



Fig. 9.

strongly to the fact that the above relationship is apparently more than a fortuitous one.

TABLE III

APPROXIMATE^a PHOTOELECTRIC THRESHOLDS OF SILVER, GOLD AND COPPER

Metal	Metal in solution	Threshold wave length, Å.		
		No Metal in a vacuum outgassing	Partial outgassing	Extended outgassing
Silver	4900	3200-3400	2900-3100	2600-2700
Gold	4900	2625	2600-2800	2650-2610
Copper	4900	2700-3000	2700-3000	

^a Column 2, this research; columns 3, 4, and 5, compiled from those given by Hughes and DuBridge, ref. 3, p. 75.

Summary

The spectral sensitivities of copper, silver and gold electrodes have been determined for a number

of lines of monochromatic radiation ranging from $\lambda = 3650$ to $\lambda = 6908$ Å. The photovoltaic threshold values for these metal electrodes have been determined.

The sensitivity of coated metal electrodes and some metal electrodes at $\lambda = 5461$ Å. is attributed to the coating on the electrode.

A similarity in the mechanism of the photovoltaic and photoelectric effects is suggested from a comparison of the photoelectric threshold values of metals at various stages of outgassing and the photovoltaic threshold value.

A vacuum tube circuit employing an F.P.-54 Plotron tube is described as suitable for the measurement of photopotentials.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

The Preparation and Identification of Three Alkali Molybdotellurates¹

BY S. R. WOOD AND ARTHUR CARLSON

The systematic preparation and study of salts of the complex heteropolyacids of molybdenum and tellurium are comparatively recent developments in inorganic chemistry. In 1910 Miolati² prepared a compound of apparent formula $\text{Te}_2\text{O}_{11} \cdot \text{K}_{10} \cdot 12\text{MoO}_3 \cdot 18\text{H}_2\text{O}$, or possibly $\text{TeO}_6 \cdot \text{K}_5\text{H} \cdot 6\text{MoO}_3 \cdot 8\text{H}_2\text{O}$. In 1929 Meloche and Woodstock³

(1) This is an abstract of a thesis submitted by S. R. Wood in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin in 1933, and of a thesis submitted by Arthur Carlson to the faculty of the Department of Chemistry of Oklahoma A. and M. College in partial fulfillment of the requirements for the degree of Master of Science in 1938.

(2) Miolati, *Z. physik. Chem.*, **70**, 330-334 (1910).

(3) Meloche and Woodstock, *THIS JOURNAL*, **61**, 171-174 (1929).

isolated and analyzed two ammonium molybdotellurates, which proved to have the empirical formulas $3(\text{NH}_4)_2\text{O} \cdot 2\text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 10\text{H}_2\text{O}$ and $3(\text{NH}_4)_2\text{O} \cdot \text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 7\text{H}_2\text{O}$. Since that time Hansen⁴ prepared and described a potassium salt, $3\text{K}_2\text{O} \cdot \text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 8\text{H}_2\text{O}$; Thomsen⁵ studied a sodium molybdotellurate, $3\text{Na}_2\text{O} \cdot \text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 22\text{H}_2\text{O}$; and Dyess⁶ reported the composition of the lithium salt to be $3\text{Li}_2\text{O} \cdot \text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 13\text{H}_2\text{O}$. Specimens of the salts of sodium, lithium, cesium,

(4) H. F. Hansen, unpublished thesis, University of Wisconsin, 1930.

(5) Thomsen, unpublished thesis, University of Wisconsin, 1933.

(6) Dyess, unpublished thesis, Oklahoma A. and M. College, 1934.

ammonium (monotellurate) prepared by Wood and the ammonium ditellurate prepared by Meloche were subjected to crystallographic and optical examinations by Donnay and Melon.⁷

Thus most of the alkali metals form corresponding compounds of the type $3M_2O \cdot TeO_3 \cdot 6MoO_3 \cdot nH_2O$. The work here reported was undertaken to learn whether rubidium and cesium yield similar complex salts. By evaporating a solution containing alkali metal hydroxides, telluric acid, and molybdenum trioxide in the proper proportions, we have indeed obtained a rubidium salt, $3Rb_2O \cdot TeO_3 \cdot 6MoO_3 \cdot 6H_2O$ and a cesium salt, $3Cs_2O \cdot TeO_3 \cdot 6MoO_3 \cdot 7H_2O$. We also have duplicated the preparation of the sodium salt already mentioned and verified its composition. All of these salts are beautifully crystalline, but effloresce rapidly when exposed to the open air.

It is worthy of note that all the alkali metal molybdotellurates can be formulated satisfactorily according to the Miolati-Rosenheim theory⁸ as $M_6[Te(MoO_4)_6] \cdot nH_2O$. The original salt of this type prepared by Miolati was apparently an acid salt, $K_3H[Te(MoO_4)_6] \cdot 8H_2O$, having the same degree of hydration as the normal salt.

Materials Used: Telluric Acid.—Pure telluric acid was prepared by a modification of the Staudenmeyer⁹ method. This procedure depends on the chromic acid oxidation of pure tellurium dioxide in dilute nitric acid solution. Six recrystallizations were carried out to ensure a very pure product. Analyses of the telluric acid for tellurium showed that it was 99.86% pure.

Molybdic Oxide.—Analyzed molybdic anhydride of 99.9% purity was used.

Cesium Nitrate.—Pure cesium nitrate was used.

Rubidium Hydroxide.—The rubidium hydroxide was prepared by treating pure rubidium chloride with the stoichiometrically calculated amount of pure silver oxide. The precipitated silver chloride was filtered off, leaving rubidium hydroxide in solution. This base was recovered by evaporation.

Sodium Hydroxide.—C. P. sodium hydroxide was used.

Preparation.—In the preparation of these salts, the reagents were dissolved in water, in the ratios of 0.06 mole of the respective alkali metal compounds, sodium hydroxide, rubidium hydroxide, or cesium nitrate, to 0.01 mole of pure telluric acid to 0.06 mole of molybdenum trioxide. The clear solution was then evaporated to a small volume on a water-bath. On cooling, colorless crystals appeared. Each of the three compounds was recrystallized from water six times. In order to prepare

samples for analysis, the crystals were dried by successive washings with alcohol and ether.

Methods of Analysis: Tellurium.—The tellurium content of the compounds was determined by the Lenher-Homberger¹⁰ method in which elementary tellurium was precipitated by the combined action of water saturated with sulfur dioxide and a solution of hydrazine hydrate upon a dilute acid solution of the sample.

Molybdenum Trioxide.—The filtrate from the tellurium analysis was evaporated to dryness on a hot-plate and fumed with 10 ml. of concentrated sulfuric acid. After the resulting solution had been diluted until the acid concentration was about 6%, the molybdenum was determined by reduction in a Jones reductor and titration with potassium permanganate. The titration was corrected by a blank. Standardization of the permanganate was made upon both sodium oxalate and pure molybdenum trioxide.

Alkali Metals.—Original samples were taken for the determination of rubidium, cesium, and sodium in the respective salts. The sample was placed in a previously weighed porcelain boat, and the boat placed inside a combustion tube. It was then heated to 500° for several hours in a stream of dry hydrogen chloride gas, the temperature being observed by the use of a thermoelectric pyrometer. Tellurium and molybdenum were thus converted to volatile oxychlorides, which sublimed away to the cooler portions of the tube. This left as residue the respective alkali chlorides which were weighed.

Water.—According to the usual practice, the hydrated salt was weighed, then dried at 110° to constant weight.

Thomsen in his analysis found the sodium molybdotellurate to contain 22 moles of water to each mole of salt. His method of determining water lay in heating a 0.5-g. sample in a combustion tube for several hours at 200°, the evolved water being swept into a tared phosphorus pentoxide tube with dried air. One of us determined the water by drying to constant weight, thus verifying the formula previously found by Thomsen.

Properties.—In appearance, all of the salts are composed of crystals of very definite and characteristic qualities. The crystals in the pure state are colorless, hexagonal rhombohedra. The cesium salts tend to crystallize out as somewhat larger crystals. When the sodium salt was allowed to crystallize slowly, crystals of enormous size were obtained, some being 2–3 cm. in length. All three of the salts are of a highly efflorescent character. When newly crystallized, they are transparent to translucent and possess a decided luster. When removed from the mother liquor and left exposed to the air, the surface turns white and opaque in a few hours time, and in a few days they crumble away to an opaque white powder.

Anal. Calcd. for $3Cs_2O \cdot TeO_3 \cdot 6MoO_3 \cdot 7H_2O$: Cs_2O , 42.02; TeO_3 , 8.73; MoO_3 , 42.98; H_2O , 6.27. Found: Cs_2O , 42.06; TeO_3 , 8.62; MoO_3 , 42.92; H_2O , 6.25.

Anal. Calcd. for $3Rb_2O \cdot TeO_3 \cdot 6MoO_3 \cdot 6H_2O$: Rb_2O , 32.82; TeO_3 , 10.27; MoO_3 , 50.58; H_2O , 6.33. Found: Rb_2O , 32.77; TeO_3 , 10.15; MoO_3 , 50.53; H_2O , 6.26.

Anal. Calcd. for $3Na_2O \cdot TeO_3 \cdot 6MoO_3 \cdot 22H_2O$: Na_2O , 11.47; TeO_3 , 10.82; MoO_3 , 53.27; H_2O , 24.44. Found: Na_2O , 11.55; TeO_3 , 10.78; MoO_3 , 53.16; H_2O , 24.37.

(7) Donnay and Melon, *Am. Mineral.*, **18**, 225–247 (1933); **21**, 125–127, 250–257, 299–311 (1936); *Am. Soc. Geol. Belg. Bull.*, **57**, 39–52 (1933–1934).

(8) Ephraim, "Textbook of Inorganic Chemistry," translated by Thorne, Gurney and Jackson, London, 1934, pp. 435–437.

(9) Staudenmeyer, *Z. anorg. Chem.*, **10**, 189 (1895).

(10) Lenher and Homberger, *THIS JOURNAL*, **30**, 387 (1908).

Summary

A rubidium molybdotellurate, $3\text{Rb}_2\text{O}\cdot\text{TeO}_3\cdot 6\text{MoO}_3\cdot 6\text{H}_2\text{O}$, and a cesium molybdotellurate, $3\text{Cs}_2\text{O}\cdot\text{TeO}_3\cdot 6\text{MoO}_3\cdot 7\text{H}_2\text{O}$, have been isolated and analyzed for the first time. The sodium molybdotellurate described by Thomsen has again been

prepared and its composition verified. The alkali metal molybdotellurates form a corresponding series with the general formula $3\text{M}_2\text{O}\cdot\text{TeO}_3\cdot 6\text{MoO}_3\cdot n\text{H}_2\text{O}$, perhaps to be written as $\text{M}_6[\text{Te}(\text{MoO}_4)_6]\cdot n\text{H}_2\text{O}$.

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Molecular and Cybotactic Weight Measurements of Resinous and Crystalline Materials¹

BY HOWARD L. BENDER

Introduction

In the analytical determination of molecular weight numbers for phenol-formaldehyde resins, for crystalline abietic acid, and for some crystalline materials used as standards, irregularities were noted in the boiling points of their solutions. These changes are considered as a function of the time and of the initial temperature used in making the solutions. The molecular weights calculated from the boiling points of the solutions thus showed wide fluctuations. It is not considered that actual molecular structures are varying to the extent shown by these measured changes.

Irregular variations occur in resin solutions as shown² by increasing and decreasing viscosity measurements on the same solution held under constant conditions. Also thixotropic and similar structural changes occur under experimental variations.

These changing viscosity data imply a very puzzling shift in the determined molecular weight where the Staudinger viscosity rule is used to calculate the magnitude of the chemical molecules.

For solutions of resins, these calculated "molecular weights" shift with change of time conditions, even though boiling point temperature measurements were made with the same solvent, same resin sample and same temperature conditions. Thus for such solutions, analytical molecular weight values are an uncertain foundation upon which to build structural molecular formulas.

Stewart³ has coined an apt term for application to changing liquid particles to meet such a diffi-

culty of stability phenomena in the field of pure liquids. According to this concept, the term "cybotaxis" is applied to describe the state wherein easily changed cybotactic groups of molecules are changing in particle size from dimolecules to a factor of approximately one thousand molecules. By Stewart's theory, when liquid molecules collide they temporarily adhere into groups but move from group to group so rapidly that actual particle detection is very difficult in low viscosity liquids.

It is now suggested that this term cybotaxis gives an apt and convenient term to describe the unstability state manifested by the unstability of supercooled liquid particles. Measurements are here given for this type material suspended in solvent solutions. The term cybotactic weight is thus proposed to replace the molecular weight number calculated from the effect of such resinous particles in solution. The proposed cybotactic analytical weight is thus a determined but transitory average value obtained by the use of ordinary molecular weight constants. Hence choice of terms between molecular weight and cybotactic weight depends upon a factor of constancy over an extended time period. This cybotactic weight value thus is a convenient analytical method for expressing the momentarily average particle size of an easily changed particle which will vary directly with the average disintegration of the mass in the solvent medium used. The values found for resins will vary with the conditions used for the determination so the conditions, including time, should always be carefully stated. The term cybotactic weight thus emphasizes the supercooled liquid state of resins. The high viscosity of undercooled liquids at the temperature of solidi-

(1) Delivered at the Baltimore Meeting of the A. C. S. Paint and Varnish Division, April, 1939.

(2) Alexander, "Colloid Chemistry," Vol. IV, The Chemical Catalog Company, New York, N. Y., 1926, p. 360.

(3) C. W. Stewart, *Trans. Faraday Soc.*, **33**, 238 (1937).