5. On some Vapour Densities at High Temperatures. By Alexander Scott, M.A., D.Sc.

The apparatus used in the following determinations is that of Victor Meyer, modified as described in a paper published in 1879, "On the Vapour Densities of Potassium and Sodium,"* by Professor Dewar and the author. In the experiments here described, the platinum vessel was further protected by a casing of iron, and the intervening space filled with magnesia, the iron casing being embedded in sand enclosed between two crucibles. In Series I. hydrogen was the gas used to fill the apparatus, but in all the others nitrogen prepared from the atmosphere by mixing it with ammonia and drawing the mixture over red-hot copper, then through dilute sulphuric acid into large glass gasholders, from which it was expelled after drying into the vapour-density apparatus. The nitrogen thus prepared almost invariably contains a small quantity of hydrogen, and this is a decided advantage for most of the substances used. The temperature of the furnace (which was an ordinary wind furnace, with 35-feet draught, and fed with coke) was considerably above the melting-point of cast iron, but was barely hot enough to volatilise rapidly potassium iodide and silver chloride, and this gives their results rather high. The best way of weighing the potassium and sodium was found to be to cut rapidly a piece of the required weight as nearly as possible, and instantly wrap it up in a tared piece of thin platinum foil and weigh again. The sodium kept remarkably well thus, but the potassium was not so satisfactory. To check the weights, pieces were similarly weighed and thrown into water, when it was found to require 23·8 to 24·3 milligrams of sodium to give 11·16 c.c. of hydrogen, according as an ordinary Becker's balance, turning with a milligram was used, or a finer one turning with ·1 milligram, the more rapid though coarser one giving thus the best results; of potassium similarly 46·3 milligrams were required.

The weight in milligrams of the substance which would be required to give 22·33 cubic centimetres of vapour is taken as the molecular weight.

* *Proc. Roy. Soc. Lond.*, vol. xxxii., 1879.

This illustration belongs to paper by Dr Alexander Scott, p. 410.

SERIES I.—Apparatus filled with hydrogen, which tended to escape when the substance was introduced, and so give too high a number for the molecular weight; coarser balance used.

Gram.							Molecular weight.
·030	sodium	gave	23·3	c.c.,	at 0° C.	and 760 mm. pressure,	giving 28·7
·035	„	„	23·6	„	„	„	„ 33·1
·037	„	„	30·4	„	„	„	„ 27·1
·033	„	„	27·9	„	„	„	„ 26·4
Mean for sodium,							28·8

SERIES II.—Same arrangement, but the apparatus filled with nitrogen.

Gram.							Molecular weight.
·029	sodium	gave	26·8	c.c.,	at 0° C.	and 760 mm. pressure,	giving 24·1
·032	„	„	29·7	„	„	„	„ 24·0
·034	„	„	31·2	„	„	„	„ 24·3
·030	„	„	27·6	„	„	„	„ 24·3
·032	„	„	30·5	„	„	„	„ 23·4
·029	„	„	25·6	„	„	„	„ 25·3
·024	„	„	22·6	„	„	„	„ 23·7
·026	potassium	„	13·9	„	„	„	„ 41·8
·045	„	„	25·1	„	„	„	„ 40·0
·042	„	„	21·9	„	„	„	„ 42·9
·052	„	„	28·4	„	„	„	„ 40·9
Mean for sodium,							24·2
Mean for potassium,							41·4

SERIES III.—Same arrangement as Series II.

Gram.							Molecular weight.
·042	sodium	gave	36·9	c.c. at 0° C.	and 760 mm. pressure,	giving	25·4
·026	„	„	21·0	„	„	„	„ 27·7
·028	„	„	23·4	„	„	„	„ 26·7
·036	potassium	„	18·2	„	„	„	„ 44·2
Mean for sodium,							26·6

SERIES IV.—Same arrangement as above, but the finer balance was used in the weighings.

Gram.							Molecular weight.
·046	potassium	gave	23·2	c.c. at 0° C.	and 760 mm. pressure,	giving	44·2
·056	„	„	27·4	„	„	„	„ 45·7

SERIES IV.—*continued.*

Gram.							Molecular Weight.
·059	potassium	gave	25·0	c.c. at 0° C. and 760 mm. pressure,	giving	52·8	
·052	„	„	22·8	„ „ „	„	51·0	
·071	„	„	35·2	„ „ „	„	45·1	
·060	„	„	20·6	„ „ „	„	43·8	
·023	sodium	„	19·2	„ „ „	„	26·7	
·032	„	„	25·9	„ „ „	„	27·6	
·035	„	„	28·5	„ „ „	„	27·4	
·029	„	„	22·0	„ „ „	„	29·4	
·033	„	„	24·6	„ „ „	„	30·0	
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·119	pot. iodide	„	14·3	„ „ „	„	185·6	
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Mean for sodium,							28·2
Mean for potassium,							47·1

SERIES V.—Same arrangement of apparatus; fine balance.

Gram.							Molecular weight.
·267	mercury	gave	29·3	c.c. at 0° C., and 760 mm. giving	203·3		
·249	„	„	27·4	„ „ „	„	202·8	
·305	lead chloride	„	25·6	„ „ „	„	265·4	
·293	„	„	25·2	„ „ „	„	260·0	
·319	cadmium bromide	„	29·7	„ „ „	„	240·0	
·340	„	„	{ 31·1 35·3 }	„ „ „	„	{ 244·4 214·8 }	
·340	cadmium iodide	„	31·2	„ „ „	„	243·3	
·411	„	„	35·4	„ „ „	„	259·0	
·162	silver chloride	„	22·4	„ „ „	„	161·5	
·191	potassium iodide	„	22·4	„ „ „	„	190·5	
·203	„	„	24·3	„ „ „	„	186·7	
·277	mercuric sulphide	„	37·2	„ „ „	„	166·6	

The mercury was used to test the apparatus, and indicates that the results obtained are a little too high.

The cadmium bromide seemed to cease giving off gas like the other substances, but if the measuring tube be left in position, an additional quantity of gas is obtained, most probably from further dissociation of the vapour into its elements. The cadmium iodide dissociated very largely as indicated by its low vapour density and by expelling the vapours, when large quantities of free iodine were observed. Silver chloride and potassium iodide volatilised very slowly; the vapour of the latter seemed to be free from every trace of free iodine.

SERIES VI.—Same arrangement of apparatus.

Gram.						Molecular weight.
·227 chromic chloride	gave 29·8 c.c. at 0° C. and 760 mm., giving					170·0
·100 " "	" 14·7 " " " "					152·2
·120 " "	" 18·8 " " " "					142·5
·149 manganous chloride	" 25·0 " " " "					133·0
·142 " "	" 24·1 " " " "					131·6
·164 mercuric chloride	" 25·8 " " " "					142·0
·167 " "	" 22·0 " " " "					169·3
·180 mercuric sulphide	" 25·3 " " " "					158·7
·145 " "	" 20·2 " " " "					160·1
·250 mercurous chloride	" 28·9 " " " "					193·4
·223 " "	" 25·6 " " " "					194·1
·068 sulphur	" 23·2 " " " "					65·8

The results of the chromium chloride are not very concordant, and may be due to traces of water. The sample used was sublimed and raised to a red heat before using; green oxide was observed on the tube for expelling the vapours. Mercuric chloride seems to dissociate largely into its elements, as do the sulphide and mercurous chloride. Sulphur was used to check the apparatus.

SERIES VII.—Same arrangement of apparatus.

Gram.						Molecular weight.
·288 caesium iodide	gave 24·0 c.c. at 0° C. and 760 mm., giving					268·0
·305 " "	" 25·7 " " " "					265·0
·270 " "	" 22·5 " " " "					267·9
·203 rubidium iodide	" 19·3 " " " "					234·6
·199 " "	" 20·1 " " " "					221·5
·202 " "	" 20·3 " " " "					221·8
·185 potassium iodide	" 22·5 " " " "					183·5
·176 " "	" 21·9 " " " "					179·0
·143 " "	" 17·8 " " " "					179·3
·196 caesium chloride	" 23·4 " " " "					187·2
·157 " "	" 19·5 " " " "					179·5
·175 " "	" 21·8 " " " "					178·9
·114 rubidium chloride	" 18·6 " " " "					136·9
·121 " "	" 19·2 " " " "					140·4
·130 " "	" 20·6 " " " "					141·0
·147 silver chloride	" 20·5 " " " "					160·2

The substances in this series were fused before use, so as to be perfectly dry. They were also very pure, their equivalents being determined by titration with silver nitrate.

SERIES VIII.—Same arrangement of apparatus.

Gram.						Molecular weight.
·173	ferric chloride	gave 28·5 c.c., at 0° C. and 760 mm., giving				135·7
·093	„	„ 16·0 „ „ „ „ „				129·6
·120	„	„ 19·3 „ „ „ „ „				138·6
·076	„	„ 12·0 „ „ „ „ „				140·7
·145	iodine	„ 18·7 „ „ „ „ „				173·1
·171	„	„ 20·6 „ „ „ „ „				185·5
·070	sulphur	„ 22·8 „ „ „ „ „				68·5
·055	„	„ 18·0 „ „ „ „ „				68·0

The ferric chloride was sublimed immediately before use, but its extremely hygroscopic nature renders it highly probable that the vapour would contain hydrochloric acid.

The iodine indicates the dissociation of its diatomic molecules, as has already been shown by V. Meyer.

Sulphur again used as a check.

The values obtained for the molecular weights from the above experiments may be thus tabulated :—

	Experimental.	Values. Theoretical.	Molecular formula indicated.
Sodium, . . .	25·5	23	Na
Potassium, . .	37·7	39	K
Mercury, . . .	203	200	Hg
Sulphur, . . .	67·3	64	S ₂
Iodine, . . .	179·3	169	(I ₂ + 2I)
Cæsium iodide, .	267	260	CsI
Cæsium chloride, .	179·2	168·5	CsCl
Rubidium iodide, .	221·6	212·3	RbI
Rubidium chloride, .	139·4	120·8	RbCl
Potassium iodide, .	184·1	164	KI
Silver chloride, .	160·8	143·5	AgCl
Lead chloride, .	262·7	278	PbCl ₂
Manganous chloride, .	132·3	126	MnCl ₂
Ferric chloride, .	136·1	162·5	FeCl ₃
Chromic chloride, .	154·9	159	CrCl ₃
Cadmium bromide, .	242·2	272	CdBr ₂
Cadmium iodide, .	251·1	366	(CdI ₂ + Cd + I + I)
Mercuric sulphide, .	161·8	155	(2Hg + S ₂)
Mercurous chloride, .	193·7	2Hg + Cl ₂ = 157	} Mixtures of Hg + Cl ₂ with some HgCl ₂
Mercuric chloride, .	155·6	Hg + Cl ₂ = 135·5	

The platinum vessel after the first experiment seemed to have no action whatever on the vapours of potassium and sodium, and the tables above given contain the results of *every experiment made*

with the exception of one with sodium, which was the first done in a new platinum vessel. It may be taken then as conclusively proved that the molecules of potassium and sodium are monatomic at high temperatures.

Mercury, sulphur, and iodine were used to test the apparatus and the degree of accuracy to be expected, and gave results quite in accordance with those of other experimenters, as did also mercuric sulphide. Both chlorides of mercury seem to undergo a very large amount of dissociation into their elements, though not to the same extent as the sulphide.

The results for the chlorides and iodides of caesium, rubidium, and potassium point to the ordinarily received formulæ as the correct ones, as is the case with the chlorides of manganese, silver, and lead, which last seems to dissociate to a certain extent.

The bromide and iodide of cadmium also seem to dissociate largely at the temperature employed. Ferric and chromic chlorides give results which seem to point conclusively to the formulæ FeCl_3 and CrCl_3 as the true ones, the chromic chloride giving results very closely corresponding to this, and the ferric chloride considerably lower, which may be due to water absorbed during weighing (which was done as above described for potassium), and this giving a larger volume of hydrochloric acid than the ferric chloride from which it would be produced, gives too low a number for the molecular weight.

Potassium fluoride was tried, but gave no vapour whatever, and phosphorus at once destroyed the vessel.

One experiment with arsenic trioxide gave results pointing to As_4O_6 as its formula, but further experiments are in progress with it and several other bodies, the results of which I hope to be able to communicate shortly.

6. On the Determination of the Plane Curve which forms the Outer Limit of the Positions of a certain Point.
By Dr G. Plarr. Communicated by Professor Tait.