

## A Micromethod for the Determination of the Oxygen Content of Some Slightly Reduced Transition Metal Oxides

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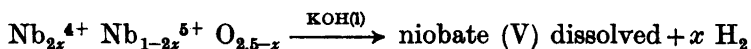
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A direct method to determine a small stoichiometry deviation  $x$  in a transition metal oxide  $MO_{n-x}$  has been developed. The sample is decomposed according to a method described by Gruehn<sup>1</sup> under vacuum in a water-free KOH-melt at 350°C, forming the highest oxidation state ( $x = 0$ ) and simultaneously liberating an amount of hydrogen equivalent to the value of  $x$ . The hydrogen is transported by a stream of argon from the reaction zone, collected in a gas sampling pump, and transferred to the carrier gas stream of a gas chromatograph. This procedure is fairly rapid and highly sensitive and specific. The method has been tested on three intermediary molybdenum oxides  $Mo_4O_{11}$  ( $x = 0.250$ ),  $Mo_8O_{23}$  ( $x = 0.125$ ), and  $Mo_9O_{28}$  ( $x = 0.112$ ). The relative standard deviation in the determination of hydrogen was ca. 2.0 %. This gives relative standard deviations in % oxygen of only ca. 0.1 %. No systematic errors were observed. Samples of  $V_5O_7$  have also been investigated with the same precision.

A precise determination of oxygen in metal oxides is an extremely difficult task. Often the oxygen content is only calculated on the basis of the metal content. Vacuum fusion and inert gas fusion methods in graphite crucibles are generally applied only to trace amounts of oxygen in metals. Occasionally these methods have also been used for metal oxides, but the results are usually not sufficiently accurate. Recently, rather good results were published for oxygen in some vanadium oxides, the relative standard deviation being approximately 0.5 %.<sup>2</sup> However, for many problems of great interest an extraordinary high accuracy is needed, e.g. to differentiate between  $Mo_8O_{23}$  (32.41 % O) and  $Mo_9O_{28}$  (32.51 % O).

For reduced oxides it may be possible to use indirect methods. Samples of  $TiO_{2-x}$  and  $NbO_{2.5-x}$  have been oxidized to  $TiO_2$  and  $Nb_2O_5$ , respectively, by heating in a stream of oxygen. The oxygen content is then determined from the increase in weight. A new approach was made by Gruehn.<sup>1</sup> His method seems to be about ten times more accurate than the "weight increase method" when applied to niobium oxides  $NbO_x$  ( $2 < x < 2.5$ ). He showed for slightly

reduced niobium oxides, that under certain circumstances a lower oxidation level is quantitatively oxidized to the highest oxidation state in a potassium hydroxide melt in vacuum. At the same time an equivalent amount of hydrogen is evolved:



This reaction is especially useful for the analysis of very slightly reduced oxides ( $x$  very small), since even rather large errors in the determination of hydrogen will give quite acceptable values of % oxygen. A prerequisite for the formation of an equivalent amount of hydrogen is that the oxidized product is soluble in the hydroxide melt. Gruehn has shown that this is the case for oxides of Nb, Mo, Ta, and W.

The present authors have used Gruehn's reaction for the liberation of hydrogen but an entirely different method for the determination. Gruehn pumped off the evolved gas with a mercury diffusion pump and determined the pressure of the total amount of gas in a fixed volume. The apparatus also contained a system for the identification of hydrogen and for the correction for other gases present.

In our device the liberated gas is transferred very rapidly from the reaction zone by means of a weak continuous stream of argon and a mercury diffusion pump. The gas is collected in an automatic gas sampling pump which takes gas samples from an evacuated system and introduces the gas quantitatively to a gas chromatograph. This arrangement has led to a fairly rapid and highly sensitive and specific procedure.

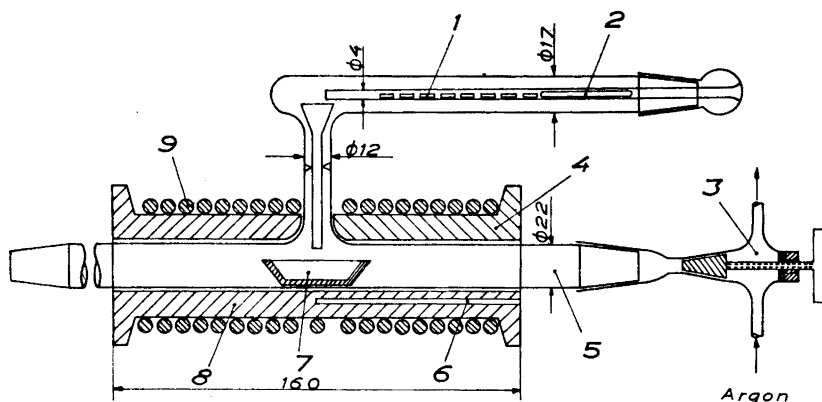
## EXPERIMENTAL

*Reagents and apparatus.* The test runs were performed on crystalline samples of the molybdenum oxides  $\text{Mo}_4\text{O}_{23}$ ,  $\text{Mo}_5\text{O}_{26}$ , and  $\text{Mo}_6\text{O}_{31}$ , kindly supplied by Dr. Lars Kihlberg, University of Stockholm. These oxides were obtained by heating appropriate oxide mixtures, carefully weighed. The synthesis of the oxides implied pro-longed heat-treatments (several weeks) of the starting materials, sealed in small evacuated silica tubes. The crystal structure determinations based on single crystal X-ray diffraction data of these oxides were made by Magnéli and Kihlberg. For a review of the synthetical and structural work, see Ref. 3.

The method has also been applied by the present authors to a new vanadium oxide  $\text{V}_3\text{O}_7$ . For details of the synthesis and the structural determination, see Refs. 4 and 5.

The reagents used were potassium hydroxide (pellets, analytical grade, EKA), potassium bromide (analytical grade, May and Baker, recrystallized), and potassium iodide (Baker Analyzed). The potassium hydroxide was first dehydrated in a tube furnace in a stream of dry nitrogen, purified from oxygen. The temperature was slowly raised from room temperature to the melting point of dry potassium hydroxide. To lower the melting point, the hydroxide was admixed with 15 mol % KBr and 2.5 mol % KI. During this procedure, the mixture was kept in a silver boat.

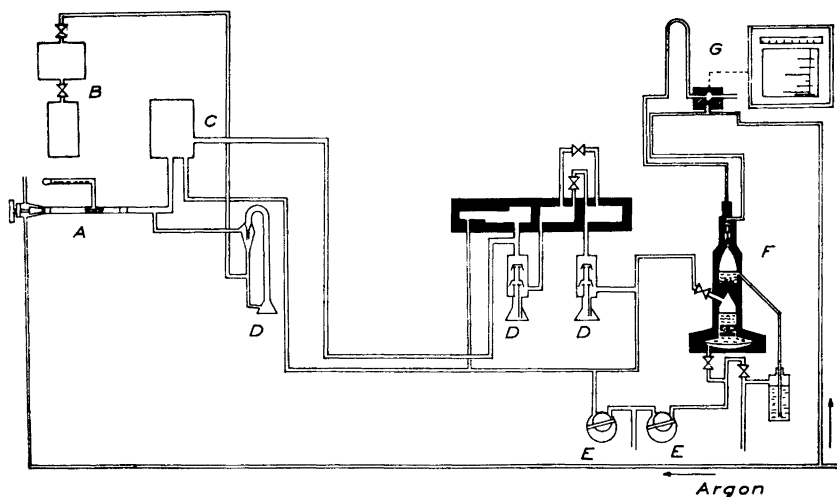
The reaction device with the sample injector is shown in Fig. 1, and is essentially according to Gruehn. As mentioned earlier, a continuous, very slow stream of argon (ca. 0.3–0.5 cm<sup>3</sup>/min) was introduced through a valve to accelerate the transport of the liberated hydrogen into the analysis system. The reaction crucibles were cut from MgO single crystals (Elektromagnesia Kristalle), kindly supplied by Dynamit Nobel AG, Werklülsdorf, 5211 Rangzel, West Germany. The dimension of the crucibles was 30 × 12 × 12 mm<sup>3</sup>. The temperature was kept within ± 3° C with the aid of a Shinko regulator,



**Fig. 1.** Reaction device with sample injector. Dimensions in mm. 1, sample tube of  $\text{Al}_2\text{O}_3$ . 2, permanent magnet. 3, valve for argon. 4, movable piece of the aluminum block. 5, tube of Pyrex glass. 6, thermo-couple connected with temperature regulator. 7, MgO-crucible. 8, aluminium block. 9, thermal trace, glasscored (Electrothermal, HC 504).

connected with a transformer and with a thermocouple in the furnace. The furnace was operated at 200 V from the secondary winding and the regulation was effected simply by the current, being switched on and off.

The Pyrex glass tube in Fig. 1 was connected with a so called Gasevolograph 0583 StRe, constructed and built by Feichtinger.<sup>6</sup> This instrument has been used for many years at the Swedish Institute for Metal Research, for the determination of gases in metals, either by vacuum fusion or by hot extraction. A simplified scheme of those parts of the instrument that were essential in the present investigation are shown in Fig. 2. The calibration was done by means of a "Gas-dosierhahn" from Ströhlein, giving 51.0  $\text{mm}^3$  with a standard deviation of 0.2  $\text{mm}^3$  when standardized by weighing mercury.



**Fig. 2.** Simplified scheme of the "Gasevolograph" showing only parts used in this investigation. A, reaction device. B, calibration system. C, system of solenoid valves. D, diffusion pumps. E, pre-vacuum pumps. F, gas sampling pump. G, gas chromatograph.

The gases evolved by the reaction in the KOH-melt are transported to the gas sampling pump in the Gasevolograph by means of diffusion pumps. Since the hydrogen is liberated continuously during a period of up to half an hour, it is necessary to collect the gas before introducing it into the gas chromatograph. In principle, it would have been possible to carry out the reaction in a stream of an inert gas instead of in vacuum, but it would not have been possible to analyse the gas directly by gas chromatography. A prerequisite for using gas chromatography is, that the gas sample is introduced during a very short period of time.

The gas sampling pump is, in its basical design, a membrane pump, the membrane being operated pneumatically. The up and down movement of this membrane is transmitted to a mercury volume, which practically operates without dead space. The transfer of gas to the carrier gas stream of the gas chromatograph is done fully automatically at preselected time intervals. The gas sampling pump is capable of collecting and transferring the gas to be analysed in volumes from a small fraction of 1 mm<sup>3</sup> to ca. 3 cm<sup>3</sup>. The last figure sets the limit for the amount of argon to be used for the transfer of hydrogen from the reaction zone between two analyses with the gas chromatograph.

A Perkin-Elmer gas chromatograph, Fractometer F6, was used. The molecular sieve (5 Å, 30–60 mesh) column (length 100 cm, internal diameter 3 mm) was kept at 100°C, and the thermistor detector at 339°C. A Hitachi Perkin-Elmer recorder, model 159, was applied. Purified argon was used as carrier gas. The introduction of an additional small amount of argon from the gas sampling pump presented no difficulties, the only effect being a peak at the beginning of each analysis, caused by the pressure deviation (cf. Fig. 3).

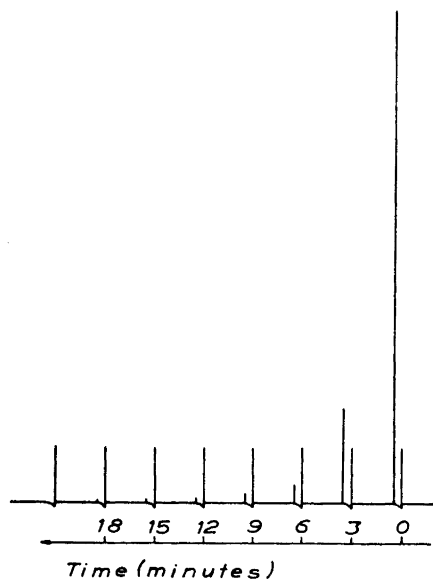


Fig. 3. Gas chromatogram of a sample of Mo<sub>2</sub>O<sub>4</sub>s. Analyses made every 3 min. The peaks of equal height originate from pressure deviations.

*Procedure.* The oxide samples (1–5 mg) were weighed with a Mettler M5 micro balance into small Morgan alumina tubes (length 6 mm, internal diameter 0.75 mm), provided with weighed KBr stoppers at both ends. Generally, the sample weights were chosen to give 35–125 mm<sup>3</sup> of hydrogen. Up to 15 sample tubes were placed in the sample injector at the same time. The magnesia boat was filled with the KOH–KBr–KI mixture and placed in position. Before the introduction of the first sample, the temperature was raised to 400°C and the system operated under the same conditions as during the analyses. Analyses were carried out with the gas chromatograph every 3 min, until the blank was negligible. The whole pretreatment of the system took less than 1 h, compared with 5–6

Table 1. Results for  $\text{Mo}_8\text{O}_{23}$ . Calculated values:  $\text{O}/\text{Mo}=2.8750$ , % O = 32.407.

Weight mg	$\text{H}_2$ calc. $\text{mm}^3$ s.t.p.	$\text{H}_2$ obs. $\text{mm}^3$ s.t.p.	O/Mo	% O
3.094	61.1	61.8	2.8735	32.396
2.691	53.1	53.5	2.8741	32.400
3.155	62.3	62.5	2.8746	32.404
2.974	58.7	58.0	2.8765	32.419
3.660	72.2	70.8	2.8775	32.426
5.014	99.0	99.3	2.8746	32.404
3.512	69.3	67.4	2.8784	32.433
4.296	84.8	84.8	2.8750	32.407
5.057	99.8	98.4	2.8766	32.419
2.797	55.2	53.3	2.8793	32.440
4.614	91.1	94.9	2.8698	32.368
4.182	82.6	85.0	2.8714	32.380
3.883	76.7	75.1	2.8774	32.426
1.670	33.0	32.5	2.8767	32.420
1.617	32.0	31.5	2.8766	32.419
2.768	54.6	53.7	2.8771	32.423
2.599	51.3	49.4	2.8796	32.442
2.569	50.7	49.7	2.8775	32.426
2.661	52.5	55.0	2.8692	32.363
3.161	62.4	62.0	2.8758	32.413
2.472	48.8	49.6	2.8730	32.392
2.431	48.0	47.1	2.8773	32.425
2.104	41.5	42.1	2.8733	32.394

Table 2. Results for  $\text{Mo}_9\text{O}_{26}$ . Calculated values:  $\text{O}/\text{Mo}=2.8889$ , % O = 32.513.

Weight mg	$\text{H}_2$ calc. $\text{mm}^3$ s.t.p.	$\text{H}_2$ obs. $\text{mm}^3$ s.t.p.	O/Mo	% O
3.561	62.4	61.6	2.8903	32.525
2.632	46.1	46.5	2.8879	32.506
2.812	49.3	49.2	2.8890	32.515
1.779	31.2	31.4	2.8881	32.508
4.180	73.2	72.5	2.8900	32.522
3.102	54.3	55.7	2.8861	32.493
3.809	66.7	67.6	2.8875	32.503
3.761	65.9	65.3	2.8899	32.521
3.639	63.8	61.1	2.8934	32.548
3.635	63.7	65.1	2.8865	32.496

h reported by Gruehn. The temperature was then decreased to 350°C, and the analyses of samples started. The reaction was generally completed in less than 30 min. The hydrogen was collected and determined automatically every 3 min, because the sampling pump could not collect the amount of argon necessary to drive out the hydrogen under a period of up to 30 min. In this way, it was also possible to follow the liberation of hydrogen during the whole reaction period and to judge carefully when the reaction had ceased. Fig. 3 shows a chromatogram taken from a sample of  $\text{Mo}_8\text{O}_{23}$ . The peaks of equal height originate from the pressure deviations mentioned earlier. The hydrogen peak heights for

Table 3. Results for Mo<sub>4</sub>O<sub>11</sub>. Calculated values: O/Mo=2.7500, % O=31.441.

Weight mg	H <sub>2</sub> calc. mm <sup>3</sup> s.t.p.	H <sub>2</sub> obs. mm <sup>3</sup> s.t.p.	O/Mo	% O
3.098	124.1	122.5	2.7530	31.463
2.871	115.0	113.0	2.7541	31.473
1.769	70.8	70.3	2.7518	31.455
2.453	98.2	98.4	2.7496	31.438
2.761	110.6	110.7	2.7497	31.439
3.546	142.0	144.0	2.7457	31.408
1.473	59.0	62.6	2.7351	31.324
3.772	151.0	153.2	2.7465	31.414
2.433	97.4	98.0	2.7542	31.474
1.480	59.3	59.0	2.7511	31.450

Table 4. Results for V<sub>5</sub>O<sub>7</sub>. Calculated values: O/V=2.3333, % O=42.290.

Weight mg	H <sub>2</sub> calc. mm <sup>3</sup> s.t.p.	H <sub>2</sub> obs. mm <sup>3</sup> s.t.p.	O/V	% O
1.236	52.3	54.0	2.3281	42.236
2.145	90.8	92.0	2.3312	42.269
0.439	18.6	19.0	2.3297	42.253
1.802	76.3	77.1	2.3316	42.273
1.598	67.6	67.9	2.3327	42.285
1.415	59.9	60.7	2.3311	42.268
1.270	53.7	54.2	2.3320	42.277
1.076	45.5	46.1	2.3313	42.269
1.058	44.8	45.6	2.3304	42.260
1.079	45.7	47.8	2.3258	42.212

each sample were measured, added and compared with results for standard volumes of hydrogen. Correction for blank was made after analysis of alumina tubes, containing no oxide samples. The blank correction was in the order of 0.5 mm<sup>3</sup> and quite invariable.

#### RESULTS AND DISCUSSION

Tables 1–3 give the results obtained for Mo<sub>8</sub>O<sub>23</sub>, Mo<sub>9</sub>O<sub>26</sub>, and Mo<sub>4</sub>O<sub>11</sub>, respectively. The ratio O/Mo was calculated using the relationship

$$\frac{O}{Mo} = 3 - \frac{M_{MoO_3}}{(w/a) + A_O}$$

$w$  = sample weight in  $\mu\text{g}$

$a$  =  $\mu\text{mol}$  of hydrogen

$M_{MoO_3}$  = molecular weight of MoO<sub>3</sub>

$A_O$  = atomic weight of oxygen

The calculation of  $\mu\text{mol}$  H<sub>2</sub> was made using 22.414 l mol<sup>-1</sup> for the volume of 1 mol at s.t.p.

Table 5. Mean values and errors for the substances investigated. % SD = relative standard deviation in per cent of the mean value.

	Mo <sub>8</sub> O <sub>23</sub>	Mo <sub>6</sub> O <sub>16</sub>	Mo <sub>4</sub> O <sub>11</sub>	V <sub>3</sub> O <sub>7</sub>
Number of det.	23	10	10	10
mm <sup>3</sup> H <sub>2</sub> /mg sample				
Calc.	19.74	17.52	40.04	42.32
Obs.	19.67	17.52	40.27	43.10
Range	1.61	1.17	3.14	1.81
% SD	2.2	2.0	2.2	1.3
Obs. - calc.	-0.07	0.00	+0.23	+0.78
O/M				
Calc.	2.8750	2.8889	2.7500	2.3333
Obs.	2.8754	2.8889	2.7491	2.3304
Range	0.0101	0.0073	0.0191	0.0062
% SD	0.09	0.07	0.21	0.09
Obs. - calc.	+0.0004	0.0000	-0.0009	-0.0029
% O				
Calc.	32.407	32.513	31.441	42.290
Obs.	32.411	32.513	31.434	42.260
Range	0.079	0.055	0.150	0.073
% SD	0.07	0.05	0.13	0.05
Obs. - calc.	+0.004	0.000	-0.007	-0.030

Table 4 gives the results for V<sub>3</sub>O<sub>7</sub> and the ratio O/V derived from

$$\frac{O}{V} = 2.5 - \frac{M_{\text{VO}_2}}{(w/a) + A_o}$$

A summary of the mean values and the errors obtained is given in Table 5 together with the theoretical values for the oxides studied. It can be seen that if an oxide is only slightly reduced, like Mo<sub>8</sub>O<sub>23</sub>, a rather large relative standard deviation of 2.2 % in the determination of hydrogen will result in an extremely low relative standard deviation in the ratio O/Mo (0.09 %) and % O (0.07 %). The same error for the slightly more reduced Mo<sub>4</sub>O<sub>11</sub> gives for O/Mo and % O the relative standard deviations 0.21 % and 0.13 %, respectively. In this case, the error in the determination of hydrogen was mainly caused by one single value, 6.1 % higher than the calculated one. The mean value of the ratio O/Mo for Mo<sub>4</sub>O<sub>11</sub> (2.7491, see Table 5) will increase to 2.7506, if this result is omitted.

A simple statistical calculation shows that there were no significant deviations from the theoretical values of O/Mo for the molybdenum oxides studied. When the statistical *t*-test was applied to V<sub>3</sub>O<sub>7</sub>, the small difference for O/V between the calculated value 2.3333 and the observed value 2.3304 showed to be statistically significant at the 99 % probability level. This deviation can be due to the method of preparation. The compound was formed by several heat-treatments with intermediate grindings of a relatively large amount

of a mixture (about 25 g) of  $V_2O_5$  and  $V_2O_3$  in a sealed Vycor tube at  $550^\circ\text{C}$ . At this temperature, the vapour pressure of  $V_2O_5$  is rather high, and small amounts of  $V_2O_5$  may have escaped from the bulk during the procedure. Further studies, using large single crystals made by hydrothermal methods will show if the same accuracy can be achieved as in the case of molybdenum oxides.

The work is also being continued, in order to test the applicability of the method for the analysis of samples with very low deficiencies in oxygen. It seems possible that the techniques will be useful for studies on degrees of reduction very much below those treated in the present study.

The "Gasevolograph" is of course not necessary for the analysis. A much simpler and cheaper arrangement, including oil and diffusion pumps and the gas sampling pump in connection with a gas chromatograph will be adequate. The gas sampling pump SPGC 10 is available from Dr. H. Feichtinger, Schaffhausen, Switzerland, as a separate unit. The amount of hydrogen, liberated in the experiments in this investigation, was not at all near the detection limit using the equipment described. The sensitivity may be raised 10–15 times without any serious effects on the precision of the determinations. On the other hand, the amount of argon used for the transport of hydrogen from the reaction zone is rather critical. The simple device used for this purpose was sufficient, but a more precise regulation will be tried later.

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