829. *Reactions of Liquid Sodium with Transition-metal Oxides. Part I. The Dioxides of Molybdenum, Tungsten, and Uranium*

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This Paper is the first of a Series describing the products (which often include ternary oxides) formed by reaction of liquid sodium with oxides of transition metals in a range of valency states, and at temperatures up to 600°. Liquid sodium does not react with uranium dioxide, but reacts with both MoO_2 and WO_2 in a very similar manner at temperatures about 295 and 320°, respectively, to give the transition metal and an oxide $Na_3M_2O_6$. From the *X*-ray diffraction patterns the two ternary oxides are indexed on the basis of a hexagonal unit cell, and cell dimensions are recorded. The composition of the ternary oxide of molybdenum has been determined by *X*-ray phase analysis; the mechanism of its formation and its reactions with water and alcohol are discussed.

WHEN a transition-metal oxide is reduced by liquid sodium the product may contain the free transition metal, or a ternary oxide having the metal in a different valency state, or both. The investigations to be described in this Series are relevant to the mechanism of wetting,[1] corrosion,[2] and wear behaviour [3] of transition metals in liquid sodium, with special reference to the use of pure transition metals, alloys, steels, etc., in fast nuclear reactors employing sodium for heat transfer; however, some new ternary oxides of transition metals in low valency states are produced, and the products have therefore been examined by *X*-ray powder crystallography also.

The use of a liquid metal as reducing agent allows much closer definition of the temperature at which reaction commences than is possible when the reducing agent is a solid. In the latter case, the extent of physical contact between solid particles is an important factor in determining reaction rate, and the limited contact between the reagents tends to obscure the influence of temperature changes. In our experiments, the transition metal oxide is stirred in liquid sodium, and a critical temperature at which reaction first occurs can be observed. The temperature range used has been limited to that at which sodium is liquid under atmospheric pressure of an inert gas (98—883°); most reactions have been studied at 400 and 600°.

The term " ternary oxide " is defined as representing a phase containing two metals and oxygen, in which some form of chemical interaction between the two binary oxides has occurred, whereas the term " mixed oxide " represents a physical mixture of two or more binary oxides, each of which can be recognised as a separate phase by *X*-ray crystallography. The term " double oxide " leads to confusion, and will not be used.

RESULTS AND DISCUSSION

The dioxides of molybdenum, tungsten, and uranium are discussed in this first Paper so that the principles involved can be employed later in the interpretation of reactions of other (and in particular the higher) oxides.

Molybdenum Dioxide.—On the basis of free-energy values,[4] reduction of molybdenum

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[1] C. C. Addison, E. Iberson, and J. A. Manning, *J.*, 1962, 2699, and refs. therein.

[2] V. W. Eldred, A.E.R.E. Rept. X/R. 1806 (1955); R. F. Koenig, *Iron Age*, 1953, **172**, 129; M. Davis and A. Draycott, Proc. 2nd Geneva Conf. on Peaceful Uses of Atomic Energy, 1958, **7**, 94; S. W. Mausteller and E. F. Batatis, U.S.A.E.C. Report NP5583 (1955); G. W. Horsley, *J. Iron Steel Inst.*, 1955, **182**, 43; E. G. Brush, *Corrosion*, 1955, **11**, 299t.

[3] W. H. Roberts, ASLE/ASME Lubrication Conference, Washington D.C., 1964; Paper 64 LC-25.

[4] " Selected Values of Chemical and Thermodynamic Properties," Nat. Bureau of Standards, Circ. 500, 1952.

dioxide ($-\Delta G_{298}$ = 60·8 kcal./g. atom O) by sodium should, and does, occur. Differential thermal analysis (see Experimental section) showed that an exothermic reaction occurred within the range 277—304°, and there was no other apparent reaction at higher temperatures. Molybdenum dioxide was added to an excess of liquid sodium contained in a nickel crucible at about 150° under an atmosphere of pure argon in the glove-box attached to the sodium loop. There was no visible reaction. (Any sodium oxide formed is very obvious, since the bright sodium surface becomes coated immediately with a white film.) Sodium was then distilled off at 400°/10^{-5} mm., leaving a black powder of composition $NaMoO_2$. This product is of interest because of the exact stoicheiometry, which was reproducible, and the apparent reduction in the oxidation state of molybdenum from (IV) to (III). The magnetic susceptibility χ_g was 1·20 × 10^{-6} c.g.s. units, compared with 0·33 × 10^{-6} c.g.s. units for molybdenum dioxide.

The *X*-ray powder diffraction pattern of the product showed that it consisted of two distinct phases; one was molybdenum metal, and the other a ternary oxide phase which could be indexed on the basis of a hexagonal unit cell with dimensions a = 6·47 Å, c = 16·14 Å. Attempts to separate the two phases by chemical methods were unsuccessful, and concentrated acids decomposed the ternary phase to leave an insoluble residue which contaminated the metal. The ternary phase was therefore studied by *X*-ray phase analysis, and found to have the composition $Na_3Mo_2O_6$, so that the reaction can be represented by the overall equation:

$$3Na + 3MoO_2 \longrightarrow Mo + Na_3Mo_2O_6 \qquad (1)$$

This equation represents the reaction at 600° also. A nickel crucible containing the Na–MoO_2 mixture was sealed into the distillation vessel, under a pressure of argon to prevent distillation of sodium, and heated at 600° for 20 hours. The unreacted sodium was then distilled off, and the *X*-ray diffraction pattern of the product found to be identical with that of the product obtained at 400°. Equation (1) also represents the initial reaction detected by differential thermal analysis. An experiment similar to those described above was carried out at 300°; distillation of unreacted sodium at this temperature is tedious, and it was therefore removed by washing with ethanol. When allowance is made for the known reaction between the phase $Na_3Mo_2O_6$ and alcohol (described below), the reaction is again represented by equation (1).

The first steps in the reaction mechanism must involve penetration of sodium atoms into the MoO_2 lattice, accompanied by transfer of electrons from one or more sodium atoms to each molybdenum ion. In cases where the penetration step can be observed separately (*i.e.*, with V_2O_3 and Cr_2O_3), the heat evolved is very small, so that the strongly exothermic reaction observed with MoO_2 is to be attributed largely to electron transfer. There are two possible mechanisms for reaction, which differ in the extent of electron transfer.

(*a*) *Disproportionation mechanism.* Transfer of a single electron to Mo^{IV}, *i.e.*,

$$Na + MoO_2 \longrightarrow NaMoO_2 \qquad (2)$$

gives directly a product having correct stoicheiometry, and which may exist as a single phase so long as liquid sodium is present in excess. There is little evidence for the existence of oxides of molybdenum lower than Mo^{IV}, and references to the preparation of such compounds generally lack *X*-ray evidence to confirm that a single phase is, in fact, present.[5] It is plausible, then, that the Mo^{III} ion in an anhydrous oxide system can only be maintained as such in the strongly reducing liquid sodium environment, and that when excess sodium is removed on distillation, the disproportionation:

$$3NaMoO_2 \longrightarrow Mo + Na_3Mo_2O_6 \qquad (3)$$

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[5] G. W. Watt and D. D. Davies, *J. Amer. Chem. Soc.*, 1948, **70**, 3751.

occurs; the stoicheiometry of the phase $Na_3Mo_2O_6$ is then a direct consequence of production of molybdenum metal on disproportionation. This mechanism also accounts satisfactorily for the fact that one of the products of reaction of molybdenum(IV) oxide with sodium contains molybdenum in an oxidation state higher than four. This could only occur if the mechanism of reaction included a step which took place in the absence of sodium.

(*b*) *Direct reduction to molybdenum metal.* If the initial reaction is

$$4Na + MoO_2 \longrightarrow 2Na_2O + Mo \tag{4}$$

then the sodium monoxide produced will combine with the (acid) oxide MoO_2 immediately,

$$Na_2O + MoO_2 \longrightarrow Na_2MoO_3 \tag{5}$$

The compound Na_2MoO_3 has not been identified as a product of the MoO_2 reaction, and it is reduced by liquid sodium much less readily than is molybdenum dioxide itself. A relationship between the compounds Na_2MoO_3 and $Na_3Mo_2O_6$ is suggested by the work of Herold and Hatterer.[6] From the reaction of molybdenum trioxide with potassium vapour, only the compound K_2MoO_3 was obtained between 250 and 300°, but $K_3Mo_2O_6$ was also formed above 300°; these species are related by the equilibrium:

$$2K_2MoO_3 \rightleftharpoons K_3Mo_2O_6 + K \tag{6}$$

According to this mechanism, the original products of the Na–MoO_2 reaction are molybdenum metal and the compound Na_2MoO_3; on heating at 400°, the excess of liquid sodium first distils off, and decomposition corresponding to equation (6) then occurs.

Evidence on the nature of the solid phases present before sodium is distilled off is clearly desirable; at present we find that removal of the excess of sodium at low temperatures by the use of solvents involves liquids which also interact with the ternary oxide $Na_3Mo_2O_6$, and which may therefore react with other ternary oxides which could be present. Examples of this are given below.

Reaction of the compound $Na_3Mo_2O_6$ *with water and ethanol.* The product from the Na–MoO_2 reaction at 400° was used, since the molybdenum metal content was unreactive. Refluxing with water for four hours gave an alkaline solution and a black residue consisting of molybdenum metal and a second phase of composition $Na_{1\cdot5}Mo_2O_6$, which gave a diffuse *X*-ray-diffraction pattern, but which could be indexed as having cubic structure, $a = 6{\cdot}251$ Å. Half the sodium content of the original ternary oxide was therefore lost during reaction; this is attributed either to reduction by the low-valency molybdenum (Mo^{V} and Mo^{IV}) or to replacement of appropriate sodium ions in the lattice by protons from solution. In an identical experiment using dry ethanol, the residue consisted of molybdenum metal with a ternary phase of composition close to $Na_2Mo_2O_6$. The reaction with ethanol may be much slower than with water, or may reach an equilibrium involving loss of a smaller amount of sodium from the ternary oxide.

These experiments cast doubt on claims by Herold and Hatterer [7] to have produced the oxide MoO. Reaction of potassium vapour with molybdenum dioxide gave a product K_xMoO_2 ($0{\cdot}66 < x < 1{\cdot}16$), which was said to react with water as follows (taking $x = 1$)

$$6KMoO_2 + 2H_2O \longrightarrow 4MoO + 2KOH + 2K_2MoO_4 + H_2$$

X-Ray-diffraction data for the residues were given by Herold, but those given for the compound MoO correspond closely with the diffraction data we obtain for the residue from water treatment of (Mo + $Na_3Mo_2O_6$) mixtures, and also include the lines of molybdenum metal.

Tungsten Dioxide.—The behaviour of this oxide towards liquid sodium is very similar

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[6] A. Herold and A. Hatterer, *Compt. rend.*, 1954, **238**, 479.

[7] A. Herold and A. Hatterer, *Compt. rend.*, 1954, **239**, 880.

to that of molybdenum oxide; an exothermic reaction occurs at a slightly higher temperature (about 320°) and $-\Delta G_{298}$, 62·3 kcal./g. atom O, is also slightly greater than for molybdenum dioxide. The product of reaction at 400°, after distillation of excess sodium, was a dark brown powder consisting of tungsten metal and a phase $Na_3W_2O_6$, identical in structure type with the corresponding molybdenum compound.

Uranium Dioxide.—No reaction occurs between sodium and uranium dioxide up to 400°; this is consistent with the very high free energy of formation of uranium dioxide ($-\Delta G_{298} = 122{\cdot}8$ kcal./g. atom O). The oxide was recovered by dissolving away the excess of sodium in dry ethanol, and its *X*-ray-diffraction pattern shown to be unchanged by treatment with sodium. Uranium dioxide and sodium were then heated together for some hours at 600°, and sodium removed by distillation. Again, the *X*-ray-diffraction pattern of the dioxide was unchanged. The fact that ternary oxides of sodium and uranium are only formed with uranium oxides higher than the dioxide is directly relevant to the mechanism of wetting of non-stoicheiometric UO_2 by liquid sodium.[8]

EXPERIMENTAL

The sodium was taken from a uniform stock held in a laboratory loop kindly supplied by U.K.A.E.A., Culcheth. The loop carried a cold trap which maintained the oxygen content in the region of 5 p.p.m. (by analysis of the residue after distillation of sodium). The only significant metallic impurity, calcium, was found to be 0·016 wt.-% by analysis, using ethylenediaminetetra-acetic acid.

Preparation of dioxides. AnalaR molybdenum trioxide was heated in hydrogen at 450° for 36 hr.;[9] the product was washed with 6M-hydrochloric acid, distilled water, and 6M-ammonium hydroxide in turn, and dried *in vacuo* at 200°. *X*-Ray-diffraction patterns gave only the lines for MoO_2,[10] and analysis for molybdenum using oxine indicated a purity of 98·9% MoO_2.

To prepare tungsten dioxide,[11, 12] a compressed pellet made from a 2 : 1 mixture of tungsten trioxide with powdered tungsten metal was heated in pure argon at 1200°. After 24 hr., an *X*-ray study of the product showed only the diffraction pattern of pure tungsten dioxide.[13]

AnalaR uranyl acetate was heated in air to the green oxide U_3O_8; this was reduced to the dioxide by treatment with hydrogen at red heat. The reduction was continued until the diffraction pattern showed only UO_2 lines.[14] Analysis for uranium by precipitation as ammonium diuranate and ignition to U_3O_8 gave U, 88·6% (calc. for UO_2, 88·1%). The sample was probably slightly oxygen deficient; this was desirable, since it was known that the oxides UO_3 and U_3O_8 do react with liquid sodium.

Differential thermal analysis. This technique is normally employed with solids, but proved readily adaptable to liquid metals. For reaction temperatures up to 400°, the apparatus shown in Figure 1 was used. Two Pyrex glass 12 × 2 cm. vessels were fitted with B19 joints which carried sleeves permitting exit of argon. Through these sleeves passed the stems of glass stirrers, and the stems carried equal pulleys linked together so that stirring conditions were identical in each vessel. Thermocouples were fitted into depressions in the base of each vessel as shown. The reaction vessels were placed near the centre of a cylindrical aluminium block furnace which was wound on the outside with nichrome heaters, and lagged. Furnace temperature was controlled from a chromel–alumel thermocouple (placed between the reaction vessels) by an Ether temperature controller fitted with cams which gave a steady heating rate (3·3° per minute in these experiments) throughout the temperature range. Temperature differences between the two vessels were registered on a Honeywell–Brown recorder, employing full-scale deflection for 2·5 mv.

Liquid sodium (~5 ml.) was first added to the reaction vessels in an argon atmosphere, the

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[8] B. M. Abraham, H. E. Flotow, and R. D. Carlson, *Ind. Eng. Chem.*, 1959, **51**, 189.

[9] R. Ward, *J. Amer. Chem. Soc.*, 1957, **79**, 5410.

[10] A. Magneli and G. Andersson, *Acta Chem. Scand.*, 1955, **9**, 1378.

[11] F. Sittig, *Z. anorg. Chem.*, 1925, **145**, 127.

[12] J. A. M. von Liempt, *Z. anorg. Chem.*, 1923, **126**, 183.

[13] A. Magneli and G. Andersson, *Analyt. Chem.*, 1952, **24**, 1998.

[14] I. F. Ferguson and P. G. T. Fogg, *J.*, 1957, 3679.

quantities in the two vessels being as nearly identical as possible. When the sodium solidified, the transition-metal oxide ($\sim$0·1—0·2 g.) was added to the metal in one vessel, and the two vessels assembled in the furnace with the stirrers resting on the surface of the solid sodium. The furnace was then heated, and stirring commenced as soon as the stirrer blades sank into the molten metal. Since the quantities of sodium in the reaction and reference vessels were not precisely the same, melting was also indicated by a deflection on the recorder plot.

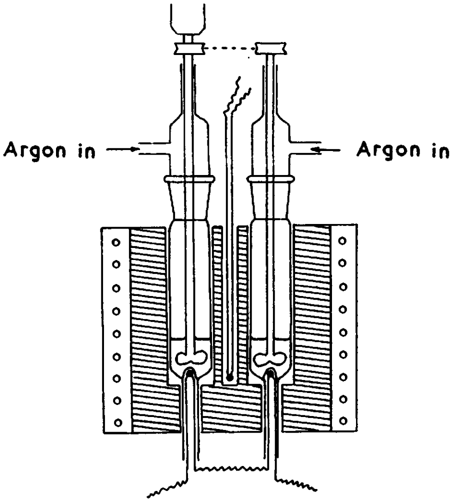

FIGURE 1. Apparatus for differential thermal analysis using liquid sodium

Typical recorder plots for three samples of molybdenum dioxide are shown in Figure 2.

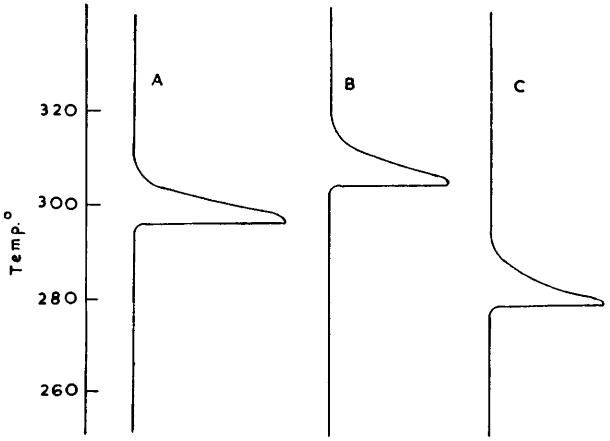

FIGURE 2. Differential thermal analysis of liquid sodium–molybdenum dioxide reactions

Peak	Oxide used (g.)	Temp. rise	Reaction temp.
A	0·194	6°	296°
B	0·122	5	304
C	0·108	5	277

In each case onset of reaction is sudden, and is complete within half a minute; no further reaction occurred up to 400°. The behaviour of tungsten dioxide was similar. These reactions (Figure 2) occurred at temperatures within a 27° range. This may be due to such factors as variation in particle size, and we believe that under more carefully standardised conditions the reaction temperature is reproducible within a much narrower range. Heats of reaction are proportional to the areas under the D.T.A. peaks, and are reproducible within the rather broad limits of this apparatus. From the data given in the caption to Figure 2, the ratios of oxide used to peak area are 1·02, 0·94, and 1·08. (arbitrary units), respectively.

Procedure for liquid sodium–metal oxide reactions.—The procedure employed for all transition metal oxides to be discussed in this series involves two basic items of equipment. Firstly, a stainless steel glove-box, which could be evacuated or filled with argon, was mounted on the liquid sodium loop, and had access through a port to a sodium reservoir which formed part of the loop. Secondly, the reaction was carried out inside a stainless steel vessel which could also be used for subsequent distillation of sodium. This apparatus (designed and supplied by U.K.A.E.A., Culcheth) consisted essentially of a cylindrical container 20 cm. tall and 8 cm. diameter, carrying a large water-cooled cold-finger, and a vacuum connection passing through the cold-finger to avoid transport of sodium vapour into the vacuum system. The vessel had appropriate heating coils, lagging, and thermocouple controls. Into the space below the cold-finger was fitted a portable stirrup, holding four cylindrical nickel crucibles each 2 cm. diam. and 2·5 cm. deep, capacity 7 mls.

The distillation vessel, nickel crucibles, and dry, powdered oxide were first placed into the glove-box, which was evacuated for some hours and then filled with argon. The crucibles were filled with sodium (about 5 ml.) by dipping into the liquid-sodium reservoir; the use of several separate crucibles enabled the chemical identity of the products to be checked. The oxide (about 0·5 g.) was added quickly to the sodium (at about 150°) in each crucible, with stirring, and any reaction observed. The crucibles were then fitted into the distillation vessel which was assembled in the glove-box to maintain an atmosphere of pure argon. After heating the sodium–metal oxide mixtures for the required time in argon, the vessel was evacuated and excess sodium removed from the crucibles by distillation on to the cold-finger. Reaction products were then transferred from the crucibles in an argon atmosphere.

Analysis of reaction products. Sodium was determined by flame photometry. The black product from the molybdenum dioxide reaction gave Na, 15·4; Mo, 62·3; O (by diff.), 22·3. $NaMoO_2$ requires Na, 15·2; Mo, 63·6; O, 21·2%.

X-*Ray examination of products.* All products were examined in a Phillips X-ray diffractometer using the PW 1010 stabilised generator, PW 1050 high-angle goniometer in conjunction with scintillation counter, and PW 1051 circuit panel. Cu K_α-radiation was used throughout, and the generator operated at 30 kv, 20 mA. Samples were mounted in holders based on the design by Smallman.[15] Since the sample can be pressed firmly into a cavity between an aluminium plate and a glass slide (which is then removed), this method gives a uniform, hard-packed and very flat sample surface.

All samples studied in this work were highly hygroscopic, so that protection from the atmosphere during X-ray examination was essential. Mylar foil was found to be suitable for this purpose, and was fitted into the radiation shield in such a position that the radiation passed at right angles through the foil at all stages in the measurement; the diffraction pattern of the foil was thereby eliminated, and absorption was at a minimum. The foil enclosed a small space around the sample, and a constant flow of dry nitrogen was maintained through this space by means of inlet and outlet tubes fitted to the radiation shield. The sample was loaded into the holder in an argon-filled dry box, and protected by a glass cover during transfer to the diffractometer.

Diffraction patterns of products. The complete patterns are given in the Table. The diffraction lines marked as due to molybdenum and tungsten metals agree with known patterns.[16] The two ternary oxides are isostructural, with hexagonal cell dimensions $a = 6{\cdot}47$ Å, $c = 16{\cdot}14$ Å ($Na_3Mo_2O_6$), and $a = 6{\cdot}48$, $c = 16{\cdot}23$ Å ($Na_3W_2O_6$).

X-*Ray phase analysis.* The distribution of molybdenum in the reaction product between the metallic form and the ternary oxide was determined by comparison of an appropriate diffraction peak in the metal and the mixed product; the method has been described by Klug and Alexander[17] and by Parrish.[18] Molybdenum powder (L. Light & Co., 99·9%) was used,

[15] C. R. Smallman, *Rev. Sci. Inst.*, 1952, **23**, 135.

[16] H. E. Swanson and E. Tatge, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 318.

[17] H. P. Klug and L. E. Alexander, " X-ray Diffraction Procedures," Wiley, New York, 1959, p. 410.

[18] W. Parrish, " Advances in X-ray diffractometry and X-ray spectrography," Centrex Publ. Co., Eindhoven, 1962.

X-Ray-diffraction patterns of products of reaction of sodium with molybdenum and tungsten dioxides

d Å	I/I_1	*hkl*	d Å	I/I_1	*hkl*	d Å	I/I_1	*hkl*
(*a*) Molybdenum dioxide product								
5·385	40	003	1·62	35	220	1·12	10	Mo(220)
3·26	70	110	1·58	30	Mo(200)	1·08	10	330
2·77	80	201	1·45	10	225	1·06	5	333
2·48	15	203	1·39	5	400	0·997	40	Mo(310)
2·25	100	Mo(110)	1·29	70	Mo(211)	0·887	50	512
1·87	30	300	1·22	10	410	0·842	30	Mo(321)
1·77	30	303	1·19	15	413			
(*b*) Tungsten dioxide product								
5·27	40	003	1·55	20	W(200)	1·08	10	330
3·25	90	110	1·45	10	225	1·06	5	333
2·76	100	201	1·39	5	400	1·00	40	W(310)
2·24	10	W(110)	1·29	70	W(211)	0·92	20	W(222)
1·87	70	300	1·22	50	410	0·89	50	512
1·76	30	303	1·19	20	413	0·85	30	W(321)
1·62	40	220	1·12	10	W(220)			

and the diffraction peak chosen was that for the 110 plane, d = 2·25 Å. The maximum of the peak occurred at 2θ = 40·7°, with peak width 0·80° 2θ. The goniometer was therefore set to scan the range 39·9° 2θ to 41·5° 2θ, at a rate of 1° 2θ per minute, running the tube at 30 kv and 20 mA; 1° divergence slit, 0·1° receiving slit, and 1° scatter slit were used. The settings of counts and rate meter were adjusted to find the settings for minimum error, which was 1·03% in the case of the molybdenum powder. The peak was then counted for the mixture over the same angular range, the error in this case being 1·24%.

After allowing for background count, the peak counts for molybdenum metal and the mixture were 24,487 and 7,248, respectively. The mass absorption coefficients for molybdenum metal, sodium, and oxygen are 137, 29, and 11·5, respectively,[19] so that the mass absorption coefficient of the mixture (represented as μ_{NaMoO_2}, since $NaMoO_2$ represents the overall chemical composition) was 93·95. The weight fraction of molybdenum metal in the mixture, given by

$$\mu_{NaMoO_2} I_{NaMoO_2} / \mu_{Mo} I_{Mo}$$

was therefore 0·203. Subtraction of this from the total molybdenum content of the mixture gave the molybdenum content of the unknown *phase* (Found: Na, 19·1; Mo, 54·3; O, 26·6. $Na_3Mo_2O_6$ requires Na, 19·3; Mo, 53·8; O, 26·9%).

Products of reaction of ternary oxide with water and with alcohol. In reactions of the original (Mo + $Na_3Mo_2O_6$) mixture with these solvents, the metal was unchanged but ternary oxides deficient in sodium were produced. After treatment with water, the composition of the *ternary oxide* was Na, 10·2; Mo, 59·0; O (by diff.), 30·8. $Na_{1\cdot5}Mo_2O_6$ requires Na, 10·6; Mo, 59·6; O, 29·8%. After treatment with ethanol a *product* of composition $Na_{2\cdot12}Mo_{2\cdot00}O_{6\cdot12}$ was obtained (Found: Na, 14·4; Mo, 56·7; O (by diff.), 28·9. $Na_2Mo_2O_6$ requires Na, 13·8; Mo, 57·4; O, 28·7%).

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[19] J. A. Victoreen, *J. Appl. Phys.*, 1949, **20**, 1141.