XIV.—*The Oxides of the Elements and the Periodic Law.*

By R. M. DEELEY, F.G.S.

LAST session I had the honour to communicate to the Chemical Society a paper describing "A New Diagram and Periodic Table of the Elements" (Trans., 1893, 63, 852). Since this was written, my attention has been called to a very interesting paper, by Professor K. W. Zenger, of Prague, published in the *Sitzungsberichte könig. Bohm. Ges. Wissenschaft.* (1881, p. 408). In this communication the author points out that the products obtained by multiplying the specific heats by the densities of the elements have values which are very similar for many elements having analogous properties. To show this, he arranges the elements in 11 groups, the first group containing bromine and iodine, and the eleventh manganese, iron, cobalt, and nickel. Of course the result is only partially satisfactory, for we now know that elements belonging to the same classes have volume heats which, on the whole, decrease with increasing atomic weight, and that even series elements must be separated from odd series elements, although their volume heats may be nearly identical.

I now purpose laying before the Society the outcome of some further work undertaken with a view to ascertain to what extent a consideration of the oxides supports or modifies previous conclusions; for although in my previous paper some reliance was placed on the oxide-forming power of the elements, the diagrams were almost wholly based upon other periodic phenomena. Of course it is improbable that any one periodic table can express the whole truth, for elements closely resembling each other in some respects may differ widely in others. Still there does seem to be a fundamental periodic basis, in accordance with which the elements may be classified, but several other derived forms may be drawn to illustrate the periodicity of the several physical or chemical properties.

In my previous paper, certain values (volume heats and volume atoms) were plotted as ordinates upon a diagram, the abscissæ of which were atomic weights. So regular were the curves and lines obtained by joining the summits of the ordinates, that it was possible to make use of the diagram for the purpose of separating the elements into classes and series, and, therefore, for constructing a periodic table based upon direct numerical values.

Lothar Meyer (*Modern Theories of Chemistry*, English Translation, § 63) very clearly pointed out how such a diagram may be inter-

preted. He found that, as a general rule, elements having similar properties occupied similar positions on the several curves, and also that each wave of the diagram constituted a complete period. So useful has this method of interpreting the atomic diagram proved to be, that we may, I think, regard with some confidence the periodic variations of the ordinates with increasing atomic weight as valuable and trustworthy aids in investigations relating to the Periodic Law. Unfortunately our knowledge of the relative densities and specific heats of the elements, and even of their compounds, is by no means complete. In the case of many elements, no determinations have been made, whilst other elements are known to exist in more than one physical condition, and to have two or more specific heats or densities. The fact that there is sometimes more than one value for the same element does not, however, seriously interfere with the symmetry of the volume heat diagram.

The diagram Lothar Meyer had previously drawn had atomic volumes plotted upon it. He also interpreted the curves obtained in accordance with the periodic table drawn up by Mendeléeff. Being, however, led by the volume heat diagram to somewhat modify this table, especially as regards the grouping of the elements of low atomic weight, I have attempted to further elucidate the matter by plotting upon diagrams some other values calculated from the relative densities of the oxides and the atomic weights of the elements.

Although Brauner and Watts (*Ber.*, 14, 48) have already proved that the molecular volumes of the oxides do show periodic variations, there do not appear to be any methods other than such as may be regarded as purely empirical, of diagrammatically illustrating the periodicity of the oxide-forming power of the elements and the periodic changes which the relative densities of the oxides undergo. One such method I have followed in constructing Diagrams 1, 2, and 3, (p. 115) which show some interesting results.

On these diagrams the ordinates = $\frac{\text{Relative densities of oxides}}{\text{Atomic weights of elements}}$

If the combination of the elements with oxygen produced compounds having densities which were the mean of their constituent atoms, ordinates calculated in this manner, and plotted upon a diagram, would give results similar to those of a volume atoms diagram. But the densities of the oxides do not follow such a law, and it is on this account that the ordinates calculated in the above manner are interesting. Still, there is frequently a close agreement between the periodic variations in the densities of the elements and of their most stable oxides.

In my previous paper, (*loc. cit.*, p. 864) the elements were arranged in duplicate in one table, the odd and even series, 1, 2, 3, &c., giving

what may be called the fundamental basis of the Periodic Law, and the duplicates $1a$, $2a$, $3a$, &c., actual or possible departures from it. The fundamental basis is shown in Table I (p. 111), and a special form in Table II (p. 112).

In the third series, there are ten substances, all of which are regarded as elements. If there are really 10 elements in this series, there should also be 10 in the first, fifth, &c.; but rather than adopt this view, I would suggest that either one of the substances in Series 3 is not an element, or if it be an element, its atomic weight is not correctly given. Although Ni and Co have been placed in the same group, it is quite possible that they are both true elements. Omitting the "typical element" fluorine, Mendeléeff, in his table, makes manganese the only member of the left-hand column of his seventh group, spaces being left for the undiscovered elements required to complete the table as far as this group is concerned. It would, therefore, perhaps, be better to regard either manganese or iron as the redundant element.

Diagrams 1, 2, and 3, although they do not furnish any evidence bearing on this particular point, show much the same general features as does the volume heat diagram, and in some respects confirm, or rather give additional support to, the fundamental periodic basis shown in Table I. The vertical scale of Diagram 1 has been made smaller than that of the other two diagrams, so as to admit of the ordinate of hydrogen being plotted upon it. Although I have drawn in curves and lines to render clear the general nature of the variation in the magnitude of the ordinates with increasing atomic weight, it must not be supposed that the variations from these curves or lines are necessarily due to incorrect determinations of the densities, &c. Indeed there seems to be evidence that the lines and curves should have been drawn in duplicate, one set cutting the ordinates of the perissads, and the other those of the artiads. For instance, the perissads boron, nitrogen, aluminium, and phosphorus all stand above the curves, whilst the artiads carbon, silicon, and sulphur fall below.

In Table III (p. 113) are given, A, the elements; B, the atomic weights of the elements; C, the densities of the elements; D, the oxides; E, the densities of the oxides; F, the volume atoms of the elements; and G, the last column, $E \div B$.

Diagram 1 has plotted upon it the values in column G corresponding to those elements having atomic weights less than that of potassium. The ordinate plotted for hydrogen is calculated from the density of ice, whilst for lithium it is calculated from the density of Li_2O , and so on. As on the volume heat diagram, the ordinate for lithium is shorter than that of hydrogen. The small numerals on the

DIAGRAM I

DIAGRAM 2

DIACRAM 3

diagrams give the valencies of the oxides plotted. As a general rule, these are the oxides of which the relative densities are well known. Many non-consecutive oxides, the relative densities of which are known, have been omitted.

In Table I (p. 111), showing the probable fundamental periodic basis, a space occurs for an element having an atomic weight greater than that of hydrogen, and less than that of lithium. Also, owing to the low density of amorphous carbon, and the anomalous properties of the "typical elements," it was suggested in my previous paper that the volume heats of the elements of the first series, for some reason or other, did not occupy positions on a line such as that of Series 3. Sodium and magnesium were also regarded as having departed from their positions on the curve of Series 2. These views receive additional support from the diagram of the oxides, for, omitting hydrogen, the ordinates plotted on Diagram 1 fall on two short lines and two curves, the lines and curves following each other alternately. On the first line, we have Li_2O and BeO , and on the second line, Na_2O and MgO . On the first curve fall Be_2O_3 , CO_2 , and N_2O_5 ; whilst on the second curve there are Al_2O_3 , SiO_2 , P_2O_5 , and SO_3 . The series from lithium to fluorine is, therefore, exactly similar to that from sodium to chlorine, and they should be placed in the same order on the derived Table II, although the fundamental order is as shown on Table I. However, on the derived Table II, which has been reproduced from my previous paper, the typical elements have not been tabulated exactly in this manner, the properties of the pure elements seeming to demand a rather different arrangement. To agree with the diagram of oxides, the following arrangement (p. 110) would be better. Here Li and Be are in Series 1'.

I may here call attention to the fact that the space measured on the atomic scale between hydrogen and potassium is shorter than that between potassium and rubidium, and also than that between rubidium and caesium. No doubt this is in some way connected with the anomalous group properties of the "typical elements." Indeed it might be urged that on this account the elements of the first and second series should not be classed at all with those of the third, fourth, fifth, and sixth. At present our periodic arrangement should not be regarded as more than tentative; but the accumulation of more data will doubtless eventually enable the true significance of what has already been called the Periodic Law to be realised.

Turning now to Diagram 2, on which are plotted the ordinates for the oxides of the elements between chlorine and rubidium, we have, on the first line, K_2O , CaO , Sc_2O_3 , and TiO_2 . But here a change takes place in the value of the ordinates, for V_2O_5 and CrO_3 have considerably shorter ordinates than those of the four preceding oxides.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
2 α	H		F	O	N	C	B	—	—
1'	Li	Be	—	—	—	—	—	—	—
2			Cl	S	P	Si	Al	—	—
1 α	Na	Mg	—	—	—	—	—	—	—
3	K	Ca	Se	Ti	V	Cr	Fe	Mn	Ni Co
Classes.									
									Series.
									—
									—

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TABLE I.

[illegible]

TABLE II.

Classes of oxides.

Series of elements.										
	R_2O_1	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	R_2O_8	R_2O_9	R_2O_{10}
2a	H	—	—	O	N	C	—	B	Be	Li
1a	Na	—	—	—	—	—	—	—	—	—
2	—	—	—	S	P	Si	—	Al	Mg	—
3	K	Ca	Sc	Ti	V	Cr	Fe	Mn	Zn	Ni Co
4	—	—	—	Se	As	Ge	—	Ga	—	Cu
5	Rb	Sr	Y	Zr	Nb	Mo	Ru	Rh	Pd	—
6	—	—	—	Tc	—	—	—	In	—	Ag
7	Cs	Ba	La	Ce	—	—	—	—	—	—
8	—	—	—	—	—	—	—	—	—	—
9	?	?	Yb	?	Ta	W	Os	Ir	Hg	Au
10	—	—	—	—	—	—	—	—	—	—
11	?	?	?	Th	—	U	Pb	—	—	—
	I	II	III	IV	V	VI	VII	VIII	IX	

TABLE III.

A.	B.	C.	D.	E.	F.	G.
Elements.	Atomic weights.	Densities.	Oxides.	Densities.	Volume atoms of elements.	E/B.
Hydrogen.....	1.0	0.62	H ₂ O	0.917	0.6149	0.9170
Lithium.....	7.02	0.59	Li ₂ O	2.102	0.0806	0.2994
Beryllium.....	9.1	1.85	BeO	3.086	0.2029	0.3392
Boron.....	11.0	2.68	B ₂ O ₃	1.79	0.2429	0.1627
Carbon.....	12.0	1.7	CO ₂	1.457	0.1416	0.1214
Nitrogen.....	14.03	—	N ₂ O ₅	1.64	—	0.1168
Sodium.....	23.04	0.985	Na ₂ O	2.805	0.0419	0.1217
Magnesium....	24.3	1.743	MgO	3.64	0.0716	0.1498
Aluminium....	27.01	2.583	Al ₂ O ₃	3.94	0.0955	0.1458
Silicon.....	28.33	2.48	SiO ₂	2.65	0.0875	0.0935
".....	"	"	"	2.22	—	0.0783
Phosphorus....	31.03	2.22	P ₂ O ₅	2.38	0.0714	0.0767
Sulphur.....	32.06	2.07	SO ₃	1.936	0.0645	0.0603
Potassium....	39.14	0.865	K ₂ O	2.656	0.0221	0.0678
Calcium.....	40.08	1.57	CaO	3.25	0.0390	0.0810
Scandium.....	44.1	—	Sc ₂ O ₃	3.8	—	0.0561
Titanium.....	48.13	—	TiO ₂	4.25	—	0.0883
".....	"	—	"	4.56	—	0.0947
Vanadium.....	51.4	5.87	V ₂ O ₅	3.35	0.1141	0.0651
Chromium.....	52.3	7.00	CrO ₃	2.8	0.1168	0.0535
Manganese.....	55.0	7.39	Mn ₂ O ₃	4.75	0.1342	0.0863
Iron.....	56.02	8.00	Fe ₂ O ₃	5.3	0.1424	0.0946
Cobalt.....	58.7	8.9	CoO	5.6	0.1515	0.0954
".....	"	"	Co ₂ O ₃	4.8	—	0.0817
Nickel.....	58.6	9.0	NiO	5.6	0.1534	0.0955
".....	"	"	Ni ₂ O ₃	4.8	—	0.0819
Copper.....	63.4	8.95	Cu ₂ O	6.13	0.1367	0.0966
".....	"	"	"	5.75	—	0.0906
Zinc.....	65.3	7.15	ZnO	5.5	0.1094	0.0842
".....	"	"	"	5.73	—	0.0877
Germanium....	72.3	5.47	GeO ₂	4.7	0.0755	0.0650
Arsenic.....	75.09	4.7	As ₂ O ₅	3.7	0.0624	0.0492
".....	"	"	"	4.2	—	0.0559
Selenium.....	79.0	4.2	SeO ₂	3.954	0.0531	0.0500
Strontium.....	87.5	2.54	SrO	4.51	0.029	0.0515
Yttrium.....	89.0	—	Y ₂ O ₃	5.03	—	0.0565
Zirconium.....	90.0	4.15	ZrO ₂	5.85	0.0461	0.0650
Niobium.....	94.0	7.06	Nb ₂ O ₅	4.46	0.0751	0.0474
Molybdenum..	95.7	8.6	MoO ₃	3.92	0.0897	0.0409
Ruthenium....	101.65	12.26	RuO ₂	7.4	0.1217	0.0728
Silver.....	107.93	10.57	Ag ₂ O	7.52	0.0987	0.0696
".....	"	"	"	8.2	—	0.0759
Cadmium.....	112.1	8.65	CdO	8.11	0.0771	0.0723
Indium.....	113.7	7.42	In ₂ O ₃	7.18	0.0651	0.0631
Tin.....	119.1	7.29	SnO ₂	6.7	0.0611	0.0562
Antimony.....	120.3	6.7	Sb ₂ O ₅	3.78	0.0556	0.0314
".....	"	"	"	6.52	—	0.0541
Tellurium.....	125.0	6.23	TeO ₃	5.1	0.0497	0.0408
Iodine.....	126.85	4.95	I ₂ O ₅	4.25	0.0393	0.0335
".....	"	"	"	5.02	—	0.0395

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TABLE III—*continued.*

A.	B.	C.	D.	E.	F.	G.
Elements.	Atomic weights.	Densities.	Oxides.	Densities.	Volume atoms of elements.	E/B.
Barium.....	137·0	4·0	BaO	4·0	0·0291	0·0291
".....				5·72	—	0·0417
Lanthanum....	138·6	6·163	La ₂ O ₃	5·94	0·0445	0·0428
".....				6·53	—	0·0471
Cerium.....	140·3	6·68	CeO ₂	6·0	0·0476	0·0427
".....				6·93	—	0·0493
Tantalum.....	182·5	10·78	Ta ₂ O ₅	7·35	0·0574	0·0402
".....				8·01	—	0·0438
Tungsten.....	184·0	19·2	WO ₃	7·32	0·1042	0·0397
Mercury.....	200·2	14·19	HgO	11·34	0·0709	0·0566
Lead.....	206·93	11·35	PbO ₂	8·89	0·0542	0·0429
Bismuth.....	208·1	9·76	Bi ₂ O ₃	8·08	0·0469	0·0388
Thorium.....	232·4	11·1	ThO ₂	9·86	0·0476	0·0424
".....				10·2	—	0·0438
Uranium.....	240·0	18·7	UO ₃	5·26	0·0779	0·0219

On Diagram 3, this is repeated, for we have (Rb?), SrO, Y₂O₃, and ZrO₂ on a line, and then a decrease in the values of the ordinates of Nb₂O₅ and MoO₃. Tantalum and tungsten also show a similar change. In all three series the change first shows itself in elements of the fifth class of Table I.

Owing to the high density ascribed to tungsten, the volume heat and volume atom of that element did not agree, on the volume heat diagram, with those of osmium and tantalum. From Table III, it will be seen that the density of the oxide is not abnormal.

Where, on the diagrams, the ordinates are denoted by circles, the ordinates are not consecutive ones, and where halfmoons are given, the values have not been determined.

By placing another element to fill in the gap between hydrogen and lithium, boron becomes the fifth element of the first series; indeed it becomes the analogue of vanadium, niobium, and tantalum. The same decrease in the value of the ordinate then occurs in all four cases (with consecutive oxides) to the fifth element of the odd series, and although the chemical properties, and therefore the class oxides, of the elements of the first series are not in agreement with those of the third, fifth, and ninth, the fact that this change of density is common to all the series appears to give considerable support to the fundamental periodic basis indicated in Table I.

Of course this classification somewhat alters the basis upon which Mendeléeff predicted some new elements, for he makes scandium

ekaboron, because it forms an oxide, Sc_2O_3 , and because it occurs in the same group as boron in his table. Fundamentally scandium is probably ekalithium, and vanadium probably ekaboron. Similarly copper is ekasodium, and zinc is ekamagnesium.

In column F, Table III, I have given the volume atoms, so that they may be compared with the values in Column G. In the even series, there is, on the whole, a fairly concurrent change in the two values.