

Thus it is noticed that the amount of association decreases with rising molecular weight, which fact is of universal occurrence for homologous bodies in the liquid state (Ramsay and Shields; Traube) as well as for substances in solution (Biltz).

In this case, however, it happens that the amount of association is inversely as the square of the molecular weight:—

	Per Cent. Amount of Association.	Numbers Proportional to Inverse of Square of Molecular Weight.
Acetic acid ...	54	52
Propionic acid ...	38	36
Butyric acid ...	25	26

Further experiments are in progress with the object of ascertaining whether the same law holds for the higher members of the series.

ART. XLIX.—*The Latent Heats of Fusion of the Elements and Compounds.*

By P. W. ROBERTSON, Junior Scholar in the University of New Zealand.

Communicated by Professor Easterfield.

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ABSTRACT.

CROMPTON states that $\frac{Aw}{Tv} = K$, where A is atomic weight, w latent heat of fusion, T melting point on absolute scale, and v the valency of the element. Now, the valency of an element is known to vary, and as the results were not very concordant the author, from theoretical grounds, replaced this by the relation $\frac{Aw}{T\sqrt[3]{A}} = d$ where d is density and $\sqrt[3]{\frac{A}{d}}$ repre-

sents the space between the atoms. Just as the atomic heat of the elements is only constant for elements with atomic weights over about 40, so is this relation only true under the same conditions. In the case of the fourteen elements with atomic weights over 40 the value varies between 1 and 1.3, with the exception of the three, gallium, lead, and bismuth. But applying this rule to the compounds, and changing the atomic weight into molecular weight, still more concordant results are obtained. Out of thirteen inorganic compounds, with the exception of two the results vary from 1.9 to 2.3, being mostly near the mean 2.1. There is also good agreement among the organic bodies examined, the mean being about 2.4. The author intends to calculate more results, and to present fuller tables to the Society.

Various attempts have been made to arrive at a definite

law connecting the latent heats of fusion with the atomic weights and other physical constants. Berthelot (1895), after proving that in the case of the latent heads of vaporization $MW/T' = \text{constant}$ (where M is the molecular weight, W the latent heat of vaporization, and T' the boiling-point on the absolute scale), supposed a similar law to be true in the case of the latent heats of fusion.

Holland Crompton, in a paper entitled "Latent Heat of Fusion,"* endeavoured to show that the equation $Aw/Tv = \text{a constant}$ for the elements, A being the atomic weight, w the latent heat of fusion, and v the valency. The difficulty first encountered in this relation is due to the fact that the valency of an element varies with its mode of combination and with different physical conditions.

Shortly afterwards Deerr† concluded that the relationship Aw/T is constant only for certain groups of "similar" elements.

In 1897 Crompton published another paper,‡ in which he attempted to disprove the hypothesis of electrolytic dissociation. He arrives at the result $dw/T = \text{constant}$ for monomolecular liquids, where d is the density of the liquid. In the same paper the results are given for the elements, the densities in many cases being taken in the solid state. As shown below, the numbers are exceedingly divergent.

De Forcrand§ showed that $M(W+w)/T'$ is approximately constant: M is the molecular weight of the substance in the state of a gas at its boiling-point T' , and W and w are the latent heats of vaporization and fusion respectively. But W is generally about ten times as great as w ; and, as $MW/T' = \text{a constant}$ is true (Trouton's law), the value of w will make little difference in the result. Further, if the equation $M(W+w)/T'$ be divided by the constant MW/T' , it follows that $W/w = \text{a constant}$. Using Traube's numbers for the latent heats of vaporization of the following elements, which gave very satisfactory numbers for Trouton's constant, the values of W/w are—Mercury, 26; zinc, 14; cadmium, 15; bromine, 3; iodine, 3.2; bismuth, 17. Since these numbers should be equal if De Forcrand's relationship is a physical law, his generalisation may be dismissed without further consideration.

Now, let it be assumed for the present that $Aw/T = 8.8$ (this value is only empirical, but its magnitude will not affect the following argument). On dividing the values of A thus obtained by the real atomic weights, the result is a series

* Journ. Chem. Soc., 1895, 67, 315.

† Proc. Chem. Soc., 1895, and Chem. News, 1897.

‡ Journ. Chem. Soc., 70, 925.

§ "Comptes Rendus," 1901, 132, 878.

of numbers which appear to be periodic functions of the atomic weights:—

TABLE I.

Cu.	Zn.	Ga.	Ge.	As.	Se.	Br.
3.8	3.1	1.7	2.4
Ag.	Cd.	In.	Sn.	Sb.	Te.	I.
3.7	3.4	..	2.6	2.3
Au.	Hg.	Tl.	Pb.	Bi.		
3.8	3.6	3.6	4.4	1.9		

It will be noticed that the values tend to increase from top to bottom and from right to left—*e.g.*, zinc to mercury and iodine to silver. It would seem, therefore, that some periodic quantity must take the place of the v in Crompton's formula to make the relation true for all the elements.

It can be proved that $TS/w = a$ constant, where S is the specific heat of the element, by using the relation $TC = a$ constant, C being the coefficient of expansion. But Pictet proves $TC \sqrt[3]{\frac{A}{d}} = K$, the expression $\sqrt[3]{\frac{A}{d}}$ representing the mean distance between the atoms if d is the density. Applying this, it follows that—

$$\frac{TS \sqrt[3]{\frac{A}{d}}}{w} = \text{constant.}$$

But $AS = \text{constant}$ (Dulong and Petit);

$$\therefore \frac{Aw}{T \sqrt[3]{\frac{A}{d}}} = \text{constant.}$$

In Table II. are given the values thus calculated for the elements with atomic weights above 40 whose latent heats are known. As in the case of Dulong and Petit's law, the relationship does not hold for the elements with low atomic weights. The values of d are taken at ordinary temperatures for the substances in the solid state, except in the case of bromine, the specific gravity of which in the solid state is unknown. Most of the constants required have been obtained from the papers of Crompton and Deerr, while the values for silver and copper are due to Heycock and Neville.*

* Trans. Royal Soc., 1897, 189, 25.

TABLE II.—ELEMENTS.

Element.	Aw.	T.	$\sqrt[3]{\frac{A}{d}}$	$\frac{Aw}{T\sqrt[3]{\frac{A}{d}}}$
Mercury	565	234	2.41	1.00
Zinc	1839	688	2.12	1.28
Cadmium	1531	593	2.35	1.10
Bismuth	2602	540	2.77	1.75
Gallium	1336	286	2.28	2.05
Palladium	3873	1773	2.09	1.05
Gold	3227	1335	2.15	1.12
Tin	1573	503	2.55	1.22
Lead	1212	600	2.61	0.76
Thallium*	1183	562	2.62	0.82
Bromine	1295	266	2.97 (?)	1.63 (?)
Iodine	1485	387	2.96	1.28
Copper	2140	1355	1.91	1.22
Silver	2920	1230	2.16	1.10
Platinum	5295	2052	2.10	1.23

The greatest discrepancies are observed in the cases of bismuth and gallium, the only two metals which are known to expand on freezing.

By using the results of Heycock and Neville for the freezing-points of alloys the value for lead becomes about 1. Their experiments confirm the values of zinc, cadmium, tin, and bismuth, the first three of which give concordant results for the constant. Using this value for lead, and excluding bismuth and gallium, the results vary from 1 to 1.3 for twelve elements with melting-points ranging from -40° to $+1,800^{\circ}$ C. The mean value is 1.16. In the table below the results are compared with those of Crompton:—

TABLE III.

Element.	A.	B.	C.	D.	E.
Mercury	1.00	-14	1.21	- 8	1.65
Zinc	1.28	+10	1.34	+ 3	2.65
Cadmium	1.10	- 5	1.29	- 1	1.84
Palladium	1.05	-10	1.09	-16	2.83
Platinum	1.23	+ 4	1.29	- 1	2.33
Tin	1.22	+ 5	1.56	+21	1.86
Silver	1.10	- 5	2.37	+80	2.08
Gold	1.13	- 3	0.80	-40	2.36
Copper	1.22	+ 5	1.16	-10	3.26
Iodine	1.28	+10	1.27	- 2	1.48
Lead	1.00	-14	0.97	-25	1.00
Thallium	1.02	-12	2.62	+100	1.52

* Since the paper was communicated to the Society the latent heat of fusion of thallium has been directly determined by the author. The value thus found (mean of ten observations) gives a value of 1.02 for the final expression. Thallium thus conforms to the general law.

A represents $Aw/T\sqrt[3]{\frac{A}{d}}$.

B represents percentage difference from mean.

C represents Crompton's 1895 relation, Aw/Tv .

D represents percentage difference from mean.

E represents Crompton's 1897 relation, $10 \times wd/T$.

Thus the relationship $Aw/T\sqrt[3]{\frac{A}{d}}$ is much the most satisfactory, the mean deviation being ± 8 per cent., a deviation of the same order as observed in the law of Dulong and Petit. But it must be borne in mind that the latent heat of fusion is one of the most difficult physical constants to determine, and that if the densities were taken at some corresponding temperatures, such as at the melting-points, the results would perhaps be even closer. There is a large number of wide deviations in Crompton's first relation, while in the case of bromine and iodine it was assumed that the valencies were 3, which assumption is decidedly open to criticism.

In the case of compounds, if A is replaced by M (molecular weight) the values for $Mw/T\sqrt[3]{\frac{M}{d}}$ are also found to be constant. The following are the data for those substances whose density in the solid state I have been able to find. The values for lead-bromide and silver-chloride are from the results of Weber, who deduced them from electrical experiments. The latent heats of antimony chloride and bromide and the bromides of tin and arsenic have been calculated from their depression constants. The remaining numbers are taken from Crompton's paper.

TABLE IV.
A. INORGANIC COMPOUNDS.

Compound.	Mw.	T.	$\sqrt[3]{\frac{M}{d}}$	$\frac{Mw}{T\sqrt[3]{\frac{M}{d}}}$	$\frac{10 \times aw}{T}$
Lead-chloride	5810	758	3.64	2.10	1.60
Lead-bromide	5100	763	3.80	1.76	1.23
Lead-iodide	5300	648	4.17	1.98	1.10
Silver chloride	4400	730	3.07	1.96	2.35
Antimony-chloride ..	2920	345	4.19	2.01	1.24
Tin-bromide	2910	303	5.11	1.90	0.73
Antimony-bromide ..	3490	369	4.42	2.15	1.10
Arsenic-bromide	2740	295	4.39	2.11	1.14
Water	1439	273	2.70	1.96	2.93
Iodine-chloride	2297	289	3.70	2.14	1.52
Potassium-nitrate ..	4949	606	3.65	2.24	1.69
Sodium-nitrate	5520	578	3.40	2.81	2.46

With the exception of lead-bromide and sodium-nitrate, the numbers vary from 1.9 to 2.2, with the value 2.07 as mean.

B. ORGANIC COMPOUNDS.

Compound.	Mw.	T.	$\sqrt[3]{\frac{M}{d}}$	$\frac{Mw}{T\sqrt[3]{\frac{M}{d}}}$	$\frac{10 \times dw}{T}$
Acetic acid	2661	277	3.84	2.50	1.61
Phenylacetic acid	4293	348	4.80	2.56	1.00
Azobenzene	5187	342	5.31	2.85	0.87
Benzoic acid	4607	396	4.56	2.55	1.08
Orthonitrophenol	3725	316	4.60	2.56	1.10
P. dichlorobenzene	4395	325	4.90	2.76	1.15
P. dibromobenzene	4962	358	5.04	2.70	1.06
Diphenyl	4391	343	5.36	2.39	0.83
Naphthalene	4559	353	4.81	2.67	0.99
Resorcinol	4906	383	4.41	2.90	1.37
Paratoluidine	4177	312	4.67	2.87	1.21
Parabromphenol	3961	337	4.62	2.55	1.09
Parachloraniline	4742	342	4.73	2.74	1.30
Phenanthrene	4450	369	5.50	2.19	0.71
Thymol	4130	321	5.36	2.41	0.81
Nitropapthalene	4383	329	5.06	2.64	0.97
Anethoil	4070	294	5.30	2.61	0.94
Nitrobenzene	2743	264	4.45	2.35	1.02
Acetophenone	35.0	293	4.86	2.53	1.02
Benzophenone*	4320	321	5.38	2.50	0.90
Chloroacetic acid*	3850	334	4.04	2.90	1.71
Acetoxime*	3022	333	4.22	2.15	1.12

With the exceptions of acetoxime and phenanthrene, the numbers vary from 2.35 to 2.9. The mean value 2.57 is distinctly greater than the value obtained for the inorganic compounds. Whether this difference is due to the large number of atoms in the compounds of carbon or whether it is one of those peculiar properties of this element remains to be seen. The value of the constant is about twice as great as that obtained for the elements themselves.

I have neglected to compare Crompton's 1895 relation Mw/TEV with the others, because until chemists can agree as to what is really meant by the sum of the valencies (EV) in a compound the results thus obtained will be of no value. In the last column of Table IV. is placed his second relationship, $10 \times wd/T$. Regarding this, he says that when the result is about unity the liquids are non-associated, and when greater the liquid is proportionately associated. It may be remarked that about 25 per cent. of the values are considerably "below" unity.

* Specific gravity in the solid state determined by the author.

By combining the equation $Mw/T\sqrt[3]{\frac{M}{a}}$ with the well-known law of Van t'Hoff, $D = \cdot 02T^2/w$, the result is $D = KMT\sqrt[3]{\frac{M}{a}}$, where D is the molecular depression of the solvent and K a constant. Hence the molecular depression of any body can now be calculated without a knowledge of the latent heat of fusion.

Trouton's law states that—

$$MW/T^2 = K^1.$$

$$\text{But } Mw/T\sqrt[3]{\frac{M}{a}} = K;$$

$$\therefore w/W = c T\sqrt[3]{\frac{M}{a}}/T^2.$$

That is, the latent heat of fusion is to the latent heat of vaporization as the freezing-point multiplied by the cube root of the specific volume is to the boiling-point. This, of course, is only true when Trouton's law is true—that is, when the molecular condition of the body is unchanged in passing from the liquid to the gaseous state.

ART. L.—Some Observations on the Fourth Dimension.

By the Rev. HERBERT W. WILLIAMS, M.A.

[Read before the Hawke's Bay Philosophical Institute, 9th September, 1901.]

HELMHOLTZ was the earliest writer to attempt to present the conception of transcendental space in a form inviting popular investigation, and his efforts have been ably seconded in recent times by the author of "Flatland,"* in the first place, and by Mr. C. H. Hinton,† in the second place. The former has produced a work which has attractions beyond the mere consideration of the fairyland of mathematics; while the latter, beginning with pamphlets of a distinctly popular nature, has in his latest work laid down, still without abuse mathematics, a scheme of mental training the avowed object of which is to enable the student to form a perfect mental image of a figure in four dimensions.

* "Flatland, A Romance in Two Dimensions, by a Square." Seeley and Co.

† Author of "Scientific Romances" and "A New Era of Thought." Swann, Sonnenschein, and Co.