

of  $T_c$  equal to 669, 628, 602 and 560°K., respectively. However, allotropy of the liquid nitroparaffins, whether due to changes in molecular aggregation or to other causes, would probably affect surface tension. Within the temperature range here reported, such effects seem to be absent.

### Summary

1. The surface tensions of the aliphatic nitroparaffins at 25.0° vary from 35.78 for nitromethane to 29.20 dyne cm.<sup>-1</sup> for 1-nitrobutane. The secondary isomers show characteristically lower free surface energies, with 2-nitrobutane giving 28.65 ergs cm.<sup>-2</sup>.

2. The total surface energies of the nitroparaffins at 25.0° vary from 77.11 ergs cm.<sup>-2</sup> for nitromethane to 58.39 ergs cm.<sup>-2</sup> for 1-nitrobutane. The secondary isomers, however, exhibit a higher surface energy, with 2-nitrobutane giving 60.46 ergs cm.<sup>-2</sup>.

3. The parachor values calculated from the measured surface tension and density are in good agreement with the predictions of Sugden.

4. Values of the critical temperatures calculated from the Ramsey-Shields equations are: nitromethane, 623°K.; nitroethane, 662°K.; 1-nitropropane, 675°K.; 2-nitropropane, 618°K.; 1-nitrobutane, 669°K.; and 2-nitrobutane, 624°K.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Composition and Structure of Molybdenum Blue

By F. B. SCHIRMER, JR., L. F. AUDRIETH, S. T. GROSS, D. S. McCLELLAN AND L. J. SEPPI

The composition of molybdenum blue has been the subject of controversy ever since it was first discovered by Berzelius<sup>1</sup> in 1826. Even modern investigators are not yet in agreement as to its formula, the most recently reported values varying from  $\text{Mo}_5\text{O}_{14}$  to  $\text{Mo}_5\text{O}_{23}$ .<sup>2,3,4</sup> There is little doubt but that products of different composition are obtained when heteropoly acid formers such as phosphoric and arsenic acids are present, or when oxidizing agents such as nitric acid are used in acidifying solutions of molybdate. There is also the very good possibility that the common practice of "purifying" molybdenum blue by extraction from aqueous solution by means of organic solvents gives products which are different. For these reasons the authors undertook to develop methods of synthesis which would avoid these complicating factors.

Molybdenum blue has been prepared by a number of methods, carefully purified and analyzed. Samples were subjected to an X-ray examination and found to yield identical diffraction patterns. The colloidal nature of molybdenum blue was verified subsequently by a study of these products under the electron microscope.

(1) Berzelius, *Pogg. Ann.*, **6**, 380 (1826).

(2) Auger and Ivanoff, *Compt. rend.*, **204**, 1815 (1937).

(3) Auger, *ibid.*, **205**, 1070 (1937).

(4) Lautié, *Bull. soc. chim.*, [5] **1**, 105 (1934).

### Experimental

#### Preparation

(a) **Reduction of Molybdate with Trivalent Molybdenum.**—The recommended procedure, by which the majority of the samples were prepared, involves interaction of a solution of trivalent molybdenum, obtained by reduction of molybdate in a Jones reductor, with an acidified molybdate solution (pH 0.4). Specific directions follow: a receiver containing 500 ml. of 0.4 *M* sodium molybdate,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , and 200 ml. of 6 *N* hydrochloric acid is attached to the reductor. A solution containing 40 ml. of 0.4 *M* sodium molybdate, 60 ml. of 6 *N* hydrochloric acid and 100 ml. of water is passed slowly through the column and the resulting olive-green solution of trivalent molybdenum is allowed to drop directly into the solution of hexavalent molybdenum. The last of the solution in the reductor is washed into the receiver with dilute hydrochloric acid. The precipitate of molybdenum blue forms in the flask.

The precipitate and the solution are separated by centrifugation and the slightly colored supernatant liquid, containing an excess of trivalent molybdenum, is either discarded or treated as in method (c). The precipitate is washed by centrifuging three to five times with a solution of 5 ml. of 6 *N* hydrochloric acid in 100 ml. of distilled water. This is followed by similar treatment of the precipitate with successive portions of distilled water until both the supernatant liquid and the precipitate are chloride free. After each washing the suspension is centrifuged and the supernatant liquid decanted.

During the washing with dilute hydrochloric acid very little of the product is lost. As the electrolyte is subsequently removed by washing with distilled water considerable peptization takes place with the result that the

supernatant solutions assume a deep blue color. While the yield of molybdenum blue is decreased by this final treatment, a purer product is obtained which more than compensates for this loss. The molybdenum blue is then dried and stored in a vacuum desiccator. Using the quantities specified above yields of 16 to 18 g. of purified molybdenum blue may be obtained. These yields correspond to about 45–55% calculated on the assumption that the hydrate obtained has the average composition  $\text{Mo}_8\text{O}_{23} \cdot 10\text{H}_2\text{O}$ .

(b) **Oxidation of Trivalent Molybdenum with Molybdate.**—This method is essentially similar to (a), but involves addition of acidified molybdate to an excess of a solution containing trivalent molybdenum prepared by reduction with zinc in a Jones reductor.

(c) **Oxidation of Lower Valent Molybdenum.**—The supernatant liquid which remains upon centrifugation of the reaction mixture in (a) above contains an excess of lower valent molybdenum. An additional yield of the blue can be obtained by passing oxygen through the solution for several days. The precipitated molybdenum blue is centrifuged, washed and dried as described under (a).

**Analysis.**—The water content was determined by heating gradually a weighed sample of the blue to a temperature of  $500^\circ$  in a stream of oxygen and absorbing the moisture in tared bulbs containing magnesium perchlorate. The residual molybdenum trioxide was either weighed directly or dissolved in dilute ammonium hydroxide and its molybdenum content determined volumetrically as outlined by Scott.<sup>5</sup> Samples of molybdenum blue were also analyzed directly for their molybdenum content. The oxygen content was calculated by difference.

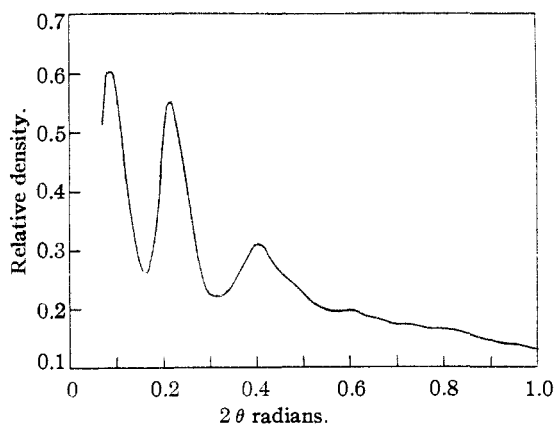


Fig. 1.—Relative density curve made from X-ray diagram of molybdenum blue using Leeds and Northrup microphotometer; filtered molybdenum radiation, circular camera (radius 6.4 cm.), wedge sample.

The analytical results presented in Table I indicate that the composition of molybdenum blue, prepared by four different methods and purified carefully, may be represented approximately by the empirical formula  $\text{Mo}_8\text{O}_{23} \cdot x\text{H}_2\text{O}$ , where  $x$  varies from six to fourteen depending

(5) "Standard Methods of Chemical Analysis," Vol. 1, D. Van Nostrand Co., Inc., New York, N. Y., 1930, p. 594.

upon how long the product has been dried.

TABLE I  
COMPOSITION OF MOLYBDENUM BLUE

Method of prepn.	Samples analyzed	Value of $x$ in $\text{Mo}_8\text{O}_{23}$
<i>a</i>	14	$23.04 \pm 0.12$ (extremes, 22.85–23.31)
<i>b</i>	2	$23.31 \pm 0.10$
<i>c</i>	2	$22.97 \pm .06$
<i>d</i> <sup>b</sup>	2	$23.41 \pm .06$

#### X-Ray and Electron Microscope Study.

Molybdenum blue preparations were examined by the X-ray diffraction method using both filtered molybdenum and filtered copper radiation with the wedge technique. Three intense and four faint halos or diffuse bands were observed. The intense interferences correspond to the following "d" values.

Cu K-alpha, Å.	Mo K-alpha, Å.
8.43	8.57
3.28	3.25
1.79	1.76

Measurements of the remaining halos are uncertain, two of them partly overlapping more intense interferences, and the remaining two corresponding to very faint diffuse bands. A tracing of the microphotometer curve obtained for molybdenum blue from an X-ray pattern with molybdenum radiation is shown in Fig. 1. This pattern is apparently perfectly characteristic of the purified material regardless of the method of preparation.<sup>7</sup> It seems significant that this halo pattern shows little resemblance to the diffraction pattern of molybdenum trioxide, a fact which suggests the presence of a definite structure other than any known form of molybdenum trioxide.

In view of a question raised by one of the referees relative to the interpretation of the broad X-ray diffraction interferences obtained with molybdenum blue, it was suggested by Professor G. L. Clark that electron photomicrographs be made of these preparations.<sup>8</sup> The sample was

(6) Prepared by reduction of acidified molybdate with stannous chloride.

(7) Burgers and van Liempt, *Z. anorg. Chem.*, **202**, 325 (1931), examined qualitatively molybdenum bronzes by the X-ray method, but give no experimental details, measurements, calculations or interpretation. They reproduce photographs of patterns obtained (a) from a so-called molybdenum blue, (b) from an ignited product and (c) from a sample of sublimed molybdenum trioxide. They describe the first of these as different from the other two which are identical. All of their samples are crystalline materials. The patterns obtained consistently by the authors bear no resemblance to those published by Burgers and van Liempt.

(8) The R. C. A. instrument was employed by Dr. Martha Barnes Baylor at a magnification of 15,500 X and the photographs were then enlarged fourfold for a final magnification of 62,000 X.

shaken up with water, allowed to settle and a drop of the top of the aqueous suspension applied to the collodion film and dried. The remarkable dispersion of particles is shown in Fig. 2 (magnification 62,000 X). A fairly uniform distribution of single primary particles some of which are only 100 Å. in diameter, appears in the background. These particles are narrower in one dimension than the other and probably lie flat as still thinner flakes. As might be expected otherwise, these are too small to show definite crystalline faces. Some small flocs representing the first stages of agglomeration of the individual particles appear in the center of the photograph. Finally, there is a distribution of larger, darker and more nearly spherical particles which must represent larger primary particles of the order of several hundred Ångström units in size.

This proof of a typical colloidal structure, therefore, confirms the interpretation of the broad X-ray interferences by means of which calculations can be made of a particle size of the order of 100 Å., or somewhat less. It is not necessary to claim absolute crystalline perfections of these extremely small particles. That some lattice organization is present is indicated by the number of diffraction halos on the patterns—several more than for carbon black which is known to be built up into particles from crystalline layers which are stacked at random like a twisted deck of cards.

### Summary

Molybdenum blue has been prepared by a number of new methods and purified carefully.

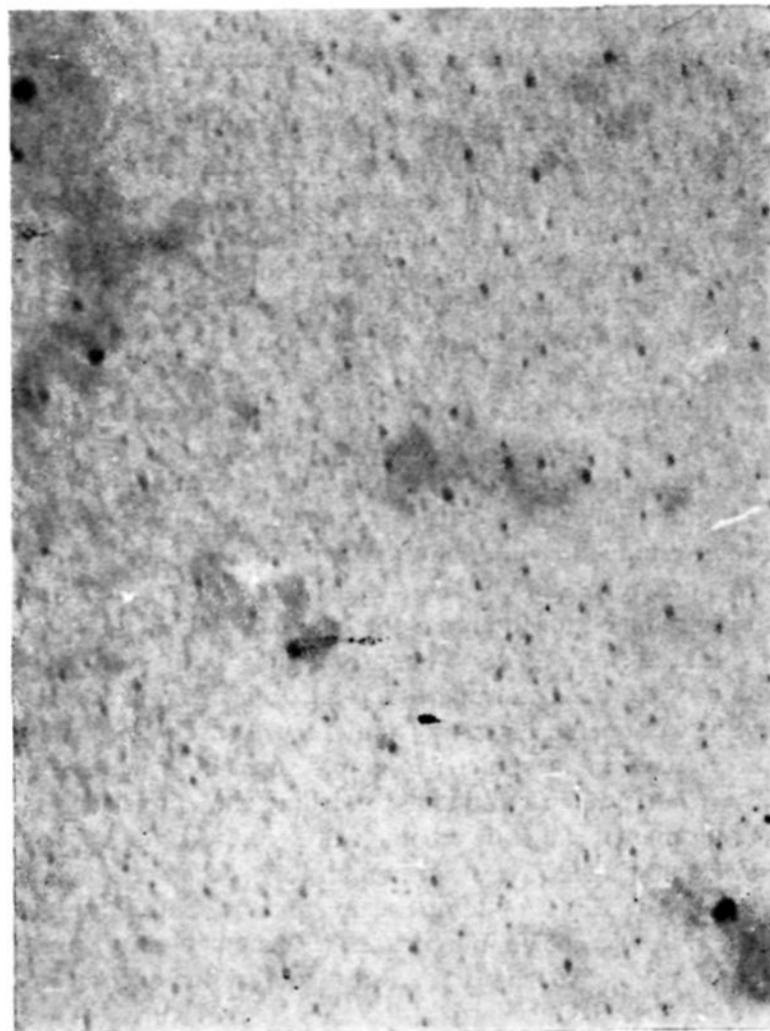


Fig. 2.—Electron photomicrograph of molybdenum blue (62,000 X).

Its composition may be represented by the empirical formula,  $\text{Mo}_8\text{O}_{23}\cdot x\text{H}_2\text{O}$ . Samples prepared under the prescribed conditions yield identical and characteristic diffraction patterns. Electron photomicrographs confirm the colloidal nature of molybdenum blue.

URBANA, ILLINOIS

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## The Adsorption of Gases at Low Temperature and Pressure on Smooth Silver

BY MARION H. ARMBRUSTER

This paper reports the results of measurements of the adsorption of hydrogen, nitrogen, argon, carbon monoxide, carbon dioxide and oxygen at pressures up to 0.1 cm. on a substantially plane, reduced surface of silver over the temperature range  $-195$  to  $20^\circ$ . The investigation was undertaken to determine the nature and properties of the smooth surface of a typical, pure, homogeneous metal as a first step toward a better understanding of the characteristics of the surface of a

less pure or less homogeneous metal, such as steel. Silver was selected chiefly because it is readily obtainable in a high degree of purity in the form of foil, a form which provides a large, smooth and reproducible surface; it is also relatively inert so that, aside from the sorption of oxygen, there should, in the range of experimental conditions covered, be no complex chemisorption which might confuse interpretation of the results.