THE ATOMIC WEIGHT OF MOLYBDENUM.

By Edgar F. Smith and Philip Maas.

Received September 25, 1893.

THE present atomic value assigned this element is based upon the results obtained by Dumas (*Ann. Chem.*, **105**, 84, and **113**, 23), Debray (*Compt. rend.*, **66**, 734) and Lothar Meyer (*Ann. Chem.*, **169**, 365). The method pursued by Dumas consisted in the reduction of molybdenum trioxide. Debray also adopted this procedure, but in addition made several experiments upon the precipitation of the trioxide in an ammoniacal solution by silver nitrate. Lothar Meyer's value (95.9) is deduced from results obtained by Liechti and Kemp (*Ann. Chem.*, **169**, 344) in their analyses of the chlorides $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$. The chlorine in each was determined as silver chloride and the molybdenum as disulphide. Clarke (A Recalculation of the Atomic Weights, Washington, 1882) expresses the opinion that the most reliable results are those obtained by the reduction of the trioxide. Of the works of Liechti and Kemp he remarks, "traces of oxychlorides may possibly have contaminated the chlorides and augmented their atomic weights." Rammelsberg (*Ber. d. chem. Ges.*, **10**, 1776) made one experiment in the reduction of the trioxide, from which he calculated the atomic weight of molybdenum to be 96.18.

Thinking that additional light could be thrown upon the magnitude of this constant, by proceeding in a different direction, we utilized a reaction first observed by Debray (*Compt. rend.*, **46**, 1098, *Ann. Chem.*, **108**, 250), which in the hands of others (Pechard, *Compt. rend.*, **114**, 173; *Ztschr. anorgan. Chem.*, **1**, 262; Smith and Oberholtzer, *J. Am. Chem. Soc.*, **15**, 18, and *Ztschr. anorgan. Chem.*, **4**, 237) has proved to be a most excellent means of determining molybdenum and separating it from its intimate associate—tungsten. We refer to the action of hydrochloric acid gas upon molybdic acid and molybdates, whereby the molybdic acid is volatilized with ease in the form of an hydroxychloride—$MoO_3,2HCl$. Numerous trials have demonstrated that the reaction expressed by the equation, $Na_2MoO_4 + 4HCl = 2NaCl + MoO_3,2HCl + H_2O$, is quantitative. We exposed pure anhydrous sodium molybdate (at 150–200°) to the action of hydrochloric acid gas, volatilized the molybdenum trioxide, and from the weight of the residual sodium chloride calculated the atomic weight of molybdenum.

The sodium molybdate employed by us was Merck's purest preparation. We recrystallized it many times, and then by a careful examination satisfied ourselves that it did not contain silica, sulphates, tungstates, or alkaline carbonates,—substances that might have been present. The purified salt was dried with extreme care, until no further loss in weight was observed. In this anhydrous condition, it was preserved in clean weighing bottles, which were kept in desiccators to exclude dust and moisture. The specific gravity of the anhydrous salt was determined, alcohol being used for the purpose. The value found was 6.9780. The balance employed by us was of the Sartorius design.[1]

The weights of brass and platinum were of Westphal make and had been previously carefully adjusted for the purpose.

Tared porcelain boats were used to carry the anhydrous sodium molybdate, which was exposed in hard glass tubes to the action of pure and dry hydrochloric acid gas. This was prepared from salt and pure sulphuric acid. The gas as it was evolved, was first conducted through a U tube half-filled with damp silver chloride, it next passed through two flasks containing sulphuric acid, then through a tower of dry calcium chloride, and finally through clean cotton, after which it was admitted to the combustion tube, where it came in contact with the sodium molybdate. A very gentle heat was applied to the latter and gradually increased to from 150 to 200°C., beyond which the temperature was not permitted to rise. Moisture was excluded as much as possible. The volatilized $MoO_3 2HCl$ was collected in water. The boats containing the residual sodium chloride were allowed to cool in a slow current of hydrochloric acid gas, then transferred to vacuum desiccators, and the vapor repeatedly exhausted. The weights were taken after the boats had stood one hour. Second weighings were made, after the

[1] We would here acknowledge our indebtedness to Dr. John Marshall, of the Medical Department, University of Pennsylvania, for the privilege of using this excellent instrument.

boats had remained over night in the dry desiccators, and showed no appreciable alteration. Barometric pressure and temperature were carefully observed and all weighings reduced to the vacuum standard. Our results are as follows:

Na_2MoO_4 in grams.	NaCl. in grams.	Atomic weight of Mo.
1.14726	0.65087	96.130
0.89920	0.51023	96.094
0.70534	0.40020	96.108
0.70793	0.40182	96.031
1.26347	0.71695	96.087
1.15217	0.65367	96.126
0.90199	0.51188	96.067
0.81692	0.46358	96.077
0.65098	0.36942	96.073
0.80563	0.45717	96.078
	Mean	96.087
Maximum		96.130
Minimum		96.031
	Difference	0.099

In our calculations we used the following values: Na = 23.05, Cl = 35.45, and O = 16. These have been taken from a revised table of atomic weights published by Clarke, October, 1891.

The sodium chloride in five of the determinations just given was converted into silver chloride. From the calculated silver contained in the chloride we deduced the atomic value of molybdenum to be 96.10, the mean of five determinations. This figure we regard as confirmatory of the rest of our work.

The sodium chloride which we obtained dissolved readily, and to a clear solution in water. Molybdic acid was not found present in it. This was one of the points that we watched very closely, although its presence would have tended to diminish rather than augment the atomic weight found. Another cause of like result would have been moisture absorbed by the sodium chloride. Against this source of error we likewise took every precaution, and consequently feel that the result 96.08 obtained by us, approaches very closely to the true atomic magnitude of molybdenum.

UNIVERSITY OF PENNSYLVANIA.
September 16, 1893.