

Citation:

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of these ionic conductivities is 326. This number may be derived in another way. H. E. JONES gives 380 as the limiting value for HF at 25°. The value as calculated above for 18° is 364. The difference per degree is 2.3 units, hence the value at 0° is 324. The approximate correctness of the number 325 is shown by the fact that if we assume the amount of dissociation to be little affected by temperature, at any rate in the more concentrated solutions, we get $\alpha = \frac{\mu_v^{0^\circ}}{\mu_\infty^{0^\circ}} = \frac{\mu_v^{18^\circ}}{\mu_\infty^{18^\circ}}$. Substituting 0.0576 for α and 18.30 for μ_v which is the value for the acid of 29.83 %, we get $\mu_\infty = 318$ (at 0°).

“The temperature coefficient for H at 18° is about 0.0153. If this is used to calculate the limiting value for the hydrogen ion at 0°, the number for $\mu_\infty^{0^\circ}$ becomes very much lower than any of these 3 numbers given above, and as a coefficient is only correct in the neighbourhood of 18° we discard this method of calculating.”

It is evident that HILL and SIRCAR have calculated μ_∞ at 0° for HF assuming a very high value for H°. Their value for H° at 0° is about 100 units higher than the value obtained in this investigation in the direct way. Consequently all their calculations for the degree of dissociation of HF with this value for H° are not reliable.

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Chemistry. — “*Properties of elements and the periodic system*”. By NILRATAN DHAR. (Communicated by Prof. ERNST COHEN).

In a former paper (DHAR Zeit. Elektro-Chem. (1913) it has been shown that the heats of ionisation of elements and the temperature coefficient of mobility of ions are periodic functions of their atomic weights. In this paper it will be shown that some other properties are also periodic functions of their atomic weights.

Surface tension, capillary rise etc.

The surface tension of liquids being an important property has been investigated by various workers. There are several methods of determining the value of the surface tension of liquids, the most important ones are (1) the rise in a capillary tube, (2) measurements

of bubbles and drops by QUINCKE, MAGIE and WILBERFORCE, (3) determination by means of ripples (Lord RAYLEIGH Phil. Mag. XXX p. 386), (4) LENARD'S (Wied. Ann. XXX p. 209) method of determination by oscillations of a spherical drop of liquid, (5) determination by the size of drops (RAYLEIGH Phil. Mag. 48, p. 321) (6) WILHELMY'S method of measuring the downward pull exerted by a liquid on a thin plate of glass or metal partly immersed in the liquid, (7) JAEGER'S method of measuring the least pressure which will force bubbles of air from the narrow orifice of a capillary tube dipping into the liquid, (8) by measuring the pull required to drag a plate of known area away from the surface of a liquid etc.

Besides (y) the surface tension, another constant is sometimes employed; it is called specific cohesion, and is usually denoted by α^2 . The relation between α^2 and (y) is expressed as follows:

$\alpha^2 = \frac{2y}{d}$ = specific cohesion, where d = density of the liquid, whence since (y) = $\frac{1}{2} r h d$ (where r = radius of the capillary tube, h = rise in the tube), it is seen that the specific cohesion is measured by the height to which a liquid rises in a capillary tube of unit radius.

WALDEN [Zeit. Phys. Chem. 65, 129, 257 (1908)] has recently found that specific cohesion may be applied in another way to estimate the degree of association of both liquids and solids. A comparison of the experimental data showed the relationship

$$\frac{T_v}{\alpha^2} = \text{constant} \approx 17.9$$

where T_v is the latent heat of vaporisation at a boiling point and α^2 , the specific cohesion at the same temperature. Combining this expression with TROUTON'S rule, we see that the molecular cohesion of a liquid at its boiling point is proportional to the boiling temperature expressed on the absolute scale. This relation holds only for non-associated liquids.

Moreover WALDEN points out that if substances are in corresponding states at their melting points, there would be a similar relation between the latent heat of fusion and the specific cohesion at the melting point.

The specific cohesion of fused metals and salts has been investigated by QUINCKE in a very thorough manner. The measurements were obtained from the weight of falling drops of a liquid, or from the curvature of flat drops of the solidified material.

It was found (Pogg. Ann. 135, 643, 1868) that all salts and metals and some organic substances near their melting points have

specific cohesions which are simple multiples of the constant number 4.3. For various reasons it seems clear that these relations are only apparent. In the first place, the divergence from the constant is in many cases considerable.

Moreover there are errors of experiment [cf. MEYER. Wied. Ann. 54, 415 (1895); LOHNSTEIN. *ibid.* 54, 722 (1895) etc]. Under the stress of criticism (*ibid.* 53, 1070 (1894), 61, 267 (1897)), QUINCKE somewhat modified his views.

It has now been found out that the specific cohesion of elements is a periodic function of their atomic weights.

The following data are collected from the works of various investi-

Name of elements.	Specific Cohesion.
Sb	7.635
Pb	8.339
Br	3.895
Cd	16.84
F	25.81
K	85.74
Cu	14.44
Na	52.97
Pd	25.26
P	4.475
Pt	17.88
Hg	8.234
S	4.28
Se	3.42
Ag	15.94
Bi	8.019
Zn	24.05
Sn	16.75
Cl	4.176
O	3.018
N	2.541

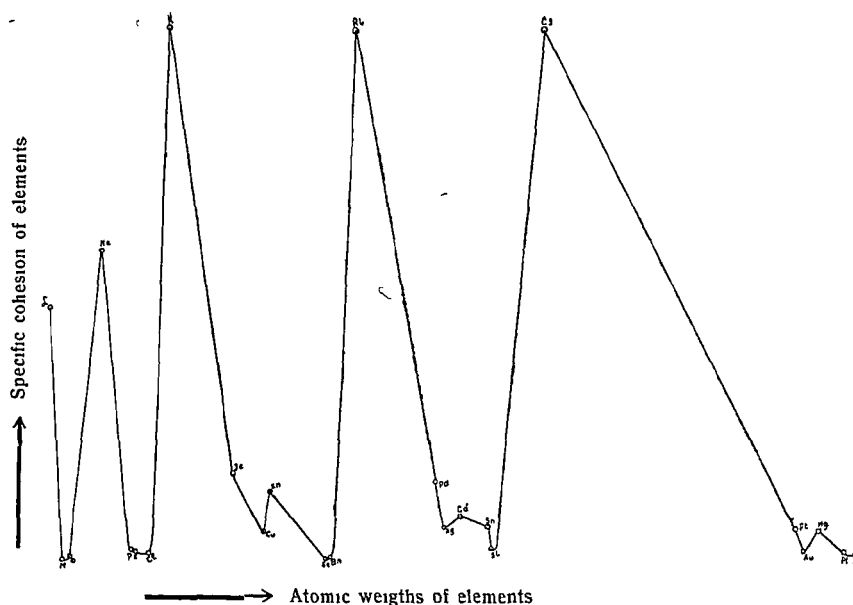


Fig. 1.

gators using the previously described methods. By plotting the following data, well-defined periodic curves are obtained.

From the curve it is seen that the alkali metals lie on the top most points, whilst Zn, Cd and Hg lie on a straight line on the descending portion of the curve. P, As, Sb, and Bi occupy similar positions in the minima.

Temperature coefficient of electric conductivity of elements.

The reciprocal of the resistance of a conductor is called its conductivity. Thus if S is the conductivity of a wire, OHM'S LAW is expressed by $C = SE$. In the same way the specific conductivity is the reciprocal of the specific resistance and is connected with the conductivity by the relation $S = ms/l$, where l is the length and s the cross section, the conductivity is directly proportional to the cross section and inversely proportional to the length.

In the case of pure metals the specific conductivity always decreases with increase of temperature. DEWAR and FLEMING have shown that at absolute zero the resistance of all pure metals approximates to zero. As a result it has been found that if R_t is the resistance of a platinum wire at the temperature t° C. on the air thermometer and R_0 is the resistance at a temperature of 0° C., then the connection between these quantities can be expressed by an equation of the form

$$R_t/R_0 = 1 + at + \beta t^2.$$

In the expression a and β are constants which vary very slightly from one specimen of wire to another. The value of these constants

is determined by measuring the resistance of the wire at three known temperatures. Just as KOHLRAUSCH has shown that the effect of temperature on the conductivity of a solution is very nearly linear, so over comparatively small ranges of temperature the increase of resistance of pure metals is very nearly proportional to the increase in temperature. Hence if R_0 is the resistance at a standard temperature, say 0°C . and R_t , the resistance at a temperature t , then we may express the relation between R_0 and R_t by an expression of the form $R_t = R_0(1 + \alpha t)$, where $\alpha = 0.00366$. There are distinct variations in the value of α , from one element to another.

It has now been observed that the temperature coefficient of electric conductivity of elements is distinctly a periodic property of the elements.

By plotting the values of the temperature coefficients given in LANDOLT and BORNSTEIN'S tables well marked periodic curves are obtained.

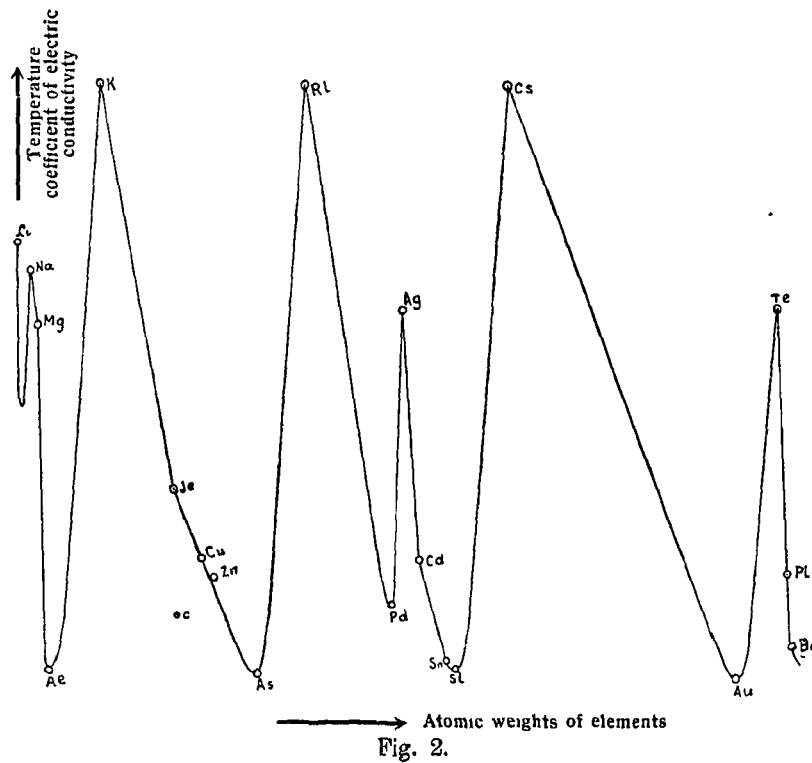


Fig. 2.

Elements of the same group lie very nearly on a straight line and occupy similar positions on the curve.

This curve resembles the one that is obtained by plotting the temperature coefficient of ionic mobility of elements (cf. DHAR loc. cit.).

Temperature coefficient of conductivity of heat.

The change of thermal conduction with temperature was noticed by FORBES [Phil. Trans. Roy. Soc. Edin. Vol. **33** (1862), p. 133]. Generally there is a decrease of conductivity with increase of temperature and as a similar decrease takes place in the electric conductivity of metals, it was supposed by FORBES that in general the thermal conductivities of metals like their electric, diminished with rise of temperature.

WIEDEMANN and FRANZ [Pogg. Ann. **89**, (1853), 497] appeared to show that there is some connection between conducting power for heat and for electricity.

For the metals were found not only to follow the same order for the two conductivities, but in many cases the numbers bore nearly the same ratio to each other.

More recent work has confirmed this supposition. The following are some of the values for metals of the ratio of the thermal conductivity and the electrical conductivity or k/c at 18° C. as determined by JAEGER and DIESELHORST [Phys. Tech. Reichsanstalt Wiss. Abh. **3**, (1900)], together with the temperature coefficient of the ratio.

	$10^{-10} \frac{K}{c}$	Temp. coeff.
Cu	6.65	0.0039
Ag	6.86	0.0037
Au	7.09	0.0037
Zn	6.72	0.0038
Cd	7.06	0.0037
Pb	7.15	0.0040
Sn	7.35	0.0034

The electron theory of conduction for heat and for electricity gives an explanation of the connection between the two quantities.

According to that theory the ratio should be proportional to the absolute temperature i. e. should have a temp. coeff. 0.00367 and at 0° C., its value should be 6.3×10^{10} . The temperature coefficient of heat conductivity has been determined by LORENZ [Wied. Ann. **13**, 422, 582 (1881)], STEWART [Proc. Roy. Soc. **53**, 151 (1893)], LIES (Phil. Trans. A. **183**, 481 (1892)] etc.

But the data of only a few elements are available, so it is impossible to obtain a curve with the insufficient data, which at present

we can have. It has already been found that the conductivity of heat and electricity is a periodic function of the atomic weights of elements and now it is seen that the temperature coefficient of electric conductivity of metals is also a periodic function of the atomic weights and as the two properties, as has been already observed, are very much related, it seems very probable that the temperature coefficient of the conductivity of heat of elements would also be a periodic function of their atomic weights.

Torsional rigidity, YOUNG'S modulus and their temperature coefficients.

The following table is obtained from LANDOLT und BÖRNSTEIN'S

Metals	E	Δ_1	T	Δ_2
Al	6570	21.3	2580	24.7
Pb	1493	—	550	78.7
Cd	7070	—	2450	46.7
Cs	—	—	—	180
Fe	18347	2.25	7337	3.04
Au	7580	—	2850	3.01
K	—	—	—	150
Cu	9897	3.63	3967	4.49
Li	—	—	—	120
Mg	4260	—	1710	30.2
Na	—	—	—	130
Ni	20300	2.46	7820	3.28
Pd	11284	1.98	4613	2.7
Pt	16029	0.73	6594	1.78
Rb	—	—	—	170
Ag	7790	7.65	2960	8.21
Bi	3190	—	1240	—
Zn	10300	—	3880	—
Sn	5410	—	1730	82

Tabellen. E represents the YOUNG'S modulus, Δ_1 its temperature coefficient. T indicates the values of torsional-rigidity and Δ_2 its temperature coefficient.

From the above table it is seen that in these properties also there are distinct indications of periodicity. The transitional elements Fe and Ni have practically equal values for these properties.

As the atomic weight of elements in the same periodic group increases the value for YOUNG'S modulus and torsional rigidity decreases. In the sub group *B* of the first group of periodic classification (Cu, Ag, Au), gold having the highest atomic weight has the smallest values for YOUNG'S modulus and torsional rigidity. Similar are the behaviours of zinc, cadmium, tin and lead.

Sufficient data are available in the case of the temperature coefficient of torsional rigidity and hence distinct periodic curves are obtained; the alkali metals, Li, K, Na, Rb and Cs lie on the topmost points whilst copper, silver and gold lie on a straight line on the minima.

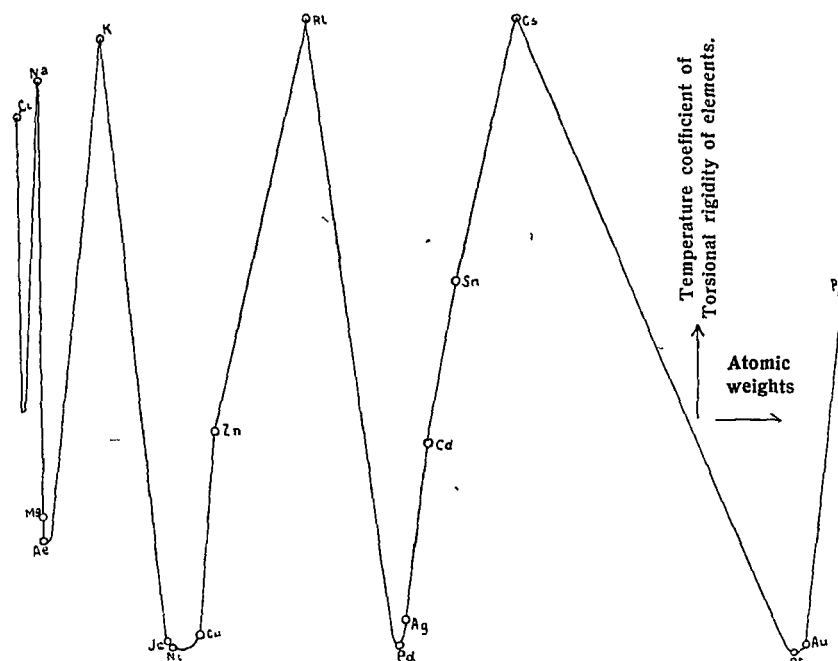


Fig. 3.

Specific heat. During recent years the determination of specific heats of substances at low temperatures was attracting the attention of numerous investigators.

RICHARDS and JACKSON (Zeit. Phys. Chem, 1910. **70**, 414) have carefully determined the specific heats of various elements between -188° and $+20^{\circ}$. From their experimental data, they come to the conclusion that the atomic heats of various elements between the above range of temperature conform approximately to DULONG and PETIT'S law, the value of the constant being 5.3. *There are*

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certain deviations and these show distinct periodicity, the general tendency being towards increasing atomic heat with increasing atomic weight.

SCHIMPF (Zeit. Phys. Chem. 1910. **71**, 257) has determined the specific heats of many elements at various temperatures (e.g. -150° , -100° , -50° etc.).

From his work he concludes that the atomic heats diverge in a marked way as the temperature falls, whilst conversely a rise of temperature produces, as is well known, a marked convergence towards a fixed value for all elements.

Evidently, it is seen from the above investigations, that there are distinct indications showing the period nature of atomic heats at low temperatures.

Very recently a decided advance in this direction was made by DEWAR [Proc. Roy. Soc. A. Vol. 89 p. 158 (1913)]. He determined the specific heats of 53 elements between the boiling points of liquid nitrogen and hydrogen at about 50° absolute.

When the atomic heats are plotted in terms of their atomic weights they reveal definitely a periodic variation resembling generally the well-known LOTHAR MEYER atomic volume curve.

The author concludes that if experiments were similarly made between the boiling points of hydrogen and helium then in all probability the atomic heats would be all very small and nearly constant.

However interesting these results may be there is a great difficulty in these investigations. The temperature range is very high with these workers. In the case of RICHARDS or JACKSON'S experiments it was about 200° and in the case of DEWAR'S it was $57^{\circ}.5$.

From these works only the mean specific heat between so large a range of temperature is available and not the specific heats at a fixed temperature. Since there is a marked variation of specific heats with temperature, the results obtained in experiments carried on with large range of temperature lose much of their significance.

NERNST and his pupils have determined the specific heats at low temperatures (Jour. de Phys. tome IX, 1910, p. 721); E. H. GRIFFITHS and E. GRIFFITHS have also attacked the same problem (Phil. Trans. 1913 A, **213**, 119.). These experiments are advantageous, since the temperature range is very small. In NERNST'S experiments it is only $2^{\circ}.7$ C. It is well known that the atomic heats of elements can be calculated from EINSTEIN'S formula

$$C = 3R \frac{e^{-\frac{a}{T}} \left(\frac{a}{T}\right)^2}{\left(e^{-\frac{a}{T}} - 1\right)^2} + b T^{\frac{3}{2}}$$

where R is a gas constant, equal to 1.98 gram calories, for Pb $a = 58$, $b = 7.8 \times 10^{-5}$.

In the following tables (see p. 431) the values of atomic heats of lead and silver at various temperatures are recorded.

Lead (atomic heat).

Absolute temp.	NERNST's observed value	Calc. from EINSTEIN	Calc. from GRIFFITHS
62°	5.63	5.58	5.62
66°	5.68	5.63	5.64
79°	5.69	5.75	5.68

DEWAR's value at about 50° abs. = 4.96

Silver (atomic heat).

64°	3.72	3.61	—
84°	4.43	4.44	—
86°	4.40	4.50	—

DEWAR's value at 50° abs. = 2.62.

Though NERNST's, EINSTEIN's and GRIFFITHS' values agree with each other, DEWAR's values are divergent owing to a large range of temperature.

GRIFFITHS and GRIFFITHS have calculated the following values of the atomic heats at -273° C., Al = 3.54, Fe = 0.73; Cu = 4.73, Zn = 4.294, Ag = 5.378, Cd = 4.95, Sn = 4.997, Pb = 4.527.

These figures also do not agree with the statement of DEWAR that atomic heats of elements between the boiling points of liquid hydrogen and helium would be all very small and nearly constant. Evidently DEWAR's data show the mean atomic heat between his experimental range of temperature.

Since the product of atomic weight and specific heat at the ordinary temperature is very nearly constant, if we plot the atomic heats at the ordinary temperature against the atomic weights, we shall get a straight line parallel to the axis representing the atomic weights. On the other hand by plotting the specific heats of elements at the ordinary temperature against their atomic weights, very nearly a rectangular hyperbola is obtained, since the product of specific heat and atomic weight is constant.

This non-periodic curve is quite unique amongst the physical

properties of the elements, since almost all important physical properties are periodic functions of their atomic weights.

By plotting DEWAR'S values of specific heat at about 50° absolute, we get a distinct periodic curve; evidently at about 50° absolute,

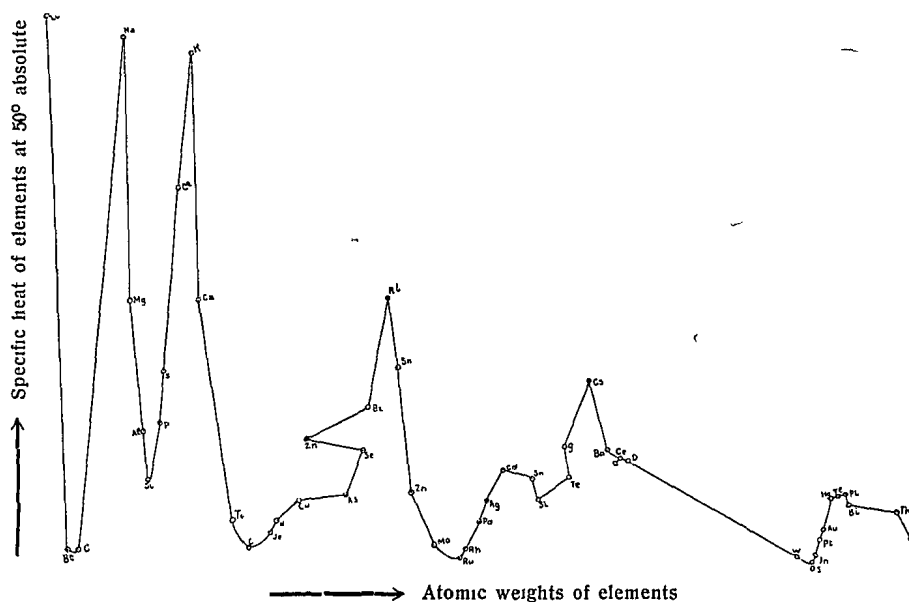


Fig. 4.

specific heat, like other physical properties of elements, is a periodic function of the atomic weight of the elements. The alkali metals, lithium, sodium, potassium, rubidium, caesium etc. lie on a straight line at the top of the curve. The halogen elements lie on a straight line on the ascending portion of the curve near the alkali metals, on the descending portion nearing the alkali metals lie Mg, Ca, Sr etc. S, Se and Te may be connected by a straight line. So also Zn, Cd and Hg. The platinum metals, (Osmium, iridium, platinum, ruthenium, rhodium, and palladium) lie on the minima of the curves.

Coefficient of linear expansion. The researches of FIZEAU show that the volatile elements occurring in the ascending curve possess, almost without exception, a larger coefficient of expansion by heat between 0° and 100° than the not easily fusible elements occupying the minimum of LOTHAR MEYER'S curve.

Similar vague suggestions are collected in LOTHAR MEYER'S "Theories of Chemistry" Eng. Trans. p. 131 from the works of CARNELLY (Journ. Chem. Soc. 1879, 565); WIEBE (Ber. 1878, 2289; 1880, 1258); RAOUL PICTET (Compt. rend. 1879 LXXXVIII, 855) on the

relations between melting point, expansion etc. But no definite statement of the periodicity of coefficient of linear expansion of elements with their atomic weights is available.

GRUNEISEN [Ann. Phys. 1910 (IV), **33**, 33—64] has found that the observed expansion of metals by heat is, in general, in close agreement with that required by THIESEN's (Ber. Deut. Phys. Ges. 1908, **6**, 947) exponential formula $l_2 - l_1 = \gamma (T_2^{1+e} - T_1^{1+e})$ and this agreement is particularly good at low temperatures. The experimental given e is a periodic function of the atomic weight of the metal and that its maximum values are reached when the atomic volumes are at their respective minima. It has now been found out that the coefficient of linear expansion of elements is also a periodic property.

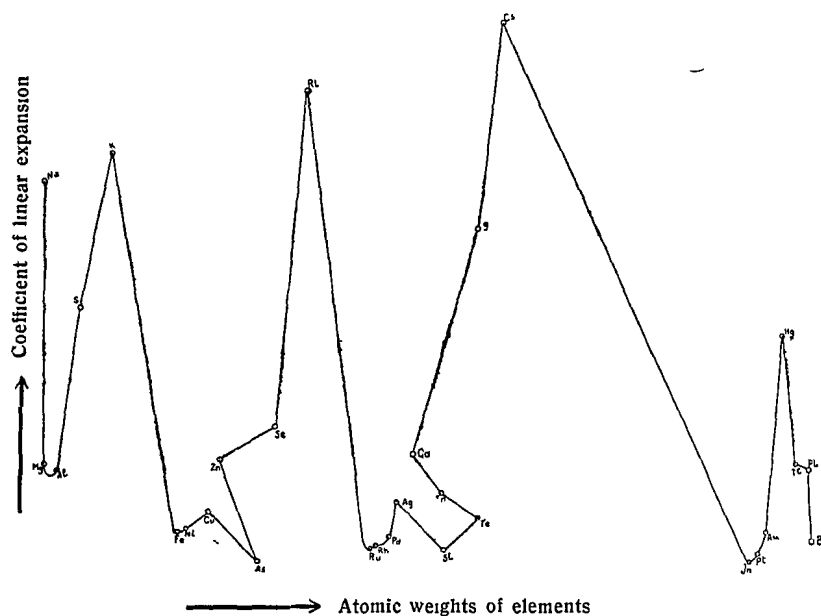


Fig. 5.

By plotting the values given in LANDOLT und BORNSTEIN's Tabellen well defined periodic curves are obtained. The alkali metals lie on the topmost points, whilst S, Se and Te lie on a straight line on the ascending portions of the curve.

Cu, Ag and Gold, as well as As, Sb and Bi occur in similar positions in the minima.

Molecular Magnetic Rotation.

If we imagine a layer of unit length of any substance placed in a magnetic field of unit intensity and traversed by a beam of homo-

geneous plane polarised light in the direction of the lines of force of the field, then the rotation which the plane of polarisation undergoes at a known temperature is the absolute magnetic rotation of the substance.

Generally we do not require the absolute value and the relative value with reference to a standard substance is sufficient.

PERKIN, the veteran worker in this line, chose water as the standard substance.

Hence denoting the specific rotation by r we have the expression,

$r = \frac{a}{d}$, where a is the rotation of the given substance $\therefore M$ (molecular magnetic rotation) $= \frac{a \delta m}{\alpha d \mu}$, where m and d are respectively

the molecular weight and density of the substance and μ and δ the corresponding values for the standard (since in PERKIN's work, tubes of equal length were always used).

The magnetic rotation of the plane of polarised light is measured in the same way as the permanent rotation of a substance, but the apparatus is more complex, since an arrangement for placing the substance in a magnetic field is provided. The tube containing the liquid is placed either between the poles or as in PERKIN's latest form of apparatus in the hollow cone of a powerful electromagnet. The chief precaution to be observed in addition to those of an ordinary polarimetric determination, is in preserving a constant strength of the magnetic field.

The rotations of the standard and of the substance are measured in the same tube under identical conditions of temperature and magnetic intensity [PERKIN, Trans. chem. Soc. 421 (1884); 69 1025 (1896); 89, 605 (1906)].

From an exhaustive study of organic compounds, PERKIN has shown that the addition of CH_2 causes an approximately constant increase in molecular rotation and this increase is very nearly the same in different classes of compounds. PERKIN has calculated the average value for CH_2 from a wider range of material and he found that $\text{CH}_2 = 1.023$.

If there are n CH_2 groups in a compound whose molecular rotation is M , then the expression $M - n(1.023) = S$ represents the rotatory effect of the remainder of the molecule. In a large number of organic compounds it is seen that S is approximately constant for all the higher members of a given series. Thus S is called the series constant. The series constant 0.508 of the normal paraffins $\text{C}_n \text{H}_{2n+2}$ is obtained by subtracting the value of $n \text{CH}_2$ from the

rotation of any member of the series. This residue must represent the value for $2H$, since $C_n H_{2n+2} - n CH_2 = 2H$. Hence we may write $2H = 0.508$, or the value of hydrogen as 0.254. Then again, it is known that $CH_2 = 1.023$, whence by deducting the value of $2H$ we may obtain the value for carbon = 0.515. Again, when hydrogen is removed from a compound and replaced by chlorine, there is an increase in rotatory power of 1.480; hence the value for chlorine may be assumed to be $1.480 + 0.254 = 1.734$. Similarly, bromine and iodine may be calculated to be equivalent to 3.562 and 7.757 respectively.

It has been found out that molecular magnetic rotation of elements is also a periodic function of their atomic weights.

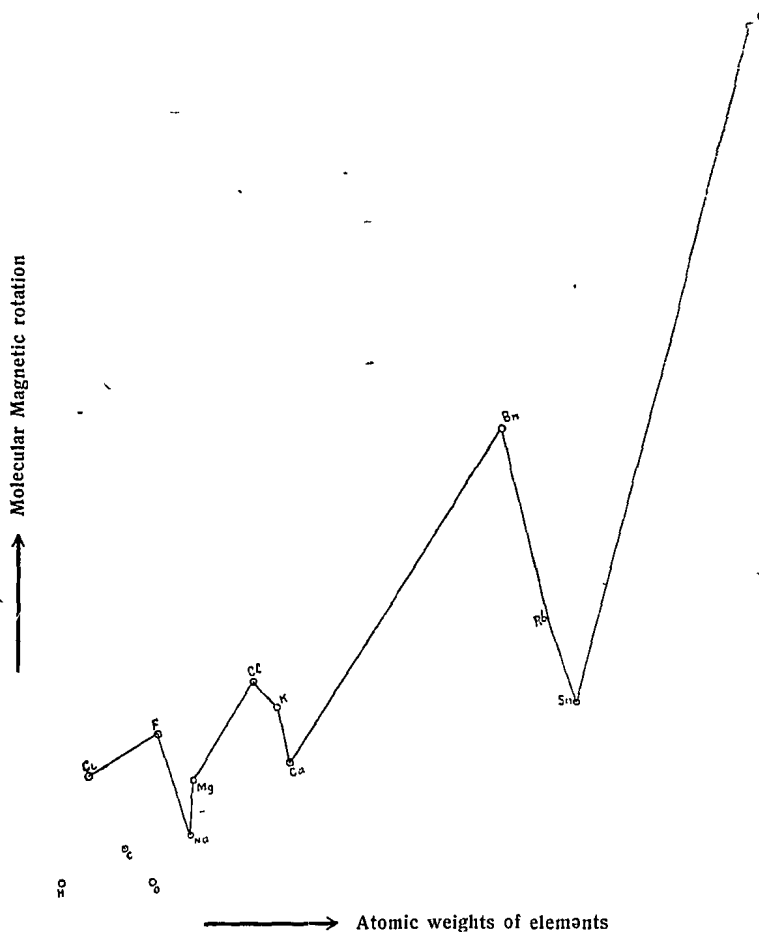


Fig. 6.

The curve is obtained from the following data (see table p. 436) collected from the works of different investigators.

Magnetic rotatory power.

Name of element	Observed by	
	PERKIN	HUMBURG
H	0.254	—
C (in Ketones)	0.850	—
O (in OH)	0.191	—
Br	3.562	3.563
Cl	1.734	1.675
I	7.757	—
N	0.717	—
Na	0.558	—
K	1.535	—
Li	1.124	—
Ca	2.143	—
Mg	2.029	—

Distinct periodic curves are obtained. The halogen elements occupy the topmost points.

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Physics. — “FRESNEL'S coefficient for light of different colours.”
(Second part). By Prof. P. ZEEMAN.

(Communicated in the meeting of May 29, 1915)

A first series of experiments was made with yellow, green, and violet (4358) mercury light. As FRESNEL'S coefficient changes only slowly with the wavelength, such a high homogeneity of the incident light is unnecessary. With regard to the intensity of the light it is even recommendable to work with a limited part of a continuous spectrum. In a second series of experiments I therefore analysed the light of an electric arc (12 Amp.) with a spectroscope of constant deviation, which I had arranged as a monochromator by taking away the eye-piece and replacing it by a slit. The monochromator had been calibrated with mercury and helium lines. The prism stood on a table, which could be turned by means of a screw. Each.