

other considerations to be presented subsequently. In a recent article Thiele<sup>1</sup> has assigned hydronitric acid the same structure as that advanced in this note. While the conclusions are similar, the one was arrived at through organic considerations, while the other was reached through a study of the inorganic chemistry of the acid. That the conclusions were arrived at quite independently may be further attested by the fact that the matter here presented was communicated by correspondence, and otherwise, to various members of the chemical profession almost a year ago, and months before the appearance of the article in the *Berichte*.

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## SOLUBILITY OF WROUGHT TUNGSTEN AND MOLYBDENUM.

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Since the production of tungsten and molybdenum metals in a malleable and ductile form,<sup>2</sup> various interesting applications have been found for these metals. Probably the most extensive use for tungsten at present is in metal filament lamps, but this metal, combining the physical properties of high melting point (3000°), high specific gravity (19.3), low vapor pressure and high heat conductivity, has found use as a contact metal in numerous current interrupting devices, as a target in Röntgen tubes, and as a possible projectile material.<sup>3</sup>

It is the purpose of this paper to point out some of the chemical properties of these wrought metals, which, combined with their physical properties already described, may broaden the field of application of these two interesting metals.

### Tungsten.

In the following experiments the samples of metal used were all of the same surface and shape. They were discs, of sheet tungsten, such as are now being used for X-ray targets, and are 18 mm. in diameter and about 2.5 mm. thick. The surface area was  $510 + 140 = 650$  sq. mm. on the average. The weight, according to thickness, varied from 9 to 12 grams.

*Solubility in Hydrochloric Acid.*—Wrought tungsten is insoluble in hydrochloric acid of any concentration at room temperature and only very slightly so at 110°. After 45 hours the hot, concentrated acid (sp. gr. 1.15) showed no effect upon the tungsten. After 175 hours, however, a black coating of oxide formed and the metal lost 0.5% in weight.

In dilute acid, at 110°, it lost 0.05% after 22 hours but showed no further loss after 50 hours. After 175 hours the metal was coated with tungstic oxide and there was a gain in weight of 1% due to oxidation. This

<sup>1</sup> *Ber.*, 44, 2522 (1911).

<sup>2</sup> Fink, *Trans. Am. Electrochem. Soc.*, 17, 229-234. Coolidge, *Proc. Am. Inst. E. E.*, 29, Part II, 961-965.

<sup>3</sup> Coolidge, *J. Ind. Eng. Chem.*, 4, 2 (1912).

oxide formed an adherent coating and protected the metal against further loss.

*Solubility in Sulfuric Acid.*—At room temperature this acid has no effect upon wrought tungsten nor has the dilute acid at  $110^{\circ}$ . Concentrated acid attacks it very slowly at  $110^{\circ}$ , the loss in weight being 0.1% after 18 hours, 0.16% after 40 hours, and 0.63% after 175 hours. Increased temperature hastens the action, for at  $200^{\circ}$  0.62% was lost in four hours. In another experiment 1.18% dissolved in 8 hours.

*Solubility in Nitric Acid.*—Concentrated nitric acid at  $110^{\circ}$  showed no action on tungsten after 48 hours other than a slight dulling of the bright, metallic surface. The dilute acid, however, produces the yellow oxide on the surface. There is a slight gain in weight after 15 hours and then no further change even after 175 hours' immersion.

*Solubility in Aqua regia.*—Aqua regia, at room temperatures, oxidizes the surface to tungstic oxide. After 215 hours the loss in weight was 0.31%. At  $110^{\circ}$  the chlorine was all driven off in about 4 hours and the tungsten disc had lost 0.1% and it was covered by a tough, greenish yellow deposit. If this coating of oxide was allowed to remain, continued boiling in fresh aqua regia had no further effect upon the metal.

*Solubility in Hydrofluoric Acid.*—This acid, hot or cold, did not attack tungsten, not even to the extent of dulling its polished surface, during numerous evaporations of the acid.

*Solubility in Potassium Hydroxide.*—Potassium hydroxide solution, of any concentration, does not attack wrought tungsten but the fused alkali attacks the metal slowly. In this case there was 31% loss in weight after 15 hours and in about 40 hours the disc had all dissolved.

*Solubility in Alkaline Carbonate.*—In fused sodium carbonate, potassium carbonate, or mixtures of the two, tungsten dissolves slowly. About 2.5% loss was noted in four hours. The addition of potassium nitrate hastens the solution considerably. In this experiment 32% dissolved in six hours.

*Other Experiments.*—A saturated sodium hypochlorite solution was found to attack tungsten at the rate of 4.27% in twenty hours. A mixture of sulfuric acid and chromic anhydride did not act upon the metal. A mixture of hydrofluoric and nitric acids dissolves tungsten very rapidly with the evolution of nitric oxide and the production of tungstic oxide.

### Molybdenum.

In the following experiments small strips of sheet molybdenum were used. These were  $30 \times 9 \times 0.4$  mm., having a total surface of 540 sq. mm.

*Hydrochloric acid*, diluted, slowly dissolves molybdenum at  $110^{\circ}$  to a brown solution with the formation of some black oxide, probably  $\text{Mo}_2\text{O}_3$ . The loss in weight was 20.3% after 18 hours. The more concentrated acid (1.15) has a much slower action. After keeping the metal for 18

hours in this acid at  $110^{\circ}$  C. the total loss of metal was only 0.34% and the surface was still bright.

*Sulfuric acid*, diluted (sp. gr. 1.30), at  $110^{\circ}$  does not attack molybdenum. The concentrated acid (sp. gr. 1.82) attacks it but very slowly at this temperature. Only 0.29% loss in weight was found after 18 hours. With elevated temperatures, however ( $200-250^{\circ}$ ), the metal dissolves rapidly to a green solution, with the evolution of sulfur dioxide.

*Nitric acid*, concentrated (sp. gr. 1.40), dissolves molybdenum slowly with the formation of molybdic anhydride,  $\text{MoO}_3$ , which deposits on the surface of the metal and retards the action. The more dilute acid (sp. gr. 1.15), however, attacks the metal rapidly.

*Aqua regia* also dissolves the metal rapidly, especially if heated.

*Hydrofluoric acid* (hot or cold) does not attack molybdenum.

*Potassium hydroxide* solutions do not attack molybdenum, but it is soluble in the fused alkali.

It will be noted that both of these metals are to a certain extent acid-resisting and this is due principally to the formation of an acid-resisting coating of oxide. Tungsten is attacked most rapidly by fuming sulfuric acid, and this only to the extent of 1.2% in 8 hours.

*Molybdenum* is much more easily dissolved than tungsten. It resists concentrated hydrochloric and sulfuric acids at moderate temperatures (below  $125^{\circ}$ ) fairly well and is untouched by hydrofluoric acid.

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## PERCHLORIC ACID IN ELECTROCHEMICAL ANALYSIS.

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In the latter part of the academic year 1910-'11 the writer made electrolytic separations of certain metals from perchloric acid solution with good results. The pressure of other duties made it necessary to discontinue the work for a time. In the meantime Henryk Golblum<sup>1</sup> has published a paper on the determination of perchloric acid in the perchlorates of nickel and cobalt, his method being to deposit the metals electrolytically and titrate the acid left in solution. Though the determination of the metals was apparently not his object, he states that they were deposited quantitatively, and that the method for the determination of the acid would probably be found applicable in all perchlorates whose metals can be deposited in weak acid solutions. Since these statements seem to foreshadow work in the direction of my own, it seems desirable to publish a brief statement of the work done in this laboratory.

<sup>1</sup> *Z. anal. Chem.*, 1911, 741.