XLIX.—*The Molecular Weights of the Metals.*

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THE means at the disposal of chemists for determining the molecular weights of elements or compounds have, until recently, been limited to the determination of their vapour-densities. Starting with Avogadro's assumption, which by the investigation of the kinetic theory of gases has now been given the precision of a law, the relative weights of gases under similar conditions of temperature and pressure are proportional to the relative weights of their molecules. The standard of reference is hydrogen, which on chemical grounds is supposed to exist in the free state as a diatomic molecule, and this assumption has been rendered almost certain by Kundt and Warburg's determination of the ratio of the specific heat of mercury gas at constant volume to that at constant pressure, whereby it is shown that all the energy imparted in the form of heat to gaseous mercury can be accounted for by supposing it to impart increased translational velocity to the molecule; no energy appears to be absorbed, produc-

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ing internal oscillation of *parts* of a molecule. Hence the conclusion that the atom of mercury constitutes the molecule. Naumann, moreover, has pointed out that that energy which disappears in producing internal work when presumably diatomic gases, such as oxygen, hydrogen, nitrogen, carbon monoxide, &c., are heated, and which doubtless causes oscillation or rotation of the atoms within the molecule, in all probability bears a constant proportion to the translational energy of the gaseous molecules. Such gases as NO, CO, HCl, &c., are not easily conceived other than diatomic; hence oxygen, nitrogen, and hydrogen may, from their similarity of behaviour as regards heat with these unmistakably diatomic gases, be also regarded as diatomic.

The method of replacement by stages, although it has rendered excellent service in determining the molecular weights of compounds and, indirectly, the atomic weights of elements, is from its very nature not adapted to the determination of the molecular weights of elements. A knowledge of the molecular weight of potassium chloride, for example, throws no light on the molecular weight of the element potassium, although it may serve as an assistance in deducing the atomic weight of potassium from its equivalent.

On the supposition, then, that the molecular weight of hydrogen is expressible by the formula H_2 , the vapour-density method has fixed the molecular weights of the following elements in the state of gas:—

	Name.	Molecular formula.	Investigators.
<i>Monatomic</i>	Mercury ..	Hg	Dumas; V. Meyer.
„	Cadmium ..	Cd	Dewille and Troost.
„	Zinc	Zn	Mensching and V. Meyer.
„	Sodium ..	Na	Scott.
„	Potassium	K	Scott.
<i>Diatomic, changing to monatomic at high temperatures</i>	Iodine	I ₂ and I	Dumas; Dewille and Troost; V. Meyer; Crafts and Meier.
	Bromine ..	Br ₂ and Br? ..	Jahn; V. Meyer and Zublin.
	Chlorine ..	Cl ₂ and Cl? ..	Ludwig; V. Meyer; Crafts.
<i>Diatomic, not altered by rise of temperature</i>	Hydrogen ..	H ₂	Regnault; V. Meyer.
	Oxygen	O ₂	Regnault; Jolly; V. Meyer.
	Nitrogen ..	N ₂	„ „ „
<i>Triatomic</i>	Ozone	O ₃	Andrews and Tait.
	Phosphorus	P ₄ P ₂ (?)	Dumas; Dewille and Troost; V. Meyer.
<i>Tetratomic</i>	Arsenic	As ₄ ·As ₂ (?) ..	Mitscherlich; Dewille and Troost; V. Meyer.
	Antimony ..	Sb ₄ (?)Sb ₂ (?) ..	V. Meyer.
<i>Hexatomic, changing to diatomic at high temperatures</i>	Sulphur ..	S ₆ (?)S ₂	Dumas; Bineau; Dewille and Troost; V. Meyer; Biltz.
	Selenium ..	Se ₆ (?)Se ₂	Dewille and Troost.
	Tellurium ..	Te ₆ (?)Te ₂	Dewille and Troost.

About the molecular formulæ of mercury, cadmium, zinc, sodium, and potassium there can be no doubt, so far as the gaseous density reveals them; nor are those of hydrogen, oxygen, and nitrogen uncertain. But the remaining elements in this table, which, it may be remarked in passing, are all commonly called non-metallic, exhibit densities varying with temperature, and from what we know regarding similar behaviour of compounds, and especially of those which dissociate into like molecules, it may be concluded that they exist in different molecular aggregates, according to their pressure and their temperature. It is, to say the least of it, remarkable that the majority of elements, about the molecular complexity of which anything is known, should exhibit such a marked contrast to the majority of compounds, where dissociation is the exception and not the rule.

The theory of the analogy between the condition of matter in dilute solutions and in gases under moderate pressure and moderately high temperature, so beautifully developed by Van't Hoff (*Phil. Mag.*, Aug., 1888), and the clear and incontrovertible deduction of the necessary sequence of Raoult's law of the connection between the molecular weight of a dissolved substance and the depression of the vapour-pressure of the solvent, or the lowering of its melting point, have placed in the hands of chemists a new means of investigating the molecular weights of substances inconvenient or impossible to gasify. This method has been applied to the determination of the molecular weights of the following elements:—

*Method of Depressing the Vapour-pressure of the Solvents.**

Iodine dissolved in solvents with brown colour	I ₄ .
Iodine dissolved in solvents with violet colour	I ₂ to I ₄ .

Method of Depressing the Melting Point of the Solvent.†

Bromine in water and in acetic acid	Br ₂ .
Iodine in benzene (very dilute)	I ₂ .
„ (more concentrated)	I ₂ to I ₄ .
Sulphur in benzene	S ₈ .
Phosphorus in benzene	P ₂ to P ₄ .

It would thus appear that iodine, like phosphorus and arsenic, but at far lower temperatures, tends to form a molecule of the complexity I₄ whilst the complexity of the sulphur molecule at low temperatures is confirmed (see Biltz, *Zeit. physikal. Chem.*, **2**, 920; also Ramsay, *ibid.*, **3**, 67).

* Loeb, *Zeit. physikal. Chem.*, **2**, 606.

† Paternò and Nasini, *Ber.*, **21**, 2153.

It is unlikely that the method of vapour-densities will render any further service in determining the molecular weights of other elements. Their temperatures of volatilisation are so high that Dumas' method, the only one adapted to settle the point decisively, cannot be employed.

It occurred to me that by using mercury as solvent, many of the metals might be investigated. But as Raoult's method presupposes a knowledge of the molecular weight of the solvent, the question arises, what is the molecular weight of liquid mercury? I think it very unlikely, in view of the investigations of Dr. S. Young and myself, that in condensing from gas to liquid the molecular weight of mercury is altered. Our experiments with stable liquids, such as the alcohols and ether, have shown that their molecular formulæ are not increased, even at low temperatures, when the vapours are in contact with their respective liquids. And further proof, which cannot be gainsaid, of the non-association of mercury-atoms is furnished by the research of Kundt and Warburg, previously alluded to (*Pogg. Ann.*, **127**, 497; also **135**, 337 and 527). It will be remembered that they showed that the total energy communicated to mercury vapour as heat, *even when the vapour was in contact with liquid mercury*, was employed in effecting translational motion of the molecule, whence it may be concluded that even the saturated vapour of mercury consists of single atoms. Hence it appears just to consider the molecular weight of liquid mercury as equal to its atomic weight, 200.

The simple formula connecting the molecular weight of the dissolved substance with the depression of vapour-pressure which the dissolved substance produces in the solvent is—

$$MW = \frac{M'W' \times P \times p}{100 \times d};$$

where MW is the molecular weight to be found; M'W' the molecular weight of the solvent; P/100 the percentage weight of dissolved substance in the solution; p , the vapour-pressure of the solvent; and d , the depression in the vapour-pressure of the solvent produced by adding the substance dissolved.

This expression becomes for mercury as solvent—

$$MW = \frac{200 \times P \times p}{100 \times d} = \frac{2P.p}{d}.$$

Apparatus Employed.—The first form of apparatus used was a U-tube, one limb of which was about 160 mm. long, and sealed; about 30 mm. from the sealed end a trap was provided. The other limb was about 400 mm. in length, and was connected at its upper end by sealing with a gauge standing in the same trough with a

barometer-tube of similar bore. This U-tube was jacketed with pure bromonaphthalene, which, by means of the arrangement described on another occasion (*Phil. Trans.*, 1887, A, p. 59), could be made to boil under various pressures alterable at will; hence it was possible, from data given in the *Trans.*, 1885, 640, to heat the U-tube to such temperatures as 260° or 270° , with the certainty that the error in temperature was a small one.

Previous to the experiment, the U-tube was filled with the required amalgam, and all air was expelled by boiling it past the trap. The U-tube was then placed in position, and a little more mercury was added. Both limbs of the U-tube were graduated in millimetres, so that, when the mercury fell in the shorter limb and rose in the longer one, the difference of pressure in the two limbs could be read. But as the open end of the U-tube was connected with a gauge, it was possible to vary the position of the mercury in both limbs, and so to obtain a set of readings at the same temperature.

To control the accuracy of the process, determinations were made of the vapour-pressures of mercury alone at 260° and 270° . In the following table all the data are given, so as to afford an idea of the method and its trustworthiness:—

Temperature 260° . Pressure under which Bromonaphthalene boiled 488.95 mm. at 19.5° , the Atmospheric Temperature.

Open.	Close.	Gauge.	Barometer.	Δ_1 .	Δ_2 .	Δ'_1 .	Δ'_2 .	Δ_3 .
mm.	mm.	mm.	mm.					mm.
61.0	25.4	276.8	145.5	35.6	131.3	34.0	130.8	96.8
61.0	25.5	276.7	145.5	35.5	131.2	33.9	130.7	96.8
55.4	31.0	266.3	145.65	24.4	120.65	23.3	120.2	96.9
49.2	37.0	254.95	145.9	12.2	109.05	11.65	108.65	97.0
49.1	36.95	254.9	145.95	12.15	108.95	11.60	108.55	96.95
44.4	41.7	245.95	146.0	2.7	99.95	2.6	99.55	96.95
44.4	41.6	245.9	146.0	2.8	99.9	2.7	99.50	96.80
							Mean ..	96.87

In this table, the first two columns refer to the U-tube, the open end being the one connected with the gauge. Δ_1 and Δ_2 are respectively the differences between the readings in the U-tube and those of the gauge and barometer. Δ'_1 is Δ_1 corrected from 260° to 0° ; Δ'_2 , Δ_2 corrected from 19.5° to 0° ; Δ_3 is the difference between the two, and gives the observed vapour-pressure of mercury.

At 270° , the following results were obtained:—

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Pressure under which Bromonaphthalene boiled, corrected to Atmospheric Temperature, 21°, 771 mm.

Open.	Close.	Gauge.	Barometer.	Δ_1 .	Δ_2 .	Δ'_1 .	Δ'_2 .	Δ_3 .
mm.	mm.	mm.	mm.					mm.
78·8	7·95	337·3	145·0	70·85	192·3	67·4	191·6	124·2
78·8	7·95	337·2	145·0	70·85	192·2	67·4	191·5	124·1
68·6	17·8	318·9	145·15	50·8	173·75	48·3	173·15	124·85
68·4	18·0	318·7	145·1	50·4	173·6	47·9	172·95	125·05
59·4	26·95	301·3	145·3	32·45	156·0	30·85	155·45	124·6
59·35	27·0	301·25	145·25	32·35	156·0	30·75	155·45	124·7
51·4	34·8	286·5	145·4	16·6	141·1	15·8	140·6	124·8
47·65	38·0	279·9	145·5	9·65	134·4	9·15	133·9	124·75
47·75	37·9	279·85	145·45	9·85	134·4	9·35	133·9	124·55
43·7	41·9	272·0	145·55	1·8	126·45	1·70	126·0	124·3
43·8	42·0	272·05	145·6	1·8	126·45	1·70	126·0	124·3
							Mean ..	124·56

We have here two determinations of the vapour-pressure of mercury, viz., at 260°, 96·87 mm., and at 270°, 124·56 mm. These figures assume that the vapour-pressures of bromonaphthalene have been correctly determined at these temperatures. The vapour-pressures of bromonaphthalene were determined by Dr. Sydney Young and myself by the method described by us in *Trans.*, 1885, 42. But we have also shown (*Trans.*, 1886, 47), that the vapour-pressures of mercury follow the law pointed out by us in the *Philosophical Magazine* for December, 1885, and January, 1886; and that it is possible from two trustworthy observations of the vapour-pressures of a substance at any two temperatures not too close to each other, to calculate the temperature corresponding to any vapour-pressure below 6000 mm. By means of these relations we calculated the vapour-pressures of mercury at intervals of 5° from 135° to 520°. The calculated vapour-pressure of mercury at 260° is 96·66 mm. I have now found 96·87 mm. The difference, 0·21 mm., corresponds to an error in temperature of the bromonaphthalene of 0·27°; and at 270°, the calculated vapour-pressure of mercury is 123·90 mm.; whereas the vapour-pressure found is 124·56 mm., the difference is 0·66 mm., corresponding to a difference in temperature of 0·21°. The error as thus calculated may be wholly ascribable to the determination of the vapour-pressures of bromonaphthalene, in which case those given by Dr. Young and myself are at such temperatures low by a pressure equivalent to about 0·2°; or it may be ascribed to error in the determination of the vapour-pressures of mercury. I am disposed to believe the former supposition; but whichever be taken, the difference

is a minute one for such high temperatures, and the observations furnish further proof of the accuracy of the work already referred to.

In carrying out similar experiments on amalgams by means of this apparatus, two difficulties were met with which led to its abandonment. These were, first, the difficulty of introducing the amalgams of easily oxidisable metals without considerable oxidation; this caused a difference in the surface tension of the mercury in the closed limb and the open limb of the U-tube; and although it is easy to introduce such a correction as would approximately restore the surfaces of the mercury to the position which they would occupy on the scale provided both menisci were plane surfaces, yet this correction does not show the true position of the mercury, inasmuch as a greatly curved meniscus means that the mercury is considerably depressed in that limb of the tube on which the meniscus is so curved. It is impossible to estimate the value in millimetres of this depression; and hence no allowance is possible. This unknown error may bear a considerable proportion to the whole depression observed, which is not a very great one. The second difficulty is, that the solubility of many metals in mercury at 260° or 270° is very slight. Now as the depression of the vapour-pressure of mercury by a dissolved metal depends on the total amount of metal dissolved, and is inversely proportional to the molecular weight, a very weak solution cannot be employed, else the probable error bears too large a proportion to the total quantity measured. But the results of measurements with cadmium and with sodium bear out the conclusions of subsequent experiments, hence they are worth quoting here. I should mention that attempts were also made to determine the behaviour of zinc, magnesium, barium, and silver, but owing to the oxidation of the first three of these metals during their introduction, the glass was wetted by the metal, and it was almost impossible to obtain readings; with silver, the solubility was too small at 270° to permit of trustworthy measurements.

1. *Cadmium*.—Temperature = 260° ; percentage in amalgam, 2.074; vapour-pressure (mean of 11 measurements), 93.02 mm.; highest measurement, 93.6 mm.; lowest, 92.2 mm.; calculated molecular weight, 104.1; temperature = 270° ; percentage, the same; vapour-pressure (mean of 9 measurements) 120.17 mm.; highest measurement, 120.75 mm.; lowest, 119.45 mm.; calculated molecular weight, 117.7; mean of both determinations, 110.9; atomic weight of cadmium, 112.1.

2. *Sodium*.—Temperature = 270° ; percentage in amalgam, 0.6255; vapour-pressure (mean of 18 measurements), 112.9 mm.; highest

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measurement, 114.2 mm.; lowest measurement, 111.3 mm.; calculated molecular weight, 13.36; atomic weight of sodium, 23.04.

Owing to the difficulty of experiment, this process was abandoned in favour of a simpler one. A U-tube with a shorter limb was employed, of the shape shown in the figure. Close beside, almost in

contact with it, was a perfectly similar U-tube. Both of these tubes were surrounded by a bath of mercury vapour. The one containing the amalgam was connected with a gauge standing in the same trough with a barometer so that the pressure could be slightly altered, and various separate readings of pressure could be taken. As the temperature of the boiling mercury was not invariably that corresponding to the atmospheric pressure of the day, some slight difference being always caused by radiation, or by convection currents, the second U-tube, which contained pure mercury, served to correct the reading; for, had the temperature been exactly that of mercury vapour, the levels of the mercury in the two limbs of the second U-tube would have been the same; this was sometimes the case; but as a rule, the temperature of the bath was slightly below that of the temperature of the vapour of boiling mercury at the pressure of the day, and by sub-

tracting the difference in level of the mercury in the two limbs of the second U-tube from the height of the barometer, the pressure truly corresponding to the temperature of the mercury vapour was obtained.

In this way, a series of determinations at the boiling point of mercury were obtained; it was unnecessary to know the temperature, for that corresponded to the pressure of the atmosphere of the day, subject to the correction mentioned.

Various methods of filling the experimental U-tube with amalgam were resorted to, according to the nature of the metal experimented with. The usual method of procedure was as follows:—The tube was pumped empty by means of a Sprengel's pump, and hydrogen was admitted to restore the pressure. The tube was again evacuated, and the amalgam, previously prepared, was introduced through the side-tube. The determinations having been made, the percentage composition of the amalgam was ascertained by analysis. This plan was pursued with oxidisable metals, such as lithium, sodium, potassium, barium, and manganese. With metals easily obtained and not readily oxidisable, the requisite amount of mercury, weighed out, was introduced into the tube. The tube was then exhausted and filled with hydrogen; the metal, weighed out, was dropped on to the mercury, and the stopper replaced; and the tube was again exhausted and again filled with hydrogen. Before each experiment, the contents of the U-tube were well boiled for about an hour under diminished pressure, so that all gas might be carried round the bend. On increasing the pressure, it is necessary that the mercury column should quickly touch the glass, leaving no trace of a gas-bubble. During each experiment, often between each two readings, the pressure was again reduced so as to ensure the expulsion of any residual gas. It was seldom found that this operation was necessary, for, as a rule, the readings obtained were identical within the limits of experimental error.

The proportion which the experimental error bears to the result obtained differs in each individual case. It was not common to obtain two readings from any set with so great a difference as 1 mm. in pressure. But when the total lowering of vapour-pressure amounts to 10 mm. this represents an extreme error of 10 per cent. In cases where larger amounts were used the error was proportionately smaller, and often did not amount to more than 1 or 2 per cent. The mean result is of course still more trustworthy.

The source of an error which cannot be very great, and yet which cannot well be estimated, has been previously mentioned, viz., that the form of the meniscus in the closed limb differs from that in the open limb. Here it is not the mere differences in level which

require correction, that can easily be approximated to, and has been uniformly allowed for; it is the unknown diminution or increase in pressure produced by the tendency of the curved surface to occupy a lower position in the tube than a plane surface would. The general concordance of the results would, however, show that this error is not a serious one. The depression in one limb is partially balanced by that in the other, and the algebraic sum is probably negligible.

The results will now be considered in the order in which the metals occur in the periodic table:—

1. *Lithium*.—Prepared by electrolysing a solution of the chloride, mercury forming the negative electrode. Long, lustrous, needle-shaped crystals separated on standing, which rapidly become dull, and melted on exposure to air. The constants were determined, and the lithium in the portion of amalgam employed was subsequently estimated as chloride. The amalgam was admitted through the side tube.

2. *Sodium*.—Sodium amalgam, prepared in the usual way, was employed. It was admitted through the side-tube into a rarefied atmosphere of hydrogen. Five sets of experiments were made, the percentage of sodium in the amalgam being different in each case. The sodium was afterwards estimated as chloride.

3. *Potassium*.—The results with potassium amalgam were similarly obtained, two sets of experiments being made.

4. *Barium*.—Barium amalgam was prepared in the same manner as lithium amalgam. Before introducing it into the U-tube, it was warmed so as to bring all the barium amalgam into solution. When cold it was filled with needle-shaped crystals. After the experiments had been made, the barium was estimated as sulphate.

5, 6, and 7. Repeated attempts were made to prepare beryllium, calcium, and strontium amalgams in a similar manner, but without success. The amalgams can be made, but are so easily attacked by water, even when the tube in which the electrolysis took place was surrounded by a freezing mixture, that they were not of sufficient concentration to give trustworthy results. All of them oxidise very rapidly on exposure to air, beryllium amalgam becoming covered with a black film, whilst strontium and calcium are covered by a grey film of oxide. During the electrolysis of calcium chloride, the solution is filled with black particles; this is not the case with strontium or barium. Attempts were also made, but without success, to prepare the metals by the electrolysis of the fused chlorides; for no coherent lumps were obtained which would have been suitable for such determinations. The depression produced by these amalgams was always too small to give trustworthy results. The result for calcium, however, will be given in its place, but it must not be considered as of

8. *Magnesium*.—A sample of commercial magnesium was sublimed in a vacuum by heating it to redness in a piece of hard combustion tubing. It sublimed with difficulty; but the resulting metal had a silver-white colour, and was obviously pure. A weighed piece was dropped on the surface of the mercury in the U-tube; the tube was then exhausted and filled with hydrogen. Two sets of experiments were made with different quantities.

9. *Zinc*.—This metal was also carefully purified by distillation in a vacuum. The pure zinc was barely attacked by hydrochloric acid, even at boiling temperature. The method was the same as with magnesium. Three sets of experiments were made.

10. *Cadmium*.—The sample was also purified by distillation. Three sets of experiments were made.

These amalgams are also unstable in moist air. The amalgam of magnesium turns black, and it was conjectured that the black substance might prove to be a suboxide of magnesium; but on analysis it proved to be a mixture of magnesia with finely divided mercury. Zinc amalgam is more stable in air than magnesium amalgam; and the cadmium compound may be exposed for some time without much oxidation.

11. *Aluminium*.—A sample of aluminium wire, which contained on analysis 99.1 per cent. of aluminium, was employed. It was cut into short lengths and dropped into a weighed amount of mercury contained in the U-tube. After exhaustion and filling with dry hydrogen, the aluminium dissolved readily on boiling the mercury. The resulting amalgam possesses a most curious property. A drop, allowed to stand in ordinary air, sends out a loose, porous, white mass of aluminium oxide, which grows from hour to hour and presents the appearance of a long, white worm, often attaining the length of a foot. All the aluminium is thus expelled from the mercury, and the alumina may be ignited and weighed. Two sets of experiments were made.

12. *Gallium*.—By the kindness of M. Lecoq de Boisbaudran, I was furnished with 0.5 gram of gallium. It dissolved easily in the mercury. One estimation was made. The gallium amalgam does not tarnish in air.

13. *Thallium*.—A sample of commercial thallium was purified by precipitation as chloride, and reduction by fusion with potassium carbonate and cyanide. The amalgam is easily made, and does not tarnish. Five experiments were made.

14. *Tin*.—The metal was reduced from the dioxide as with thallium. The amalgam is stable in air. Two experiments were made.

15. *Lead*.—The metal was prepared from the chloride, as above. Two sets of readings were taken.

16. *Arsenic*.—Attempts to prepare an amalgam of arsenic failed;

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the element is insoluble in mercury, even at the boiling point of mercury; and on electrolysis of the dilute chloride, the element is deposited on the surface of the mercury; none enters into solution. Hence experiments could not be carried out.

17. *Antimony*.—Antimony dissolves in mercury freely at the boiling point, but crystallises out in spangles on cooling. The amalgam is permanent in air; four estimations were made.

18. *Bismuth*.—Two experiments were made with this amalgam. It is permanent in air.

19. *Copper*.—Although copper amalgamates readily, yet its amalgam is almost insoluble in mercury, even at the boiling point, giving too small a depression of vapour-pressure, hence experiments made with it failed.

20. *Silver*.—The same remark applies to silver. But the amalgam is much more soluble in boiling mercury than the corresponding one of copper. One set of readings was taken. The composition of the amalgam, after it has been heated to dull redness, appears to be HgAg.

21. *Gold*.—This amalgam is also not freely soluble; yet sufficient dissolved for the purpose.

22, 23. *Platinum and Palladium*.—These metals do not dissolve in mercury to a sufficient extent to make it possible to carry out experiments.

24, 25. *Iron and Nickel*.—Attempts to produce these alloys by electrolysis succeeded in so far as dilute solutions were obtained; but the amount present was too small to allow of an estimation of their molecular weights.

26. *Manganese*.—This element was amalgamated by electrolysis of its chloride. The amalgam rapidly turns black in air, but may be preserved for some time under water in a closed vessel, on which it has little or no action. Under alcohol, in an open vessel, it rapidly becomes oxidised, owing to absorption of the oxygen of the air. A successful series of readings was obtained.

The results of these experiments are given in the table (p. 533).

On inspecting the table it will be seen that the molecular weights of the elements lithium, magnesium, zinc, cadmium, gallium, tin, lead, bismuth, silver, and gold are expressed by numbers almost identical with their atomic weights. But here the question of probable error of experiment should be considered. It may be taken that no two readings of any set differed by more than a millimetre. The total depression with different elements, however, is represented by numbers of very different magnitude. Thus with the smallest quantity of sodium taken, 0.86 atom per 100 atoms of mercury, the mean total depression observed was 6.7 mm. The probable error is, however,

Tabulation of Results.

	No. of readings.	Percentage.	No. of atoms per 100 atoms of mercury.	Pressure of mercury vapour.	Depression.	Molecular weight found.	Atomic weight.
				mm.	mm.		
(1.) Lithium	7	0·0597	1·70	763·6	12·9	7·1	7·02
(2.) Sodium	7	0·0985	0·86	736·4	6·7	21·6	23·04
(3.) „	8	0·1768	1·54	767·2	15·0	18·1	„
(4.) „	9	0·2147	1·87	766·8	17·9	18·3	„
(5.) „	9	0·3205	2·79	755·0	29·3	16·5	„
(6.) „	7	0·6616	5·35	772·1	62·7	15·1	„
(7.) Potassium	9	0·3023	1·55	752·8	15·6	29·1	39·14
(8.) „	7	0·0180	5·26	742·5	49·6	30·2	„
(9.) Calcium	8	0·0373	0·19	750·4	2·9	19·1	40·08
(10.) Barium	9	0·6107	0·90	762·0	12·3	75·7	137·00
(11.) Magnesium	5	0·0855	0·70	758·0	5·4	24·0	24·30
(12.) „	5	0·5820	4·82	749·8	40·6	21·5	„
(13.) Zinc	6	0·3459	1·07	751·7	7·4	70·1	65·43
(14.) „	7	0·6282	1·93	766·1	15·5	62·1	„
(15.) „	5	1·0214	3·16	755·4	23·6	65·4	„
(16.) Cadmium	5	0·04187	0·75	752·6	6·3	100·2	112·1
(17.) „	5	1·0785	1·95	753·4	16·3	99·7	„
(18.) „	5	1·9220	3·51	740·0	27·4	103·8	„
(19.) Aluminium	7	0·2043	1·52	755·0	8·4	36·7	27·01
(20.) „	9	0·3950	2·94	758·5	18·1	33·1	„
(21.) Gallium	5	0·7855	2·27	767·1	17·3	69·7	69·9
(22.) Thallium	4	0·8191	0·81	758·9	7·6	163·6	204·2
(23.) „	9	1·666	1·66	745·6	13·3	186·8	„
(24.) „	4	2·894	2·92	765·5	24·6	180·1	„
(25.) „	5	3·290	3·33	759·8	25·3	197·6	„
(26.) Tin	6	1·142	1·94	754·1	14·7	117·4	119·1
(27.) „	5	2·292	3·94	753·4	23·1	149·5	„
(28.) Lead	4	2·020	2·00	762·1	15·4	199·9	206·93
(29.) „	5	4·348	4·39	762·6	26·5	250·2	„
(30.) Antimony	5	1·117	1·86	769·6	12·6	136·5	120·30
(31.) „	5	1·526	2·58	742·6	14·3	158·5	„
(32.) „	5	2·257	3·84	754·2	17·2	197·9	„
(33.) „	5	3·289	6·22	755·4	16·5	301·2	„
(34.) Bismuth	5	3·772	3·77	762·1	26·8	214·5	208·1
(35.) „	5	4·636	4·68	763·9	30·5	232·2	„
(36.) Manganese	6	0·3122	1·14	755·0	8·5	55·5	55·0
(37.) Silver	5	1·709	3·22	750·0	22·8	112·4	107·93
(38.) Gold	6	1·541	1·59	760·4	11·3	207·4	197·22
(39.) „	6	2·690	2·80	742·5	19·2	208·1	„

reduced by the number of observations, and cannot be considered so great as 1 mm. It would have been easily possible to calculate the true mean probable error; but the result would have given a fallacious impression of the amount of error. For, as has been previously remarked, there is a source of error impossible to estimate, due to

unequal capillary depression in the open and closed limbs of the U-tube. It must however be held that those measurements in which a large depression was observed are more accurate than measurements of a small depression, inasmuch as the total quantity measured bears a much greater proportion to the sources of error.

The element sodium, present in small proportion to the solvent mercury, has apparently a molecular weight lower than the atomic weight, the number 21.6 being found, whereas the atomic weight is 23. On increasing the proportion of sodium, the apparent molecular weight falls, till with 5.35 atoms per 100 atoms of mercury, the number 15.1 is reached. This behaviour is not observable with potassium, the numbers obtained with 1.55 and 5.26 atoms of metal per 100 atoms of mercury being sensibly identical. The low number cannot be due to the existence of stable alloys of these metals with mercury, for if these were present a higher and not a lower weight would be observable. One possible cause, and that appears an improbable one, is that the presence of sodium tends to produce an association of atoms of mercury so that it would no longer be justifiable to assume the atomic weight of mercury as identical with its molecular weight. It may, on the other hand, be the case that a definite stable alloy of sodium and mercury is formed, with a definite vapour-pressure, and that such a substance acts as a solvent. It is, however, remarkable that lithium, an element closely related to sodium, gave no sign of such irregularity, while alteration of dilution with potassium is apparently without influence on the molecular weight, which nevertheless was found lower than the atomic weight, viz., 29 and 30, instead of 39.

But little weight can be attached to the result with calcium; the difficulty of producing a sufficiently concentrated amalgam hindered any further experimental investigation. Various attempts were made without success. But with both calcium and barium the same peculiarity is seen, viz., molecular weights lower than the atomic weights of these elements. No doubt the cause of this behaviour, whatever it may be, is the same as determines it with sodium; but as a study of the influence of varying amounts did not throw light on the anomaly with sodium, series of experiments with metals much more difficult to manipulate were not executed.

Perhaps the same tendency may account for the results with magnesium; but as the total depression with 0.7 atom present per 100 of mercury amounted to only 7.4 mm., too much weight must not be attached to the number 24.0. With cadmium, again, the numbers obtained are somewhat low; and about these results there can be no doubt; the cadmium was free from zinc, and was redistilled in a vacuum before use.

The metal thallium, of which the atomic weight is approximately 204, again gives low results, varying from 164 to 198; but the tendency is here to rise with increase of metal proportionately to solvent. Still there can be no doubt here as to the molecular weight indicated.

The metals tin, lead, antimony, and bismuth show distinct tendency towards association of atoms. The more concentrated the amalgam the higher the apparent molecular weight. As regards the number 301.2, obtained for antimony, with 6.22 atoms per 100 of mercury, such a high result may well be due to the limit of solubility of antimony in mercury having been reached. The amalgam, on cooling, was filled with crystals of antimony, and there may well have been free antimony in the hot amalgam. This would have the effect of apparently raising the molecular weight; for that portion which did not dissolve in the mercury would still appear on the numerator of the fraction in the equation given on p. 524, and would cause the quotient to be too high. I do not think that this was the case with 3.84 atoms of antimony present per 100 of mercury, for the amalgam on cooling deposited few crystals. And the remark is also inapplicable to the three metals tin, lead, and bismuth, all of which are readily soluble in mercury.

The metals gallium, silver, and gold give numbers sufficiently near their atomic weight to render it probable that the molecule and atom are with them identical.

The only other elements to be considered are manganese, with which the normal number was obtained, and aluminium, which gave invariably high results. Good commercial aluminium was used, which on analysis was found to contain over 99 per cent. of that metal. The result can hardly be attributed to impurity, but must be connected in some way with the metal itself. The numbers 36.7 and 33.1 were found instead of 27. It is possible but not probable that such a high result is due to association of atoms; for very different amounts were used in each case, viz., 1.52 atoms and 2.94 atoms per 100 atoms of mercury.

It is interesting to compare these results with those of two experimenters who have published their results since the preliminary note of this research was read. Messrs. Heycock and Neville made use of the method of freezing in a similar series of observations; their preliminary note is published in the *Proceedings of the Chemical Society*, 1889, No. 65. Employing tin as solvent, they find concordant results for the metals zinc, copper, silver, cadmium, lead, and mercury. The elements antimony and aluminium gave abnormal results. With antimony they obtained a rise, connected possibly with the formation of a compound of antimony and tin, and its serving as

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solvent; and with aluminium the fall was only 1.34° per atom of metal per 100 atoms of solvent instead of about 2.4° . This would imply a high molecular weight for aluminium; in fact, assuming the other metals to have molecular weights identical with their atomic weights, the molecular weight of aluminium should be represented by the formula Al_2 when dissolved in tin.

G. Tamman has also published a memoir in Ostwald's *Zeitschrift für physikalische Chemie*, 1889, 441, in which he gives results similar to those of Messrs. Heycock and Neville. He used mercury as solvent, and with the metals potassium and sodium obtained what he considers normal results; taking as the molecular depression of freezing point of mercury 425, the mean numbers for these metals are 424 and 420. Very dilute solutions were used, varying from 0.048 atom to 0.353 atom per 100 atoms of mercury. With thallium and with zinc, lower numbers were obtained, viz., 365 and 390, while with bismuth the number 570 expresses incipient association. With lead, cadmium, gold, and tin his results, when only small amounts were employed, were also normal; but with larger amounts, either association of atoms or formation of stable alloys occurred, rendering the results inconclusive.

Similar experiments, in which sodium was employed as solvent, gave erratic results—in every case appearance of association of atoms being observed. But Tamman points out that it is improbable that such association can take place, as it would contradict experience. We have, however, no knowledge of molecular weights of metals at low temperatures; which, moreover, are eminently favourable to chemical association of atoms to form molecules. No opinion can be pronounced on Tamman's suggestion in the present state of our knowledge. It is, however, noteworthy that the solvent in this case is a substance which gives curious results as regards its own molecular weight as determined by the boiling point method; and it may be that its molecular aggregation is disturbed by the presence of foreign metals dissolved in it.

So far, then, as conclusions can be drawn from these experiments, it would appear legitimate to infer that in solution, as a rule, the atom of a metal is identical with its molecule, as the physical properties of those metals which have been vaporised would lead us to suppose.