ON

THE TRUE FORMULA

FOR

PERMANGANATES.

DISSERTATION

PRESENTED TO THE FACULTY OF THE UNIVERSITY
OF VIRGINIA.

In application for the Degree of Doctor of Philosophy.

BY

CHARLES M. BRADBURY,
OF VIRGINIA.

THESIS:—*Permanganic acid is monobasic, and the permanganates are represented by the general formula* $\overset{n}{R}(MnO_4)_n$.

To

His Father,

John W. Bradbury, Esq.

This Paper is Inscribed

IN TOKEN OF AFFECTION,

BY

The Author.

Preface.

The greater part of the following paper was written nearly a year ago. As it was nearing completion, I found, from an allusion in an article by M. Raoult, of Paris, (see *Bulletin de Soc. Chim. de Paris,* XLVI, p. 805), that my conclusion as to the true formula for permanganates had been reached already by that eminent chemist, by means of a new method, originated by himself, for determining molecular weights. Upon examining M. Raoult's original paper in the *Ann. de Chim. et de Phys.*, (6), VIII, July, 1886, p. 330, however, it was found that nothing was given concerning permanganates, beyond the simple statement that they were shown by the method to be monobasic.

Dr. Victor Meyer and Dr. Auwers, of Göttingen, have recently extended and simplified the method of M. Raoult, (see *Berichte der Deuts. Chem. Gesells.*, for February 27 and March 12, 1888), and I am therefore enabled to add materially to the evidence already collected in the dissertation, by a convincing application of this method. Had the detailed results of M. Raoult's investigation of the permanganates been accessible, they would, of course, have been made use of in the dissertation as first written. In the absence of this information, it has been necessary for me to do what would in any case have been more satisfactory—that is, to apply the method for myself.

The results of this work may be found on p. 28, sq.

I am unwilling to lose this opportunity of acknowledging the deep obligation under which my honored teacher, Dr. Mallet, has placed me, not only by his helpful supervision of my work, but by numberless acts of kindness and good will. To my friend and former teacher, Professor Dunnington, also, I return hearty thanks for his unfailing kindness during our three years' intercourse in the laboratory, and especially for valuable aid in my post-graduate work.

University of Virginia, *June, 1888.*

ON THE TRUE FORMULA FOR PERMANGANATES.

INTRODUCTORY NOTE.

The material obtained by fusing alkali and peroxide of manganese together, which was investigated by Scheele about 1740, and named by him "mineral chameleon," had, as is well known, been observed nearly a hundred years before by Glauber. Up to the early part of the present century, however, but little was known as to its chemical constitution. In 1817 Chevillot and Edwards examined this subject with considerable care[1], and concluded that mineral chameleon contained a peculiar acid of manganese, but they did not assign to this supposed acid any formula, nor did they recognize the fact (afterwards ascertained by Forchammer) that they were dealing with two acids of manganese instead of one. The first reliable quantitative analyses of these acids were made in 1832 by Mitscherlich[2], who assigned to them the respective formulas that (if we translate from the old to the new chemistry) have been nearly always accepted until very recently. His conclusions have not, however, been unchallenged. Schönbein, in 1848, endeavored to show that permanganates are properly compounds of manganese dioxide with a tetroxide of the base[3]; and in 1859 Phipson denied the existence of permanganic acid, while allowing that of manganic[4].

Chemical literature from 1832 to 1835 inclusive, contains many discussions on the permanganates; they are again frequently noticed from 1851 to 1856; and from 1859, when their usefulness as disinfectants was pointed out, they have continued to attract attention and to increase in variety of application.

---

[1] Ann. de Chim. et de Phys., (2) IV, 287; also VIII, 237.

[2] Ann. der Chem. und Pharm., II, 10.

[3] L. Gmelin, *Handbook of Chemistry*, tr. by H. Watts, IV, 213.

[4] *Comptes Rendus*, L, 694.

Since the establishment of the new system of chemical nomenclature, and until quite recently, permanganic acid has been almost universally regarded as dibasic, so that the permanganates have been represented as $\overset{I}{R}_2Mn_2O_8$ or $\overset{II}{R}Mn_2O_8$. Some of the newest treatises[5] have, however, substituted for this expression one indicating just half its molecular weight, i. e., $\overset{I}{R}MnO_4$ or $\overset{II}{R}(MnO_4)_2$, without giving any reason for so doing. It was to determine, if possible, whether this change was justified by the facts in the case, that the present inquiry was undertaken.

Is Permanganic Acid Dibasic?

In searching for the correct answer to this question, it will be well to examine in the first place the facts that seem to favor the affirmative.

Let us take, for the sake of convenience, potassium permanganate as a type of the entire class. Then, so far as the manner of writing the formula is concerned, it may be remarked that under the old system of atomic weights no simpler formula than the one we now write, $K_2\ Mn_2\ O_8$, was possible; for K_2O was KO, and permanganate of potash was $KOMn_2O_7$[6], or, according to Berzelius, $KOMnO_7$. But inasmuch as the adoption of the new system has resulted in halving the formulas of many compounds, e. g. nitric acid, which before were in a precisely similar condition, this fact, taken alone, has no greater weight than attaches to the mere priority of the dibasic formula; which is scarcely worthy of mention.

In the second place, however, there is what seems to be a very good reason indeed for retaining the formula $K_2Mn_2O_8$, namely, that manganese undoubtedly deports itself in many

---

[5] See, for example, Richter's *Inorganic Chemistry*, (Dr. E. F. Smith's trans.) 1883; *Principles of Chemistry*, M. M. Pattison Muir, 1884; *Treatise on Chemistry*, Roscoe and Schorlemmer, 1886.

[6] See, for instance, analysis by Machuca, (*Comp. Rend.*, LI, 140).

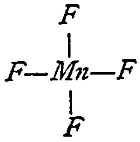
cases as an artiad(7 element and hence to write potassium permanganate $K\ Mn\ O_4$ is to violate Gerhardt's law of even numbers. Without giving to this law greater credence than is proper, the fact that it holds in most cases is hardly deniable. Unless good reasons can be shown for disregarding it, it should be observed in this instance.

A few examples of the even valence of manganese will help to show the weight of the evidence in favor of the formula $K_2Mn_2O_8$:—

The manganous and manganic chlorides both display this even valence; so do the fluorides,

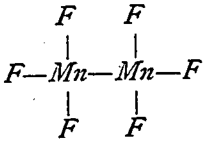
(1) $F—Mn—F$

(2)



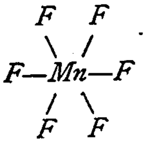
$$\begin{array}{c} F \\ | \\ F—Mn—F \\ | \\ F \end{array}$$

(3)



$$\begin{array}{ccc} & F & F \\ & | & | \\ F— & Mn— & Mn—F \\ & | & | \\ & F & F \end{array}$$

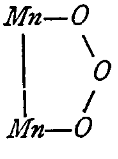
(4)



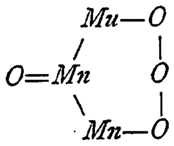
The oxides best known are MnO, Mn_2O_3, Mn_3O_4 and MnO_2, which may be written, respectively,

(1) $Mn=O$

(2)



(3)



(4) $O=Mn=O$

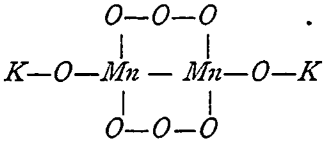
According to the law that quantivalence always varies, if

---

7) With regard to the whole subject of quantivalence I have endeavored to follow what seem to be the prevailing ideas, as exemplified in Odling's article, "Metals, atomic weights and classification of," in Watts' Dictionary.

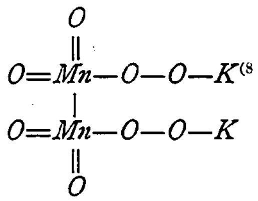
at all, by *pairs* of equivalents, such evidence as the above would seem to prove conclusively that manganese is artiad in all of its compounds.

It is evident that by retaining the molecular formula $K_2Mn_2O_8$, not only is Gerhardt's law satisfied, but it becomes easy enough to write structural formulas of probable correctness. For example, supposing manganese to be tetravalent,



$$\begin{array}{ccccccc} & & O & -O- & O & & \\ & & | & & | & & \\ K & -O- & Mn & - & Mn & -O- & K \\ & & | & & | & & \\ & & O & -O- & O & & \end{array}$$

or, as is more usual, making it hexvalent,



$$\begin{array}{ccl} & O & \\ & \| & \\ O= & Mn & -O-O-K\,[8] \\ & | & \\ O= & Mn & -O-O-K \\ & \| & \\ & O & \end{array}$$

So far as I have been able to discover, the facts just stated—namely, the even valence of manganese, taken in connection with Gerhardt's law, and the impossibility, in view of this even valence, of writing a graphic formula corresponding $KMnO_4$—have determined the retention of the molecular formula $K_2Mn_2O_8$ so long after other apparently double formulas have been simplified. It is clear that with the nitrates, chlorates, perchlorates, etc., neither of the reasons exists for retaining the double formula that seem to make that course necessary with the permanganates; for the nitrogen and chlorine of these salts, and the elements that bear similar relations to others whose molecular weights have been divided by two since the introduction of the new system, are perissad.

If, then, the dibasic formula corresponds so well with

---

[8] From Watts' Dict., 1st Supp., 236.

known facts, why should it be called into question, much less rejected? A general answer to this may be found without much difficulty. Stated briefly, it may be divided into two propositions: First, there has been up to the present time *no positive evidence* of dibasicity in permanganic acid, in the shape of acid or double salts. Second, there are theoretical considerations, partly of recent development, that permit and indeed require the use of the monobasic formula. In other words, at least one of the two laws that indicate so positively the correctness of the old formula must, in the light of later research, be accepted in a modified sense only.

With regard to the first proposition, it is clear that it could hardly be true of a really dibasic acid as well known as permanganic. That in all the experimental study of the permanganates that has been made in the past(9, this particular question could, by an accidental coincidence, have been entirely overlooked, is highly improbable. In fact, there is one acid permanganate—that of barium—spoken of in one of the older treatises(10, but, as will be shown, this fact increases the improbability just alluded to. If even this one acid permanganate could be proved to exist, further discussion as to the basicity of the acid would be unreasonable; but the whole account of it is indefinite, improbable, and contradictory, and recent works do not speak of it at all.

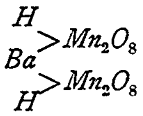
It appears that according to some observers, if aqueous permanganic acid (obtained by treating a solution of barium permanganate with sulphuric acid) be evaporated at a gentle heat till quite concentrated, it deposits, on cooling, "dark carmine-red needles which yield 8.411 per cent. of water." This is certainly singular, to say the least, when compared with the admitted fact that a similar solution evaporated over oil of vitriol merely deposits hydrated peroxide of manganese. But without denying that such crystals have been obtained, the

9) See, for instance, an account by Gorgeu [*Comptes Rendus*, L, 610] of a "manganate and permanganate," (?) $Mn_2O_7K_2O.2MnO_3K_2O$.

10) Gmelin's *Handbook*, IV, 210.

question as to what they were is an open one, for Fromherz regarded them, not as acid barium permanganate, but as crystallized permanganic acid. Mitscherlich and Wöhler are said to have inclined to the opinion that they were acid barium permanganate. It does not appear, however, from the account given, that any analysis of the crystals had been made, and it is difficult to see how, after enough sulphuric acid had been added to precipitate all the barium, and the solution decanted, enough barium could still remain in solution to form an essential constituent of "dark carmine-red needles" or of anything else at all noticeable.

Besides this, the percentage of water given is about three times as much as acid barium permanganate would contain. For, assuming that the acid is dibasic and acid barium permanganate possible, it must be



$$\begin{array}{l} H \\ \quad > Mn_2O_8 \\ Ba \\ \quad > Mn_2O_8 \\ H \end{array}$$

or $H_2Ba\,(Mn_2O_8)_2$, the molecular weight of which is 615. It could yield only one molecule of water, and $\frac{18}{615} = 0.029$. That the excess could be water of crystallization is unlikely, whether the substance be compared with other acid salts or with other permanganates; nor is any allusion made to the excess, nor any explanation offered. Finally, attempts to make this "acid barium permanganate" met with no success. Of this more will be said in another place

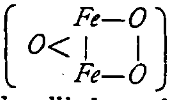
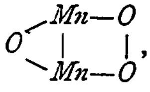
The assertion that the dibasic formula has not been supported by *experimental* evidence is, then, justifiable. It will now be shown that the *theoretical* defenses of this formula must give way to known facts.

It will suffice for my present purpose to speak of the statement that is the very keystone of the supports of the double formula; namely, that manganese is an artiad element. The evidence in favor of this conclusion is too strong to be set aside without exceedingly good reasons. There is no doubt that, in general, this element has an even number of atomicities.

If, however, it can be proven that there are exceptions to the rule—that the statement in question, while generally true, is not rigidly so—the *possibility* of the monobasic formula for permanganates will be established.

As a matter of fact, while manganese is most frequently of even valence, it can nevertheless exist in a state that (unless the meaning of "valence" be modified, as some have proposed) can only be described as one of uneven or perissad valence. There is ample evidence to prove that the law that quantivalence always varies by twos, while it very generally holds good, does not always do so. The fact that mercury appears to be both monad and dyad is well known; nitrogen also is frequently recognized as peris-artiad. That tungsten does not conform to the law, is evident from the list of chlorides of that metal,

$$WCl_2,\ WCl_4,\ WCl_5,\ WCl_6.$$

The same is true of vanadium, which forms the series of chlorides VCl_2, VCl_3, VCl_4, and the oxides V_2O, V_2O_2, V_2O_3, V_2O_4, V_2O_5.(11 According to Odling,(12 iron, which is dyad in ferrous oxide ($Fe = O$), is triad in the ferric oxide  and similar differences exist in the salts of the allied metals nickel, copper, cobalt and manganese. This would make the graphic formula for Mn_2O_3, , instead of that given on page 7. Without accepting even Odling's views with regard to the iron metals (including manganese) as decisive, no reasonable doubt remains that either there are genuine exceptions to the law under discussion, or the meaning of "valence" must be restricted so as to exclude some of the

---

[11] Roscoe and Schorlemmer, *Treatise*, II, ii, 293, 283.

[12] Watts' *Dict.*, III, 595 sq.

phenomena usually designated by that word. In the present instance it can make no difference which alternative is chosen; it will be sufficient to show that manganese is as much an exception to the law as any other element.

As evidence to this effect, it is fair to mention the fact that some eminent authorities, as Odling, have come to this conclusion by observing the analogy (1) between aluminic and ferric and (2) between ferric and manganic oxides.

Again, although the supposed heptachloride of manganese of Dumas turned out to be an oxychloride, the formula MnO_2Cl_2, assigned to it by H. Rose,(13 in which the manganese is perhaps most naturally regarded as hexad, had been changed by Roscoe(14 to MnO_3Cl, and no structural formula can be written corresponding to this, without making the manganese heptad, or at least a perissad of some sort.(15

These reasons for regarding manganese as peris-artiad may not be conclusive, but are worthy of attention. Strong and direct evidence may be obtained, however, by a consideration of the *periodic relations* of the element.

The Periodic System of the elements has been brought to a stage of development which places it, at least as to its main facts, in the realm of accepted truth; and it may be appealed to for the decision of many doubtful questions with great confidence in the answers given by it. Now the atomic weight of manganese is well established; and according to the Periodic Law, i. e., that the chemical properties of the elements are a periodic function of their atomic weights, manganese is forced, by virtue of its atomic weight, into the group of *heptad elements*, at the same time preserving its close relationship with the metals of the iron group. This may be seen by reference to a scheme or table of the periodic system.(16 Even

---

13) Watts' *Dict.*, 1st Supp., 246.

14) R. and S. *Treatise*, II, ii, 22.

15) According to Lossen's system (Muir's *Principles of Chemistry*), this statement does not hold good; but according to most authorities it does.

16) See page 14.

this bare fact would be conclusive, unless manganese could be shown to be an exception to the periodic law. Moreover, the relationship of manganese to the halogens may be received as not by any means incredible; for the behavior of the elements in general, when viewed in the light of this system, indicates that under the influence of varying valence elements which are commonly far from alike may develop strong similarity. We may take, as examples of this variation in character of the same element, the marked differences between the *ous* and the *ic* compounds of iron, chromium, copper and other metals, and between the acid and basic oxides; and the evident tendency of the metals, in their higher oxides, to assume functions identical with those of acidic elements.

THE PERIODIC SYSTEM.

The following table is from Richter's *Inorganic Chemistry*, except that the atomic weight of titanium (48) has been supplied from Roscoe and Schorlemmer's *Treatise*.

		I Group.	II Group.	III Group.	IV Group.	V Group.	VI Group.	VII Group.	VIII Group.		
H Compounds. Highest salt-forming oxides.		------- M_2O	------- MO	------- M_2O_3	MH_4 MO_2	MH_3 M_2O_5	MH_2 MO_3	MH M_2O_7	MO_3	MO_2	M_2H MO
Periods. 1st.	Series. 1st	H 1 Li 7	Be 9	B 11	C 12	N 14	O 16	Fl 19			
2d	2d	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35			
3d	3d	K 39	Ca 40	Sc 45	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 58	Ni 58
	4th	Cu 63	Zn 65	Ga 70	---- 73	As 75	Se 79	Br 80			
4th	5th	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	---- 100	Ru 104	Rh 104	Pd 106
	6th	Ag 108	Cd 112	In 113	Sn 118	Sb 122	Te 126	I 127			
5th	7th	Cs 132	Ba 137	La 139	Ce 140 Di 144	-------	-------	-------	-----	-----	-----
	8th	-------	-------	-------	-------	-------	-------	-------			
	9th	-------	-------	Yb 173	-------	Ta 182	W 184	-------	Os 193	Ir 193	Pt 196
	10th	Au 197	Hg 200	Tl 204	Pb 206	Bi 210	-------	-------			
		-------	-------	-------	Th 234	-------	M 240	-------			

An obvious objection to the verdict of the periodic system is, that it seems to leave no room for the perfectly well-established dyad, tetrad, and hexad valence of manganese in many of its compounds, but declares it simply heptad. As to this, similar objections hold with many elements. The answer for all is found either in Prof. Muir's definition of valence(17: "The valency of an elementary atom is a number which tells the *maximum number* of monovalent atoms, (i. e. atoms of H, F, Cl, Br, I, or Tl), with which the given element combines to form a molecule;" or, perhaps better, in the distinction made by Prof. Richter(18 between hydrogen valence and halogen or oxygen valence; or, finally, what amounts to the same thing, in the difference between true valence and the "index of affinity,"(19 deduced from consideration of the highest oxides. The first of these explanations is simple and, I believe, applicable in every case, but it seems likely that the others must also be reckoned with, in interpreting the indications of the periodic system. However this may be, it is clear that we may either limit the meaning of "valence," as Muir does, in which case no room remains for any law whatever about variable valences; or we may use Richter's or Meyer's distinction between "hydrogen" or "real valence," subject to the law of variation by twos only, and "oxygen or halogen valence" or "index of affinity." In either case, the impossibility of supposing that manganese can display an odd number of atomicities can no longer be alleged.

If, then, we assume that the valence of the manganese in permanganates is identical with that displayed in the highest oxide, Mn_2O_7 (this being, like that of the halogens in their highest oxides, heptad(20) the chief objections to the formula $\overset{I}{R}MnO_4$—that it violates the law of even numbers, and that it

---

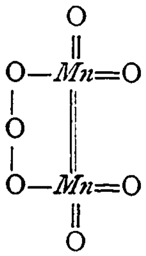
17) *Principles of Chemistry*, 122.

18) *Inorganic Chemistry*, 164.

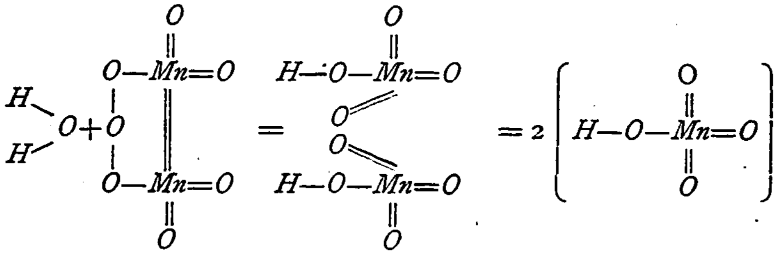
19) Lothar Meyer. See R. and S., II, ii, 511.

20) R. and S., II, ii, 512.

does not correspond to any structural formula—disappear at once. If we represent manganese heptoxide as



(which suggests that loose union, which really exists, of a portion of the oxygen) then, upon contact with water,



or $H_2O + Mn_2O_7 = 2\ HMnO_4$, and similarly for K_2O, Na_2O, etc.

It now remains to be shown that $KMnO_4$ is not merely a possible formula for the salt it represents, but that it is the only correct one. This I hope to do by appeal (I) to the results of certain experiments made with reference to this question, and (II) to facts and principles generally recognized as parts of chemical science.

I

(1)

If permanganates really contain two atoms of a monad base, there is no good reason why one of these may not be replaced by some other monad, thus producing a double salt. To test the possibility of producing such a salt, the following experiment was made:

11.70 grams of silver permanganate and 1.48 grams potassium chloride were separately dissolved in the least quantity of hot water. The two solutions were then thoroughly mixed by shaking in a bottle with a well-ground glass stopper, and the mixture was set aside in a dark place for about twelve hours. The reaction to be expected (assuming the correctness of the formula $\overset{I}{R}_2Mn_2O_8$) was

$$Ag_2Mn_2O_8 + KCl = \left.\begin{matrix}K\\Ag\end{matrix}\right\} Mn_2O_8 + AgCl \; . \; . \; . \; (A.)$$

The purple liquid was decanted from the precipitated silver chloride and placed under a bell-glass, with a vessel containing strong sulphuric acid. The crystallization occupied nearly a month. The mother-liquor was then poured off, and the small crystals were washed, dried over sulphuric acid and analyzed. The analysis gave, from 0.8120 grams supposed double permanganate,

Ag	0.3802
Mn	0.2025
K	0.0030

or,

		Calculated for $KAgMn_2O_8$
Ag	46.83 per cent. . . .	28.05
Mn	24.93 " " . . .	28.55
K	00.30 " " . . .	10.16

So that the crystals examined were clearly not the double permanganate. Upon comparing the analysis with the calculated percentages of the elements in silver permanganate, it appears that the material was merely silver permanganate with a trace of potassium permanganate in it. The difference in solubility of the two salts readily accounts for the small proportion of the latter. Calculating the oxygen, there are found

					Calculated for $Ag_2Mn_2O_8$
Ag_2	0.3802				
O	0.0281		Ag	46.83 per ct.	47.58
K_2	0.0030	or	Mn	24.93 " "	24.23
O	0.0006		O	28.84 " "	28.19
Mn_2	0.2025		K	00.31 " "	....
O_7	0.2062				

Instead of reaction (A), the change that took place on mixing the two solutions was therefore merely

$$2\ Ag_2Mn_2O_8 + 2KCl = K_2Mn_2O_8 + Ag_2Mn_2O_8 + 2\ AgCl,$$

or, as seems more probable,

$$2\ AgMnO_4 + KCl = KMnO_4 + AgMnO_4 + AgCl.$$

(2)

An attempt was now made to prepare a double permanganate of potassium and sodium. The method first adopted was based on the suggestion that

$$2K_2Mn_2O_8 + Na_2SO_4 . 10H_2O = 2\left.\begin{matrix}Na\\K\end{matrix}\right\} Mn_2O_8 + K_2SO_4 + Aq$$

ought to be a possible reaction, since potassium, being more basylous than sodium, might be expected to take sulphuric acid from that element. Hot solutions of the two salts were mixed in proper proportion and set in a dessicator to crystallize. After ten days an abundant deposit of crystals, in general appearance reminding one of silver permanganate, was found. Upon analysis, however, they proved to be only potassium permanganate in crystals of rather unusual 'habit.'

			Calculated for $KMnO_4$
K	.2463	24.60 per cent	24.73
Mn	.3526	35.22 " "	34.80
O (calcul.)	.4091	40.87 " "	40.47

So that there seems to have been no chemical change of any kind.

A second trial was made on a different plan. Sodium sulphate, barium permanganate and potassium permanganate were mixed in proportions to produce the reactions

$$(1)\ Na_2SO_4 . 10H_2O + BaMn_2O_8 = Na_2Mn_2O_8 + BaSO_4 + Aq.$$

$$(2)\ Na_2Mn_2O_8 + K_2Mn_2O_8 = 2\left.\begin{matrix}K\\Na\end{matrix}\right\}Mn_2O_8$$

The first of these, of course, took place as soon as the solutions were mixed; but the second did not occur. After allowing the mixture to stand for some hours, the clear solution was decanted into an evaporating dish, concentrated at a gentle heat, and placed in a dessicator. Within twelve hours potassium permanganate was deposited from the solution in small prismatic crystals of the appearance, in shape and color, so characteristic of that salt.

(3)

If potassium permanganate really contains two atoms of potassium, it ought to be possible to replace one of these by hydrogen, thus forming an acid salt. Accordingly five grams of potassium permanganate was dissolved, and treated with a quantity of hydrofluosilicic acid corresponding to one-half the potassium. The potassium silicofluoride was caught on an asbestos filter, and the filtrate concentrated over sulphuric acid. After a few days sufficient crystals were deposited for examination. They did not differ in appearance from many specimens of potassium permanganate, and upon attempting to determine water in 0.8193 grams, none was found. Hence the substance contained no hydrogen, and was, in fact, merely recrystallized potassium permanganate.

(4)

The untrustworthy character of the only description accessible to me of the "acid permanganate of baryta" alleged by some to exist, has already been alluded to. As it would be unreasonable to reject assertions, which if true ought to be so easy to prove, without testing them by experiment, I endeavored to prepare some of these crystals. An accurately weighed portion of barium permanganate was dissolved, and treated with just the amount of normal solution of sulphuric acid necessary, theoretically, to precipitate all the barium. After a couple of hours, the clear solution was decanted and evaporated on a water-bath at a very gentle heat. When quite concentrated it was allowed to cool, but yielded no crystals of any kind, nor did further evaporation produce any; the final product was a black powder insoluble in water—MnO_2. A second portion of barium permanganate was now dissolved, and treated in the same way, except that rather less sulphuric acid was purposely used than would precipitate all of the barium. But not even this, in which the conditions for forming an acid barium permanganate (if it can exist) were almost certainly present, yielded, on gradual evaporation, anything but a crust of manganic oxide and a little barium permanganate.

(5)

While it might be desirable to multiply experiments like those already described, which bear directly upon the question at issue, so as still further to reduce the chance of error in drawing a conclusion, circumstances have prevented this. But before passing on to further theoretical reasons (which are very strong) for receiving the monobasic formula, it may be well to describe a few other practical tests that have a less direct, but scarcely less important bearing on the subject.

The arguments to be used in (II) are largely dependent upon the isomorphism of the permanganates with the perchlorates. The *fact* can scarcely be questioned, as it seems to be recognized by all authorities. As opinions appear to differ as to its degree, an endeavor was made to determine this.

Several attempts were made to establish the exact isomorphism of potassium permanganate and potassium perchlorate according to the rule proposed by Kopp, that the test of strict isomorphism should be the growth of crystals of one of the substances, when suspended in a saturated solution of the other. This was found to be impracticable. Crystals of permanganate suspended in a saturated solution of perchlorate in every case dissolved entirely, and crystals of perchlorate, while easily coated or stained with permanganate, did not have the appearance of having grown, in a crystallographic sense.

There was no difficulty, however, in getting the salts to crystallize together, the crystals of the mixture being in some cases remarkably perfect in shape and beautiful in color, varying according to the proportions of the constituents, when examined with a lens.

Twelve different mixtures were prepared, six as nearly as possible in varying integral proportions—as one to two, one to three, five to one—the remainder being mixtures of accurately weighed portions of the salts, without any attempt at exact proportion. These were dissolved in hot water, and left to evaporate in the air, loosely covered with filter paper to exclude dust.

The result was, in each case, a mass of minute crystals, with every indication in color, shape, and size, of being mixtures of permanganate and perchlorate. One or two of the solutions, which were allowed to evaporate to dryness, yielded what seemed to be two kinds of crystals, a lighter and a darker. The others gave crystals which, when drained, washed, and dried, had the appearance of being the same throughout, and were often, as before remarked, exceedingly well developed.

In no single instance, however, did analysis of these crystals indicate the proportions of permanganate and perchlorate that had been used in making them. In all of the analyses(21

---

21) The method used with the first six samples was to ignite with excess of alkaline carbonate, dissolve the fused mass in water, acidify with nitric acid and precipitate chlorine with silver nitrate. The silver chloride was caught on a filter, washed, the excess of silver nitrate removed from the filtrate by adding

that I considered most trustworthy, (the amount of material taken was in most cases smaller than would have been desirable for accuracy), more perchlorate was found than was expected—often largely more—and less permanganate. As this excess was quite balanced by deficiency of the manganese, and was found even when especial care had been taken to exclude chlorine from any other source than the salt under examination, it must be accounted for otherwise than by supposing repeated error in the analyses. Two considerations, at least, would lead one to expect results similar to those found; first, that the perchlorate is the less soluble of the two salts, and would therefore crystallize in advance of the other; second, that the solution of permanganate is liable to decomposition when exposed to the air, while the perchlorate is stable.

As examples of this variation, I will give the results of analysis of specimens 7 and 8: Eighty-five milligrams of No. 7 ought to have given, according to the proportions used in making the solution, (0.7309 gm. permanganate to 0.3012 perchlorate), 25 mg. perchlorate and 60 mg. permanganate. The actual result was

	Gm.		Gm.	
Instead of	0.025	. . . . . .	0.070	perchlorate.
" "	0.060	. . . . . .	0.013	permanganate.
	0.085		0.083	

These crystals were well formed but small, not more than half a millimeter thick. Under the lens they appeared translucent, with a beautiful crimson color.

No. 8 was in crystals so minute that to the naked eye they appeared as a purple-red crystalline powder. The lens, however, revealed that the crystals were as well formed indi-

hydrochloric acid and again filtering, and the filtrate finally treated with ammonia and bromine to precipitate manganese. The other six were treated similarly except that the manganese was precipitated first from the alkaline solution, with hydrogen dioxide.

vidually as No. 7, and that their color, by transmitted light was a rather faint red. The solution from which these separated had been made of 1.6814 gm. perchlorate and 0.3261 gm. permanganate. The 148 mg. used in analysis should have contained, therefore, 124 mg. of perchlorate and 24 of permanganate. The result was :—

	Gm.	Gm.	
Instead of	0.024	0.011	permanganate.
" "	0.124	0.138	perchlorate.
	0.148	0.149	

The results, on the whole, agree with the statement usually made, that these two salts are isomorphous to the extent of crystallizing together in all proportions. Hence the right to make deductions from this isomorphism cannot be doubted.

II.

If it were possible to ascertain the vapor density of potassium permanganate, there would be no difficulty in choosing between the formula $KMnO_4$ and $K_2Mn_2O_8$, as, according to the law of Avogadro, the molecular weight of the compound would thereby be decided. But since this is impracticable, owing to the decomposition of the salt at a temperature as low as 240° C.,(22 the problem must be attacked by methods less direct.

It is assumed that the received formula for the perchlorates, $\overset{n}{R}(ClO_4)_n$, is correct. Granting this, it follows almost necessarily that the permanganates are represented by the analogous formula $\overset{n}{R}(MnO_4)_n$, from the following considerations :

---

22) R. and S., II, ii, 22.

(1)

THE SPECIFIC HEATS OF POTASSIUM PERMANGANATE AND POTASSIUM PERCHLORATE.

According to the law of Dulong and Petit, the specific heats of elements in the solid state vary inversely as their atomic weights. In the present state of chemistry this law is received with reservations, yet a high degree of probability attaches to deductions from it.(23

Although the fact established by Kopp,(24 that the molecular heats of compounds are the sums of the atomic heats of their constituent elements, cannot be directly applied to fixing molecular weights by means of specific heats; yet it has been observed, in connection with the specific heats of solid compounds, that there is in general an inverse variation between their specific heats and molecular weights, similar to that established by Dulong and Petit for the solid elements, *where the substances compared are of analogous composition.*(25 Without assuming any closer analogy between permanganates and perchlorates than is actually revealed by analysis (thus leaving the question of the molecular weight of the former open) it would seem fair to expect from them conformity to this rule; for the only difference that analysis shows is the replacement of manganese in the one salt by chlorine in the other.(26

It follows, then, that if the specific heats of potassium perchlorate and potassium permanganate as determined by experiment are nearly alike, their molecular weights will also be similar. According to Kopp,(27 the specific heat of potassium permanganate is 0.179; that of potassium perchlorate

---

23) R. and S. II, i, 16.

24) R. and S. II, i, 20

25) Watts' *Dict.*, IV, 36.

26) Cf. Mitscherlich, *Ann. Chem. Phar.* II, 10; Serullas, *Ann. Chim. Phys.* (2) XLVI, 303; Mitscherlich, ibid., XLIX, 113.

27) Watts' *Dict.*, 1st Supp., 667.

0.190. The molecular weight of $KClO_4$ is 138.25; that of potassium permanganate should, then, be somewhere near $(138.25 \times \frac{190}{179} =)$ 147 +. But the formula $K_2Mn_2O_8$ requires a molecular weight of 314.42. By taking the formula $KMnO_4$, with half of this molecular weight, there is an evident agreement (even though it be not very close) between the molecular weight as usually calculated, and as indicated by specific heat, i. e. 157.21 and 147 + respectively.

(2)

THE SPECIFIC VOLUME RELATIONS.

The isomorphism of perchlorates with permanganates was announced by Mitscherlich[28], who made comparative measurements of the two classes of crystals. His results have been very generally received and confirmed by subsequent investigators.

According to the general law that *isomorphous compounds have equal specific volumes, while those whose crystal forms are approximately the same have also approximately equal specific volumes*[29], the specific volumes of potassium perchlorate and potassium permanganates must be very nearly the same. But if $K_2Mn_2O_8$ be the correct formula for the permanganate, this is not the case; for the specific gravity of potassium permanganate is 2.644[30], giving a specific volume (with this formula) of $(\frac{314.42}{2.644} =)$ 118.9; whilst the sp. gr. of the perchlorate is 2.47[30], which gives a sp. vol. of $(\frac{138.25}{2.47} =)$ 55.9. It is evident that this wide difference disappears when the formula $KMnO_4$ is substituted for $K_2Mn_2O_8$. The sp. vol. of potassium permanganate then becomes 59.4, which is not far from 55.9.

---

[28] *Ann. Chim. Phys.* (2) XLIX, 129.

[29] Fownes' Chem., 232. Also Watts' *Dict.*

[30] See Notes on Work (1) infra.

(3)

THE GENERAL CHEMICAL RELATION OF ISOMORPHOUS BODIES.

The relation referred to is thus concisely expressed by Richter[31]: "From the isomorphism of two compounds may be concluded an analogous chemical composition, a similar number of atoms in the molecule." This statement is qualified in its context as accuracy requires. With all necessary limitations, it yet adds something to the evidence which, as a whole, points so unmistakably to the monobasic character of permanganic acid, and the heptad valence of the manganese in it. Potassium permanganate must, like potassium perchlorate, contain six and not twelve atoms in its molecule.

This paragraph, of course, is practically the same as the preceding, but presents the argument in more general form. As both are dependent on the isomorphism of the two salts compared, it should be noted that it is not essential to their validity that this isomorphism should be perfect, which is probably not the case. No investigator has been found, however, to deny at least a general isomorphism between the two classes of salts. Mitscherlich stated that the primitive form of both permanganate and perchlorate of potash is the right rhombic prism[32], and this was afterwards alluded to by Gmelin, curiously enough, as an exception to the recognized rule that isomorphism argues chemical similarity, on the ground that "manganese bears no relation to chlorine"[33]. That manganese does bear relations to chlorine is, as has been remarked, an unavoidable inference from the periodic system.

[31] *Inorg. Chem.*, 251.
[32] *Ann. Chem. Pharm.*, II, 9.
[33] *Handb. of Chem.* I, 88.

SUMMARY AND CONCLUSION.

It appears from the foregoing that there has not been, and is not now, any tangible proof, in the shape of double salts, to show that permanganic acid is dibasic; but that unless manganese be regarded as heptad in this acid, the monobasic formula is abnormal.[34] But it is tolerably clear that manganese may be so regarded[35], notwithstanding its artiad character in most of its compounds; and it follows that the monobasic formula does not violate any law of chemistry[36], and being the simpler of the two should, according to the law of parcimony, be given precedence of the dibasic for this reason alone. In addition to this, however, it has been shown that the relations of permanganic acid to another acid known to be monobasic, point conclusively to the monobasic formula as the only correct one; the relations, namely, between its potassium salt and that of perchloric acid with regard to (1) specific heat, (2) specific volume and (3) crystal form.

The above arguments are not offered as a rigid demonstration of the thesis. The intrinsic difficulties of the subject are such as well nigh forbid an unanswerable course of reasoning, since the evidence is to a large extent merely negative in character. Nevertheless, the accumulated weight of the facts adduced in favor of the thesis—the facts of experiment, of authority, and of chemical law—are such as give to it a degree of probability that is only short of actual certainty.

[34]) Pp. 7, 8.
[35]) Pp. 10–15.
[36]) P. 15.

Addendum,

May, 1888. (See Preface.)

Dr. Auwers, of Göttingen, has recently given special attention to Raoult's method of determining molecular weights by observing the freezing points of solutions. His published results have been obtained from organic substances, and with other solvents than water; and although M. Raoult himself seems to have determined "depression-coefficients" for various inorganic substances, I have not been able to find any detailed account of his work. It seemed worth while, therefore, to make an examination, even though a very brief one (as it necessarily was, owing to pressure of other work) of the relations between the freezing points of solutions of substances whose molecular weights are well known, and of potassium permanganate.

Seven salts of potassium were examined—K_2SO_4, $KHCO_3$, K_2CrO_4, KNO_3, $KClO_3$, KIO_3 and $KClO_4$. In each case, an accurately weighed portion (either one or two grams) was dissolved in 100 molecules of water, or the least multiple of 100 molecules that would dissolve it readily, and the solution was then frozen, the temperature of solidification being carefully noted. Where 200, 300, etc., molecules of water were used instead of 100, the observed depressions were multiplied by 2, 3, etc., respectively, since, other things being equal, the depression varies inversely as the amount of the solvent. The values thus found were as follows:—

	T.
1. K_2SO_4	2.38
2. $KHCO_3$	1.86
3. K_2CrO_4	2.60
4. KNO_3	1.65
5. $KClO_3$	1.73
6. KIO_3	2.00
7. $KClO_4$	1.80
Average value of T	2.00

If we reject the first three salts from consideration, on the ground that they are dibasic and not analogous to the others, the average value of T becomes 1.80.

Three separate solutions of potassium permanganate were made, of uniform strength, i. e., 2 grams of permanganate in 136.7 c. c. of water, or 600 molecules of water to 1 molecule of permanganate, supposing the permanganate to be $KMnO_4$. The solutions were frozen, and the *observed* depressions of the freezing point below 0°C. were $0.^\circ 33$, $0.^\circ 32$ and $0.^\circ 35$, an average of $0.^\circ 33\frac{1}{3}$.

Supposing the true formula of the salt to be $K_2Mn_2O_8$, it is evident that the amount of water used was not really 600 molecules to one of the permanganate, but 1200, since on this hypothesis the same weight of the salt would have only half the number of molecules. Hence the observed depression, $0.^\circ 33\frac{1}{3}$, must be regarded as $\frac{1}{12}$ of T, and $T = 4.00$.

Such a value of T is altogether in excess of any other value found, even for the salts known to be dibasic.

If, however, $KMnO_4$ be the correct formula, T becomes 2.00, which is exactly the average value for all the salts examined, and is not much greater than the average value (1.80) for the monobasic salts.

Hence $KMnO_4$ is the true formula, and permanganic acid is monobasic.

Notes on Work.

(1.) THE SPECIFIC GRAVITIES OF POTASSIUM PERMANGANATE AND POTASSIUM PERCHLORATE.

In selecting a liquid in which to take these specific gravities, the use of water being impossible, it was, of course, necessary not only that it should not dissolve the permanganate, but that it should be free from reducing action on that very easily decomposable salt. Refined petroleum was found to answer the purpose admirably. The liquid used was an illuminating oil of the best grade known as "Pratt's Astral Oil." Its sp. gr. at 20° C. was found to be 0.793. The crystals of permanganate were crushed to a rather coarse powder; 1.24 grams were put into a miniature flask of about 25 m. m. diameter with long gradually tapering neck, then covered with the oil, and gently agitated till free from air bubbles. The flask was next immersed in a bath of water at about 18° C.; it was roughly filled with oil at that temperature from another vessel already in the bath, and the whole was raised to exactly 20°. The liquid in the neck of the flask was carefully brought to the level of the mark with a very fine pipette. The flask was then removed, wiped dry, set in the balance case for a quarter of an hour, and weighed. Similar precautions were observed in all of the fillings and weighings.

The sp. gr. of the permanganate relative to the oil was found to be 3.334: which, reduced to the standard of distilled water at 20° C., gives 2.644.

The sp. gr. of the perchlorate was taken in the same way. It was found to be 2.470.

(2.) THE PREPARATION OF BARIUM PERMANGANATE.

The manufacture of barium manganate, preparatory to converting it into permanganate, was found to be hardly so simple a matter as might be inferred from the language of many of the books. It is necessary to have the materials present in as nearly the right proportion as may be, a large excess of manganese dioxide preventing the formation of the manganate. The temperature must be properly regulated, otherwise either no manganate is formed or, on the other hand, it is decomposed by excessive heat. Lastly, the reaction is very sensibly aided by blowing air into the crucible. This is in accordance with the observation of Desclabissac (Watts' *Dictionary*, VII, 771), that contact of air is essential to the formation of good oxidation products, oxidizing salts alone not being sufficient.

After several attempts with unsatisfactory results (including exposure of the material in a shallow tray in the muffle) nitrate of barium and manganese dioxide were taken in proportion of their molecular weights, the reaction—

$$Ba(NO_3)_2 + MnO_2 = BaMnO_4 + 2NO_2$$

—being assumed. That is, three parts of barium nitrate and one of manganese dioxide were finely pulverized, intimately mixed and placed in a No. 10 Beaufay crucible. The crucible was loosely covered with an iron sand-bath, through the middle of which was introduced an iron pipe reaching to the bottom of the crucible and connected with a small foot-bellows. The crucible was then placed in the wind-furnace and heated to bright redness, a current of air (sufficiently gentle to avoid blowing out the loose powder) being meanwhile kept up. The contents of the crucible now became liquid, and the air was briskly bubbled through. In a few minutes the mass stiffened. The current of air and the bright red heat were continued, however, for about three quarters of an hour longer, at the end of which time a homogeneous mass of brilliant green manganate was found. Another charge, during the fusion of which the air-pipe became stopped, was duller in color and not homogeneous. The same was true of a previous charge in which the air-blast was not used.

The manganate was pulverized and converted into permanganate with carbon dioxide, as usual.

(3.) ATTEMPT TO PREPARE SODIUM MANGANATE.

It is stated in Watts' *Dictionary* (III, 818) on the authority of Gentele, that manganate of soda is produced when equal parts of finely pulverized manganese dioxide and sodium nitrate are heated to bright redness, in a muffle, for sixteen hours. Wöhler, however, is quoted as denying that any manganate can be formed in this way, for the reason that "the nitrate is entirely decomposed before the temperature is attained at which it can act on the manganese dioxide," and (we must infer) the remaining caustic soda, unlike caustic potash under similar circumstances, does not act on the manganese dioxide.

I followed the directions of Gentele with care, using a tray of Russia iron to hold the mixture of the two salts; but the result was entirely in accordance with Wöhler's statement. Within a half-hour after introducing the tray into the muffle, nearly all visible action had ceased; and after the sixteen hours of heating to bright redness had passed, the tray contained nothing but manganese dioxide and caustic soda.

It seemed possible that by heating the MnO_2 to redness and throwing it into the fused nitrate, combination might be brought about. The attempt was made with the aid of the air-blast and wind furnace used in the preparation of the barium salt, but even thus no manganate was formed. Lack of time forbade further experiments at the furnace, and the sodium permanganate wanted was easily made by mixing solutions of barium permanganate and sodium sulphate.

(4.) THE SOLUBILITY OF POTASSIUM PERMANGANATE.

Not finding an extended statement of this solubility in any work to which I had access, I undertook to determine it.

A flat porcelain dish, about six centimeters deep and twenty-five in diameter, was covered outside with cotton wool and heavy paper, and fitted with a wooden cover. The salt was placed in a small beaker, in sufficient quantity to ensure saturation of the solution, and the beaker was immersed in the bath in the dish through an opening made in the cover to fit it. The temperature of the bath was shown by a thermometer, introduced through the cover, and that of the solution by another suspended in it.

Starting at 0°C., the temperature was gradually raised by removing the ice and adding warm water, till thirty degrees was reached; from which point the increase was continued by the aid of a jet of steam led through the cover into the bath. At every five degrees rise in the temperature of the solution, five cubic centimeters were removed to a weighed vial, which was then set in a steam bath to evaporate. The solution was stirred, and then given time for the undissolved salt to subside, previous to the removal of each sample. The practical difficulties in getting trustworthy results increased with the temperature. The pipette was kept hot, by suspension in a flask over boiling water, and rinsed with hot water each time it was used, to avoid the otherwise inevitable accumulation of solid salt in it.

The following figures show the average of three determinations. From 0° to 30° the results of the three determinations were practically identical, 0° and 5° absolutely so. From 35° up, there were occasional rather wide disagreements among the results, making the increase in the average less regular. T shows temperature, and W the weight of solid salt contained in 100 cubic centimeters of a saturated solution at that temperature.

T	W (Grams)	T	W	T	W	T	W
0	3.0	25	7.0	50	13.7	75	22.8
5	3.3	30	8.2	55	15.6	80	24.8
10	4.0	35	9.7	60	16.7	85	26.6
15	4.9	40	10.6	65	19.2	90	28.6
20	5.8	45	13.1	70	22.2	95	32.8

The approximate solubility often given of 1 in 16 at 15° agrees more nearly with that at 20° in the above.

(5.) SOLUBILITY OF POTASSIUM PERCHLORATE.

This was found by the same method as the preceding; the results given are the mean of the two most reliable determinations.

T	W (Grams)	T	W	T	W	T	W
0	.7	25	1.6	50	4.0	75	9.5
5	.8	30	2.0	55	5.2	80	9.1
10	1.0	35	2.6	60	6.1	85	11.1
15	1.1	40	3.0	65	7.4	90	13.4
20	1.3	45	3.7	70	8.2	95	13.2

The apparent interchange between 75° and 80°, and 90° and 95° shows the results as actually obtained, and confirmed by repeated determinations.