CXXVI.—*Atomic and Molecular Heats of Fusion.*

By P. W. ROBERTSON.

No satisfactory relationship has hitherto been found between the latent heat of fusion of substances and their atomic or molecular weights. Crompton (Trans., 1895, 67, 315) supposed the equation $\rho/Tv = \text{a constant}$ to be true for the elements, where ρ is the atomic latent heat, T the melting point on the absolute scale, and v the valency. Apart from the fact that the experimental numbers give but poor agreement with the formula, exception must be taken to an expression which involves such a variable "constant" as valency.

Later, Deerr (Proc., 1895, 11, 125, and *Chem. News*, 1897, 76, 234) concluded that ρ/T is a constant only in the case of certain groups of similar elements.

In 1897, Crompton arrived at the result that $dw/T = \text{a constant}$ for unimolecular liquids, w being the latent heat and d the specific gravity of the liquid (Trans., 1897, 71, 925). Concordant values were obtained in the case of a number of organic compounds which had been proved unimolecular by other methods. When the results were too high to agree with the above expression, Crompton concluded that the liquids were proportionately associated. The number varied from 0.1 to 0.4 with the elements, the results being calculated in many cases from the specific gravity in the solid state.

De Forcrand (*Compt. rend.*, 1901, 132, 878) showed that the rela-

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tionship $M(W+w)/T'$ is approximately constant, where M is the molecular weight of the substance in the state of a gas at the boiling point T' , W the latent heat of vaporisation, and w the latent heat of fusion. Owing to the large magnitude of W as compared with w , in general, the results have little dependence on the latent heat of fusion. Further,

$$MW/T' = \text{constant (Trouton's law)}.$$

By combining this with De Forcrand's formula, it follows that $W/w =$ a constant. Using the values obtained by Traube for the latent heats of vaporisation of the following elements, which give concordant results for Trouton's formula, the values of W/w are approximately :

Bromine	= 3	Cadmium	= 15
Iodine	= 3	Mercury	= 25
Zinc	= 14	Bismuth	= 16

According to De Forcrand's formula, these numbers should be identical.

When the values of Aw/T are considered, it is seen that with few exceptions they have a certain periodic character. It would seem therefore that some periodic quantity must replace the value of the v in Crompton's formula to make it 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 that $TC \sqrt[3]{V} =$ a constant, the expression $\sqrt[3]{V}$ representing the mean distance between the atoms if V is the atomic volume. Applying this, it follows that

$$\begin{aligned} TS \sqrt[3]{V}/w &= \text{a constant} \\ \text{but } AS &= \text{a constant (Dulong and Petit)} \\ \therefore Aw/T \sqrt[3]{V} &= \text{a constant} \end{aligned}$$

It will be found that this expression agrees more accurately with the results of experiment than any which has hitherto been proposed.

In Table I (p. 1235) are given the values of this expression for those elements with atomic weights above 40 the latent heats of which are known. Most of the constants required have been taken from Crompton's papers ; the values for copper and silver are due to Heycock and Neville, and the latent heats of lead and thallium have been determined by the author.

The value for lead is thus seen to be somewhat below the normal, whilst those of bromine, bismuth, and gallium are too high. It is a remarkable fact that the two latter elements expand on freezing, which occurrence is of comparative rarity. The specific volumes, except in the case of bromine, are those of the elements in the solid state. If the latent heat of bromine has been correctly determined, it would

TABLE I.

Element.	$Aw.$	$T.$	$\sqrt[3]{V}.$	Robertson, $\rho/T^3\sqrt[3]{V}.$	Percentage deviation from mean.	Crompton 1895, $\rho/Tv.$	Crompton 1897, $10 \times dw/T.$
Zinc	1839	688	2.10	1.28	+13	1.34	2.65
Cadmium	1531	593	2.35	1.10	-3	1.29	1.84
Mercury	565	234	2.41	1.00	-11	1.21	1.65
Palladium	3873	1773	2.02	1.08	-4	1.09	2.83
Platinum	5295	2052	2.10	1.23	+9	1.29	2.33
Gold.....	3227	1335	2.15	1.11	-2	0.80	2.36
Tin.....	1573	503	2.55	1.23	+9	1.56	1.86
Lead	1340	598	2.61	0.87	-23	1.12	1.22
Thallium	1470	562	2.57	1.02	+10	2.62	1.52
Iodine	1485	387	2.36	1.29	+14	1.27*	1.48
Copper	3140	1355	1.93	1.20	+6	1.16	3.25
Silver.....	2920	1230	2.16	1.10	-3	2.37	2.30
Bromine	1295	266	2.99?	(1.63)	—	1.62*	1.34
Bismuth	2602	540	2.77	1.75	—	1.60	2.32
Gallium.....	1336	286	2.28	2.05	—	1.56	3.98

* The valency of the halogens is taken as 3.

seem probable that this element, like bismuth and gallium, expands on freezing. On comparing these results with those obtained by Crompton, it is readily seen that the most definite relationship of this type yet obtained is as follows:—*For the elements with atomic weights above 40 which do not expand on freezing, the atomic heat of fusion divided by the melting point on the absolute scale into the cube root of the atomic volume is a constant.*

Excluding bromine, the mean percentage deviation is ± 10 , with 1.13 as the mean value of the constant. It is interesting to note that in Dulong and Petit's law the variation from the mean is about ± 7 per cent.

Since Dulong and Petit's law cannot be said to apply to compounds, it would seem improbable that the expression $Mw/T^3\sqrt[3]{V}$ would yield constant results with the molecular heat of fusion. As a matter of fact, however, certain definite relationships are obtained in the case of compounds also. Thus the binary inorganic compounds and certain groups of organic compounds yield numbers in close agreement with one another. But the latent heats of those organic compounds which contain a large number of atoms in the molecule show wide deviations from the law; for example, the latent heat of stearic acid (56 atoms) is about twice that calculated from the formula. This difference might be attributed (a) to the high molecular weight, (b) to the larger

number of atoms in the molecule. That it is not due to the high molecular weight is shown by the fact that tribromoaniline and tribromophenol give latent heats in accordance with the predicted values.

The most probable explanation of the irregular results obtained with compounds containing a large number of atoms in the molecule would appear to be that $\sqrt[3]{V}$ does not truly represent the mean distance between the molecules. The possibility thus presents itself that accurate latent heat determinations may serve as a means for the calculation of this constant:

TABLE II.—*Inorganic Compounds.*

Compound.	<i>Mw.</i>	<i>T.</i>	$\sqrt[3]{V}$.	$Mw/T \sqrt[3]{V}$.	$10 \times dw/T$ (Crompton).
Water	1439	273	2.70	1.96	2.93
Iodine chloride	2297	289	3.70	2.14	1.52
Antimony chloride	3020	346	4.19	2.09	1.03
Antimony bromide	3490	367	4.42	2.15	1.10 *
Arsenic bromide	2740	295	4.39	2.11	1.08 *
Tin tetrabromide	2910	303	5.09	1.89	0.73 *
Lead chloride	5810	758	3.64	2.10	1.60 *
Lead bromide	4520 ?	763	3.80	1.56	1.23 *
Lead iodide	5300	648	4.17	1.98	1.10 *
Silver chloride	4400	730	3.07	1.96	2.31 *
Potassium nitrate	4949	606	3.65	2.24	1.69 *
Sodium nitrate	5516	579	3.36	2.81	2.46 *

* Densities taken in the solid state.

Good agreement is shown amongst the binary compounds with the single exception of lead bromide. From electrical experiments, Weber has found the latent heat to be somewhat greater than that given in the table, whilst his value for latent heat of lead chloride was in close agreement with that found directly. Taking his value for lead bromide, the value of the expression $Mw/T \sqrt[3]{V}$ becomes 1.76. The mean variation for these ten compounds, with molecular weights ranging from 18 to 438, is only ± 5 per cent. from the mean. It is remarkable that water agrees with the other compounds although it expands on freezing.

TABLE III.—*Organic Compounds.*

Compound.	<i>Mw.</i>	<i>T.</i>	$\sqrt[3]{V}$	$Mw/T\sqrt[3]{V}$	$10 \times dw/T$
<i>Acids.</i>					
Formic acid	2640	266	3.33	2.98	2.71
Acetic acid.....	2661	277	3.84	2.50	1.61
Chloroacetic acid	3890	334	3.91	2.98	1.71
Benzoic acid	4607	396	4.56	2.61	1.08
Phenylacetic acid	4293	350	4.80	2.56	1.00
Phenylpropionic acid ...	3720	322	5.14	2.25	0.87
Lauric acid.....	8985	316	6.13	4.64	1.24
Stearic acid	13520	337	6.93	5.79	1.19
<i>Hydrocarbons.</i>					
Naphthalene	4559	353	4.81	2.67	0.99
Phenanthrene	4450	373	5.45	2.19	0.71
Diphenyl	4391	343	5.36	2.39	0.83
Diphenylmethane.....	4661	300	5.54	2.80	0.90
<i>Halogen derivatives.</i>					
<i>p</i> -Chloroaniline	4742	342	4.13	2.93	1.30
<i>p</i> -Dichlorobenzene.....	4395	325	4.90	2.76	1.15
<i>p</i> -Dibromobenzene	4862	358	5.04	2.70	1.06
<i>p</i> -Bromophenol ...	3961	337	4.62	2.55	1.09
Tribromophenol	4301	366	4.96	2.37	0.93
Tribromoaniline	4608	395	5.14	2.27	0.86
<i>Nitro-derivatives.</i>					
Nitrobenzene	2743	264	4.45	2.34	1.02
<i>m</i> -Dinitrobenzene	4901	363	4.81	2.81	1.21
Nitronaphthalene	4383	329	5.06	2.64	0.97
<i>o</i> -Nitrophenol	3725	316	4.60	2.56	1.10
<i>Phenols.</i>					
Phenol	2344	298	4.36	1.80	0.89
Resorcinol	4906	383	4.41	2.90	1.37
Thymol	4127	321	5.36	2.40	0.81

TABLE III.—*Organic Compounds (continued).*

Compound.	<i>Mw.</i>	<i>T.</i>	$\sqrt[3]{V}$	$Mw/T \sqrt[3]{V}$	$10 \times dw/T$
<i>Amino-compounds.</i>					
Diphenylamine	3830	324	4.72	2.51	0.78
<i>p</i> -Toluidine	4177	312	4.67	2.87	1.21
α -Naphthylamine	3720	316	4.96	2.38	0.95
<i>Aromatic Ketones.</i>					
Acetophenone	3588	293	4.86	2.52	1.05
Benzophenone	4361	321	5.40	2.51	0.90
<i>Miscellaneous.</i>					
Acetoxime	3022	333	4.22	2.15	1.12
Urethane	3631	322	4.30	2.62	1.34
Azobenzene	5187	342	5.31	2.85	0.87
Azoxybenzene	4285	308	5.42	2.57	0.88
Anethole.....	4070	294	5.30	2.61	0.94
Thiosinamine	3874	350	4.56	2.43	1.14

It is at once apparent that the agreement in the case of the organic substances is not as close as that observed amongst the inorganic binary compounds. There are, indeed, several striking exceptions. Thus phenol shows a deviation of more than 25 per cent. from the mean. Of the 36 organic substances mentioned, more than 30 give numbers which do not vary to a greater extent than ± 7 per cent. from the mean.

To test the theoretical considerations enumerated above, the latent heats of several substances of more or less importance to the result have been determined. In addition, it has been necessary to find the specific gravities of a number of organic compounds in the solid state.

In the determination of the latent heat, the simplest apparatus was employed. The substance placed in a test-tube was heated to the required temperature in a hot-air bath, and when the thermometer in the tube and the one in the bath registered the same temperature, the test-tube and its contents were rapidly plunged into a large calorimeter fitted up with the usual precautions. This operation was repeated at different temperatures. In the case of the metals, the solid piece was

caught by the stirrer as it fell from the fractured test-tube. In repeating the experiment, a tube of equal weight was employed.

The loss of heat of the calorimeter by radiation was practically *nil* when the latent heats of the metals were being found, as the final temperature was reached in so short a time. Owing to the poor conductivity of the organic compounds, however, the time taken to acquire the final temperature was considerably longer, although even in this case the change due to radiation is hardly noticeable. In general, when two observations were made at the same temperature, one was made with the water in the calorimeter slightly below the temperature of the air and the other a little above.

The solid organic compound was heated to about 20° below its melting point, and several observations made at about this temperature. It was found inadvisable to work at a higher temperature with the solid, for the presence of impurity is apt to make the specific heat increase rapidly near the melting point. Groups of observations were then made at intervals of 10 and 30° above the melting point.

TABLE IV.—*Water + Water Value of Calorimeter = 630 grams.*

Substance.	Weight.	Temperature.	Final temperature.	Rise.
Thallium.....	36	230	18·05	0·75
„	36	230	17·15	0·80
„	36	255	22·05	0·85
„	36	315	18·1	1·5
„	36	350	18·5	1·7
„	49	240	17·4	1·1
„	49	260	18·6	1·15
„	49	265	18·25	1·2
„	49	305	19·45	1·9
„	49	330	20·4	2·0
Lead	45	260	18·15	0·9
„	45	260	18·05	0·95
„	45	290	20·55	1·05
„	45	290	18·3	1·05
„	45	350	21·1	1·8
„	45	350	20·6	1·8
„	45	365	19·6	1·9
Tin	43	160	16·35	0·75
„	43	160	19·95	0·75
„	43	190	19·1	0·9
„	43	190	19·9	0·9
„	43	240	22·0	2·1
„	43	270	19·95	2·3
„	43	285	19·8	2·35
„	43	290	22·2	2·4
Phenanthrene	16	75	21·45	0·55
„	16	80	24·0	0·5
„	16	85	24·4	0·55
„	16	110	21·45	1·55

TABLE IV.—*Water + Water Value of Calorimeter = 630 grams (continued).*

Substance.	Weight.	Temperature.	Final temperature.	Rise.
Phenanthrene	16	115	19·7	1·7
Phenylacetic acid	16	130	21·8	2·0
„	25·3	60	22·35	0·5
„	25·3	60	17·95	0·55
„	25·3	80	22·2	2·1
„	25·3	80	21·8	2·2
„	25·3	90	23·05	2·4
„	25·3	95	20·2	2·6
„	25·3	115	20·8	3·15
<i>m</i> -Dinitrobenzene	20	70	20·55	0·5
„	20	70	23·5	0·5
„	20	100	20·1	1·7
„	20	100	23·2	1·75
„	20	110	23·1	1·8
„	20	120	21·0	1·95
Thiosinamine	20·2	60	20·2	0·6
„	20·2	60	19·55	0·65
„	20·2	98	18·3	2·35
„	20·2	98	23·25	2·25
„	20·2	125	20·95	2·75
„	20·2	125	22·35	2·8
Tribromophenol	16	60	19·6	0·35
„	16	60	20·6	0·35
„	16	100	19·55	1·05
„	16	100	21·1	1·05
„	16	120	22·2	1·2
„	16	120	21·05	1·3
Tribromoaniline	16	85	14·75	0·65
„	16	85	16·15	0·65
„	16	130	18·36	1·5
„	16	130	18·45	1·6
„	16	150	17·95	1·8
„	16	150	16·5	1·85

Latent Heats. (See Table IV.)

Thallium.—The metal was heated in an atmosphere of coal-gas. Two series of experiments were performed, using different amounts of material. In the first series, the latent heat was found to be 7·0, and in the second, 7·4; mean, 7·2. The melting point was assumed to be 290°. This value for the latent heat is widely different from that (5·12) obtained indirectly by Heycock and Neville (*Trans.*, 1894, 65, 31). Their value, however, is calculated from the atomic falls of only three metals. Further, the material they used contained “at least 98 per cent. of thallium.” Small quantities of impurities are known to have a noticeable effect on the latent heat; thus, 3·5 per

cent. of solid matter has been found to depress the latent heat of ice from 80 to 54 (Petterson). The thallium used by the author was shown to be almost pure by the following analyses :

0.2292 gave 0.3710 TlI. Tl = 99.81 per cent.

0.2348 „ 0.4678 Tl₂PtCl₆. Tl = 99.74 per cent.

Lead.—From these experiments, the latent heat is found to be 6.45, assuming the melting point to be 330°. The results obtained by previous observers are : (1) Rudberg, 5.858 ; (2) Person, 5.369.

The atomic falls obtained by Heycock and Neville in the case of lead vary so much that it is hardly safe to draw conclusions from them as to the latent heat of the metal. Taking the mean of the atomic falls between 4 and 6.4, the latent heat would seem to be about 6.3. The purity of the metal (Merck) used by the author is shown by the following analysis :

0.3224 gave 0.4728 PbSO₄. Pb = 100.15 per cent.

Tin.—The experimental numbers give the value of the latent heat as 14.05, which is in close agreement with Person's value 14.252. The melting point was taken as 230°.

Phenanthrene.—After separation from the anthracene present, which raises its melting point, the substance melted sharply at 100°, and the melting point was not altered by recrystallisation. The latent heat was found to be 25. This is a little higher than the number 23, calculated from the molecular depression 120, obtained by Garelli and Ferratini (*Gazzetta*, 1893, 23, i, 442).

Phenylacetic Acid.—The acid used had a melting point of 77° and gave the latent heat as 32. Bruner* (*Ber.*, 1894, 27, 2102) found the value 25.4 with a sample of the acid melting at 74.9°.

m-Dinitrobenzene.—The latent heat of this compound does not seem to have been previously determined. A sample melting at 90° gave the latent heat as 29.0.

Thiosinamine.—This compound is doubly interesting from the fact that it is the only one in the list containing sulphur, and that it contains an ethylene linking. The material used had a melting point of 77° and gave the latent heat as 33.4.

Tribromophenol.—This substance is especially interesting on account of the magnitude of its molecular weight. The material used melted at 93° and was found to have a latent heat of 13.4.

Tribromoaniline.—Two different preparations both melted at 122°. The latent heat obtained was 14.4. This is a little higher than that of tribromophenol.

* Several of the latent heats obtained by this observer are lower than those of other experimenters, and some give smaller values for the expression $Mw/T \sqrt[3]{V}$ than would be expected by analogy with similar compounds.

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These latent heat determinations are summarised in the following table:

Substance.	Melting point.	Latent heat.
Thallium	(290°)	7.2
Lead	(330)	6.45
Tin	(230)	14.05
Phenanthrene	100	25
Phenylacetic acid	77	32
<i>m</i> -Dinitrobenzene	90	29.0
Thiosinamine	77	33.4
Tribromophenol	93	13.4
Tribromoaniline	122	14.4

Specific Gravities.

It is a little remarkable that the specific gravities of comparatively few solid organic compounds are known. The values obtained in the following table were determined by means of the specific gravity bottle, water or petroleum of low boiling point being employed to fill the vacant space. The values given are the mean of two closely concordant results:

Compound.	Sp. gr. 20°/20°.	Molecular volume of solid.
Diphenylamine	1.160	105.6
<i>m</i> -Dinitrobenzene	1.521	111.1
Benzophenone	1.172	155.3
α -Naphthylamine	1.171	122.1
Azoxybenzene	1.248	158.8
Thiosinamine	1.219	95.1
Urethane	1.11	80.2
Chloroacetic acid	1.58	59.8
Acetoxime	0.97	75.3
Tribromophenol	2.55	121.9
Tribromoaniline	2.35	136.2

Summary.

(1) For the elements with atomic weights over 40 which do not expand on freezing, the expression $Mw/T \sqrt[3]{V}$ gives numbers the deviation of which from the mean is but slightly greater than that observed in the case of Dulong and Petit's law.

(2) For the binary inorganic compounds, the mean percentage deviation of the values of $Mw/T \sqrt[3]{V}$ is only ± 5 .

(3) In the case of the carbon compounds, great regularity is noticed

among those of similar constitution. Thus for the disubstituted benzenes the variation is ± 5 per cent. Compounds with two benzene nuclei give equally satisfactory results.

There still remain a number of points to be cleared up in connection with the subject of latent heats of fusion. Careful determinations with pure material of the latent heats of all the members of one or more series of organic compounds should throw much light on the relationship between latent heat, molecular weight, and chemical constitution.

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