of the electrical properties of the solvents. In a metallic solution practically the whole of the conductance is through the solvent and undissociated solutes, while the "ionoids" which are electrolytically active tend, like ions, to acquire energy in the form of electric charges, but on account of the nature of the solvent retention of this energy is impossible and it is, in consequence, transformed and dissipated in the form of heat. Thus the electrical energy transformed into heat by the "ionoids" may be expressed in terms of specific resistance and consequently the ionic concentration in solid solution in metals may be determined by deducting from the total specific resistance that due to the solvent and undissociated solutes. Under the above conceptions the dissociation theory of solution would be just as applicable to solid solutions in metals as to aqueous solutions, although the phenomena, when the two solutions were subjected to a difference of potential at two points, would manifest themselves in opposite directions. The differences, however, in electrical behavior of the two solutions are due not to any fundamental difference in the atomic relations existing between solutes and solvent, but to the differences in the electrical properties of the solvents.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ATOMIC WEIGHT OF MOLYBDENUM.

BY JOHN H. MÜLLER.

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The purpose of the present investigation was to redetermine the atomic weight of molybdenum by the oxidation of pure metal. It will be recalled that as early as 1859 Dumas[1] oxidized the sulfide, reducing the resulting oxide in hydrogen to metal. The mean of six determinations was 95.942.

In 1868 Debray used the method of Dumas.[2] The trioxide, in this case, was purified by sublimation from platinum. The mean of three determinations was found to be 95.524. Later Rammelsberg,[3] from a single experiment, obtained a result very close to that of Dumas.

In 1895 Seubert and Pollard[4] determined the indirect ratio 2.AgCl :- MoO_3, subsequently reducing the trioxide to metal in hydrogen, with the result, Mo = 96.006.

Vandenberghe[5] reduced the dibromide to metal and oxidized the latter to trioxide by means of nitric acid. The mean of five determinations by this procedure was 96.088.

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[1] *Ann. Chem. Pharm.*, 105, 84, and 113, 23.

[2] *Compt. rend.*, 66, 734.

[3] *Berlin. Monatsb.*, 1877, p. 574.

[4] *Z. anorg. Chem.*, 8, 434 (1895).

[5] "Acad. Roy. Belge Mem. couronnes T.," 56.

Reagents.

Water.—Ordinary distilled water of the laboratory was redistilled, first from alkaline permanganate, then from acid permanganate, and finally alone. A block-tin condenser and well-seasoned Jena glass receivers were used.

Hydrogen Chloride.—This gas was prepared by the action of concentrated sulfuric acid upon concentrated hydrochloric acid and dried by passage through four wash bottles containing freshly dehydrated sulfuric acid. All connections were either fused or ground glass.

Ammonia.—This was prepared by warming ordinary ammonia water and conducting the gas through a double splash trap to an inverted large funnel, under which was placed a platinum dish containing water.

Hydrogen.—The hydrogen was obtained by electrolysis of 20% solution of caustic soda. Both electrodes were of pure nickel, while the generator of two liter capacity was so constructed that the inner compartment was entirely of glass—the wires being sealed in. The exit tube from the electrolytic cell was ground to fit the drying apparatus and was held in place by an external band of rubber. All other joints throughout the entire washing and drying system were fused. A current of five amperes furnished the maximum flow of gas. The latter was passed in turn through the following: silver nitrate, alkaline permanganate, concentrated sulfuric acid, broken caustic potash, a heated tube containing palladium asbestos, concentrated solution of caustic potash, concentrated sulfuric acid, drying tower (beads and sulfuric acid), soda lime and caustic potash tower, and phosphorus pentoxide.

Oxygen.—This gas was produced electrolytically from sodium hydroxide solution from an independent cell so as to take off the gas only from the inner compartment. The generator was the same as that used for the preparation of hydrogen, with the omission of the palladium asbestos tube. The oxygen was washed and dried as described under hydrogen.

Air.—The air was washed and dried by passing it through: (*a*) Silver nitrate and moist silver oxide; (*b*) 1-1 solution of caustic potash; (*c*) concentrated sulfuric acid; (*d*) concentrated sulfuric acid (tower and beads); (*e*) broken stick potash and soda lime; (*f*) phosphorus pentoxide.

Preparation of Molybdic Oxide.—500 g. of commercial molybdic oxide were converted to ammonium molybdate and treated with a little ammonium sulfide, filtered and evaporated to crystallization. The crude salt was recrystallized five times in large porcelain vessels. The resulting product was ignited to oxide and subjected to volatilization in hydrochloric acid gas. This was done without regard to temperature regulation. The first and last portions of the sublimate were discarded, the intermediate product being converted into ammonium molybdate. Large platinum dishes were the containing vessels. After evaporation of the ammoniacal solution to dryness, the residue was transferred to quartz dishes and therein ignited.

The oxide thus obtained was placed in large quartz boats in a wide bore quartz tube and subjected to a fractional sublimation in air—at a temperature just below the fusing point, the crystalline sublimate being continuously removed from the quartz tube. About one-half of the oxide was sublimed from each charge, the remaining portions being discarded. It was noticed that the boats and a narrow strip of the quartz tube beneath the boats were superficially etched by the long-continued heating—due possibly to a small quantity of alkali present in the oxide. A portion of the sublimate, however, showed no tendency to etch a fresh boat even after twenty hours' ignition at a slightly higher temperature than that of the original sublimation. From 65 g. of oxide 45 g. of sublimate were obtained and constituted the starting product for a more careful fractionation in hydrochloric acid gas. The sublimation of molybdenum hydroxychloride was carried out in the apparatus shown in Fig. I.

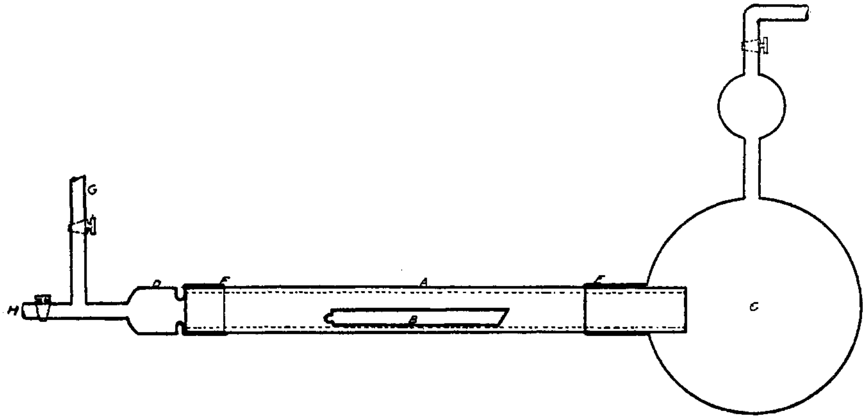

Fig. I.

A. Quartz tube 2 cm. diam., length 80 cm.
B. Large quartz boat.
C. $^1/_2$ L. jena glass bulb.
D. Adapter ground to fit A, held in place by external band of rubber at F.
G. Entrance for dry air.
H. Entrance for dry HCl.

The temperature was not allowed to exceed 250° throughout the operation. A slow current of dry air was first passed in at G to expel all traces of moisture, after which precaution it was possible to sublime large quantities of the oxychloride with no stoppage of the quartz tube. In the absence of all moisture, the very bulky sublimate showed no tendency to stick to the sides of the receiving bulb so that after removal of the excess of hydrogen chloride by dry air the contents of C could be almost completely shaken out into a quartz beaker. To avoid the taking of alkali from the Jena glass bulb, washing was omitted. The sublimate was dissolved in water and the aqueous solution transferred from the quartz vessels to ammonia water contained in platinum dishes. After evaporation to dryness the residue was ignited to oxide in vessels of quartz.

The sublimation above described was repeated four times, each operation removing smaller residues of unsublimed oxide, the last portion leaving no weighable residue after heating to 200° in HCl. The final fraction of molybdenum trioxide thus obtained was resublimed in hydrochloric acid gas, dividing it into thirds. These three portions, upon conversion to metal, constituted Fractions I, II and III, used in determining the ratio of metal to oxide.

Metallic Molybdenum.—The molybdic oxide prepared as above was reduced to metal in quartz boats. A preliminary reduction was found quite necessary because an appreciable quantity of oxide in the final reduction led to the condensation of water in the vacuum apparatus, manometer tubes, etc. Its removal was difficult and time consuming.

The writer wishes to lay particular stress on the fact that the physical condition of the metal had much to do with the ease or the difficulty with which subsequent oxidation could be carried out. A very porous, finely divided material could not be obtained from the pure oxide after the latter was ignited at a temperature high enough to cause much crystallization, but if the ammoniacal solution of the hydroxychloride was only very gently ignited so as to expel only the excess of ammonium chloride—the non-crystalline residue could be very slowly reduced with the production of metal offering maximum surface and facilitating complete oxidation. The metal obtained as outlined above was preserved in a desiccator. It was used in the following determinations: (Fractions I, II and III.) The combustion furnace K, Fig. II, was constructed of asbestos, covered externally with sheet iron. A battery of special burners developed a temperature within the quartz core of more than 1000°. The furnace was cut longitudinally in equal parts so that it could be removed from the stationary quartz tube while the latter was at white heat,

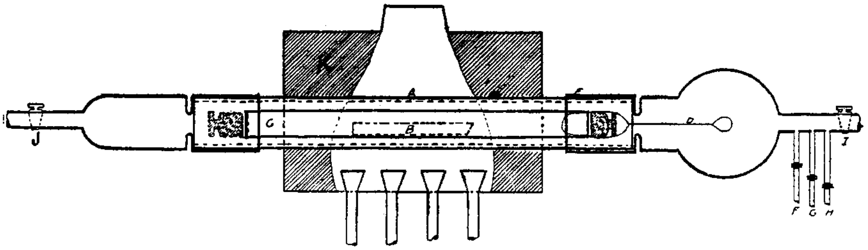

Fig. II.

This saved much time in cooling the charge and minimized error from leakage of air into the evacuated tube during the process of cooling to room temperature. The special advantage of a quartz tube here was evident as cold water could be applied to the hot tube immediately after removing the furnace sections, effecting a cooling to room temperature in a short time.

Apparatus for Reduction.—The apparatus used in the final production of metal was arranged as in Fig. II, A, a thick-walled quartz tube 90 cm. in length, internal diameter about 2 cm., into which was placed the bottling tube of clear quartz, C, containing boat B and metal. The quartz stoppers were pushed into place before removing the inner tube for transference of boat to weighing tube. Connections at J and E were ground and strong external bands of rubber were used to hold the glass adapters in close contact with the quartz tube. F was connected with a manometer to an air pump, H, to air apparatus, I, to a sulfuric acid trap for the exit of hydrogen current. The glass stopcocks at F, G, H, I, and J were all carefully reground with the finest procurable emery dust and were lubricated with metaphosphoric acid. No measurable leakage into the vacuum was noticed after one-half hour's standing, this test being applied before each reduction was carried out.

The use of a vacuum pump in the reduction of the metal served two purposes: first, the rapid and complete removal of air before each heating of metal to constant weight—as pure, dry hydrogen could be slowly admitted at J and the washing of the contents of the tube in this gas be carried out several times before applying heat; secondly, the subsequent cooling of the metal was effected *in vacuo* and the cooled metal then washed in dry air admitted at H before the bottling tube was removed by the platinum wire D.

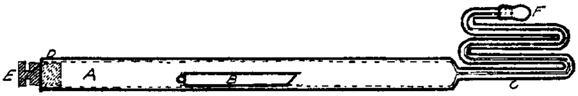

Fig. III.

A. Thick-walled transparent quartz tube, length 20 cm., inner diam. 15 mm., weight 32 grams.
B. Quartz boat containing metal.
C. Capillary tube length 14 cm., ground cap at F.
End of tube at D ground inside to fit stopper E and outside beveled to fit oxygen apparatus.

Weighing Tube and Counterpoise.—Weighing tube and counterpoise shown in Fig. III were almost identical in weight and shape, the weight of the latter being brought to within a milligram of the former by the introduction of a small quartz rod.

Apparatus for Oxidation.—Arranged as in Fig. IV. The entire apparatus was protected from dust by enclosure in a large glass compartment with a narrow opening at the top to permit the escape of heat.

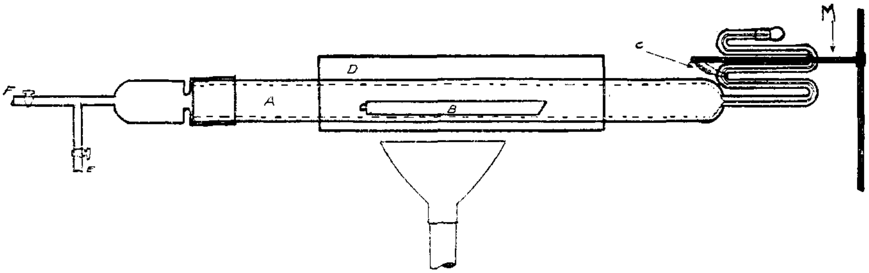

Fig. IV.

A. Quartz weighing tube boat at B.
C. Platinum wire and spring to hold A in place.
E and F. Air and oxygen.
D. Quartz jacket tube to protect A from direct flame.
M. Fork to hold platinum wire.

All of apparatus shown in figure was enclosed in a large glass chamber to avoid dust.

Balance and Weights.—The balance used was a Troemner No. 10; sensibility factor, 0.00022 g. Weights, gold plated, were calibrated by Richard's substitution method. No rider was used. To eliminate small errors in weighing from static charges upon the quartz weighing tubes some highly radioactive residues were placed within the balance case. It was observed that quartz possesses the property of holding a static charge to a degree far surpassing that of glass, and weighings carried out without the aid of radioactive material were only satisfactory after a period of several hours for the establishment of equilibrium. The above-mentioned material lessened the time required for weighing and eliminated troublesome irregularities which could only be traced to charges upon the quartz apparatus. Forefinger and thumb stalls of lint free linen much facilitated the manipulation of weighing tube and counterpoise and were found much more convenient than either tongs or handkerchief.

Specific Gravity of Metal and Trioxide.

The means of three determinations for both metal and trioxide were used for vacuum corrections. Pure toluene, freshly distilled over sodium at 110°, was selected for the determination, previous experiment having established the complete unalterability of metal and oxide in this liquid.

		Mo.		MoO_3.
D_4^{26}	(*a*)	10.270	D_4^{26}	4.659
D_4^{26}	(*b*)	10.296	D_4^{26}	4.669
D_4^{26}	(*c*)	10.278	D_4^{26}	4.760
Mean,		10.281	Mean,	4.696

Ratio Mo : MoO_3.

Mo taken *in vacuo.*	Total number of hours heating in hydrogen at 1000°.	MoO_3 found *in vacuo.*	Atomic weight.
	FRACTION I.		
(*a*) 0.52591	25	0.78879	96.027
(*b*) 0.56327	20	0.84487	96.012
(*c*) 1.12757	24	1.69117	96.031
	FRACTION II.		
(*a*) 0.53014	21	0.79517	96.014
(*b*) 1.10754	20	1.66130	96.002
(*c*) 1.62166	21	2.43181	96.080
(*d*) 1.45530	22	2.18259	96.047
	FRACTION III.		
(*a*) 0.94968	18	1.42428	96.048
(*b*) 0.65659	20	0.9870	96.054
		Mean,	96.035
		Mean omitting (*c*) Fraction II,	96.029

In the first three of the above determinations (Fraction I), the metal was heated in hydrogen for periods of about six hours each and required four weighings to obtain constant weight (error ±0.00002). In the later determinations the time of ignition was extended to over seven hours in hydrogen and averaged three weighings to secure constant weight within the same limit of error. Preceding each reheating, all air was removed by evacuating the tube—refilling the vacuum several times with hydrogen (stopcocks J and G, Fig. II).

After ignition the sectional furnace K was removed—the tube again evacuated while still hot. After complete cooling had taken place, the vacuum was refilled by a current of air through (H), several operations insuring the removal of all traces of hydrogen.

The bottling tube C, Fig. II, was closed before removal from the ignition tube and the transference of the boat to weighing tube (Fig. III) effected by bringing the ground end of C to the open end of the weighing tube, pushing the boat into place with a quartz rod. Tube and counterpoise were desiccated over phosphorus pentoxide twelve hours before weighing. The oxidation of the metal was carried out as shown in Fig. IV. Heating in a very slow current of air was continued until nearly all of the metal was oxidized. The stopcock E was then closed, admitting oxygen at F to complete the operation at a more elevated temperature. The quartz jacket D served to protect the weighing tube from direct heating and also to secure a more uniform temperature for the tube and contents.

The temperature was regulated so as to avoid all signs of sintering of the oxide and at no time was high enough to cause more than a slight volatilization of the oxide above the boat. The weighing tube A was held in the ground adapter F by the platinum wire and spiral springs at C. As the inital heatings in air and oxygen were carried out at the lowest reacting temperature, the time required to complete the oxidation was nearly as great as that expended in the reduction to metal, averaging about fifteen hours.

It will be noticed that the result of determination C, Fraction II, is considerably higher than the other values obtained, which can probably be explained by the fact that the boat was in this instance taxed to its limit of capacity—the metal requiring an abnormally long series of heatings in oxygen to constant weight while some doubt was entertained as to the complete reduction of this larger quantity of metal. In view of the above considerations, the writer feels justified in selecting the mean of the eight more concordant results (96.029) as the most probable value.

The practically perfect condition of the quartz boat and weighing tube after all of the above determinations—representing about 190 hours in hydrogen at 1000° for the former and about 150 hours for both tube and boat in air and oxygen near the subliming point of oxide, proved conclusively that metallic molybdenum and its oxides have no effect on quartz through a wide temperature range. This fact is of interest as other more commonly used substances, porcelain and platinum in particular, are very decidely affected under like circumstances.

Effort was made to prepare molybdic acid without using quartz or platinum vessels, but the product obtained could not be subsequently sublimed in quartz without a decided etching of the boat and tube. Several samples of supposedly pure oxide from different sources likewise showed a noticeable effect upon quartz when an air sublimation was attempted. Hence, it was concluded that the etching in the above mentioned cases must be laid to the presence of small quantities of alkali and not to any action of molybdenum or its oxides. Possible error from volatilization of the oxide during the long periods of heating in air and oxygen seemed to have been entirely obviated by the special construction of the weighing tube (Fig. III).

Preliminary experiments were made to establish this—using a temperature much higher than that used in the actual determinations—all of the oxide having been driven out of the boat into the weighing tube to a point close to the capillary without loss in weight.

Behavior of Metallic Molybdenum in Hydrogen.

The possible absorption of hydrogen by metallic molybdenum and consequent source of error was investigated through a range of temperature from 0° to 600°, fixing the pressure at 0.5 mm. and plotting weight against temperature.

The apparatus used was similar to that shown in Fig. II, less the furnace K and the inner tube C. The heavy quartz tube A was surrounded by an asbestos covered metal jacket furnished with a pyrometer. Approximately three grams of molybdenum were introduced into the weighing tube (Fig. III) which was then sealed off at the wide end, leaving open only the capillary C. The weighing tube containing metal was now introduced into the quartz ignition tube and the apparatus then evacuated, refilling repeatedly with hydrogen to expel all air. The tube was then raised to red heat for seven hours and finally cooled to room temperature in hydrogen. The inital weighing was taken after evacuation of the hydrogen at 20° and replacement of the latter by air. A series of weighings were then made, fixing the pressure in hydrogen at 5 mm. and cooling to room temperature at this pressure in hydrogen before replacing the latter by air.

Cooled from	Pressure in hydrogen. Mm.	Weight of metal in grams.
20° to 0°	760	3.31980
50° to 20°	760	3.31981
100° to 20°	0.5	3.31994
200° to 20°	0.5	3.32001
360° to 20°	0.5	3.31997
500° to 20°	0.5	3.31991
580° to 20°	0.5	3.31988

From these results it was concluded that any error due to absorption of hydrogen by the metal was negligible and that the evacuation of tube and replacement of hydrogen by dry air, as carried out in all of the determinations of the ratio of metal to oxide, accomplished the complete removal of hydrogen from the metal.

Conclusion.

In concluding, it may be stated that the method used in the preceding experiments for determining the ratio of molybdenum to its trioxide differs from other investigations of the same ratio in the following essentials:

1. The purification of materials was greatly aided by the use of pure quartz apparatus which proved to be quite unaffected by molybdenum and its oxides.

2. Provision was made for complete prevention of loss of molybdic oxide by volatilization.

3. An air sublimation of the trioxide in quartz and the fractionation of molybdenum hydroxychloride to constant composition under carefully regulated temperature conditions to insure complete absence of tungsten.

4. A protracted preliminary reduction of the oxide in large boats offering maximum surface for complete removal of oxygen, and, finally, the choice of an oxidation of the metal in place of the reduction of the weighed oxide, made possible through the use of the quartz bottling apparatus together with the construction of a weighing tube to prevent loss of oxide.

PHILADELPHIA, PA.