

stopped down to an aperture corresponding to the size of the mirror, the reflected image is contrasted with that seen directly, and if the definition is unchanged, the mirror is marked K.O., with a writing diamond, and returned to the maker; if the object appears distorted, its unfitness for use is similarly notified. A small fee is charged for the examination.

III. "On the Atomic Weight of Manganese." By JAMES DEWAR, M.A., F.R.S., Jacksonian Professor, Cambridge, and ALEXANDER SCOTT, M.A. Received February 9, 1883.

Our attention has been directed for some time to a new determination of the atomic weight of manganese. This communication gives a succinct account of the results of the preliminary stages of such an inquiry, and although the further progress of the investigation may reveal some errors, still we feel convinced the final numbers can in no way differ materially from the present values, and therefore further delay in publication is unnecessary.

The atomic weight of manganese has been determined by many chemists,\* but the resulting values vary considerably according to the special method selected. The results of the different investigators may be divided into two classes—those giving approximately 55 as the number, and those making it about 54. To the former class belong Turner, Berzelius, and Dumas, all of whom use the same method, viz., the determination of the silver chloride yielded by a weighed amount of chloride of manganese. Turner also made determinations from the analysis of the carbonate, and from the conversion of the monoxide into sulphate. Von Hauer used the same method as that employed by him in the determination of the atomic weight of cadmium, viz., the reduction of manganous sulphate to sulphide by ignition in a current of sulphuretted hydrogen. It is probable that this method is not very trustworthy, as, according to Schneider, the sulphide may be contaminated by oxysulphide. Schneider and Rawack belong to the second class of observers, the former employing the oxalate, and from its analysis calculating the atomic weight by deducting the weight of water and carbon dioxide obtained. Rawack, whose experiments were conducted in Schneider's laboratory, weighed the water obtained by reducing manganosomanganic oxide to manganous oxide.

One objection to the analysis of the chloride is that it may contain besides manganous chloride varying proportions of manganic salt.

\* Berzelius, "Lehrbuch," 5 Ed., 3, 1224. Dumas, "Ann. Chem. Pharm.," 113, 25, 1860. Hauer, "Wien. Acad.," xxv, 124. Rawack and Schneider, "Pogg Ann.," 107, 603.

This must be the case if, as Forchammer maintains, pure manganous salts are colourless, the pink colour of manganese salts being due to traces of a manganic compound. Forchammer has observed that on fusing manganese sulphate with potassium hydrogen sulphate, a white mass is obtained which gives a colourless solution. We have been unable to prepare any chloride or bromide without a pink or rose colour giving a correspondingly coloured solution, and this was also the case with specimens fused in hydrogen and hydrochloric acid gas. The effect of a trace of manganic salt in the chloride would be to lower the atomic weight. The chloride and bromide of manganese are both not only very hygroscopic, but if fused in hydrochloric acid gas (or hydrobromic acid in the case of the bromide) are liable to retain traces of the halogen acids, and this would consequently make the atomic weight too low.

In order to ascertain the values of the atomic weight of manganese which result from careful analysis of the halogen salts, determinations were made of the molecular weights of chloride and bromide on specimens prepared with great care. The number found for the bromide was 214·87, and for the chloride 125·825, yielding the respective atomic weights of manganese of 54·97 and 54·91. All researches on the oxides of manganese have shown that they are all difficult to obtain in anything like a definite form, with perhaps the exception of the protoxide.

It occurred to us that the analysis of silver permanganate might be employed with advantage, as this salt is found in a very definite state, and can be easily freed from all the allied metals. The selection of this substance, moreover, involved only the atomic weights of silver and oxygen, and as it seemed feasible to deduce the atomic weight of the manganese directly from the percentage loss of oxygen on heating, we expected to get very accurate results. In this we were disappointed, as we have not been able to obtain concordant results by this most direct method.

Table I.

	Weight of silver permanganate.		Weight of residue. Ag + MnO.		Oxygen lost.	Equivalent.
	In air.	In vacuo.	In air.	In vacuo.		
I. . .	5·8688	5·8696	4·6320	4·63212	1·23748	227·673
II. .	5·4981	5·4988	4·3358	4·33591	1·16293	226·965
III. .	7·6725	7·6735	6·0538	6·05395	1·61959	227·422
IV. .	13·0997	13·10147	10·3179	10·31815	2·78332	225·943
V. . .	12·5782	12·5799	{ 9·9104 9·9141	9·91065	2·66925	226·22
				9·91435	2·66555	226·53

Table I gives the results of the direct determination of the equivalent of the permanganate of silver by reduction in hydrogen.

The silver permanganate was heated in a bulb of hard glass, first in a current of pure air and then in hydrogen, at a red heat, until the resulting mixture of silver and oxide of manganese had a constant weight. The residue was allowed to cool in hydrogen, which was finally displaced by nitrogen before weighing. The results obtained by this method show great variation, the errors being probably due to the occlusion of hydrogen and the suspension of some oxide of manganese in the oxygen evolved. The method finally employed was to dissolve the permanganate of silver in dilute nitric acid in presence of various reducing agents, such as sulphurous acid, sodium formate, and potassium nitrite. The silver was then determined by adding very nearly an equivalent quantity of pure potassium bromide, and titrating the small amount of silver remaining in solution, by means of very dilute potassium bromide, containing about 1.19 mgrms. of the pure salt per gramme of solution. The solutions were in all cases weighed, thus avoiding errors due to fluid expansion, faulty graduation of burettes, &c. The titrations were performed in yellow light in an apparatus similar to that used by Stas, and with all the precautions insisted on by him as essential to the accuracy of such determinations.

The permanganate of silver crystallises readily from warm water, and is a very stable salt. It is also quite anhydrous and not in the slightest degree hygroscopic. From its small solubility it is easily freed from adhering impurities by recrystallisation. The purity of the salt was tested by reducing about 5 grms. by means of alcohol and filtering, when the total residue only weighed 1.9 mgrms. This residue when tested with the spectroscope was found to consist almost entirely of calcium salts from an accidental impurity in the distilled water, only the faintest trace of potassium being detected. The sample which was tested in this way had only been recrystallised once after precipitation. The salt was usually prepared by the precipitation of silver nitrate by means of an equivalent quantity of potassium permanganate, the solutions being warm, and the silver permanganate thus obtained in fine needles, was easily drained, washed, and recrystallised. A quantity of the salt was also prepared from crystallised barium permanganate, which was made from barium chloride and silver permanganate, the barium salt being afterwards decomposed with pure silver sulphate. This method of preparing the permanganate of silver ensures the absence of any trace of silver nitrate, which as Stas has shown adheres most persistently to many silver salts.

Permanganate of silver has several very important advantages over the other bodies previously used for the determination of the atomic weight of manganese. Its freedom from hygroscopic properties and

the improbability of its containing excess of any of the elements of which it is composed beyond what is necessary for the formation of the normal compound, recommend it especially for this purpose. Another point which rendered its selection important was to ascertain if a body liable to partial decomposition under certain circumstances could give concordant results in atomic weight determinations, thus putting to a crucial test the amount of variation in the values which may be attributed to secondary causes.

Table II gives the results of the titrations. The use of sulphurous acid as the reducing agent was found unsatisfactory, as a slight residue having the appearance of sulphide was almost always left undissolved. The production of sulphate was also more or less troublesome from its insolubility.

Table II.

No.	AgMnO <sub>4</sub> .	AgMnO <sub>4</sub> . Corrected for vacuo.	KBr.	KBr. Corrected for vacuo.	Equiva- lent of AgMnO <sub>4</sub> .	Reducing agent.
1	6·528	6·5289	3·4228	3·42385	227·094	Sulphurous Acid.
2	7·5368	7·5378	3·9541	3·9553	226·958	Nitrite of Potash.
3	6·1000	6·1008	3·20067	3·20166	226·937	"
4	5·7457	5·74647	3·00584	3·00677	227·606	Sulphurous Acid.
5	6·1651	6·16593	3·23503	3·23602	226·918	Formate of Soda.
6	5·1126	5·11329	2·68216	2·6828	226·984	"
7	5·0737	5·07438	2·6614	2·66204	227·013	Nitrite of Potash.
8	13·4466	13·4484	7·05385	7·05602	226·983	"
9	12·5782	12·5799	6·59861	6·60065	226·972	Hydrogen.
10	12·2686	12·27025	6·4361	6·43808	226·976	Nitrite of Potash.

Experiments (6) and (7) were made with a sample obtained from the barium salt, and these results are slightly higher owing to the presence of a small trace of barium sulphate easily recognisable by the slight turbidity of the reduced solution. We had hoped by the use of a larger quantity of material to arrive at results comparable in some degree at least with those of Stas; but we found the preparation of considerable quantities of material of absolute purity frequently involves sources of error not incurred in the production of smaller quantities. This we observed especially in the preparation of our pure potassium bromide, which contained traces of sulphates in every sample. This sulphate is due to the use of ordinary gas in the ignition of the pure bitartrate of potash from which the bromide of potassium was made. In order to get a pure product gas must be replaced by a powerful flame of alcohol, or all the operations conducted in a muffle.

The mean atomic weight of manganese which results from the

average of the eight determinations in which sulphurous acid was not employed as the reducing agent is 55.038, oxygen being taken as 16 and silver as Stas's value 107.93.

Thus another element is added to the list of those whose atomic weights have been found on revision to be exceedingly near whole numbers.

Further details and discussion must be reserved for another communication.

*February 22, 1883.*

#### THE PRESIDENT in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "The Effects of Temperature on the Electromotive Force and Resistance of Batteries." By WILLIAM HENRY PREECE, F.R.S., Received February 8, 1883.

It is well known that heat influences the conditions of galvanic elements so as to vary the strength of the currents generated by them in those parts of the circuits connecting their poles.

In 1840 De la Rive\* found that the action of a galvanic pair was accelerated when it was put into hot fluid instead of cold fluid, and he attributed the result to increased chemical affinity.

Faraday† repeated De la Rive's experiment, but he, on the other hand, attributed the result to improved conductivity in the liquid, and he showed that the effect was not due either to motion, to chemical action, or to thermo-electric action, or indeed to any increase in the electromotive force.

Daniell,‡ also, found an increased current due to increased temperature. According to him, one of his elements was nearly trebled in strength when raised to 212° F. He attributed the effect to the increased energy of the affinity. Said he, "Changes of temperature even have a marked influence upon the working of the voltaic battery, and must not be neglected in nice comparative experiments."

J. B. Cooke§ made careful observations on the chemical affinity in a

\* "Ann. Chem.," 1828, xxxvii, p. 242.

† "Researches," 17th Series, §§ 1925-26.

‡ "Chemical Philosophy," p. 506.

§ "Phil. Mag.," 1861, p. 95.