All the results here given must be considered in the light of the general considerations affecting Lindemann's formula put forward in Part I. of this paper†.

* Communicated by the Author.

† Phil. Mag. vol. xxxv. p. 333, April 1918.

Compounds containing water of crystallization have not been included, as in such cases it is often difficult to decide whether the recorded temperature is a true melting-point or the temperature at which the solid dissolves in the water of crystallization.

GROUP I.

Of inorganic compounds for which the density and the melting-point are known, a larger proportion belongs to the first group than to any other group in the Periodic Table. With a small number of exceptional or doubtful cases, the results show good agreement with the suggested relations. It is noteworthy that when the temperature of the melting-point is known accurately, the agreement is better than when this temperature is uncertain.

For several of the lithium compounds the melting-point has not been determined with great accuracy, yet the values of ν_λ do not differ widely from the mean value which is $20.7 \times 10^{12} \text{ sec.}^{-1}$. The mean value for the elements, given in a former paper*, was $20.9 \times 10^{12} \text{ sec.}^{-1}$, when the same factor was employed in Lindemann's formula as that here used. It has been pointed out previously† that the chance of these results for the lithium compounds (including $\text{Li}_3\text{PO}_4 \cdot \text{H}_2\text{O}$) agreeing accidentally was about 1 in 280.

GROUP I.

Lithium Compounds (N=3).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
LITHIUM				
amide	LiNH_2	12	6.073	$3\frac{1}{2} \times 20.8$
bromide	LiBr	38	3.234	6×20.5
carbonate	Li_2CO_3	36	3.435	6×20.6
chloride (a).....	LiCl	20	5.079	5×20.3
fluoride	LiF	12	9.207	$5\frac{1}{2} \times 20.1$
iodide	LiI	56	2.227	6×20.8
nitrate.....	LiNO_3	34	2.821	$4\frac{1}{2} \times 21.3$
perchlorate.....	LiClO_4	52	1.742	$4\frac{1}{2} \times 20.1$
silicate (b)	Li_2SiO_3	44	3.756	8×20.8
sulphate acid	LiHSO_4	52	1.636	4×21.3
sulphate	Li_2SO_4	54	2.680	7×20.7

- (a) Richards and Meldrum (1917) give the melting-point of pure lithium chloride as 613° C . This makes for better agreement, giving $N\nu \times 10^{-12} = 5 \times 20.6$.
- (b) The melting-point of lithium silicate is given as a standard temperature (1201° C) in the Smithsonian Physical Tables.

* H. S. Allen, *Phil. Mag.* vol. xxxiv. p. 478 (1917).

† H. S. Allen, *Phil. Mag.* vol. xxxv. p. 338 (1918).

Sodium Compounds (N=11).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
SODIUM				
borate tetra-	$\text{Na}_2\text{B}_4\text{O}_7$	98	1.596	$7\frac{1}{2} \times 20.9$
bromate	NaBrO_3	70	1.801	6×21.0
bromide	NaBr	46	3.037	$6\frac{3}{4} \times 20.7$
carbonate	Na_2CO_3	52	2.878	7×21.4
chlorate	NaClO_3	52	1.962	5×20.4
chloride (a).....	NaCl	28	4.407	6×20.6
fluoride	NaF	20	6.794	$6\frac{1}{2} \times 20.9$
hydroxide	NaOH	20	6.787	$6\frac{1}{2} \times 20.9$
iodide	NaI	64	2.268	7×20.7
nitrate.....	NaNO_3	42	2.417	5×20.3
nitrite (b)	NaNO_2	34	2.724	$4\frac{1}{2} \times 20.6$
phosphate meta	$\text{Na}_4\text{P}_4\text{O}_{12}$	200	0.829	8×20.7
sulphate	Na_2SO_4	70	2.337	8×20.4
sulphate acid (c), ...	NaHSO_4	60	1.859	$5\frac{1}{2} \times 20.3$

(a) Melting-point of sodium chloride (801°C .) has been used as a standard temperature.

(b) Melting-point of sodium nitrite, 271°C . (Divers, 1899).

(c) Melting-point of NaHSO_4 "over 315°C ." (Gmelin-Kraut).

Potassium Compounds (N=19).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
POTASSIUM				
arsenate acid	KH_2AsO_4	86	1.364	$5\frac{1}{2} \times 21.3$
bromate	KBrO_3	78	1.708	$6\frac{1}{2} \times 20.5$
bromide	KBr	54	2.575	$6\frac{1}{2} \times 20.6$
carbonate	K_2CO_3	68	2.310	$7\frac{1}{2} \times 21.0$
chlorate	KClO_3	60	1.886	$5\frac{1}{2} \times 20.6$
chloride	KCl	36	3.493	6×20.9
chromate	K_2CrO_4	94	1.882	$8\frac{1}{2} \times 20.8$
dichromate.....	$\text{K}_2\text{Cr}_2\text{O}_7$	142	0.974	$6\frac{1}{2} \times 21.4$
fluoride	KF	28	4.789	$6\frac{1}{2} \times 20.6$
formate	KCHO_2	42	1.955	4×20.5
hydroxide	KOH	28	3.431	$4\frac{1}{2} \times 21.3$
iodate	KIO_3	96	1.609	6×20.4
iodide	KI	72	1.988	7×20.4
iodide tri-	KI_3	178	0.543	$4\frac{1}{2} \times 21.5$
nitrate.....	KNO_3	50	2.080	5×20.8
perchlorate.....	KClO_4	68	2.046	$6\frac{1}{2} \times 21.4$
periodate.....	KIO_4	104	1.488	$7\frac{1}{2} \times 20.6$
phosphate	KH_2PO_4	68	1.308	$4\frac{1}{2} \times 20.9$
dihydrogen (a) }				
sulphate (b).....	K_2SO_4	86	2.121	9×20.3
" acid	KHSO_4	68	1.536	5×20.9
sulphocyanate.....	KCNS	48	1.778	4×21.3

(a) Melting-point of the anhydrous salt, 96°C ., Tilden (1884).

(b) The melting-point of potassium sulphate (1070°C .) is used as a standard temperature.

The results for sodium and potassium compounds are specially interesting, and should be compared with one another where that is possible. There are eleven cases in

which compounds of sodium are represented in the second list by the corresponding potassium salts. For five of these (the bromide, chloride, fluoride, iodide, nitrate) the frequency number is the same for the sodium as for the potassium salt. For the bromate, carbonate, chlorate, the frequency number for the potassium compound is greater by $\frac{1}{2}$ than that for the sodium compound. For normal potassium sulphate $N\nu \times 10^{-12} = 9 \times 20.3$, as compared with 8×20.4 for the sodium salt. The results for the acid sulphates and the hydroxides are less reliable.

The bromides of sodium and potassium require special consideration. For NaBr the melting-points recorded fall between the early value of Carnelley (708° C.) and that of Ruff and Plato (765° C.). Taking the latter value, $N\nu = 139.7 \times 10^{12}$. For KBr Carnelley gave the value 699° C., whilst Ruff and Plato in 1903 found 750° C. Using the highest value according to the principle adopted generally, it is found that $N\nu = 139.0 \times 10^{12}$. Thus if the melting-points of Ruff and Plato are correct, the values of $N\nu$ for NaBr and KBr are in close agreement with one another; but they cannot be represented by using frequency numbers of the form n or $n + \frac{1}{2}$ unless high values for ν_A are employed, the product for NaBr being equal to $6\frac{1}{2} \times 21.5 \times 10^{12}$ and that for KBr being equal to $6\frac{1}{2} \times 21.4 \times 10^{12}$. A redetermination of the density and melting-point for each of these salts is to be desired. It may be noticed that both LiBr and RbBr give normal results, the value of $N\nu$ for the former salt being $6 \times 20.5 \times 10^{12}$, for the latter $7 \times 20.5 \times 10^{12}$; the melting-point of CsBr is not recorded.

Assuming that the value of $N\nu \times 10^{-12}$ for NaBr is written in the form $6\frac{1}{2} \times 21.5$, calculation of the probability by the formula of Laplace shows that the chance of an accidental concordance in the values of ν_A for the sodium salts is about 1 in 36.

The agreement between the values of ν_A in the case of the compounds of rubidium and caesium is only moderately good. Perhaps it may be safe to predict from a comparison of the results with those already given that the melting-point of caesium iodide will prove to be higher than the recorded value, 621° C., so as to give a frequency number 8 instead of $7\frac{1}{2}$. It will be noticed that in general the frequency numbers for the compounds of the alkali metals tend to increase as the atomic number of the metal increases.

Rubidium Compounds (N=37).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
RUBIDIUM				
bromide	RbBr	72	1.990	7×20.5
chloride (a)	RbCl	54	2.310	6×20.8
fluoride	RbF	46	3.021	$6\frac{1}{2} \times 21.4$
hydroxide	RbOH	46	2.297	5×21.1
iodide	RbI	90	1.616	7×20.8
oxide di-	Rb ₂ O ₂	90	1.674	7×21.5
pentasulphide.....	Rb ₂ S ₅	154	0.685	5×21.1

(a) Melting-point of rubidium chloride, 714° C. (Richards & Meldrum, 1917).

Cæsium Compounds (N=55).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
CÆSIUM				
chloride (a).....	CsCl	72	2.065	7×21.2
iodide	CsI	108	1.480	$7\frac{1}{2} \times 21.3$
nitrate.....	CsNO ₃	86	1.542	$6\frac{1}{2} \times 20.4$
oxide tri-	Cs ₂ O ₃	134	1.076	7×20.6
„ tetr-	Cs ₂ O ₄	142	1.073	$7\frac{1}{2} \times 20.3$
pentasulphide.. ..	Cs ₂ S ₅	190	0.612	$5\frac{1}{2} \times 21.1$

(a) Melting-point of cæsium chloride, 645° C. (Richards & Meldrum, 1917).

Only a few copper compounds can be included; it is of interest to note that the frequency number for cupric chloride is $6\frac{1}{2}$ as compared with 6 for the cuprous salt.

Copper Compounds (N=29).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
CUPROUS				
bromide	CuBr	64	2.267	7×20.7
chloride	CuCl	46	2.726	6×20.9
iodide	CuI	82	2.048	8×21.0
sulphide	Cu ₂ S	74	3.002	11×20.2
CUPRIC				
chloride	CuCl ₂	63	2.136	$6\frac{1}{2} \times 20.7$
oxide	CuO	37	5.458	10×20.2

Silver Compounds (N=47).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
SILVER				
bromide	AgBr	82	1.935	$7\frac{1}{2} \times 21.2$
chlorate	AgClO ₃	88	1.421	6×20.8
chloride	AgCl	64	2.343	7×21.4
fluoride	AgF	56	2.609	7×21.0
iodide	AgI	100	1.657	8×20.7
nitrate (a).....	AgNO ₃	78	1.543	6×20.1
phosphate ortho.....	Ag ₃ PO ₄	188	1.309	15×20.6
„ pyro	Ag ₄ P ₂ O ₇	274	0.756	10×20.7
sulphate	Ag ₂ SO ₄	142	1.378	$8\frac{1}{2} \times 20.8$
sulphide	Ag ₂ S	110	2.004	$10\frac{1}{2} \times 21.0$
telluride	Ag ₂ Te	146	1.686	12×20.5

(a) Silver nitrate changes from the rhombic to the hexagonal-rhombic form at 159° 8 C. The density of the rhombic form has been used in the calculation.

The salts of silver show fair agreement with the proposed relation. It is doubtful whether silver nitrate should have

been included, as the density corresponds to a crystalline form different from that to which the melting-point applies.

No results are available for compounds of gold.

The melting-point and the density are known for the greater number of the halogen derivatives of Group I., so that it is possible to institute a comparison between the frequency numbers for this group of compounds. The results are collected in the Table following, which contains the atomic or molecular number in italics and the product $N\nu \times 10^{-12}$ in roman numerals. The values for the thallium compounds have been added as they resemble closely the corresponding rubidium compounds*. A close examination of the table will reveal many interesting relationships; the close resemblance between the sodium and the potassium salts is at once evident; the frequency numbers for these compounds exceed the corresponding numbers for the lithium salts by unity (the bromide excepted); the frequency numbers for cuprous chloride, bromide, iodide form the sequence 6, 7, 8; the frequency numbers for silver chloride, bromide, iodide form the sequence 7, $7\frac{1}{2}$, 8. Further, it will be noticed that silver chloride, cuprous bromide, sodium iodide have the same frequency number, 7; caesium chloride, rubidium bromide, potassium iodide form a similar chain with frequency number, 7.

Monohalides of Group I.

Element.	Fluoride F=9.	Chloride Cl=17.	Bromide Br=35.	Iodide I=53.
Li=3	<i>12</i> $5\frac{1}{2} \times 20.1$	<i>20</i> 5×20.3	<i>38</i> 6×20.5	<i>56</i> 6×20.8
Na=11	<i>20</i> $6\frac{1}{2} \times 20.9$	<i>28</i> 6×20.6	<i>46</i> $6\frac{3}{4} \times 20.8$	<i>64</i> 7×20.7
K=19	<i>28</i> $6\frac{1}{2} \times 20.6$	<i>36</i> 6×20.9	<i>54</i> $6\frac{3}{4} \times 20.6$	<i>72</i> 7×20.4
Cu=29	<i>38</i> ---	<i>46</i> 6×20.9	<i>64</i> 7×20.7	<i>82</i> 8×21.0
Rb=37	<i>46</i> $6\frac{1}{2} \times 21.4$	<i>54</i> 6×20.8	<i>72</i> 7×20.5	<i>90</i> 7×20.8
Ag=47	<i>56</i> 7×21.0	<i>64</i> 7×21.4	<i>82</i> $7\frac{1}{2} \times 21.2$	<i>100</i> 8×20.7
Cs=55	<i>64</i> ---	<i>72</i> 7×21.1	<i>90</i> ---	<i>108</i> $7\frac{1}{2} \times 21.3$
Tl=81	<i>90</i> ---	<i>98</i> 6×21.1	<i>116</i> 8×21.3	<i>134</i> 8×20.9

* Tutton, Roy. Soc. Proc. vol. lxxix. p. 351 (1907).

GROUP II.

On the whole the results for compounds containing elements belonging to the second group are less reliable than those already considered. This arises partly from the fact that in many cases there is uncertainty as to the true value of the melting-point, no values later than those of Carnelley being recorded for several compounds*; further, the product $N\nu$ is in general greater for these compounds than it is for the corresponding compounds containing elements of the first group, so that larger frequency numbers are required. Consequently the frequency numbers given in the following Tables are not to be regarded in all cases as final; some of them—especially amongst the larger numbers—may require revision when more exact data have been obtained.

In spite of such uncertainties a comparison between the compounds in these Tables, and also between these and the corresponding compounds for the first group, will show many suggestive relationships.

GROUP II.

Beryllium Compounds ($N=4$).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
BERYLLIUM				
fluoride	BeF_2	22	5.213	$5\frac{1}{2} \times 20.9$
iodide	BeI_2	110	1.339	7×21.0

Magnesium Compounds ($N=12$).

MAGNESIUM				
chloride <i>C</i>	MgCl_2	46	2.807	6×21.5
fluoride <i>C</i>	MgF_2	30	5.446	8×20.4

Calcium Compounds ($N=20$).

CALCIUM				
aluminate	CaAl_2O_4	78	3.011	$11\frac{1}{2} \times 20.4$
bromide	CaBr_2	90	1.783	8×20.1
chloride	CaCl_2	54	2.302	6×20.7
fluoride	CaF_2	38	4.757	9×20.1
iodide	CaI_2	126	1.464	9×20.5
nitrate (<i>a</i>) <i>C</i>	$\text{Ca}(\text{NO}_3)_2$	82	1.715	7×20.1
nitride	Ca_3N_2	74	2.532	9×20.8
oxide	CaO	28	7.696	$10\frac{1}{2} \times 20.5$
silicate	CaSiO_3	58	3.531	10×20.5
sulphate	CaSO_4	68	2.979	10×20.3

(a) Highest density recorded, 2.472 (Landolt-Börnstein).

* These cases are indicated in the tables by the letter C following the name of the compound.

Strontium Compounds (N=38).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
STRONTIUM				
bromide <i>C</i>	SrBr ₂	108	1.512	8 × 20.4
chloride	SrCl ₂	72	2.201	7½ × 21.1
fluoride <i>C</i>	SrF ₂	56	3.037	8 × 21.3
hydroxide	Sr(OH) ₂	56	2.204	6 × 20.6
iodide	SrI ₂	144	1.197	8½ × 20.3
nitrate <i>C</i>	Sr(NO ₃) ₂	100	1.549	7½ × 20.7
oxide	SrO	46	6.195	14 × 20.4
silicate	SrSiO ₃	76	2.940	11 × 20.3

Barium Compounds (N=56).

BARIUM				
bromide	BaBr ₂	126	1.531	9 × 21.3
carbonate (<i>a</i>)	BaCO ₃	86	2.485	10½ × 20.4
chloride	BaCl ₂	90	1.982	8½ × 21.0
fluoride	BaF ₂	74	2.768	9 × 20.5
iodide	BaI ₂	162	1.153	9 × 20.7
nitrate <i>C</i>	Ba(NO ₃) ₂	118	1.298	7½ × 20.4
silicate	Ba(SiO ₃) ₂	94	2.418	11 × 20.7

(*a*) "Schmilzt in CO₂ bei 1380° noch nicht" (Boeke).

Comparing together the compounds of calcium, strontium, and barium we find that, in general, the frequency number corresponding to a particular radicle tends to increase with an increase in the atomic number of the metal. Again, comparing the chloride, bromide, and iodide for a particular metal, it is noticed that the frequency number for the bromide is greater than that for the chloride, and the frequency number for the iodide is at least as great as that for the bromide. In the case of the fluoride, however, the frequency number is about the same as that for the iodide.

Zinc Compounds (N=30).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
ZINC				
acetate.....	Zn(C ₂ H ₃ O ₂) ₂	92	1.113	5 × 20.5
bromide <i>C</i>	ZnBr ₂	100	1.408	7 × 20.1
chloride (<i>a</i>).....	ZnCl ₂	64	1.849	5½ × 21.5
fluoride <i>C</i>	ZnF ₂	48	3.410	8 × 20.5
iodide <i>C</i>	ZnI ₂	136	1.113	7½ × 20.5
sulphide	ZnS	46	3.936	9 × 20.1

(*a*) Melting-point of zinc chloride, 365° C. "All lower values are obtained from impure material."

Cadmium Compounds (N=48).

CADMIUM				
bromide	CdBr ₂	118	1.412	8 × 20.8
chloride	CdCl ₂	82	1.846	7½ × 20.2
fluoride <i>C</i>	CdF ₂	66	2.500	8 × 20.6
iodide	CdI ₂	154	1.027	7½ × 21.1
sulphate	CdSO ₄	96	2.153	10 × 20.7

Mercury Compounds (N=80).

MERCURIC				
bromide	HgBr ₂	150	0.927	6½ × 21.4
chloride	HgCl ₂	114	1.200	6½ × 21.1
iodide	HgI ₂	186	0.798	7 × 21.2
MERCUROUS				
iodide (<i>a</i>).....	HgI	133	1.157	7½ × 21.2

(*a*) Melting-point of mercurous iodide, 290° C., Yvon (1873).

GROUP III.

The compounds met with in connexion with elements of the third group do not require much discussion. The melting-points of boron oxide and boric acid are determinations of Carnelley in 1878, whilst those for aluminium bromide and aluminium iodide are of an even earlier date, for these latter compounds the degree of molecular association is uncertain also.

The results for the compounds of thallium form a fairly consistent series, and it is of interest to compare the frequency numbers with those previously given for the compounds of the alkali metals. The mean value of ν_A deduced from the thallium salts is $21.05 \times 10^{12} \text{ sec.}^{-1}$, and the chance that the agreement should be purely accidental is about 1 in 39.

GROUP III.

Boron Compounds (N=5).

	Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
BORON					
	oxide C	B_2O_3	34	3.185	5×21.7
	sulphide tri	B_2S_3	58	1.613	$4\frac{1}{2} \times 20.8$
	„ penta	B_2S_5	90	1.271	$5\frac{1}{2} \times 20.8$
BORIC					
	acid C	H_3BO_3	32	2.387	$3\frac{1}{2} \times 21.8$

Aluminium Compounds (N=13).

ALUMINIUM					
	bromide	Al_2Br_6	236	0.858	5×20.3
	iodide	Al_2I_6	344	0.682	$5\frac{1}{4} \times 21.3$
	oxide	Al_2O_3	50	4.949	12×20.6
	sulphide	Al_2S_3	76	2.212	8×20.5

Yttrium Compound (N=39).

YTTRIUM					
	chloride	$YtCl_3$	90	1.114	5×20.1

Lanthanum Compound (N=57).

LANTHANUM					
	chloride	$LaCl_3$	108	1.693	9×20.3

Cerium Compound (N=58).

CERIOUS					
	chloride	$CeCl_3$	109	1.645	9×20.0

Thallium Compounds (N=81).

THALLIUM					
	bromide	$TlBr_2$	116	1.466	8×21.3
	carbonate	Tl_2CO_3	192	0.825	$7\frac{1}{2} \times 21.1$
	chloride	$TlCl$	98	1.623	6×21.1
	iodide	TlI	134	1.247	8×20.9
	nitrate	$TlNO_3$	112	1.137	6×21.2
	oxide (-ic)	Tl_2O_3	186	1.067	$9\frac{1}{2} \times 20.9$
	perchlorate	$TlClO_4$	130	1.310	8×21.3
	sulphate	Tl_2SO_4	210	0.981	10×20.6

GROUP IV.

The compounds of carbon are so numerous as to require separate consideration. It is only necessary to mention for the sake of comparison with compounds containing other elements of the same group, that for carbon tetrabromide ($N=146$) the value of $N\nu$ is $5 \times 20 \cdot 5 \times 10^{12}$, and for carbon trichloride (C_2Cl_6) the value is $4\frac{1}{2} \times 20 \cdot 6 \times 10^{12}$. For silicon, titanium, and zirconium only a few results can be given.

GROUP IV.

Silicon Compound ($N=14$).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
SILICON tetrabromide	SiBr ₄	154	0·553	$4 \times 21 \cdot 3$

Titanium Compounds ($N=22$).

TITANIUM	Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
tetrafluoride	TiF ₄	58	1·848	$5 \times 21 \cdot 4$	
tetrabromide (a).....	TiBr ₄	162	0·545	$4 \times 22 \cdot 0$	
dioxide	TiO ₂	38	5·536	$10 \times 21 \cdot 0$	

(a) Melting-point, 39° C., Duppa (1856).

Zirconium Compound ($N=40$).

ZIRCONIUM	Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
dioxide	ZrO ₂	56	5·283	$14 \times 21 \cdot 1$	

Disregarding the high value for ν_A in the case of titanium bromide, for which no modern determination of the melting-point is recorded, the values of ν_A for the compounds of this group are generally higher than those for the earlier groups. In the case of the lead salts, however, a lower value is found for the chloride, bromide, and iodide; but the close agreement between the values of the product $N\nu$ for these three salts deserves special notice, as also the agreement for the oxide and the sulphide.

Tin Compounds ($N=50$).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
STANNIC				
fluoride	SnF ₄	86	2·049	$8\frac{1}{2} \times 20 \cdot 7$
iodide	SnI ₄	262	0·491	$6 \times 21 \cdot 4$
oxide	SnO ₂	66	3·353	$10\frac{1}{2} \times 21 \cdot 1$
STANNOUS				
bromide	SnBr ₂	120	1·075	$6 \times 21 \cdot 5$
sulphide	SnS	66	2·780	$9 \times 20 \cdot 4$

Lead Compounds (N=82).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
LEAD				
bromide	PbBr ₂	152	1·067	8 × 20·3
chloride	PbCl ₂	116	1·414	8 × 20·5
iodide	PbI ₂	188	0·863	8 × 20·3
oxide	PbO	90	2·443	10½ × 21·0
selenide	PbSe	116	2·029	11 × 21·4
sulphate	PbSO ₄	130	1·795	11 × 21·2
sulphide	PbS	98	2·274	10½ × 21·2

Thorium Compound (N=90).

THORIUM				
chloride.....	ThCl ₄	158	1·214	9 × 21·3

GROUP V.

Almost all the compounds so far considered have been metallic salts. In the fifth group a number of non-metallic compounds are met with; and although many of these conform to the proposed relation with frequency numbers n or $n + \frac{1}{2}$, several require the use of values $n + \frac{1}{4}$ or $n + \frac{3}{4}$. It is at present impossible to decide whether this means that the relation fails to hold in these two cases, or whether the apparent failure is to be attributed to our ignorance of the degree of molecular association in such compounds. It may be pointed out that the compounds in question belong to the "non-polar" type*. According to Langmuir solid polar compounds are built up of atoms bound together by secondary valencies, whilst solid non-polar compounds consist of "group molecules" in which the atoms are usually held together by primary valencies; these group molecules in turn are bound together by secondary valencies to form a large "crystal molecule." As data for determining the molecular frequency are available for only a small number of inorganic non-polar compounds, further discussion may be deferred till organic compounds are considered.

GROUP V.

Nitrogen Compounds (N=7).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
NITROGEN				
chlorophosphide ...	N ₃ P ₃ Cl ₆	168	0·580	4½ × 21·6
pentoxide	N ₂ O ₅	54	1·278	3¼ × 21·2
sulphide	N ₄ S ₄	92	1·117	5 × 20·5

* See Langmuir, Amer. Chem. Soc. Journ. vol. xxxviii. p. 2221 (1916).

Phosphorus Compounds (N=15).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
PHOSPHORIC				
acid ortho-.....	H ₃ PO ₄	50	1.470	3½ × 21.0
PHOSPHOROUS				
acid hypo-.....	H ₃ PO ₂	34	1.855	3 × 21.0
„ ortho-.....	H ₃ PO ₃	42	1.794	3½ × 21.5
PHOSPHORUS				
oxide tri-.....	P ₄ O ₃	108	0.761	4 × 20.5
oxybromide	POBr ₃	128	0.706	4½ × 20.1
oxybromdichloride. .	POBrCl ₂	92	0.807	3½ × 21.2
oxychloride.....	POCl ₃	74	0.920	3½ × 20.9
sulphobromide	PSBr ₃	136	0.659	4½ × 21.1
sesquisulphide	P ₄ S ₃	108	0.913	4¾ × 20.7
pentasulphide	P ₂ S ₅	110	1.024	5½ × 20.5

Vanadium Compound (N=23).

VANADIUM				
pentoxide	V ₂ O ₅	86	1.841	7½ × 21.1

Columbium Compound (N=41).

COLUMBIUM				
pentachloride	CbCl ₅	126	0.876	5½ × 20.1

Arsenic Compounds (N=33).

ARSENIC				
disulphide	As ₂ S ₂	98	1.299	6 × 21.2
ARSENOUS				
bromide	AsBr ₃	138	0.688	4½ × 21.1
iodide	AsI ₃	192	0.629	6 × 20.1
oxide	As ₄ O ₆	180	0.712	6 × 21.3
selenide	As ₂ Se ₃	168	0.910	7½ × 20.4
sulphide	As ₂ S ₃	114	1.144	6 × 21.7

Antimony Compounds (N=51).

ANTIMONY				
bromide tri-	SbBr ₃	156	0.702	5 × 21.9?
chloride tri-	SbCl ₃	102	0.907	4½ × 20.6
fluoride tri-.....	SbF ₃	78	1.602	6 × 20.8
iodide tri-	SbI ₃	210	0.615	6 × 21.5

Bismuth Compounds (N=83).

BISMUTH				
bromide	BiBr ₃	188	0.749	7 × 20.1?
chloride di-.....	BiCl ₂	117	0.999	5½ × 21.2
chloride tri-	BiCl ₃	134	0.943	6 × 21.1

Tantalum Compounds (N=73).

TANTALUM				
chloride	TaCl ₅	158	0.777	6 × 20.5
fluoride	TaF ₅	118	0.930	5 × 21.9?

GROUP VI.

In the sixth group of the Periodic Table only a dozen compounds need be considered. Several of these are oxides, and it is noticeable, both here and elsewhere, that these in general necessitate large values for ν_{Λ} .

It is interesting to find that salts of the heaviest metal, uranium, appear to conform to the same rule as salts of the lightest metal, lithium. Thus lithium fluoride, with molecular number 12, has for $N\nu$ the value $5\frac{1}{2} \times 21.0 \times 10^{12}$, uranium hexafluoride, with molecular number 146, has the value $5 \times 21.0 \times 10^{12}$; lithium iodide ($N=56$) gives $N\nu=6 \times 20.8 \times 10^{12}$, whilst uranium tetra-iodide, with the large molecular number of 304, gives $N\nu=9 \times 20.7 \times 10^{12}$.

GROUP VI.

Sulphur Compounds ($N=16$).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
SULPHUR trioxide β	(SO ₃) ₂	80	0.816	3 \times 21.7
SULPHURIC acid pyro	H ₂ S ₂ O ₇	90	0.890	4 \times 20.0

Selenium Compounds ($N=34$).

SELENIUM dioxide	SeO ₂	50	2.473	6 \times 20.6
oxychloride.....	SeOCl ₂	76	0.984	3 $\frac{1}{2}$ \times 21.4
SELENIC acid	H ₂ SeO ₄	68	1.269	4 \times 21.6

Tellurium Compound ($N=52$).

TELLURIUM tetrabromide	TeBr ₄	192	0.792	7 $\frac{1}{2}$ \times 20.3
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Chromium Compounds ($N=24$).

CHROMIUM trioxide	CrO ₃	48	2.030	4 $\frac{1}{2}$ \times 21.7
CHROMIC oxide	Cr ₂ O ₃	72	3.876	13 \times 21.5
CHROMOUS fluoride	CrF ₂	42	4.300	8 $\frac{1}{2}$ \times 21.2

Molybdenum Compound ($N=42$).

MOLYBDENUM trioxide	MoO ₃	66	2.576	8 \times 21.2
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Uranium Compounds ($N=92$).

URANIUM fluoride hexa.....	UF ₆	146	0.719	5 \times 21.0
iodide tetra-	UI ₄	304	0.614	9 \times 20.7
oxide di-.....	UO ₂	108	3.182	16 \times 21.5

GROUP VII.

In the seventh group the only metallic compounds represented are those of manganese. The four salts in question give concordant values for ν_A . The chance of an accidental agreement is about 1 in 180.

GROUP VII.

Manganese Compounds (N = 25).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
MANGANESE				
chloride	MnCl_2	59	2.252	$6\frac{1}{2} \times 20.4$
fluoride	MnF_2	43	3.756	8×20.2
silicate	MnSiO_3	63	3.057	$9\frac{1}{2} \times 20.3$
sulphate	MnSO_4	73	2.107	$7\frac{1}{2} \times 20.5$

In the same group are a number of compounds containing chlorine or iodine. Most of these require the provisional use of frequency numbers of the form $n + \frac{1}{4}$ or $n + \frac{3}{4}$.

Chlorine and Iodine Compounds.

Chlorosulphonic acid...	$\text{ClSO}_2 \cdot \text{OH}$	58	1.335	$3\frac{3}{4} \times 20.6$
Iodine monochloride α .	ICl	70	1.125	$3\frac{3}{4} \times 21.0$
Iodine tetrachloride ...	ICl_3	104	0.836	$4\frac{1}{4} \times 20.5$
Iodine fluoride	IF_5	98	0.869	4×21.3
Iodic acid	HIO_3	78	1.342	5×20.9

GROUP VIII.

In the eighth group the data are scanty, only six compounds of iron being represented, two of cobalt, and one each of nickel, ruthenium, and osmium. Rhodium, palladium, platinum, and iridium are not represented at all. The results, as far as they go, tend to show that the compounds of this group fall into line with the metallic salts of the earlier groups, the only serious discrepancy being the case of cobalt carbonyl where it is possible that molecular association occurs.

GROUP VIII.

Iron Compounds (N=26).

Name.	Formula.	N.	$\nu \times 10^{-12}$.	$N\nu \times 10^{-12}$.
IRON				
disulphide	FeS ₂	58	3·748	10½ × 20·7
phosphide	Fe ₂ P	67	3·653	12 × 20·4
FERRIC				
chloride	FeCl	83	1·498	6 × 20·7
oxide	Fe ₂ O ₃	76	3·330	12 × 21·1
FERROUS				
sulphide	FeS	42	4·856	10 × 20·4
FERROSO-FERRIC				
oxide	Fe ₃ O ₄	110	2·762	15 × 20·3

Cobalt Compounds (N=27).

COBALT				
carbonyl	Co(CO) ₄	83	0·927	3¾ × 20·5
COBALTOUS				
sulphate	CoSO ₄	75	2·477	9 × 20·6

Nickel Compound (N=28).

NICKEL				
sulphide mono-	NiS	44	3·914	8¼ × 20·3

Ruthenium Compound (N=44).

RUTHENIUM				
tetroxide	RuO ₄	76	1·399	5 × 21·3

Osmium Compound (N=76).

OSMIUM				
tetroxide	OsO ₄	108	1·079	5½ × 21·2

In the foregoing pages a number of cross-correspondences between the values of the frequency numbers for related compounds have been noticed. But instances might also be cited in which the frequency number has not the value which might have been predicted for it by analogy. For example, the chlorides of potassium and rubidium have the same frequency number 6, but though the frequency number for calcium chloride is 6 that for strontium chloride is 7½; again the iodides of calcium, strontium, barium give the unexpected sequence of numbers 9, 8½, 9. In view of the hypothesis that has been put forward relating the frequency number to the number of valency electrons, it may be suggested that the frequency number determined from the melting-point may not have, in all cases, a unique value,

In consequence of the presence of traces of impurity, or through imperfect crystallization, it is at least possible that fusion may sometimes occur when the number of valency electrons is smaller than the normal value.

It is noticeable that for a large number of compounds the frequency number is one of the series $4\frac{1}{2}$, 6, $7\frac{1}{2}$, 9, — — ; suggesting that the factor 3 plays an important part in the determination of its value. It may not be entirely accidental that a number belonging to this series frequently occurs when the compound contains an element of valency 3 (*e. g.* amongst the compounds of As, Sb, Bi, and Fe). It is not unlikely that the factor 3 should occur in such cases if it is supposed that the chemical valency is associated with a certain number of valency electrons.

The facts recorded in this paper are regarded as proving that the characteristic frequency calculated for a metallic compound by means of Lindemann's formula can, in general, be expressed in the form $n\nu_A$ or in the form $(n + \frac{1}{2})\nu_A$, where n is an integer and ν_A is approximately 21×10^{12} sec.⁻¹. The evidence for this may not be considered conclusive when compounds of one single metal are examined, but the evidence in the present case is cumulative. The degree of probability of this result may be small when compounds of a single element are found to conform to the rule; but it is larger when the compounds of all the elements in a group are found to give concordant values for ν_A , and becomes very great when the number of compounds is extended to include all the groups in Mendeléeff's classification. Further, these results for compounds and those recorded previously for the elements mutually support one another, and lead to the conclusion that we have to deal with a property that is fundamental and characteristic of the solid state of matter. It is to be borne in mind that the formula of Lindemann is looked upon as giving only an approximate value for the characteristic frequency, and the final justification for the proposed relation must come from observations on the specific heat of compounds at low temperatures.