

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON.]

THE PLACE OF MANGANESE IN THE PERIODIC SYSTEM.

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Received April 22, 1918.

It is customary, following Mendeléeff, to assume that manganese has a normal valence of 7 and hence belongs in the seventh group of the periodic system. If the classical or Mendeléeff tabulation of the periodic system is accepted this makes manganese the only member of Section B of the seventh group and places it in close relation with chlorine and bromine which precede and follow it in Section A of the same group.

The reasons that are usually given¹ for this position for manganese can be summed up as follows:

(1) **Arguments from the Periodic Law.**—In the periodic system as ordinarily arranged most of the groups can be divided into 2 sub-groups, the A and B series as they are usually called. If manganese and the unknown elements with the atom numbers 43 and 75 are removed from the seventh group and placed in the eighth group with iron, cobalt and nickel, and with the palladium and platinum metals, respectively, Moseley's law requires that the entire B series of the seventh group be abolished. Otherwise there would be too many vacant places in the table, but for reasons of symmetry it does not seem that the B section of this group could be fictitious. This argument, however, loses its force when it is noted that the zero group is also lacking its B section. The table is hence really more symmetrical, omitting the B section of the seventh group than with it, especially when the eighth group which lacks its A section is used as a link between the incomplete zero and seventh groups.

A second reason, under this head, against placing manganese with iron is that this shift would disturb the pretty but apparently meaningless triads of this group, but this reason disappears when it is noted that it will replace this triadic arrangement by an equally pretty and apparently more significant tetradic arrangement, for, of course, placing manganese with iron carries with it the placing of eka-manganese (Moseley's element 43) with ruthenium and diva-manganese (Moseley's element 75) with osmium. The advantages from the standpoint of the periodic table of placing manganese in the eighth group can be most succinctly pointed out by giving in Table I the periodic arrangement as modified by the proposed changes.

This table is not essentially different from the ordinary Mendeléeff arrangement given in Table II. Consider the Mendeléeff table as wound around a cylinder so as to bring fluorine and neon into juxtaposition and then cut this cylindrical strip between boron and carbon and one has the

¹ Mendeléeff, *Principles of Chemistry*, Eng. Ed., London, II, 1905, p. 329; Miolati, Abegg's *Handbuch* (Leipzig), IV, 2, 629 (1913).

earths into a hypothetical and very doubtful two rows between the rows of caesium and gold (vacant spaces that according to Moseley's rule cannot exist), (c) that they place Mn, Pr, Nd, Sa, Eu, Gd, Dy, Er, Tm₁, Tm₂ with their natural neighbors and not, respectively, with Cl, V, Cr, Fe, Co, Ni, Pr, Nd, Cs and Ba, (d) that Ni and Cu, Pd and Ag, Pt and Au are brought into their natural juxtaposition, and (e) that the triads are replaced by tetrads and a group of 16 which accords better with the preference of the periodic system for powers of two.

The open and spacial arrangements of the periodic systems¹ are not in question here, as arguments for the natural valence of manganese can hardly be based on them.

(2) **Arguments Based on Isomorphism.**—The second group of arguments for placing manganese in the seventh group is based on the fact that the crystals of KMnO₄ and KClO₄ are isomorphous. From this fact it is argued that the normal valence of manganese must be 7. Now from the modern point of view concerning crystal structure, the point of view which takes X-ray analysis as its starting point, the general argument of isomorphism² has lost much of its weight. Crystal structure seems to depend far more on the number and arrangement of different kinds of atoms in the compound than on the valence forces. In any event the most that can be proven about valence by the argument based on the isomorphism of 2 crystals is that the valence³ of an element in one of the crystals is the same as that of an analogous element in the other. Thus from the isomorphism of KMnO₄ crystals with those of KClO₄ it is legitimate to argue that manganese has a valence of +7 in that crystal, but it is not legitimate to argue from that fact that manganese belongs to the seventh group of the periodic system. If one could prove such a deduction by means of this sort of an argument, then since K₂MnO₄ is isomorphous with K₂SO₄,⁴ since Mn⁺⁺⁺ alum is completely isomorphous with Al⁺⁺⁺, Ti⁺⁺⁺, V⁺⁺⁺, Cr⁺⁺⁺, and Fe⁺⁺⁺ alums,⁵ and since MnCl₂ is completely isomorphous

¹ Staigmüller, *Z. phys. Chem.*, **39**, 243 (1902); Werner, *Ber. Chem. Ges.*, **38**, 914 (1905); Adams, *THIS JOURNAL*, **33**, 684 (1911); Soddy, "The Chemistry of the Radio Elements," London, II, **1914**, p. 11; Harkins and Hall, *THIS JOURNAL*, **38**, 169 (1916).

² The word isomorphism seems to have no very precise meaning. We shall use it in the ordinary sense meaning "the state of having closely similar crystallographic properties." By complete isomorphism we shall mean isomorphism where the substances, besides having similar crystallographic property, form a series of mixed crystals.

³ When we speak of the valence of an element in a crystal state we mean the state of oxidation of the element in that state. We mean the number of gram atoms of electricity (the number of faradays) necessary to reduce enough of the crystal to give one gram atom of that element in the elementary state.

⁴ Miolati, Abegg's *Handbuch*, IV, 2, 629 (1913).

⁵ Arzruni, "Relation between Crystalline Form and Chemical Composition," Braunschweig, **1903**.

with CaCl_2 ,¹ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, one could prove with equal propriety that manganese belongs to the first, second, third, fourth, fifth, sixth and eighth groups.

(3) **Arguments Based on Chemical Properties.**—The third type of arguments used to show that manganese belongs in the seventh group is based on the fact that the highest known oxide of manganese is Mn_2O_7 , and on certain similarities of the chemical properties of the perchlorates, perchloric acid, perchloric anhydride and chlorine dioxide with the permanganates, permanganic acid, manganese heptoxide and manganese dioxide. Now it is true as a general rule that the valence of the highest known oxide corresponds to the element's position in the periodic table, but the first row of the eighth group is just where this rule fails most conspicuously. Thus the highest known valence of iron is 6, of cobalt 4 (?), and of nickel 3, and therefore it is unsafe to argue from this rule in regard to the position of manganese. It is also true that there is a certain similarity between the compounds cited, as all of them are unstable oxidizing agents, and the acids and oxides have certain physical resemblances,² but here the resemblance between chlorine and manganese stops. All other compounds are about as different as possible. Try to compare, for example, AlCl_3 with AlMn_3 , or CCl_4 with Mn_3C or ClI with MnI_2 . Even the resemblance of permanganates to perchlorates is not close. Permanganates are unstable in alkali, and are reduced by I_2 , Fe^{++} , SO_2 and even by H_2O_2 ; perchlorates are stable in alkali and are not reduced by these reagents—indeed in dilute solutions it is difficult to reduce the perchlorate ion under any circumstances. But it is unnecessary to carry this rebuttal further, for if one could argue from the pseudo-similarities of MnO_4^- and ClO_4^- one could, with equal propriety, argue from the exactly analogous relations between ClO_3^- and VO_3^- ion that vanadium belongs in the seventh group. As a matter of fact the chemical differences between the A and B series of any group are likely to be so marked that one cannot safely base the position of any element in the periodic system on such minor (and largely formal) similarities as do exist.

Arguments for Placing Manganese in the Eighth Group.—It is possible, however, to get reasonably definite information concerning the place of manganese in the periodic table from the chemical resemblances, not between A and B series of the same group but between the various members of the row Ti, V, Cr, Mn, Fe, Co, Ni. These elements all belong to the B series of their respective groups and form a row of elements which

¹ Miolati, *Op. cit.*, p. 697. KMnO_4 is itself isomorphous with a substance as chemically different from it as BaSO_4 .

² The similarity of density and hardness or crystalline KClO_4 with crystalline KMnO_4 cited by Mendeléeff does not concern us here as these properties are dependent mostly on crystal structure and so have been disposed of already.

are quite analogous. It is therefore possible by comparing the gradation of the properties in the row Ti, V, Cr, with that in the row Fe, Co, Ni to see whether Mn is the last member of the row Ti, V, Cr, Mn or the first member of the row Mn, Fe, Co, Ni.

Now as a matter of fact many of the properties of analogous compounds of these elements form a continuously graded series with no break in the properties either before or after manganese. Such properties are the stability of the oxides, the magnetic properties of the divalent salts and many others. These properties naturally cannot be used to determine the place of manganese in the periodic table. On the other hand, there are many cases where there is a distinct break in the series of properties either before or after manganese which make its affinities fairly certain.

The first of these broken sets of properties are the physical properties of the element such as melting point. Titanium melts above 2000° K., vanadium at 1990° K., chromium at 1788° K., manganese at 1533° K., while iron, cobalt and nickel melt, respectively, at 1793° , 1763° and 1725° K. The compressibilities and atomic volumes¹ of the elements form similar series. This certainly looks as if manganese belongs to the Ti, Cr, V row rather than to the Fe, Co, Ni row. However, there is no obvious relation between the valence properties of the atom and these physical properties of the free element. And, moreover, the position of manganese as so determined contradicts the much more cogent direct chemical evidence.

Chemical Evidence.—(1) As one proceeds along any row in the periodic system from the first to seventh group the stability of compounds in which oxygen is attached to the metallic element to form a stable salt-forming group of the chromyl or uranyl type, rapidly increases. Thus no scandyl salts are known. $TiOCl_2$ seems to be the only titanyl salt described. Vanadyl salts are known but are very unstable, while chromyl salts have comparatively high stability. We should therefore expect that if manganese belongs to the B series of the seventh group it would form very stable manganyl salts, but as a matter of fact as with all elements of the eighth group, salts of this type are unknown.

(2) The barium salts of meta- or orthotitanic, meta- or orthovanadic, and the corresponding chromic acids are all slightly soluble. Barium permanganate is very soluble.²

(3) Unstable per-acids (acids in which the element has an apparent valence higher than its group in the periodic system) are known for titanium, vanadium and chromium.³ We would therefore expect that man-

¹ But compare Heydweiller, *Ann. Physik*, **42**, 1273 (1913).

² Comey, *Dictionary of Solubility*, London, 1896.

³ Gmelin Kraut, *Handbuch*, Heidelberg, III, **1**, 375, 435 (1912); III, **2**, 92, 1086 (1908).

ganese, if it belonged to the seventh group, would form an acid with an apparent valence higher than manganese in the so-called permanganates, but no such acid is known.

(4) *m*-Titanates, *m*-vanadates and chromates are stable in alkaline solution and are unstable in the presence of acid. Permanganates are more stable in acid than alkali. Their oxidizing power is also widely different.

(5) Ti^{++} , V^{++} , Cr^{++} are all powerful reducing agents, Cr^{++} being one of the most powerful known, Mn^{++} , Fe^{++} , Co^{++} , Ni^{++} are either very mild reducing agents as Mn^{++} or Fe^{++} , or have almost no reducing power as Co^{++} or Ni^{++} .¹

(6) $MnCl_2$ and $MnBr_2$ and their hydrates are completely isomorphous with the corresponding Fe, Co, and Ni compounds and are not isomorphous with $CrCl_2$ (apparently nothing is known about the crystal form of $TiCl_2$ and VCl_2). Here the argument from isomorphism is used in its only valid form to show lack of chemical relation between structurally analogous substances.²

(7) $MnCl_2$ forms the same hydrates, as for instance, $CoCl_2$, namely, the bi-, tetra-, hexa-hydrates. The tetra-hydrates of both are known in two forms, α and β . All are completely isomorphous.³ In fact, resemblances of crystal form between all analogous manganous and ferrous, cobaltous, and nickalous compounds are very close; no such close crystal resemblances exist between manganous and Ti^{++} , V^{++} and Cr^{++} salts.

(8) TiS , VS and CrS cannot be made in a wet way from hydrogen sulfide; MnS , FeS , CoS , NiS are all precipitated from the neutral dilute solution of their respective ions by hydrogen sulfide, are all insoluble in water and soluble in strong acid.

(9) $TiCO_3$, VCO_3 , $CrCO_3$ are not known. $MnCO_3$, $FeCO_3$, $CoCO_3$, $NiCO_3$ are fairly stable. Siderite (natural $FeCO_3$) and rhodocrosite (natural $MnCO_3$) usually occur as solid solutions of $MnCO_3$ in $FeCO_3$, or *vice versa*. Similar arguments can be urged from the relations between other insoluble salts, from tendency to complex salt formations, etc.

(10) Trivalent manganese salts, like ferric, cobaltic, and nickelic salts, are oxidizing agents, manganic salts being powerful ones (manganic salts like ferric salts are probably mostly double complexes). Cr^{+++} , V^{+++} , Ti^{+++} are reducing agents. The existence of manganates and permanganates would be expected from the rapidly increasing stability of the upper valence states, as one goes from *higher* to *lower* atom number in any row of the eighth group. Nickelic salts are almost unknown, cobaltic salts are fairly stable, ferric salts are stable, and ferrates (analogous to the manganates) are known. The fact that in any row of the eighth

¹ Gmelin Kraut, *Handbuch*.

² Miolati, Abegg's *Handbuch*, II, 2, p. 698.

³ Startenbeker, *Z. physik. Chem.*, 16, 250 (1895).

group the high valence oxides of elements of lower atom number are more stable than corresponding ones of higher atom number is clearly brought out in the ruthenium and osmium rows. OsO_4 and RuO_4 are the only octavalent oxides known, while even the lower oxides of platinum and palladium are very unstable. Potassium perruthenate KRuO_4 is closely analogous to potassium permanganate, though not isomorphous.

(11) Another very striking argument for placing manganese in the eighth group can be found in the fact that alloys of manganese with iron, cobalt and nickel show no tendency to compound formation, while manganese forms compounds stable at the melting point with almost all the metals of lower groups including chromium, vanadium, and silicon.¹ Apparently the alloys of manganese with titanium have not been studied.

(12) The manganese compounds with the metalloids such as carbon and silicon are analogous to those of iron and not to those of chromium.

(13) The atom colors of the various valences of manganese show that the normal valence of manganese must be even, not odd, as the position in the seventh group would require.²

Summary.

(1) The older arguments placing manganese in the seventh group of the periodic system (*i. e.*, giving manganese a normal valence of 7) now appear open to question.

(2) On the other hand there are 12 different lines of argument based on purely chemical relationships which indicate its position in the eighth group.

(3) This conclusion is also in accord with the more decisive reasoning based on atom color.

(4) An improved form of the Periodic Table showing the relations of the eighth and rare earth groups to the rest of the periodic system is presented.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONSTITUTION OF DICYANODIAMIDE.³

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Received February 23, 1918.

Upon the evaporation of an aqueous solution of cyanamide, Beilstein and Geuther⁴ obtained a colorless product which they supposed to be a

¹ Guertler, *Metallographie* (Berlin), I, see index (1912).

² Bichowsky, *THIS JOURNAL*, 40, 500 (1918).

³ The work described in this article forms part of a thesis submitted by Frank C. Vibrans in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

⁴ *Ann.*, 108, 99 (1858); 123, 241 (1862).