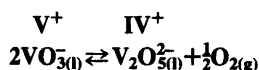


Reduction of Fused Sodium Vanadates

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Fused sodium metavanadate (NaVO_3) was reduced in a mixed atmosphere of carbon monoxide and carbon dioxide. Corresponding values of oxygen pressure and oxidation states of vanadium seem to satisfy the equation



Fused metavanadate is assumed to consist of long chains or rings in which vanadium atoms are linked together by oxygen bridges. During the reduction to tetravalent vanadium a successive introduction of double oxygen bridges may take place. The units VO_3^- and $\text{V}_2\text{O}_5^{2+}$ are assumed to be randomly distributed in the chains.

The equilibrium constants vary from $4.7 \cdot 10^{-8}$ at 800°C to $1.9 \cdot 10^{-6}$ at 1000°C . (The activity of negative groups is expressed as mole fractions.)

Sodium-rich melts are more difficult to reduce. It is suggested that the length of the chains in fused vanadates decreases with increasing basicity.

The phase diagram of the quasi-binary system $\text{V}_2\text{O}_5\text{--Na}_2\text{O}$ has been determined.¹ In addition to the solid phases Na_3VO_4 , $\text{Na}_4\text{V}_2\text{O}_7$ and NaVO_3 , several so-called "vanadium bronzes" exist in the vanadium-rich part of the system. On solidification of such vanadate melts, oxygen gas is liberated, leading to an oxidation state of less than five for vanadium. A series of phases exist with compositions $\text{Na}_x\text{V}_2\text{O}_5$ ($0 < x < 1.8$).² There are some discrepancies in the literature concerning the composition of vanadium bronzes. The existence of the solid phases NaVO_2 , Na_2VO_3 and $\text{Na}_2\text{V}_2\text{O}_5$ has been reported.^{3,4} The existence of the solid phases $\text{Na}_2\text{V}_2\text{O}_5$ and Na_2VO_3 could not be confirmed by heating of vanadate and vanadium oxide mixtures.⁵

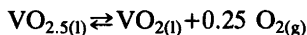
A survey of the phases reported in literature can be found.⁶ Some of the sodium vanadates are hygroscopic and the existence of several hydrates is reported.

The liberation of oxygen from mixtures of V_2O_5 and NaVO_3 has been studied gravimetrically.⁷ The fused vanadium bronzes are oxidized to the pentavalent state by air above $600\text{--}700^\circ\text{C}$.

The high temperature form of NaVO_3 has a diopside type structure, in which vanadium atoms are linked by oxygen bridges in a chain structure.^{8,9} The solid phase NaV_2O_5 has a chain structure with both single and double oxygen bridges between vanadium atoms.² In more vanadium-rich compounds the chains are cross-linked and layer structures are found. The more basic compounds, $\text{Na}_4\text{V}_2\text{O}_7$ and Na_3VO_4 , have three-dimensional structures with

small structural units, $V_2O_4^{4-}$ and VO_4^{3-} respectively. Electrical conductivity measurements of fused mixtures of V_2O_5 and $NaVO_3$ show that the sodium-rich melts exhibit ionic conduction.¹⁰ The viscosity of $NaVO_3$ is rather high¹¹, indicating large structural entities in the melt.

The reduction of fused V_2O_5 in oxygen–nitrogen gas mixtures has been examined.¹² The equilibrium constant for the equation



varied from $1.19 \cdot 10^{-3}$ (694 °C) to $17.8 \cdot 10^{-3}$ (956 °C). The corresponding enthalpy of reaction is 107 kJ mol^{-1} .

EXPERIMENTAL

Sodium metavanadate, 50–100 mg, was placed in a platinum crucible and suspended in thermobalance equipment. The fused salt was reduced in a stream of CO/CO_2 mixture regulated by calibrated gas flow-meters. The total gas pressure was one atmosphere, and the flow speed was about 50 ml min^{-1} . The experiments were performed at 800, 900 and 1000 °C. Partial pressure of oxygen was calculated using thermodynamic data.¹³ The loss of oxygen was determined gravimetrically as a function of oxygen pressure and time.

X-ray powder diffraction of the samples was carried out in a Guinier-type focusing camera using $CrK\alpha_1$ -radiation.

Some other sodium vanadates were prepared by melting together $NaVO_3$ and Na_2CO_3 or V_2O_5 and reduced in atmospheres corresponding to those used for $NaVO_3$.

RESULTS AND DISCUSSION

Sodium metavanadate. At reduced oxygen pressures, the fused sodium metavanadates could be successively reduced to oxidation states between five and four. Equilibrium condition was assumed when constant weight of the sample was obtained, often after several hours' exposure. After reoxidation of such melts with oxygen gas, the original weight was obtained. This indicated that only oxygen was liberated during the reduction. X-ray examination of the re-oxidized samples showed the presence of $NaVO_3$ only. $NaVO_3$ melts reduced to a tetravalent state, contained a mixture of V_2O_3 and $Na_4V_2O_7$ after cooling to room

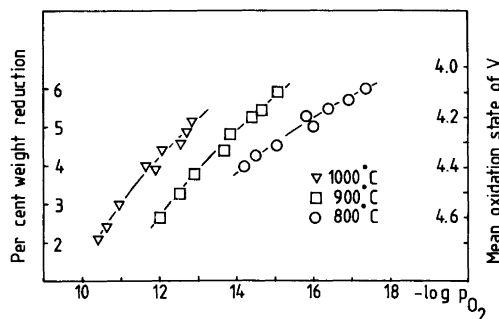


Fig. 1. Weight reduction of fused $NaVO_3$ at equilibrium versus $\log p_{O_2}$ at 800, 900 and 1000 °C.

temperature. Accordingly, a tetravalent vanadate such as $\text{Na}_2\text{V}_2\text{O}_5$ did not crystallize, but apparently disproportionated on cooling. This is also in accordance with the observations in Ref. 2.

NaVO_3 exposed to a stronger reducing atmosphere did not attain constant weight, but a slight weight loss continued. X-ray examination showed the presence of NaVO_2 and V_2O_3 in the solidified melts. Such strongly reduced melts did not obtain their original weight on reoxidation, and X-ray exposures showed the presence of vanadium bronzes, such as $\gamma\text{-Na}_5\text{V}_{12}\text{O}_{32}$. These observations indicate that also sodium was lost under the strongly reducing conditions.

Corresponding values for weight loss of the fused vanadate and partial pressure of oxygen were determined for temperature and pressure combinations where only oxygen was lost during the reduction experiments. The observations are given in Fig. 1 as % weight loss versus $\log P_{\text{O}_2}$ for the temperatures 800, 900 and 1000 °C.

Equilibrium constants for various types of reduction reactions have been calculated, and the simplest reaction that gives an acceptable interpretation of the results seems to be:



The equilibrium constant is given by

$$K_p = \frac{x_{\text{V}_2\text{O}_5^{2-}} P_{\text{O}_2}^{\frac{1}{2}}}{x_{\text{VO}_3^-}^2}$$

where the activities are represented as mole-fraction of the units $\text{V}_2\text{O}_5^{2-}$ and VO_3^- and the partial pressure of oxygen (in atmospheres). See, e.g. the analogous treatment of silicates.¹⁴ The average values of $\log K_p$ at 800, 900 and 1000 °C are -7.1 , -6.4 and -5.7 , respectively. The deviation was less than 0.3.

A Van't Hoff's plot of $\log K_p$ versus T^{-1} yields a standard enthalpy change, $\Delta H^\circ = 185 \text{ J mol}^{-1}$, and the corresponding change in standard entropy, ΔS° , is $36 \text{ J mol}^{-1}\text{K}^{-1}$, referring to the components of equation (1) in their standard state. The standard state of $\text{NaVO}_3(\text{l})$ and $\text{Na}_2\text{V}_2\text{O}_5(\text{l})$ is taken as the pure liquid components (unity mole fraction).

Solid sodium metavanadate has a chain structure where the vanadium atoms are connected through oxygen bridges. It seems reasonable to assume that the chain structure is essentially retained in the fused state, and with an average chain length distribution depending on temperature. The reduction could then result in formation of double oxygen bridges between two adjacent vanadium atoms. Such double bridges are also found in some solid vanadium bronzes.² Provided that the chains are relatively long, the units VO_3^- and $\text{V}_2\text{O}_5^{2-}$ could be randomly distributed along the chains in a partly reduced vanadate melt. This suggested model will satisfy the equation given above. On complete reduction to tetravalent vanadium an alternation of single and double oxygen bridges is assumed between vanadium atoms.

The assumed atomic arrangement in some fused vanadates is shown in Fig. 2.

More basic vanadates. Preliminary reduction experiments have been carried out on mixtures with gross composition: $\text{Na}_4\text{V}_2\text{O}_7$, $\text{Na}_5\text{V}_3\text{O}_{10}$ and a sample with approximate composition $\text{Na}_6\text{V}_4\text{O}_{13}$. Fused sodium pyrovanadate, $\text{Na}_4\text{V}_2\text{O}_7$ could not be reduced under conditions similar to those used for NaVO_3 . Use of a stronger reducing atmosphere resulted

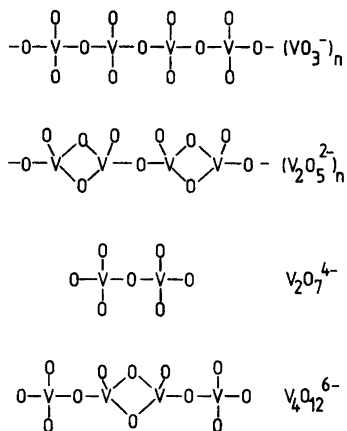
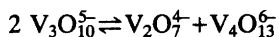


Fig. 2. Assumed structure of some vanadate chains. The negative charges should be distributed over the nonbridging oxygen atoms.

in partly reduction to V_2O_3 . $Na_5V_3O_{10}$ and $Na_6V_4O_{13}$ could, however, be somewhat reduced. The degree of reduction increases with increasing acidity of the melt.

In the solid state no crystalline phase is found between $NaVO_3$ and $Na_4V_2O_7$. In the fused vanadates one might, however, assume the existence of increasing chain lengths from $V_2O_7^{4-}$ to $(VO_3^-)_n$ on increasing acidity. It seems likely that the vanadium atoms at the ends of the chains are not reducible to the tetravalent state. The formation of a double oxygen bridge would therefore require a chain length of at least four vanadium atoms in the chain. Accordingly the ions $V_2O_7^{4-}$ and $V_3O_{10}^{5-}$ should not be reducible to a tetravalent state. One can, however, expect a certain distribution of the chain lengths in the melts, for example:



This assumption seems to give an explanation of the observed reduction of $Na_5V_3O_{10}$.

The reduction measurements on fused $Na_6V_4O_{13}$ were interpreted according to the equation:



$$K_p = \frac{x_{V_4O_{12}^{6-}} \cdot P_{O_2}^{\frac{1}{2}}}{x_{V_4O_{13}^{6-}}}$$

At this composition the “ V_4 -complexes” are supposed to be the dominating species and a possible distribution of chain lengths in this melt has not been taken into account.

According to the suggestions above, the following mean values of equilibrium constants for $Na_6V_4O_{13}$ were calculated:

$$800 \text{ }^\circ\text{C}, K_p = 1.5 \cdot 10^{-8}; 900 \text{ }^\circ\text{C}, K_p = 1.2 \cdot 10^{-7}$$

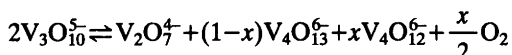
$$\text{and } 1000 \text{ }^\circ\text{C}, K_p = 1.0 \cdot 10^{-6}$$

Table 1. A roughly calculated distribution of species in partly reduced fused $\text{Na}_5\text{V}_3\text{O}_{10}$.^a

	800 °C	900 °C	1000 °C
p_{O_2} (atom)	$1.9 \cdot 10^{-18}$	$2.4 \cdot 10^{-16}$	$1.9 \cdot 10^{-14}$
$\text{V}_3\text{O}_{10}^{5-}$ (mol%)	60	55	66
$\text{V}_2\text{O}_7^{4-}$	20	22	17
$\text{V}_4\text{O}_{13}^{6-}$	1.7	2.5	2.1
$\text{V}_4\text{O}_{12}^{6-}$	18	20	15

^a The results must be only regarded qualitatively.

The reduction of $\text{Na}_5\text{V}_3\text{O}_{10}$ may then as a first approximation be regarded as



Reduction of $\text{Na}_5\text{V}_3\text{O}_{10}$ was carried out at 800, 900, and 1000 °C. On the basis of the equilibrium constants for $\text{V}_4\text{O}_{13}^{6-}$, [eqn. (2)], the molar distribution of species in partly reduced $\text{Na}_5\text{V}_3\text{O}_{10}$ could be calculated. The expression for equilibrium constant corresponds to an entropy of mixing given by a random distribution of the anions.¹⁵ Any corrections for difference in anion size would be small and are neglected here. The results are given in Table 1 and must be regarded as a qualitative approach only.

More acid vanadates, $\text{NaVO}_3 + \text{V}_2\text{O}_5$. Some reduction experiments have been carried out on fused mixtures of NaVO_3 and V_2O_5 . These mixtures are easily reduced at the beginning, possibly because of reduction of the pentoxide to V_2O_3 . Further reduction of the melts proceeds in a similar way as for the pure metavanadates.

Conclusion. The measurements of red-ox equilibria may indicate that a reduction of fused NaVO_3 leads to a formation of $\text{V}_2\text{O}_5^{2-}$ groups randomly distributed among the VO_3^- groups in a chainlike structure. Measurements on more basic systems, which presumably have shorter chains, indicate that the vanadium in the end groups $-\text{VO}_3^{2-}$ is difficult to reduce. As an example, the $\text{Na}_6\text{V}_4\text{O}_{13}$ is investigated. In this system there seems to be only one pair of vanadium atoms which can be easily reduced to a $\text{V}_2\text{O}_5^{2-}$ group. Systems between these two cases involve complex statistical calculations which would require more and accurate experimental data.

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