number equal to 4. According to the present theory, such compounds are to be regarded rather as typical primary valence compounds.

This valence theory is based on the following simple equation:

$$e = 8n - 2p$$

where e is the total number of available electrons in the shells of all the atoms in a molecule; n is the number of octets forming the outside shells, and p is the number of pairs of electrons held in common by the octets. This equation is a complete mathematical statement of the primary valence requirements, not only in organic, but in inorganic chemistry.

The theory leads to very definite conceptions as to the positions of the electrons in the molecules or space lattices of compounds. The structures of molecules of nitrogen, carbon monoxide, hydrogen cyanide, and NO prove to be exceptional in that the kernels of both atoms in the molecule are contained within a single octet. This accounts for the practically identical "physical" properties of nitrogen and carbon monoxide, and for the abnormal inertness of molecular nitrogen.

The results obtained by the use of the postulates are so striking that one may safely reason that the results establish the fundamental correctness of the postulates.

These conclusions, however, are not easily reconciled with Bohr's theory of the atom. Bohr's stationary states have a rather close resemblance to the cellular structure postulated in the present theory. There are also striking points of similarity with J. J. Thomson's theory of the structure of atoms, in which he assumes that the attractive forces are limited to certain tubes of force.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF EDINBURGH.]

MANGANOUS TARTRATE AND POTASSIUM MANGANOUS TARTRATE.

BY LEONARD DOBBIN.

Received February 25, 1919.

I. Manganous Tartrate.

Manganous tartrate was first prepared by Scheele,[1] who obtained it by the interaction of a solution of potassium tartrate with a solution of a manganous salt, but did not describe it. Bergman[2] also mentions this interaction, while J. B. Richter[3] employed it, using hot solutions, as his method of freeing manganese from iron—a purpose for which it was like-

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[1] *Kongl. Vetenskapsacad. Handlingar*, 35, 95 (1774).

[2] "Phys. and Chem. Essays" (Trans. by Cullen), 2, 221 (1784).

[3] *Neuere Gegenstände der Chemie*, Erstes Stück, 1791, p. 32, and *Crell's Chem. Ann.*, 1796, Bd. II, p. 300.

wise regarded as applicable by Hermbstädt.[1] In the first edition of his "*System of Chemistry*" Thomson refers[2] to Bergman as authority for the preparation of manganous tartrate by double decomposition, as above, but in the sixth edition he describes[3] the mixture of tartrate of potash with a solution of manganese as depositing, on standing, crystals "consisting of tartrate of potash combined with oxide of manganese." Five years later, however, in his "Attempt to establish the first Principles of Chemistry by Experiment,"[4] under the heading Tartrate of Manganese, Thomson states[4]:—"This salt has hitherto been mistaken for a triple salt, but it contains no potash," and he adds that its constituents are:

"1 atom tartaric acid,
1 atom protoxide of manganese,
2 atoms water,"

from which it is evident that the substance had been submitted to quantitative examination, although particulars of this are not given.

Döbereiner[5] obtained manganous tartrate together with manganous formate by heating tartaric acid or potassium hydrogen tartrate with manganese peroxide and water.

Notwithstanding these early references to its preparation, the information obtainable from the larger modern chemical works of reference with respect to manganous tartrate is very scanty, and, as will appear, it is not very reliable. The latest edition of Gmelin-Kraut's *Handbook* mentions,[6] as sole authority, a paper by Pfaff[7] which was published more than 100 years ago, while Wurtz's *Dictionary* refers,[8] in addition, to a more recent paper by Fleischer.[9]

On consulting Pfaff's paper it was found that the author dissolved crystallized Ilfeld grey manganese ore in hydrochloric acid, permitted the liberated chlorine to escape from the solution, "neutralized" a portion of this solution with sodium carbonate till "whitish flocks" appeared, and then added to the liquid, which "still had an acid reaction," a solution of potassium tartrate. It is stated that no precipitate appeared at first, but that small, white crystals were gradually deposited which behaved like pure cream of tartar; and that this deposit was followed by a further separation of very small crystals of yellowish color, which, on close examination, behaved like manganese tartrate and were partially decomposed

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[1] *Crell's Chem. Ann.*, **1792**, Bd. II, p. 315.

[2] Vol. III, 89 (1802).

[3] Vol. II, 583 (1820).

[4] Vol. II, 353 (1825).

[5] *Gilbert's Ann.*, 71, 107 (1822).

[6] Bd. III_2, p. 335.

[7] *Schweigger's J.*, 4, 376 (1812).

[8] Tome 3, p. 218.

[9] *Ber.*, **5**, 380 (1872).

when boiled with water—a salt consisting of the greater part of the acid, with part of the oxide, passing into solution, while the remainder of the acid, with excess of the oxide, was left undissolved. The author gives no indication of the analytical treatment employed to establish the identity of the cream of tartar or of the manganese tartrate said to have been precipitated, and quantitative data are altogether wanting.

Fleischer obtained manganous tartrate as a product of the reduction of solutions of potassium permanganate by interaction with tartaric acid in the absence of mineral acid. He describes the salt produced in this way as strongly rose-red when moist, paler after drying over sulfuric acid, and almost colorless when dried at 100° or over. He determined the proportion of water driven off at 150° and the percentage of manganese in the dried salt, and from these data he arrived at the formula $MnC_4H_4O_6.2H_2O$.

Fleischer does not mention any experiments designed to prepare manganous tartrate by ordinary double decomposition and there is not any suggestion that the possibility of its being obtainable in that way had occurred to him.

The present writer made some experiments in imitation of Pfaff's (but starting from a solution of purified manganous chloride) in an endeavor to realize his results.

1. A moderately dilute solution of manganous chloride was acidified with hydrochloric acid, and sodium carbonate was then added to it until "whitish flocks" appeared *and just remained undissolved.* When this latter condition was fulfilled, the liquid was distinctly alkaline and the addition of potassium tartrate, of course, did not produce a precipitate of cream of tartar; but on standing for a short time, a slightly rose-tinted crystalline deposit was gradually formed, and this proved on analysis to consist of manganous tartrate.

2. Sodium carbonate was added to another portion of the acidified manganous chloride in such quantity that the solution was left still slightly acid. In this case a white precipitate of potassium hydrogen tartrate appeared very shortly after adding potassium tartrate, but on standing, this precipitate gradually became mixed with some manganous tartrate which separated later and formed with it a faintly tinted deposit. In so far as the deposition of cream of tartar is concerned, this experiment is thus in accord with Pfaff's.

For convenience in preparing further quantities of manganous tartrate by double decomposition, approximately equimolecular solutions of appropriate concentration were prepared, which contained the following amounts per liter of the respective substances calculated as the anhydrous salts:

Manganous chloride, 34 g.	Potassium tartrate, 60 g.
Manganous sulfate, 40 g.	Sodium tartrate, 52 g.

Separating slowly from liquids obtained by employing these solutions in correct proportions, with or without further dilution with water, manganous tartrate appears in glistening, well-formed, very small, rose-tinted crystals, a crystallographical description of which is given further on. These crystals can be washed thoroughly with cold water without undergoing visible change. At 100° they lose over 14% of water, but water in small proportion continues to be driven away from the nearly colorless residue up to 180–185°, and at about 200° darkening occurs with incipient decomposition of the anhydrous salt. When ignited in air they leave a dark brown residue which does not impart an alkaline reaction to moistened litmus paper and is therefore free from potassium or sodium carbonate. When powdered and boiled with water for some time, only a very small quantity passes into solution, and the undissolved residue consists of the original salt, undecomposed and with its proportion of water of crystallization unchanged. Nothing is observed in this last treatment which even remotely suggests the decomposition reported by Pfaff as resulting in the formation of a soluble acid salt and an insoluble basic salt.

The crystals were submitted to quantitative analysis, when the figures given below were obtained, in agreement with the composition stated by Thomson and with the formula given by Fleischer.

	Mn.	C.	H.	O.	H_2O.
Calc. for $MnC_4H_4O_6.2H_2O$:	22.98	20.09	1.68	40.16	15.07
Found:	23.14	20.59	1.77	...	15.13

It is somewhat difficult, in view of the following facts, to understand how Richter could have adopted precipitation of manganese in the form of tartrate as a method of freeing this element from iron. On one occasion, when preparing manganous tartrate by double decomposition from a solution of an ordinary commercial sample of manganous chloride, the crystals which separated had a bright orange-yellow color and these, as well as the manganous chloride, gave a decided reaction for iron. Some experiments were therefore made by mixing known quantities of ferric chloride with solutions of pure manganous sulfate prior to precipitating with sodium tartrate. The quantities of ferric chloride were varied so that the mixed solutions contained the two metals between the proportions of 20Mn: Fe and Mn: Fe. When the latter proportion was employed, the solution did not give any precipitate, owing probably to its acidity, and the proportion which yielded a satisfactory crystalline deposit was found to be about 10Mn: Fe, whereas mixtures containing iron in a somewhat greater proportion, yielded cream-colored precipitates which were to a considerable extent flocculent. The crystals which separated from a solution containing 10Mn: Fe had the shape and the fine glistening appearance of those of pure manganous tartrate, but their color was bright orange. When examined quantitatively they were found to contain 0.92% of iron.

Report on Crystals of Manganous Tartrate.[1]

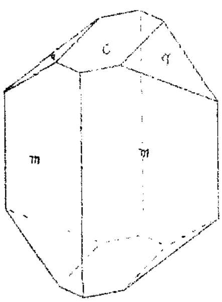

Fig. 1.

The system is monoclinic with axial ratios $a:b:c = 0.816:1:0.699$, $\beta = 100^\circ.14'$. The habit of the crystals is short prismatic, the forms observed being $m\{110\}$, $c\{001\}$, and $q\{011\}$, as is shown in Fig. 1. The faces were always somewhat curved so that the measurements are only approximate; moreover, the forms c and q were always striated parallel to the a-axis. Following are the results of measurement and calculation:

	Azimuth (φ).		Polar distance (ρ).	
Face.	Observed.	Calculated.	Observed.	Calculated.
$m\{110\}$...	*51°.13′	..	90°.0′	90°.0′
$c\{001\}$...	87 .23	90°.0′	11 .15	10 .14
$q\{011\}$...	*14 .28	..	*35 .50	..

II. Potassium Manganous Tartrate.

The earliest statement concerning the alleged existence of potassium manganous tartrate that the author has met with is that by Thomson in 1820, already quoted. No authority is mentioned, but Thomson's statement scarcely demands serious consideration since he withdrew it 5 years afterwards. Gmelin-Kraut's *Handbook* states,[2] however, that potassium manganous tartrate is obtained by dissolving manganous carbonate in aqueous solution of cream of tartar, and a reference is there given to Scheele as authority. On looking up this reference,[3] it proves to be a German abstract of the paper on tartaric acid by Retzius,[4] describing experiments in which Scheele participated. This paper has been ascribed by some to Scheele, but it is excluded from the list of Scheele's publications by Nordenskjöld.[5] It does not include any experiments with manganese compounds. In view of the statement in Gmelin-Kraut, however, numerous experiments were made by treating solutions of potassium hydrogen tartrate, under varying conditions of temperature, with manganous carbonate, in the endeavor to obtain potassium manganous tartrate, but these simply resulted in the formation of manganous tartrate which separated almost completely in crystalline form, while normal potassium tartrate remained in solution.

Frommherz[6] refers to "the double salt, potassium manganous tartrate, described by Scheele," but he does not state where it is described, and a very careful search through all the indexed writings, as well as through

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[1] By Miss M. W. Porter, University Museum, Oxford.

[2] Bd. III_2, p. 359.

[3] *Crell's Chemisches J.*, **2**, 179 (1779).

[4] *Kongl. Vetenskapsacad. Handlingar*, **31**, 210 (1770).

[5] *Nachgelassene Briefe und Aufzeichnungen*, **35**, 1892.

[6] *Schweigger's J.*, **44**, 339 (1825).

all the seemingly likely portions of the unindexed writings of Scheele, no such description has been discovered.

Crystallographical description and measurements of a salt which purported to be potassium manganous tartrate are given by Schabus,[1] who states that the salt was handed to him by Dr. J. J. Pohl for examination. The mode of preparation of the salt is not given, and a search for any account of this in Pohl's papers was unsuccessful, but Schabus mentions that the crystals were yellowish colored, in mass, and possessed a slightly acid taste.

Since the attempts by the present author to prepare this double salt had proved unsuccessful, attention was more particularly directed to the crystal measurements recorded by Schabus. Mr. T. V. Barker, M.A., B.Sc., of the University Museum, Oxford, was good enough to submit these measurements to a minute examination and he reports that the reputed potassium manganous tartrate of Pohl-Schabus is crystallographically indistinguishable from potassium hydrogen tartrate. In view of this fact, there seems to be little doubt that a mistake of some kind has occurred—most likely to be attributed to Pohl—whereby crystals of potassium hydrogen tartrate were supposed to be those of potassium manganous tartrate. The slightly acid taste of the crystals examined by Schabus, which it would be difficult otherwise to account for, would be easily explicable on the assumption that they consisted of potassium hydrogen tartrate, while their yellowish color could arise from iron present as impurity. As a matter of fact, experiments designed to test this latter point were made by crystallizing potassium hydrogen tartrate from solutions containing iron in small proportion, and these resulted in the separation of crystals which agreed well with the description given by Schabus—yellowish in color and exceedingly lustrous.

Besides the reference to Scheele already mentioned, Maumené[2] is quoted by Gmelin-Kraut as authority regarding the occurrence of potassium manganous tartrate in grapes. Maumené's paper mentions the separation, on cooling, from the residue obtained by evaporating a certain red wine, of crystals which, after several washings with alcohol, were of a perfectly homogeneous rose color and, on calcination in air, left a very green, fusible and soluble ash which was a mixture of potassium carbonate and manganate. Quantitative data are not given and there is no further evidence to show that the crystals were actually those of a double salt.

Quantitative analytical data with respect to potassium manganous tartrate being altogether wanting and the other facts regarding its supposed existence being as stated in the foregoing, the strongest doubts appear to be justified as to such a double salt ever having been obtained. The only

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[1] *Bestimmung der Krystallgestalten*, Wien, 1855, p. 67.

[2] *Bull. soc. chim.*, 41, 451 (1884).

point which seems to stand seriously in the way of a definite assertion that its existence has never been established is the specific statement by Frommherz, who had worked extensively among manganese compounds, as to its having been described by Scheele, while a demonstration to the contrary is not forthcoming. Perhaps some chemist may be able to say where, if at all, Scheele deals with the matter.

With regard to the compounds described by Descamps[1] and by Baudran[2] as containing potassium and manganese in combination with the tartaric acid radical, these may be assumed to contain the latter metal in the manganic state. There are difficulties in reconciling the formulas given by both authors with the analytical data which they advance, but a review of manganic compounds lies beyond the scope of this communication.

In conclusion, the author wishes to acknowledge, with thanks, his indebtedness to Miss Porter and to Mr. Barker for their valuable aid in dealing with the crystallographical matters included in this paper.

EDINBURGH, SCOTLAND.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF NATIONAL CARBON CO., INC.]

EMULSIFICATION OF WATER AND OF AMMONIUM CHLORIDE SOLUTIONS BY MEANS OF LAMP BLACK.

BY WILLIAM C. MOORE.

Received March 3, 1919.

Introduction.

Following the recent publication of results by Schlaepfer[3] on the emulsifying action of lamp black on water-kerosene mixtures, a considerable amount of time has recently been devoted in this laboratory to a study of the emulsifying action of various kinds of carbon on water and on aqueous solutions. At the outset it can be stated that the only successful emulsions with kerosene as the external phase, have been prepared by the use of lamp black as the emulsifying agent. Highly calcined lamp black and calcined petroleum coke were entirely unsuited for this work, probably owing to their inability to form a coherent film in the "dineric interface."[4]

In our work we have used successfully, as emulsifying agents for water and certain ammonium chloride solutions, several samples of commercial lamp black which had been prepared by the incomplete combustion of creosote oils. Since our results seem to bring out clearly certain surface phenomena underlying emulsion formation, it may be of interest to make them public, in the following report:

[1] *Compt. rend.*, **70**, 813 (1870).

[2] *Ann. chim. phys.*, [7] **19**, 555 (1900).

[3] *J. Chem. Soc.*, **113**, 522 (1918).

[4] Bancroft, *J. Phys. Chem.*, **19**, 275 (1915).