

Studies on Vanadium Oxides

I. Phase Analysis

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The phase relations in the composition range $\text{VO} - \text{VO}_{2.50}$ of the vanadium-oxygen system have been investigated. Phases of the following (approximate) compositions were found to exist at temperatures between 650–1 000° C:

VO (homogeneous within the range $\text{VO}_{0.75} - \text{VO}_{1.30}$), $\text{VO}_{1.50}$, $*\text{VO}_{1.87}$, $*\text{VO}_{1.75}$, $*\text{VO}_{1.80}$, $*\text{VO}_{1.84}$, $*\text{VO}_{1.86}$, $*\text{VO}_{1.87}$, $\text{VO}_{2.00}$, $\text{VO}_{2.17}$ (at 650° C), and $\text{VO}_{2.50}$; the formulae marked with an asterisk represent previously unknown oxides.

The $\text{VO}_{1.87}$ phase is monoclinic with the C centered unit cell dimensions:

$$a = 9.983 \text{ \AA}; b = 5.031 \text{ \AA}; c = 9.835 \text{ \AA}; \beta = 138.80^\circ$$

The formula of this phase is probably V_3O_5 and the unit cell thus contains 4 V_3O_5 .

Powder photographs of the phases $\text{VO}_{1.75} - \text{VO}_{2.00}$ suggest pronounced structural relationships to exist between these oxides. They may represent oxides belonging to a series with the general formula $\text{V}_n\text{O}_{2n-1}$.

The VO_2 phase is monoclinic with the unit cell dimensions:

$$a = 5.743 \text{ \AA}; b = 4.517 \text{ \AA}; c = 5.375 \text{ \AA}; \beta = 122.61^\circ$$

and the observed reflections are in accordance to the space-group $P2_1/c$. The unit cell contains 4 VO_2 .

The V_5O_{13} phase has been found to decompose into VO_2 and V_2O_5 at 700° C and higher temperatures.

PREVIOUS WORK

The system vanadium-oxygen has previously been the object of several studies. Thus, Mathewson, Spire, and Samans¹ investigated the lower vanadium oxides by means of X-ray powder photographs and microscopic examinations. They found that VO has a structure of the sodium chloride type with an extended homogeneity range and that this phase can exist in equilibrium with vanadium metal. They also supported the findings of Goldschmidt, Barth, and Lunde² and of Zachariasen³ who found V_2O_3 to have a corundum type of structure.

Klemm and Grimm ⁴ studied the vanadium-oxygen system for compositions between V and V_2O_3 . According to these authors the vanadium phase can dissolve up to 0.4 oxygen atoms per metal atom at 1 450—1 600° C. They also reported that the face-centered cubic VO phase exists between $VO_{0.9}$ and $VO_{1.3}$ at high temperatures but that this phase at lower temperatures decomposes into the metal phase and a higher oxide (not V_2O_3).

Seybolt and Sumsion ⁵ recently reported the existence of a metallic oxide with the approximate limits of homogeneity $VO_{0.15}$ — $VO_{0.25}$. Schönberg ⁶ confirmed the existence of this oxide. He also demonstrated the VO phase to be stable with an extended homogeneity range at low temperatures.

For compositions between V_2O_3 and V_2O_5 a phase analysis was performed by Hoschek and Klemm ⁷. They found some evidence for the existence of a new oxide within each of the ranges V_2O_3 — VO_2 and VO_2 — V_2O_5 but did not express a definitive inference concerning the number of phases existing. They also stated that the VO_2 phase is homogeneous between $VO_{1.8}$ and $VO_{2.0}$.

Measurements of the electric conductivity of vanadium oxides as well as X-ray studies performed by Klemm and Pirscher ⁸ were thought to confirm the existence of the phases suggested by Hoschek and Klemm ⁷.

Goldschmidt ⁹ reported that VO_2 has a tetragonal structure of the rutile type.

The composition range VO_2 — V_2O_5 was studied at this Institute by Aebi ¹⁰ who demonstrated the existence of an intermediate phase $VO_{2.17}$. He determined the crystal structure of this phase by means of X-ray methods and found the formula to be V_6O_{13} .

The crystal structure of V_2O_5 was recently determined by Byström, Wilhelm, and Brotzen ¹¹.

PRESENT INVESTIGATION

As the knowledge of the system especially for compositions between V_2O_3 and VO_2 seemed to be rather incomplete a new phase analysis was thought to be desirable. This article will present an account of investigations of the system within the composition range VO — V_2O_5 at temperatures between 650 and 1 000° C *. For compositions between V and VO a phase analysis has simultaneously been performed at this Institute by Schönberg ⁶.

EXPERIMENTAL

The starting materials for the preparations were vanadium metal (Vanadium Corporation of America, 99.7 % Grade) and vanadium pentoxide (Schering-Kahlbaum and L.K.B., Sweden, *pro analysi*) which had been heated at 400° C. Vanadium trioxide of high purity obtained by reduction of vanadium pentoxide with hydrogen at 800° C was also used for several syntheses. The vanadium content of this oxide was determined by titration with permanganate ¹².

Preparations of vanadium oxides with compositions between VO and V_2O_5 were generally obtained by heating weighed mixtures of vanadium metal powder (or in some cases vanadium trioxide) and vanadium pentoxide in evacuated silica tubes at temperatures between 650 and 1 000° C. The heating time varied between 2 days and 20 days. For lower oxides it was generally necessary to use a longer heating time to attain equilibrium

* A short note concerning this work has recently been published ¹².

than for oxides rich in oxygen. The samples were mostly quenched in cold water from the heating temperature. At temperatures above 700° C samples richer in oxygen than the dioxide appreciably affected the silica tubes with a greenish layer appearing on the inside of the walls of the tubes.

The samples obtained in this way were investigated under the microscope and by taking X-ray powder photographs in a Guinier focussing camera with monochromatized Cr-K α radiation. In the cases where single crystals could be obtained rotation and Weissenberg photographs were taken with Cu-K radiation.

PHASES OBSERVED

The present phase analysis has revealed the existence of eleven discrete oxides with the following approximate composition: VO, VO_{1.50}, VO_{1.67}, VO_{1.75}, VO_{1.80}, VO_{1.84}, VO_{1.86}, VO_{1.87}, VO_{2.00}, VO_{2.17}, and VO_{2.50}. (The existence of an oxide phase with the approximate homogeneity range VO_{0.15}

Table 1. Results of the phase analysis of vanadium oxides.

Composition of the samples	Temperature of preparation and quenching	Appearance of the samples	Phases observed
VO _{1.07}	~ 900° C	Dark or medium gray powder	VO
VO _{1.15}	»	— » —	VO
VO _{1.20}	»	— » —	VO
VO _{1.25}	»		VO(+V ₂ O ₃)
VO _{1.35}	»		V ₂ O ₃ +VO
VO _{1.45}	»		V ₂ O ₃ (+VO)
VO _{1.50}	»	Grayish powder	V ₂ O ₃
VO _{1.55}	»		V ₂ O ₃ (+VO _{1.67})
VO _{1.63}	»		VO _{1.67} (+V ₂ O ₃)
VO _{1.67}	»	{ Dark gray powder or very small crystals	VO _{1.67}
VO _{1.72}	»		VO _{1.75} + VO _{1.67}
VO _{1.75}	»	{ Dark lustrous powder or aggr. of very small crystals	VO _{1.75}
VO _{1.77}	»		VO _{1.75} + VO _{1.80}
VO _{1.80}	»	{ Nearly black lustrous powder or aggr. of small crystals	VO _{1.80}
VO _{1.82}	»		VO _{1.80} + VO _{1.84}
VO _{1.84}	»	{ Lustrous powder or aggr. of blue-black crystals	VO _{1.84}
VO _{1.85}	»		VO _{1.84} + VO _{1.86}
VO _{1.86}	»	{ Strongly lustrous blue-black powder or very small crystals	VO _{1.86}
VO _{1.865}	»		VO _{1.87} + VO _{1.86}
VO _{1.87}	»	— » —	VO _{1.87}
VO _{1.92}	»		VO ₂ + VO _{1.87}
VO _{2.00}	»	{ Needle- or rodshaped blue-black crystals	VO ₂
VO _{2.15}	≥ 700° C		VO ₂ (+V ₂ O ₅)
VO _{2.30}	»		V ₂ O ₅ + VO ₂
VO _{2.10}	~ 650° C		VO ₂ + V ₆ O ₁₃
VO _{2.17}	»	{ Black lustrous powder or small crystals	V ₆ O ₁₃
VO _{2.25}	»		V ₆ O ₁₃ + V ₂ O ₅
VO _{2.50}	»	{ Brownish yellow powder or brownish crystals	V ₂ O ₅

Table 2. X-ray diffraction data of the phases $VO_{1.67}$, $VO_{1.75}$, $VO_{1.80}$, $VO_{1.84}$, $VO_{1.86}$, $VO_{1.87}$, and VO_2 . Cr-K α radiation.

$VO_{1.67}$				VO_2			
<i>hkl</i>	<i>I</i> _{rel}	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	<i>hkl</i>	<i>I</i> _{rel}	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$
$\bar{2},0,2$	m	.0609	.0610	$\bar{1},1,1$	w	.1198	.1198
$\bar{1},1,1$	w	.0671	.0671	$0,1,1$	vst	.1283	.1283
$2,0,0$	st	.1214	.1214	$\bar{1},0,2$	w	.1830	.1830
$0,0,2$	w	.1250	.1250	$\bar{2},0,2$	w+	.2220	.2220
$\bar{1},1,1$	st	.1598	.1598	$2,1,1$	m+	.2234	.2234
$3,1,3$	st	.1892	.1892	$2,0,0$	w	.2241	.2242
$0,2,0$	m	.2074	.2073	$2,1,2$	m	.2864	.2863
$\bar{3},1,1$	vw	.2171	.2171	$2,1,0$	m	.2887	.2885
$\bar{1},1,3$	m	.2244	.2245	$\bar{1},2,1$	vw	.3124	.3127
$\bar{4},0,4$	vw	.2442	.2442	$0,1,2$	w	.3207	{ .3203 .3212
$2,2,1$	m+	.2674	.2673	$0,2,1$			
$2,2,2$	m	.2688	{ .2684 .2690	$3,0,2$	vw+	.3732	.3732
$3,1,4$				$\bar{3},1,1$	vw+	.4395	{ .4391 .4402
$1,1,2$	m	.3000	.2999	$\bar{1},2,2$	w	.4771	.4772
$2,2,0$	m-	.3287	.3287	$\bar{2},1,3$			
$0,2,2$	vw	.3325	.3324	$2,2,2$	w	.4788	.4792
$5,1,5$	m+	.4332	.4333	$2,2,0$	m+	.4814	{ .4814 .4816
				$\bar{2},1,1$			
				$\bar{1},1,3$	vw	.5022	.5027

$VO_{1.75}$		$VO_{1.80}$		$VO_{1.84}$		$VO_{1.86}$		$VO_{1.87}$	
$\sin^2\theta_{\text{obs}}$	<i>I</i> _{rel}	$\sin^2\theta_{\text{obs}}$	<i>I</i> _{rel}	$\sin^2\theta_{\text{obs}}$	<i>I</i> _{rel}	$\sin^2\theta_{\text{obs}}$	<i>I</i> _{rel}	$\sin^2\theta_{\text{obs}}$	<i>I</i> _{rel}
.0358	vw	.0220	vw	.0513	vw	.0496	vw	.0666	w
.0494	w	.0503	w	.0554	w	.0610	w-	.0983	m
.0744	m	.0832	m+	.0895	m+	.0805	vw	.1214	st+
.0960	w--	.1173	vw	.1197	st	.0942	m+	.1369	st
.1187	st	.1191	st	.1293	w+	.1204	st	.1461	st-
.1223	w	.1220	vw	.1400	st	.1244	w+	.1994	w
.1414	w	.1310	vw	.1533	st	.1380	st	.2005	w
.1485	m+	.1393	vw+	.1687	w	.1489	st+	.2109	m
.1607	w	.1432	m+	.1908	m-	.1768	vw	.2201	m
.1711	m+	.1565	vw	.1990	w	.1789	vw	.2242	m+
.1746	m-	.1602	st	.2056	m+	.1954	w+	.2376	w
.1975	m	.1847	m-	.2180	m	.1989	w-	.2584	w+
.2123	vw	.2022	m	.2234	m-	.2083	m	.2812	st
.2142	m-	.2166	m-	.2382	w	.2188	m	.2822	m
.2244	m-	.2239	m-	.2422	w	.2235	m	.2840	m
.2324	w+	.2357	w	.2708	w+	.2388	w-	.2931	st
.2550	w	.2469	vw	.2782	m	.2402	w-	.2987	w
.2756	st	.2768	w+	.2796	w+	.2633	w+	.3126	w+
.2832	m-	.2788	m+	.2812	m	.2794	m	.3211	vw
.2964	m-	.2822	w	.2924	m-	.2807	m	.4143	w-
.2991	w+	.2882	w+	.2936	m-	.2825	m	.4646	m+

vst = very strong; st = strong;
m = medium; w = weak; vw = very weak.

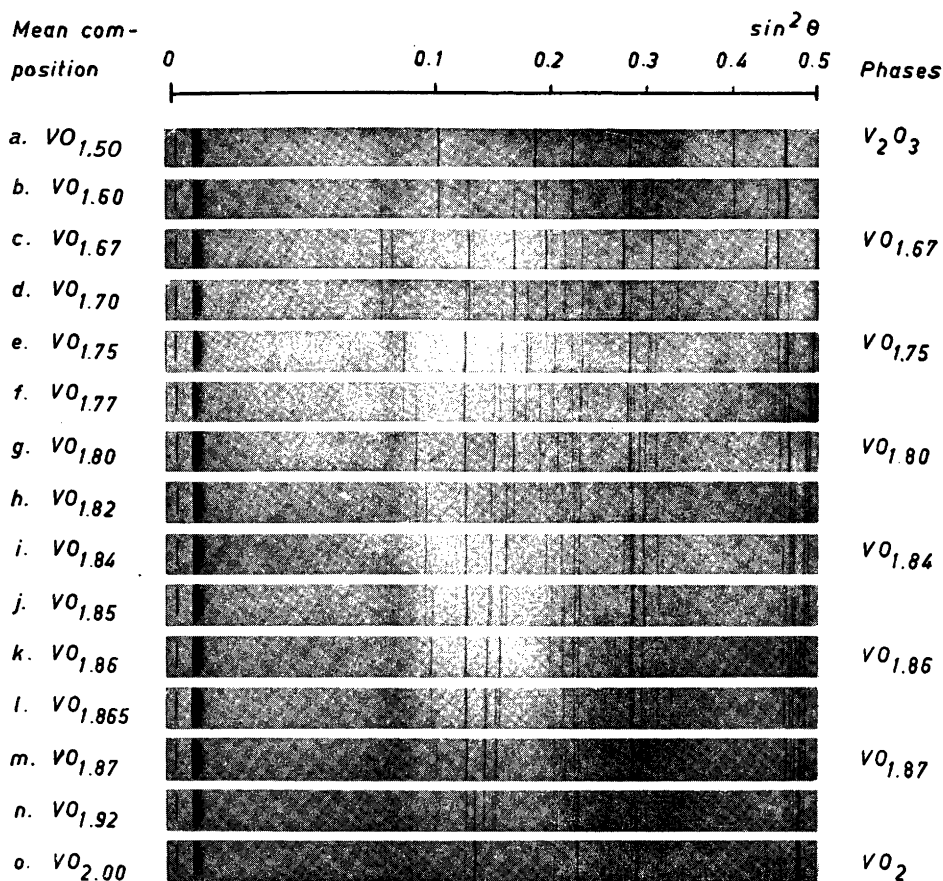


Fig. 1. X-ray powder photographs of samples VO_x (Cr-K α radiation).

— $VO_{0.25}$ has recently been demonstrated by Seybolt and Sumsion⁵ and by Schönberg⁶.) In the following these approximate formulae will be used as symbols for the various intermediate phases.

The results of the phase analysis are summarized in Table 1 while X-ray diffraction data for the oxides $VO_{1.67}$ — VO_2 are listed in Table 2. Fig. 1 represents a selection of powder photographs for compositions $VO_{1.50}$ — $VO_{2.00}$.

In agreement with the observations of Klemm and Pirscher⁸ measurements of the electric conductivity have shown the oxides VO to $VO_{2.17}$ inclusively to be semiconductors.

The VO phase. As stated by previous authors^{1,4,6} the monoxide VO of sodium chloride structure shows a wide range of homogeneity. It was found rather difficult to reach a state of equilibrium in samples of this phase. However, after prolonged heating at 900°C it was possible to obtain several samples

VO_{1.07}—VO_{1.20} the powder patterns of which did not show any traces of phases other than VO. The lattice constants derived from powder photographs are given in Fig. 2 together with lattice constants obtained by Schönberg (private communication). Contrary to the statement of Klemm and Grimm⁴ the unit cell dimensions thus were found to increase with increasing oxygen content. The upper and the lower limits of the phase range were found to be VO_{1.20} and VO_{0.75} with the axial lengths $a = 4.128 \text{ \AA}$ (VO_{1.20}) and $a = 4.043 \text{ \AA}$ (VO_{0.75}) respectively. The axial length at the composition VO_{1.00} was found to be $a = 4.09 \text{ \AA}$.

The V₂O₃ phase. Powder photographs of samples with compositions around VO_{1.25} (heated at 900° C) showed weak lines of the V₂O₃ phase while for compositions between VO_{1.40} and VO_{1.55} the V₂O₃ lines dominated the patterns. Variations in the positions of the reflections could not be detected for samples containing this phase indicating the homogeneity range to be very narrow. The corundum structure^{2,3} of the phase was verified, and the following dimensions of the rhombohedral unit cell were derived in reasonable accordance to the values given by Zachariasen³:

$$a = 5.467 \text{ \AA}; \alpha = 53.74^\circ$$

The VO_{1.67} phase. Powder photographs of the samples VO_{1.55}—VO_{1.65} showed lines of V₂O₃ together with lines of another phase. The latter lines appeared alone in photographs of the sample VO_{1.67} (Fig. 2 c) and closely around this composition (about ± 1 atom-%). The range of homogeneity was found to be very narrow. The phase was investigated by single crystal as well as powder methods (Table 2).

The crystal structure was found to be monoclinic with $C2/c$ or Cc as probable space-groups. The unit cell dimensions were:

$$a = 9.983 \text{ \AA}; b = 5.031 \text{ \AA}; c = 9.835 \text{ \AA}; \beta = 138.80^\circ$$

The density of the sample was determined to be 4.55 which corresponds to 11.6 VO_{1.67} per unit cell and suggests a cell content of 4 formula units of V₃O₅. A determination of the crystal structure is in progress.

The VO_{1.75}, VO_{1.80}, VO_{1.84}, VO_{1.86}, and VO_{1.87} phases. Powder photographs of samples with the compositions VO_{1.70} and VO_{1.72} clearly showed the phase VO_{1.67} together with the phase denoted VO_{1.75} while in photographs of the samples VO_{1.77} and VO_{1.79} the VO_{1.75} lines appeared together with lines of the VO_{1.80} phase. Samples of the composition VO_{1.75} gave reflections of only one phase, viz. the VO_{1.75} phase (Fig. 1 e). Crystals suitable for single crystal methods have not yet been obtained of this phase.

From powder photographs of samples with compositions VO_{1.77}—VO_{1.82} the next phase was found to be homogeneous very close to the composition VO_{1.80} (Fig. 1 g). Attempts to produce single crystals by prolonged heatings have, not yet been successful.

The powder photographs of the three following phases which seem to be homogeneous at compositions about VO_{1.84}, VO_{1.86}, and VO_{1.87} respectively (Fig. 1 i, k, m) resemble each other very much as well as the photographs of the two preceding oxides (Table 1). After prolonged heatings at higher temperatures very small strongly reflecting crystals without characteristic shape could

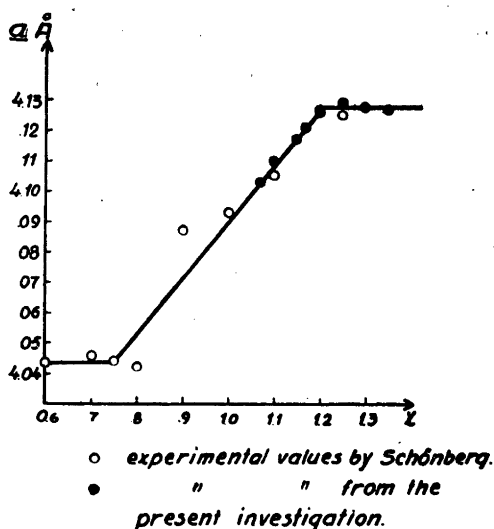


Fig. 2. The axial length (a) as a function of the composition (VO_x) at 900 °C.

be observed under the microscope but so far no crystals suitable for single crystal investigations have been obtained.

Extended homogeneity ranges have not been demonstrated for any of the oxides $\text{VO}_{1.75}$, $\text{VO}_{1.80}$, $\text{VO}_{1.84}$, and $\text{VO}_{1.86}$. In some powder photographs of samples $\text{VO}_{1.90}$ — $\text{VO}_{1.96}$ a few weak lines were observed besides the powder pattern of $\text{VO}_{1.87}$ and together with the pattern of VO_2 (Fig. 1 n). This fact possibly indicates that the $\text{VO}_{1.87}$ phase has a variable composition or possibly that still another phase may be present here.

The close similarity between the powder patterns of all the phases from $\text{VO}_{1.75}$ and to VO_2 suggests pronounced structural relationships between these phases (Fig. 1 e—o and Table 2). As their powder photographs are rather complicated further interpretation seems to require single crystal methods.

It has been pointed out to the author by Dr. A. Magnéli that these oxides within the limits of error have compositions corresponding to the general formula $\text{V}_n\text{O}_{2n-1}$, viz. $\text{VO}_{1.75}$ ($\text{V}_4\text{O}_7 = \text{VO}_{1.750}$), $\text{VO}_{1.80}$ ($\text{V}_5\text{O}_9 = \text{VO}_{1.800}$), $\text{VO}_{1.84}$ ($\text{V}_6\text{O}_{11} = \text{VO}_{1.833}$), $\text{VO}_{1.86}$ ($\text{V}_7\text{O}_{13} = \text{VO}_{1.857}$), $\text{VO}_{1.87}$ ($\text{V}_8\text{O}_{15} = \text{VO}_{1.875}$), and VO_2 ($\text{V}_n\text{O}_{2n-1}$, $n \rightarrow \infty$). This conformity together with the pronounced structural relationship suggested by the similarity of the powder patterns might indicate the existence of a "homologous series" of vanadium oxides structurally based on the rutile type structure in a way similar to the homologous series of molybdenum tungsten oxides $(\text{Mo}, \text{W})_n\text{O}_{3n-1}$ derived from the ReO_3 -type structure¹⁴⁻¹⁶.

The VO_2 phase. At first sight single crystal photographs seem to indicate a tetragonal unit cell with the a and c axes twice as long as those corresponding to the structure of rutile type reported by Goldschmidt⁹. However, the multiplet structure of several powder lines (Fig. 2 o) shows that the actual symmetry is lower, viz. monoclinic. Observed and calculated positions and

relative intensities of the powder reflections are recorded in Table 2. The dimensions of the primitive unit cell were from powder photographs found to be:

$$a = 5.743 \text{ \AA}; b = 4.517 \text{ \AA}; c = 5.375 \text{ \AA}; \beta = 122.61^\circ$$

This cell contains four units VO_2 . The space-group is probably $P 2_1/c$. No displacements of the powder lines could be observed either in photographs taken of samples of the VO_2 phase together with the lower oxide phase or together with higher oxide phases. This indicates that the homogeneity range of this phase must be very narrow. A determination of the crystal structure of VO_2 is in progress.

The V_6O_{13} and V_2O_5 phases. Powder photographs of samples with compositions between $\text{VO}_{2.05}$ and $\text{VO}_{2.15}$ quenched from about 650°C showed VO_2 lines together with lines of V_6O_{13} . Samples $\text{VO}_{2.10}$ — $\text{VO}_{2.40}$ quenched from 700°C and higher temperatures, however, only gave the patterns of VO_2 and V_2O_5 (Table 1) showing the V_6O_{13} phase to be unstable at these temperatures. The unit cell dimensions and symmetry of the V_6O_{13} phase previously found at this Institute by Aebi¹⁰ were verified.

The unit cell dimensions observed for V_2O_5 in the present investigation agree with those derived by Byström *et al.*¹¹ and by Magnéli and Blomberg¹⁷.

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