PHASE EQUILIBRIA IN THE V_2O_5–Sb_2O_4 SYSTEM

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Abstract

Differential thermal analysis (DTA) and X-ray powder diffraction (XRD) were used to study phase equilibria, established in air in the V_2O_5–Sb_2O_4 system up to 1000°C. It has been found that there is a new phase ≈$SbVO_5$. The ≈$SbVO_5$ has been prepared by two methods: by heating equimolar mixtures of V_2O_5 and α-Sb_2O_4 in air and by oxidation of the known phase of rutile type obtained in pure argon at temperatures between 550 and 650°C. Thermal decomposition of ≈$SbVO_5$ in the solid state starts at 710°C giving off oxygen. The results provide a basis for constructing only a part of the phase diagram of the investigated system (up to 50.00 mol% Sb_2O_4).

Keywords: antimony tetroxide, DTA, phase equilibrium, vanadium(V) oxide, XRD

Introduction

Vanadium and antimony oxides and phases formed in the V–Sb–O system show some properties of practical value [1].

It follows from the information published that the number and types of phases formed in the V–Sb–O system greatly depend on the atmosphere in which the oxide reagents are thermally treated. Practically, all the interested workers agree that in air the components of the Sb_2O_3–V_2O_5 system react by giving only one compound that would correspond to the 1:1 molar ratio of the oxides in the initial mixture from the investigated system [2–13]. Renaud has ascribed a formula $Sb_2V_2O_9$ to the phase obtained in air from an Sb_2O_3/V_2O_5 or Sb_2O_4/V_2O_5 mixture, and found it prone to decomposition into $SbVO_4$ and free oxygen [2]. In Renaud's opinion, a stoichiometric $SbVO_4$ [3–5] can be obtained from Sb_2O_3 only in argon atmosphere, it being then stable up to 925°C [2]. Birchall *et al.* [6] have confirmed by Mössbauer spectroscopy that a compound obtained at 800°C in air from an Sb_2O_3/V_2O_5 mixture has a formula $V_{0.28}^{III}V_{0.64}^{IV}Sb_{0.92}^{V}O_4$($SbVO_{4.35}$) and, according to the previous statements [2, 4, 5], it is a phase of a rutile structural type [6]. Berry *et al.* maintain that a reaction leading to a non-stoichiometric rutile-type phase, $V_{1-x}Sb_{1-x}O_4$, where $x< 0.1$, involves oxidation of Sb_2O_3 to Sb_2O_4 [7–11]. Antimony in the obtained phase is in +5 oxidation state and vanadium – in +4. The authors found that the compound, $V_{0.89}Sb_{0.89}O_4$, melted in air above 800°C and a solid solution of vanadium in β-Sb_2O_4 was formed in the products of melting [8,10]. Other workers have confirmed the experimental results of Birchall *et al.* [6]. They maintain that in air both Sb_2O_3 and Sb_2O_4 react with V_2O_5 giving one non-stoichiometric compound with a formula $Sb_{0.92}V_{0.92}O_4$ [12–

14]. $Sb_{0.92}V_{0.92}O_4$, which crystallises in a tetragonal system and belongs to a space group $P4_2/mnm$ [12].

Canovas *et al.* [14] have found that heating of an equimolar Sb_2O_3/V_2O_5 mixture at 800°C in O_2/N_2 atmosphere with a varying proportion of oxygen to nitrogen gives a sequence of non-stoichiometric phases of a rutile structural type, $Sb_{0.9}V_{0.9+x}\square_{0.2-x}O_4$ and α-Sb_2O_4.

Furthermore, literature search has shown that only few workers have studied phase equilibria established in the Sb_2O_3–V_2O_5 or Sb_2O_4–V_2O_5 system [2, 15]. The relevant phase diagram was constructed only by Renaud [2]. The eutectic formed by V_2O_5 and $Sb_2V_2O_9$ (the only phase found in this system) – melts at 657°C and its composition corresponds to that of an oxide mixture containing 91 % V_2O_5 and 9 % Sb_2O_4. The state of our investigations of the Sb–V–O system and the experimental results of our introductory research [16] have given rise to suggestion that it is necessary to verify the equilibria established in the Sb_2O_4–V_2O_5 system in air.

Experimental

The following reagents were used for experiments: V_2O_5, p.a., (POCh, Glivice, Poland), Sb_2O_3, p.a. (M. Merck, Darmstadt, Germany), α-Sb_2O_4, a reactant prepared by heating Sb_2O_3 in air in the following cycles:
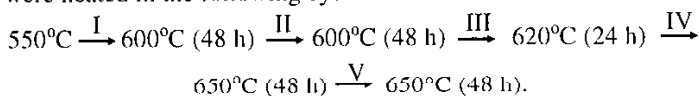
350°C (1 h) → 400°C (1 h) → 500°C (1 h) → 600°C (1 h) → 650°C (24 h).
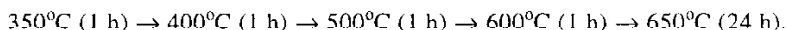
Table 1 The α-Sb_2O_4 content of α-Sb_2O_4/V_2O_5 initial mixtures and the phase composition of samples after the final heating cycle

The α-Sb_2O_4 content of a mixture/mol%	Phases found
5.00,10.00, 20.00, 25.00, 30.00, 33.33, 35.00, 40.00, 45.00	V_2O_5, $\approx SbVO_5$
50.00	$\approx SbVO_5$
55.00, 60.00	$\approx SbVO_5$, $Sb_2V_2O_9$, α-Sb_2O_4-traces
65.00, 66.67, 70.00, 75.00, 80.00, 85.00, 90.00, 95.00	$Sb_2V_2O_9$, α-Sb_2O_4

There were prepared twenty mixtures with varied V_2O_5 and α-Sb_2O_4 contents in order to present the whole component concentration range of the title system (Table 1). The oxide mixtures were homogenised by grinding. shaped into pastilles and heated cyclically in air. The results of the preliminary tests [16] decided the application of the following conditions to samples, containing up to 50.00 mol% of Sb_2O_4, so that they could reach an equilibrium state:

550°C → 600°C (48 h) → 600°C (48 h) → 620°C (24 h) →
630°C (48 h) → 630°C (48 h).
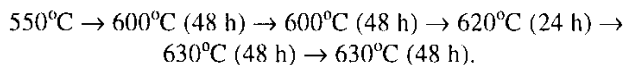
A sample with a 50/50 percentage of the V_2O_5/α-Sb_2O_4 in the initial mixture and samples presenting the other component concentration range of the V_2O_5–α-Sb_2O_4 system were heated in the following cycles:

$$550°C \xrightarrow{I} 600°C \ (48\ h) \xrightarrow{II} 600°C \ (48\ h) \xrightarrow{III} 620°C \ (24\ h) \xrightarrow{IV}$$
$$650°C \ (48\ h) \xrightarrow{V} 650°C \ (48\ h).$$

On each heating cycle the samples were gradually cooled to ambient temperature, weighed in order to find a change in their mass, then ground and analysed by XRD method. Afterwards the samples were again shaped into pastilles and heated, the procedure was repeated until identical results of XRD analysis were obtained after two consecutive heating cycles. Finally, they were analysed by DTA method.

The phase composition was established depending on the diffraction patterns taken by an X-ray diffractometer of an HZG-4/A-2 (CoK_α) type and on the data included in PDF cards [17] and on those in the publication [2, 7, 12].

Differential Thermal Analysis (DTA) was made by using a derivatograph of a Paulik-Paulik-Erdey type (MOM, Budapest, Hungary). The measurements were made in air at 20–1000°C. Samples with a 1000 mg mass were placed in quartz crucibles and heated at a rate of 10°C min^{-1}.

The solidus lines shown in the phase diagram of the system under consideration were determined depending on the onset temperatures of first endothermic effects recorded on DTA curves of the samples after the final heating cycle. The curves bordering the fields where solid phases remain in equilibrium with liquid have been drawn on the basis of temperatures of successive endothermic effects or of temperatures at which distinct shoulders on the sides of the thermal effects were recorded.

Results and discussion

The diffraction patterns of a sample with its initial V_2O_5 and Sb_2O_4 contents corresponding to an equimolar mixture of the oxides, after the first and second heating cycles, i.e. at 600°C (48 h and 48 h) covered, apart from the lines characteristic of V_2O_5 and Sb_2O_4, a set of diffraction lines whose angle position and mutual relations in terms of intensity were consistent with the diffraction pattern of $Sb_2V_2O_9$ ($SbVO_{4.5}$) published by Renaud *et al.* According to these authors, it is the sole compound to arise in air in the V_2O_5–Sb_2O_4 system [2]. On the other hand, in the light of the data published recently it can be assumed that the phase which is initially formed in the reaction mixture corresponds to the compound, $Sb_{0.92}V_{0.92}O_4$ ($SbVO_{4.35}$) [12]. A pure $SbVO_{4.35}$ – a black non-stoichiometric phase of a rutile structural type – has been obtained in air only from an equimolar Sb_2O_3/V_2O_5 mixture so far [6, 11–14, 18].

The sample we obtained from an equimolar V_2O_5/α-Sb_2O_4 mixture was greenish black after two heating cycles. Diffraction patterns of that sample on consecutive cycles of heating in air at 620°C (24 h) and 650°C (48 h) covered, apart from reflexions characteristic of the rutile type phase ($SbVO_{4.35}$), a set of lines attributable only to the phase we have recently informed about. The preliminary stage of our studies on the title system accounts for the provisional attribution of a $\approx SbVO_5$ formula to the

phase of interest [16]. On heating the sample at 650°C a noticeable increase in its volume can be seen. After the final heating cycle, that is, the fifth one, the sample was of light olive colour and contained only the new phase, ≈SbVO₃ (Table 2). The synthesis of ≈$SbVO_5$ was distinguished not only by a change in the colour and volume of the reaction product but also by its mass increment, of ~2.5% by weight after the five heating cycles.

Table 2 The interplanar distances of ≈SbVO₅ and relative intensities corresponding to the reflections

d/nm	I/%	d/nm	I/%	d/nm	I/%	d/nm	I/%
0.4638	100	0.2776	8	0.2176	6	0.1852	12
0.3567	15	0.2744	20	0.2133	10	0.1759	8
0.3382	80	0.2623	33	0.2102	8	0.1738	40
0.3302	12	0.2538	8	0.2030	5	0.1711	5
0.3277	8	0.2476	20	0.1986	5	0.1687	20
0.3094	46	0.2432	5	0.1968	20	0.1677	8
0.2889	23	0.2387	4	0.1930	5	0.1664	10
0.2862	10	0.2322	25	0.1870	6	0.1644	10
0.2794	15	0.2235	12	0.1857	20	0.1636	8

The experimental results suggest that α-Sb_2O_4 present in reaction mixtures reacts in air with V_2O_5 to produce at first the known non-stoichiometric rutile-type phase [2,12]. In next stages this phase may react with atmospheric oxygen to give ≈$SbVO_5$, the formation of which can be inferred from the mass increment of the samples observed during heating. In order to verify the reaction course of the phase synthesis, an equimolar α-Sb_2O_4/V_2O_5 mixture was prepared to be heated in the atmosphere of 99.995% pure argon (the amount of oxygen in the argon not exceeding $2 \cdot 10^{-4}$ %). The temperature and time of each argon-heating cycle were identical to those applied to the heating in air. XRD and DTA examinations of the argon-heated sample of black-graphite colour showed that it was a monophase material which contained the rutile-type phase. The diffraction pattern of the phase prepared in argon bore a lot of similarity to the pattern of the compound $Sb_2V_2O_9$ ($SbVO_{4.5}$) obtained from an Sb_2O_4/V_2O_5 mixture by Renaud [2]. The phase prepared in argon was then heated in air under the following conditions:

650°C (24 h) → 650°C (24 h) → 650°C (72 h) → 650°C (48 h) → 650°C (48 h).

X-ray phase analysis of the sample on the final heating cycle showed the presence of the ≈$SbVO_5$ phase only. The heating of the sample, the hue of which was changing from black-graphite to light olive, involved a mass increment making 2.45% by weight.
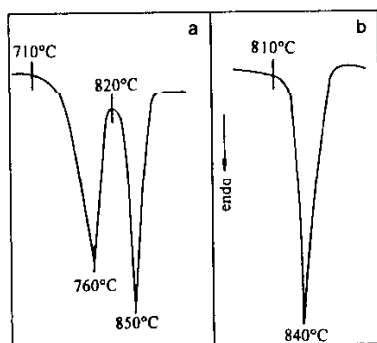
Fig. 1 The DTA curves: a) $\approx$SbVO$_5$, b) the phase obtained in argon

Figure 1 shows, for comparison, a DTA curve of the ~SbVO$_5$ phase *vs.* the DTA curve of the phase obtained in argon. The DTA curve of $\approx$SbVO$_5$ has two endothermic effects, the first starting at $710\pm5°C$, and the onset of the other – at $820\pm5°C$. The first effect entails mass decrement, recorded on TG curves (neglected in the figure), and makes up 2.8%. X-ray phase analysis of the $\approx$SbVO$_5$ sample extra heated at 760°C (3 h), that is, at the temperature of I effect extremum, to be immediately quenched to ambient temperature, has shown that the ~SbVO$_5$ phase probably decomposes releasing oxygen and giving a rutile-type phase, i.e. Sb$_2$V$_2$O$_9$ or SbVO$_{4.35}$ (Sb$_{0.92}$V$_{0.92}$O$_4$). Its thermal decomposition starts at 710°C. The resultant Sb$_2$V$_2$O$_9$ melts congruently at $820\pm5°C$ (II effect).

All things considered, it is justifiable to assume that the endothermic effect with $810\pm5°C$ onset temperature recorded on the DTA curve of the phase obtained in argon (curve b) will account for melting of the rutile-type phase, Sb$_2$V$_2$O$_9$ (or SbVO$_{4.35}$). The fact can be supported by the phase composition of a sample melted at 850°C (3 h) – identical to that of a sample comprising $\approx$SbVO$_5$ and melted at the same temperature.

On the assumption that the reaction between V$_2$O$_5$ and α-Sb$_2$O$_4$ taking place in the solid phase, in air will produce stoichiometric products that may be either intermediary or final products of the reaction, one can write the following equations:

$$V_2O_{5(s)}+Sb_2O_{4(s)} \rightarrow Sb_2V_2O_{9(s)} \tag{1}$$

$$Sb_2V_2O_{9(s)}+1/2O_2 \rightarrow 2SbVO_{5(s)} \tag{2}$$
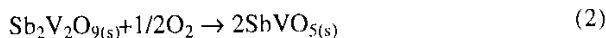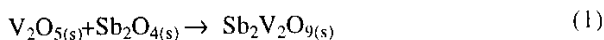
The mass increment of the product involved in the formation of the stoichiometric SbVO$_5$ phase should be 3.2% by weight according to Eq. (2). Both the mass increment observed during synthesis of SbVO$_5$, not exceeding 2.5% by weight, and the 2.8%/weight mass decrement, recorded on TG curves during decomposition of the phase, have allowed the formula of the resultant product to be written as SbVO$_{5-x}$, where $0.1>x>0.05$, or $\approx$SbVO$_5$.

Table 1 shows the contents of initial oxide mixtures representing the whole component concentration range for the V_2O_5–Sb_2O_4 system and phase composition of samples after the final heating cycle.

X-ray analysis of samples in an equilibrium state, prepared from initial mixtures composed of up to 50.00 mol% of α-Sb_2O_4, show them to be diphase products and to contain the $\approx SbVO_5$ phase apart V_2O_5. The phases remain in equilibrium in the solid state to 640±5°C, indicated by the onset temperature of the first endothermic effect recorded on DTA curves of the samples. This effect may be accounted for by melting of a eutectic formed by V_2O_5 and $\approx SbVO_5$. The contents of the eutectic mixture in terms of the system's components correspond to the amount of α-Sb_2O_4 making up 10.00 mol%, at the most. The eutectic composition can be confirmed by the magnitude of the first effect observed on the DTA curve of this sample.

X-ray phase analysis of samples with the α-Sb_2O_4 contents between 55.00 and 60.00 mol% on the final, i.e. the fifth heating cycle – 650°C for 48 h, shows them to be triphase and to contain, beside the rutile-type phase $Sb_2V_2O_9$ (or $SbVO_{1.35}$). $\approx SbVO_5$, minute quantities of α-Sb_2O_4. The samples representing the other component concentration range – upwards of 60 mol% of α-Sb_2O_4, on the last heating cycle are diphase products and contain α-Sb_2O_4 beside the known phase. Further heating. at 675°C for 48 h in air, of samples containing over 50.00 mol% of α-Sb_2O_4 could not cause changes in their phase composition. This component concentration range (of above 50.00 mol% of α-Sb_2O_4) has been deemed favourable for the phases $\approx SbVO_5$ and α-Sb_2O_4 to remain in equilibrium in the solid state. The phase composition of samples in that concentration range of the title system's components implies that $Sb_2V_2O_9$ ($SbVO_{4.35}$), found as an intermediary product in the reaction mix-
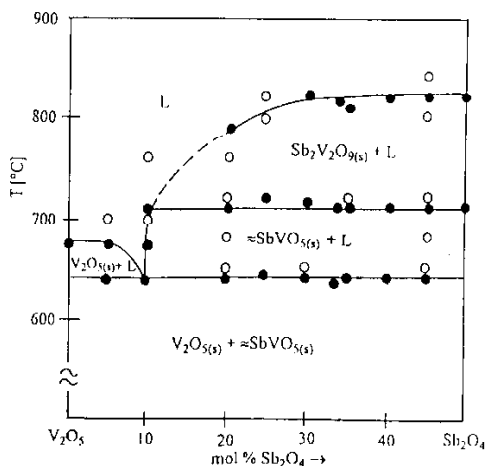

Fig. 2 Phase diagram of the V_2O_5–Sb_2O_4 system for the component concentration range up to 50.00 mol% of Sb_2O_4. • – points indicate DTA; o – X-ray investigation after air quenching

ture, will not entirely react with oxygen in the presence of α-Sb_2O_4 to produce $\approx SbVO_5$.

The results of our studies on phase equilibria established in air in the V_2O_5–Sb_2O_4 system have permitted constructing a phase diagram only for the component concentration range of 0.00–50.00 mol% of α-Sb_2O_4 (Fig. 2). The borders of fields delineated on the base of DTA and XRD analyses of phases being in an equilibrium state have been marked with a solid line. On the other hand, the borders of fields which were established depending upon XRD analysis of samples extra heated and then quenched to ambient temperature have been marked with a dashed line.

The components of the V_2O_5–α-Sb_2O_4 system react in the solid state to form a new phase, $\approx SbVO_5$. This phase decomposes at $\sim710^\circ C$ into the known rutile-type phase. The part of the phase diagram presented has provided a proof that the V_2O_5–Sb_2O_4 system is a real two-component one within the above-mentioned component concentration range.

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