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REACTIONS BETWEEN SODIUM CARBONATE AND VANADIUM PENTOXIDE

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ABSTRACT

The isothermal reactions between Na_2CO_3(X) and V_2O_5(Y) have been studied. It has been noticed that the reaction depends on both temperature and the molar X:Y ratios for the mixtures 1:6 and 1:3. For higher Na_2CO_3 contents, the reaction is more dependent on temperature. An X-ray examination of the isothermal products revealed the sequence of formation of different types of vanadates. The X-ray diffraction patterns for five sodium vanadates were investigated. The presence of two types of bronze I; $Na_2V_{12}O_{31}$ and NaV_6O_{15} was evidenced by both X-ray and differential thermal analysis. The transformation of the former compound to the latter during cooling is accompanied by oxygen evolution; a phenomenon which is reversible.

INTRODUCTION

Vanadium oxide usually occurs in combination with phosphates and other minerals of iron, lead, zinc and uranium. The usual procedure in separating vanadium oxide from its ores, consists of converting it to a soluble sodium salt and roasting with a source of soda under oxidizing conditions. The chemical behaviour during roasting vanadium oxide with soda, follows the unpredictable pattern of the transition elements in many of its compounds and there is uncertainty as to its precise reaction with alkali salts[1]. From the viewpoint of extractive metallurgy, most of the problems arise from the selection of the sodium salt and the side reactions that may proceed with the associated minerals in the ores[2–4].

Sodium carbonate is widely used in the extraction of vanadium oxide from lead–zinc deposits from African mines[1]. The indefinite composition of the sodium vanadate products together with the contradictory results given by some authors[5–7] concerning the structure of vanadium compounds, are calling attention to the mechanism of the reaction between sodium carbonate and vanadium pentoxide. The X-ray diffraction data of anhydrous sodium vanadates were not well established[7,8] before this study.

EXPERIMENTAL

Materials

V_2O_5 was prepared by heating chemically pure ammonium vanadate at 500 °C for 24 hours[9]. Analar anhydrous Na_2CO_3 from BDH was preheated at 800 °C and kept in a desiccator.

Apparatus and technique

The investigation of the interaction between Na_2CO_3 and V_2O_5 included experiments on isothermal gravimetric analysis, and differential thermal analysis. The apparatus and technique have been described in an earlier publication[10]. The X-ray diffraction analysis is performed according to Helzberg *et al.*[9], with the aid of 114.83 mm Philips Debye–Sherrer powder camera and Philips X-ray unit PW 1010 diffractometer.

RESULTS AND DISCUSSION

Isothermal studies

The change in weight isotherms for the mixtures Na_2CO_3 (X) and V_2O_5(Y) having the X:Y ratios 1:6, 1:3, 1:1, 2:1 and 3:1 between 400–800 °C are shown in Figs. 1–5. It is noticed that at all mixtures, the reaction proceeds with higher rates than the corresponding mixtures of Na_2SO_4 and V_2O_5[10,11]; a phenomenon which is expected due to the lower acidity of CO_3^{2-} ions. It is found that Na_2CO_3 decomposes by V_2O_5 at temperature as low as 400 °C. It is of interest to mention that the reaction between Na_2CO_3 and V_2O_5 at all mixtures except 3:1, takes place in the solid state at temperatures < 650 °C. At 550 °C, however, semifusion starts and the

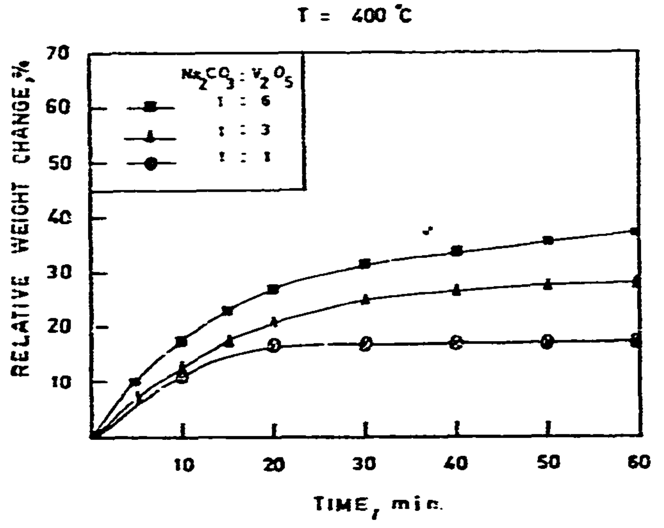

Fig. 1. Relative weight changes of the mixtures Na_2CO_3:V_2O_5 at 400 °C.

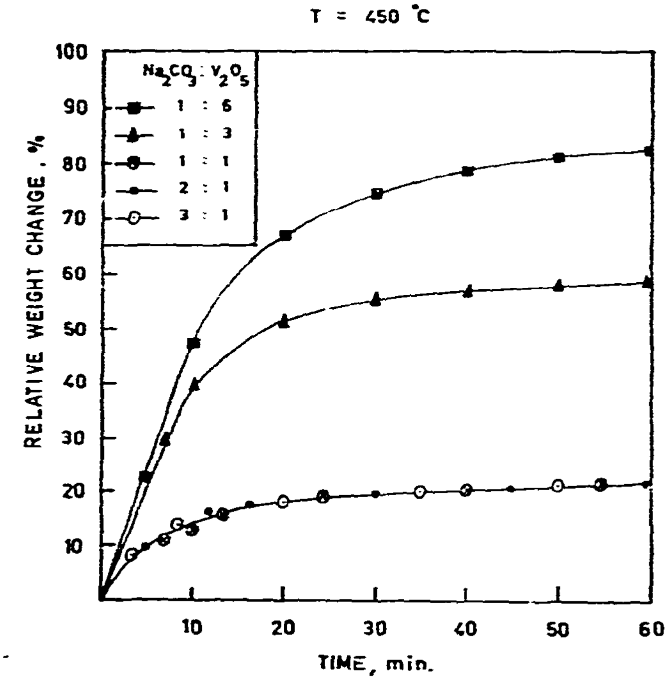

Fig. 2. Relative weight changes of the mixtures Na_2CO_3:V_2O_5 at 450°C.

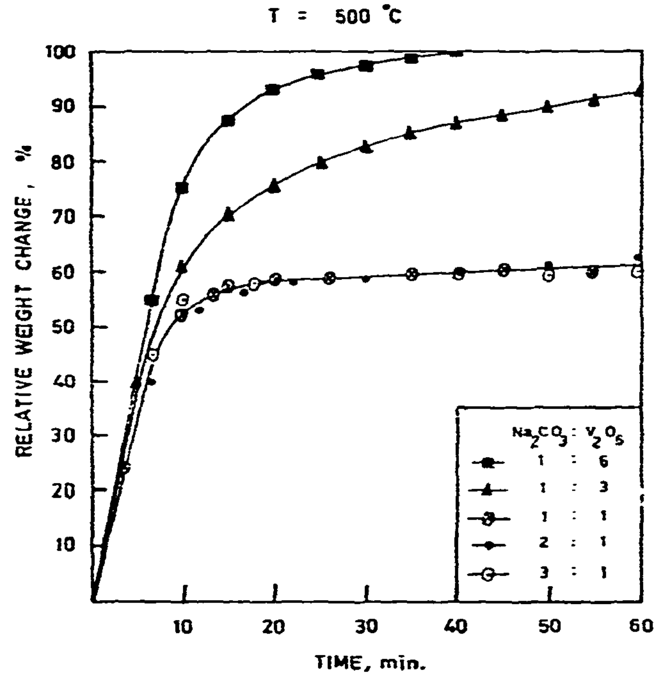

Fig. 3. Relative weight changes of the mixtures Na_2CO_3:V_2O_5 at 500°C.

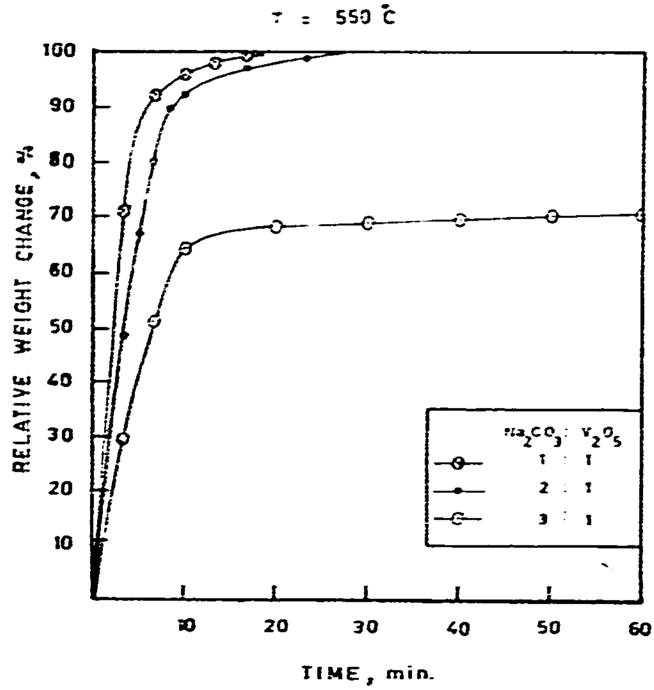

Fig. 4. Relative weight changes of the mixtures Na_2CO_3:V_2O_5 at 550 °C.

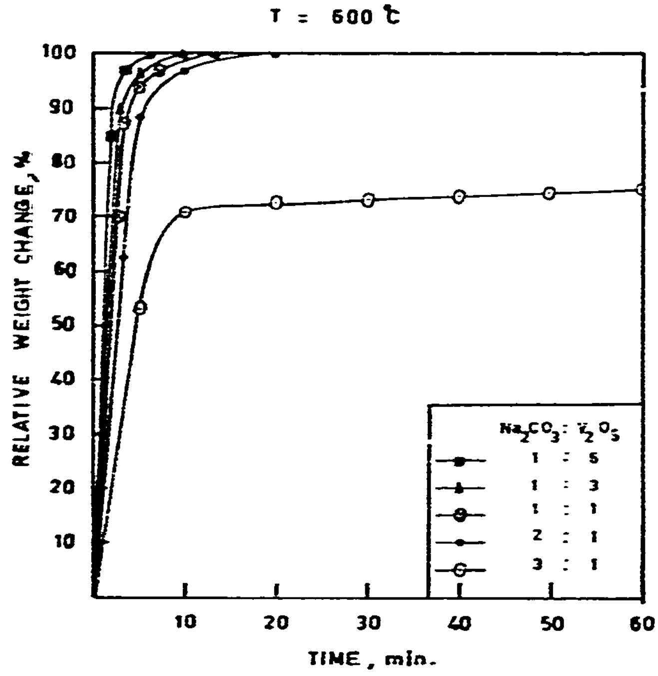

Fig. 5. Relative weight changes of the mixtures Na_2CO_3:V_2O_5 at 600 °C.

reaction proceeds in a molten phase at temperatures > 650 °C. The reaction is vigorous at relatively higher temperatures, especially at lower Na_2CO_3 concentrations.

The reaction is considered to take place in the five different ratios, according to the following equations

$$Na_2CO_3 + 6V_2O_5 \rightarrow Na_2V_{12}O_{31} + CO_2 \quad (1)$$

$$Na_2CO_3 + 3V_2O_5 \rightarrow 2NaV_3O_8 + CO_2 \quad (2)$$

$$Na_2CO_3 + V_2O_5 \rightarrow 2NaVO_3 + CO_2 \quad (3)$$

$$2Na_2CO_3 + V_2O_5 \rightarrow Na_4V_2O_7 + 2CO_2 \quad (4)$$

$$3Na_2CO_3 + V_2O_5 \rightarrow 2Na_3VO_4 + 3CO_2 \quad (5)$$

leading to the formation of vanadium bronzes I and II, metavanadate, pyrovanadate and orthovanadate respectively. In the temperature range 400–500 °C, the rate of reaction in eqns (1)–(3) is greatly dependent on both the temperature of reaction and the V_2O_5 content. On the other hand, the rate of reaction in the same temperature range for the mixtures 1:1, 2:1 and 3:1, is only dependent on temperature, where similar rates are achieved with variable V_2O_5 contents at the same reaction temperature. However at temperatures >550 °C, another behaviour is noticed. With all mixtures except that of the highest Na_2CO_3 content (3:1), the reaction proceeds very fast and reaches completion after short periods; decreasing with the increase in Na_2CO_3 content. This behaviour may be attributed to the fact that in this temperature range, semifusion or melting of the mixture takes place, leading to an acceleration of the diffusion process of ions and consequently an increase in the interactions between Na_2CO_3 and V_2O_5. This assumption is further evidenced by our differential thermal analysis (*vide infra*).

The rate of reaction of the mixture 3:1 decreases suddenly after few minutes and the reaction tends to limiting values specially at temperatures <800 °C, as represented in Fig. 6. This sudden decrease is noticed at about 67% reaction extent, where $Na_4V_2O_7$ is the product of the limiting values. Accordingly, the reaction between the latter vanadate and the remaining Na_2CO_3 can be assumed to be the rate-determining step for the formation of the orthovanadate. This assumption was substantiated by the X-ray analysis of the products at different temperatures as discussed in another part of this paper, and by three experiments performed according to the equation

$$Na_4V_2O_7 + Na_2CO_3 \rightarrow 2Na_3VO_4 + CO_2 \quad (6)$$

where the mixtures of $Na_4V_2O_7$ and Na_2CO_3 are heated at 600, 700 and 800 °C. The rates of reaction are nearly identical to the corresponding experiments illustrated in Fig. 6. Despite the fact that according to eqns (5) and (6) reactions proceed completely[11] in a semifused state at 800 °C, yet they reach completion after 60 minutes.

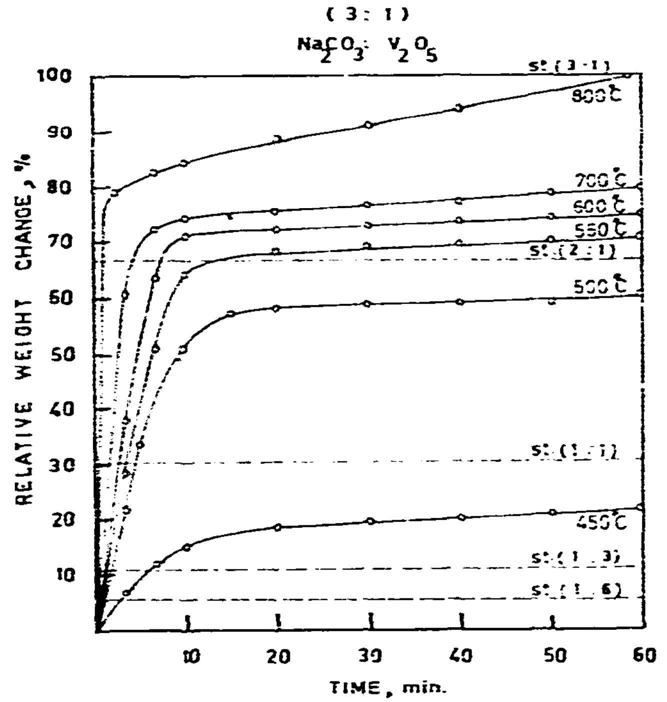

Fig. 6. Relative weight change of the reaction: $3Na_2CO_3+V_2O_5 \rightarrow 2Na_3VO_4+3CO_2$.

Differential thermal analysis (DTA)

The DTA curves of the reactions between Na_2CO_3 and V_2O_5 mixtures are represented in Fig. 7. The DTA heating curves (Fig. 7A), represent the successive reactions that may proceed during formation of the five vanadates. It is noticed that the reaction between V_2O_5 and Na_2CO_3 can proceed at low temperatures even in the solid phase. In the mixture 1:6 (Na_2CO_3:V_2O_5), the formation of vanadium bronze I starts at 320°C as noticed from an endothermic peak. This peak represents the dissociation of Na_2CO_3 to Na_2O and CO_2; a process which is initiated[1] by V_2O_5. This peak is incomplete due to the heat evolved from the spontaneous reaction between V_2O_5 and the Na_2O formed. The succession of the two reactions continues with rise of temperature and is accomplished at 500°C (semifusion point), where the rate of Na_2CO_3 decomposition is relatively high and interactions between Na_2O and V_2O_5 are vigorous. This is illustrated by a sharp exothermic peak at 520°C which immediately follows as incomplete endothermic peak. The complete formation of bronze I ($Na_2V_{12}O_{31}$) is achieved at 550°C, as also confirmed by the isothermal gravimetric curve (Fig. 2). In this temperature range (near the melting point of bronze I), there is a probability of formation of another form of bronze I, having the structural formula NaV_6O_{15}. This compound is easily transformed at high temperatures to $Na_2V_{12}O_{31}$; a process which is accompanied by oxygen uptake and represented by an endothermic peak in the temperature range of 550–600°C. This peak

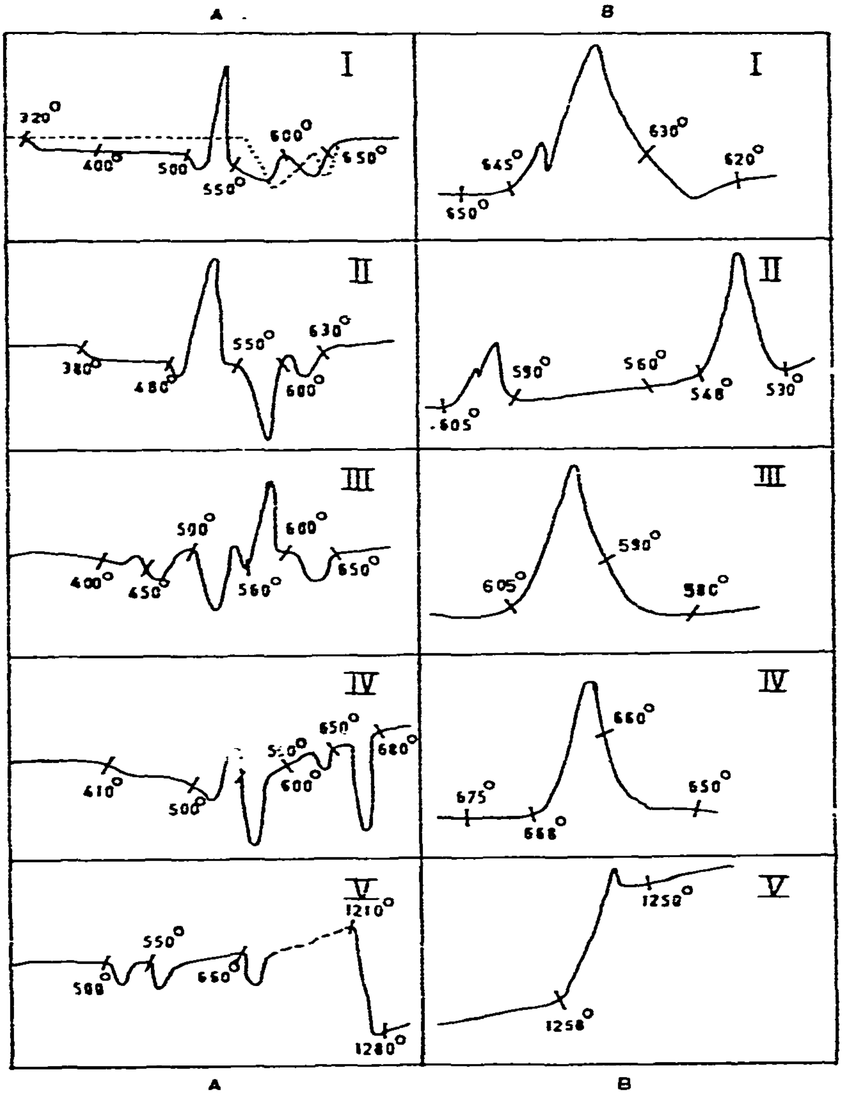

Fig. 7. DTA curves of the reactions between Na_2CO_3 and V_2O_5. I: $Na_2CO_3 + 6V_2O_5$; II: $Na_2CO_3 + 3V_2O_5$; III: $Na_2CO_3 + V_2O_5$; IV: $2Na_2CO_3 + V_2O_5$; V: $3Na_2CO_3 + V_2O_5$; A = heating curves, B = cooling curves for mixtures preheated in the molten phase for 60 minutes, rate of heating and cooling = 7°/min.

is followed by another endothermic peak (600–650 °C) indicating the melting of $Na_2V_{12}O_{31}$. The above assumptions are confirmed by the following experiments:

(i) The cooling DTA curve of the molten bronze I (preheated at 700 °C) is carried out; the result is illustrated in Fig. 7BI. The exothermic peak representing the solidification of bronze I is displayed at 645 °C, and is closely followed by another exothermic peak at 640 °C. The latter peak represents the dissociation of $Na_2V_{12}O_{31}$ to NaV_6O_{15} with oxygen evolution according to the following equation:

$$Na_2V_{12}O_{31} \rightleftharpoons NaV_6O_{15} + \tfrac{1}{2}O_2 \qquad (7)$$

Phase diagram studies indicate[11] that this compound melts congruently without any solidus points. It is important to note that oxygen splitting and heat evolved accompanying this reaction can be easily observed during the above experiment.

(ii) Another heating DTA experiment was performed on solid bronze I and the result is illustrated by the curve with dotted line in Fig. 7AI. Two endothermic peaks are displayed: one broad in the temperature range of 560–660 °C and another sharp at 645 °C. The former represents the polymerization of bronze I according to eqn (7), proceeding to the left-hand side with oxygen uptake, while the latter peak represents the melting of bronze I ($Na_2V_{12}O_{31}$).

(iii) In order to determine the melting point of NaV_6O_{15}, which is assumed to be the bronze I in the solid phase, the above experiment is performed in a nitrogen atmosphere to avoid oxygen uptake and formation of $Na_2V_{12}O_{31}$. It is noticed that only one peak is displayed at 690 °C, a temperature which is higher than the melting point of the polymerized compound ($Na_2V_{12}O_{31}$).

(iv) The X-ray analysis of the products formed at different temperatures substantiates the formation of both compounds: details are given in another part of this investigation.

The DTA heating curve for the mixture 1:3 (Na_2CO_3:V_2O_5) is shown in Fig. 7AII. The endothermic peak representing the dissociation of Na_2CO_3 is only detected at 380 °C in this mixture. It is also broad and incomplete and the formation of bronze I is accomplished below 550 °C and represented by an exothermic peak. A sharp endothermic peak follows the exothermic one and may represent the interaction between sodium carbonate (remaining after the formation of bronze I) and newly formed bronze I with the liberation of CO_2 according to the equation

$$Na_2CO_3 + Na_2V_{12}O_{31} \rightarrow 4NaV_3O_8 + CO_2 \quad (8)$$

leading to the formation of bronze II. The melting of the latter compound takes place in the temperature range of 600–630 °C, and is represented by a broad endothermic peak. The cooling DTA curve for bronze II (preheated at 700 °C) is illustrated in Fig. 7BII, showing two exothermic peaks representing the liquidus and solidus points[11].

The DTA curve for the reaction between Na_2CO_3 and V_2O_5 in the molar ratio 1:1 is represented by the curves AIII and BIII. The formation of two endothermic peaks at 400 and 450 °C illustrates the successive formation of bronzes I and II. The newly formed bronze II interacts with Na_2CO_3 to form the metavanadate with the liberation of CO_2 with an endothermic peak at 525 °C. The reaction is represented by the equation:

$$Na_2CO_3 + NaV_3O_8 \rightarrow 3NaVO_3 + CO_2 \quad (9)$$

The abovementioned reactions proceed in the solid phase. At ~540 °C, a small endothermic peak is detected, that may represent the melting of $NaVO_3$ which is contaminated with other compounds (bronze II and Na_2CO_3). The succession of these reactions was also deduced from the X-ray analysis of the products at different temperatures (*vide infra*). The formation of a sharp exothermic peak at 550°C may be attributed to the transformation that accompanies the melting of $NaVO_3$; a process which was suggested[12] at ~600°C. The last endothermic peak is broad (600–650°C) and may represent the reaction of some remaining bronze II with Na_2CO_3. This assumption is substantiated by a thermal gravimetric experiment of the mixture (with the same rate of heating) showing that completion of the reaction is only achieved at 660°C. The melting point of $NaVO_3$ is 605°C as shown in DTA cooling curve (Fig. 7B III).

The DTA heating curve illustrated in Fig. 7A IV shows the successive formation of the two bronzes and the metavanadate prior to the formation of the pyrovanadate that is accomplished at 650°C. At 670°C the melting of the latter compound is indicated by a sharp endothermic peak at 670°C. A more accurate melting point for this compound (688°C) is achieved by DTA cooling curve shown in Fig. 7B IV.

The mixture of Na_2CO_3:V_2O_5 in the molar ratio 3:1, behaves similarly in the DTA heating curve Fig. 7A V to that leading to pyrovanadate, but with three small and broad endothermic peaks for the formation of meta-, pyro-, orthovanadate successively. The peaks representing the formation of the two bronzes are not detected. The same is noticed in the X-ray analysis of the products at 450°C. The melting point of sodium orthovanadate is 1258°C, as indicated by the DTA cooling curve in Fig. 7B V.

X-ray diffraction analysis

This series of experiments is performed on the products of isothermal reactions of the previously mentioned five mixtures. The Debyograms illustrated in Figs. 8–9 reveal that the formation of different vanadates are greatly dependent on temperatures rather than on molar ratios of Na_2CO_3:V_2O_5. The patterns of the reactants are only noticed in the products of reaction at 450°C—a phenomenon which is noticed with those of five mixtures.

It is noteworthy that in the products of reaction mixture 1:6, two different X-ray patterns are represented, one at 400°C and another at 700°C. It was suggested that at 400°C, the reaction proceeds in the solid phase, leading to the formation of $Na_2V_{12}O_{31}$, displaying the main characteristic lines at 7.31, 3.39, 2.93 and 2.71 Å. On the other hand, the reaction at 700°C proceeds in the molten phase. The formed bronze $Na_2V_{12}O_{31}$ decomposes by cooling to form NaV_6O_{15} with oxygen evolution (eqn 7). This reaction was mentioned by some authors[12–14] who noticed oxygen evolution during cooling this bronze. The same phenomenon was noticed in the cooling curves of the mixture ($Na_2CO_3+6V_2O_5$) as studied by DTA. Accordingly, the X-ray pattern of the final product of this mixture (700°C) illustrates only the pattern of NaV_6O_{15}. It was difficult to determine the exact pattern of $Na_2V_{12}O_{31}$, as it is formed admixed with the reactants at this low temperature.

It is also noticed from Figs. 8 and 9 that the sequence of formation of vanadates, takes place in the order

$$NaV_6O_{15} \rightarrow NaV_3O_8 \rightarrow NaVO_3 \rightarrow Na_4V_2O_7 \rightarrow Na_3VO_4.$$

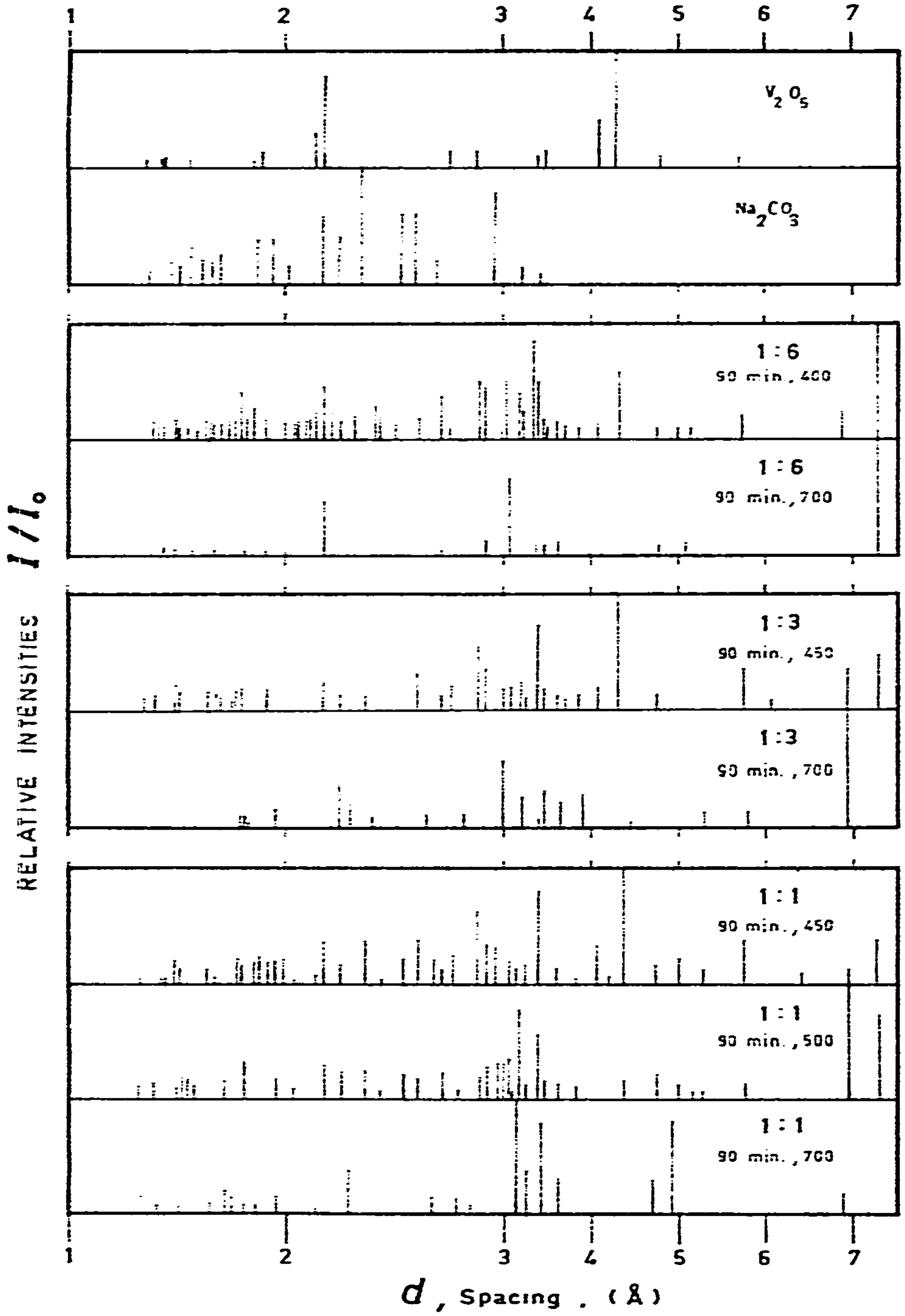

Fig. 8. X-ray diffraction analysis of the products of the reactions: $Na_2CO_3+6V_2O_5$, $Na_2CO_3+3V_2O_5$ and $Na_2CO_3+V_2O_5$.

At 700°C, the patterns of pure vanadates are represented for the reaction products of the respective mixtures except that at the highest Na_2CO_3 concentration ($3Na_2CO_3$

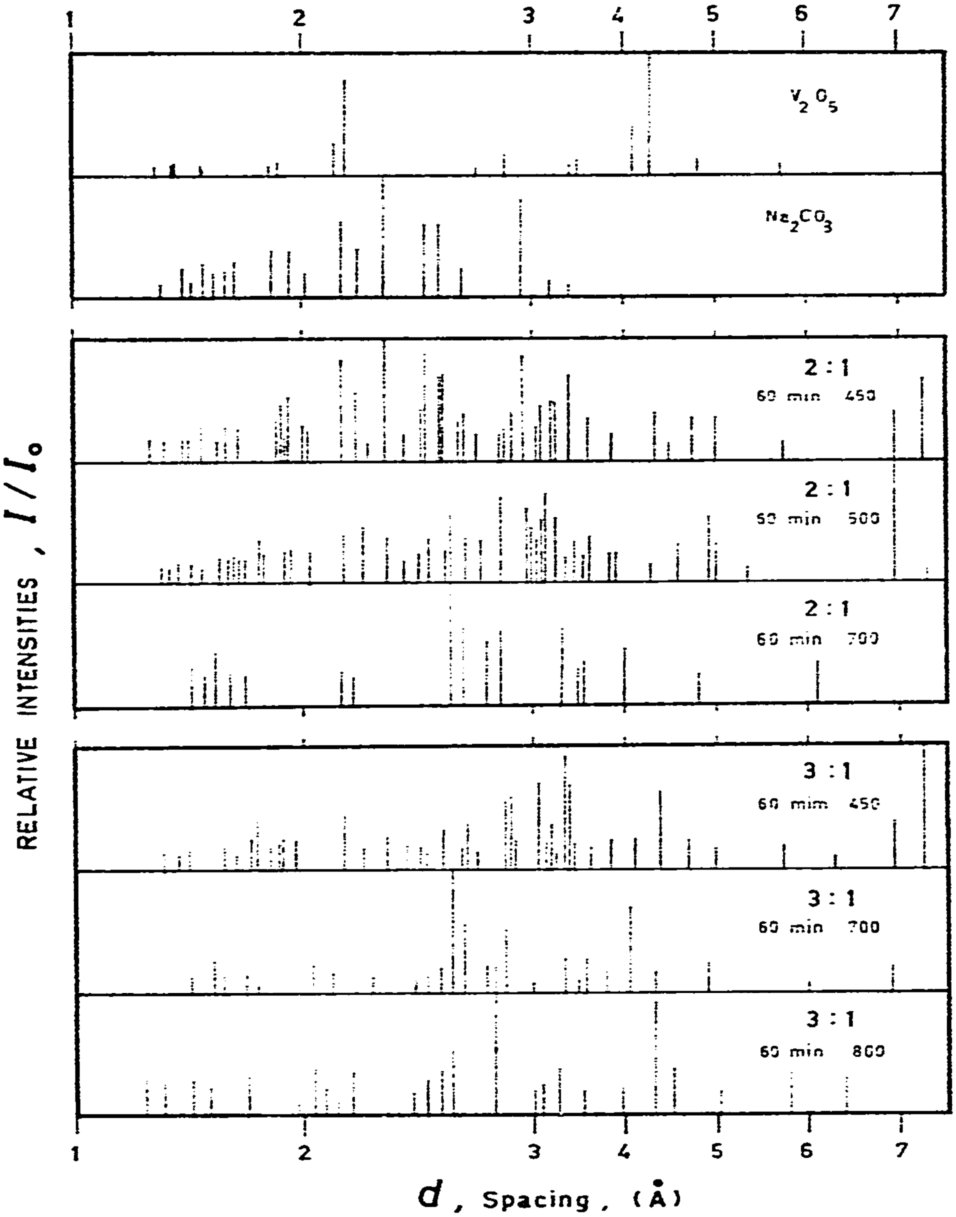

Fig. 9. X-ray diffraction analysis of the products of the reactions: $2Na_2CO_3+V_2O_5$ and $3Na_2CO_3+V_2O_5$.

$+V_2O_5$), where the reaction of the latter mixture is only accomplished at 800°C. At lower temperatures compounds of higher V_2O_5 content are investigated.

The exact X-ray patterns of the samples representing different anhydrous sodium vanadates (prepared by accurate methods[9]) are illustrated in Table 1. These data are different from that of the corresponding hydrated materials given in ref. 15. They illustrate also the absence of any diffraction lines of V_2O_5, Na_2CO_3 or any

TABLE I

X-RAY DIFFRACTION LINES OF SODIUM VANADATES

NaV_6O_{15}		NaV_3O_8		$NaVO_3$		$Na_4V_2O_7$		Na_3VO_4	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
7.31	100[a]	9.51	16	6.89	19	9.88	26	8.00	21
5.87	4	6.97	100[a]	4.93	82[a]	6.09	36	6.39	30
5.50	4	5.79	16	4.71	32	4.80	29	5.79	35
5.09	9	5.32	14	3.62	29	4.01	43	5.02	21
4.77	10	4.56	5	3.43	82[a]	3.55	36	4.52	40
3.84	7	4.47	8	3.27	38	3.49	33	4.32	95[a]
3.63	9	3.88	23	3.16	100[a]	3.33	62[a]	3.97	19
3.48	12	3.64	18	2.85	6	2.86	62[a]	3.54	19
3.37	9	3.47	34	2.79	12	2.80	50	3.28	37
3.18	6	3.38	9	2.67	15	2.70	60	3.11	26
3.07	60[a]	3.21	26	2.29	39	2.65	100[a]	3.04	23
2.92	12	3.01	55[a]	2.14	6	2.22	26	2.84	100[a]
2.73	5	2.92	13	2.09	6	2.17	29	2.66	53[a]
2.60	3	2.65	10	1.959	16	2.01	18	2.60	40
2.52	4	2.41	12	1.859	11	1.920	7	2.54	30
2.45	3	2.31	21	1.810	13	1.748	24	2.48	14
2.37	4	2.25	39[a]	1.754	17	1.684	26	2.21	37
2.25	4	1.961	14	1.722	22	1.612	43	2.15	10
2.18	44[a]	1.834	6	1.648	9	1.572	26	2.10	23
1.997	15	1.819	11	1.576	5	1.516	38	2.05	40
1.912	10	1.805	13	1.506	13	1.330	37	1.986	10
1.866	4	1.768	7	1.462	5	1.302	24	1.766	33
1.806	6	1.758	7	1.412	7	1.278	24	1.590	20
1.754	3	1.716	10	1.378	14			1.526	30
1.677	4	1.641	11	1.251	5			1.380	23
1.650	3	1.587	8					1.324	33
1.584	15	1.579	10						
1.536	4	1.557	8						
1.496	16	1.546	7						
1.450	5	1.527	9						
1.372	3	1.503	9						
1.256	3	1.445	10						
1.232	3	1.426	9						
1.172	4	1.412	5						
		1.390	6						
		1.332	11						
		1.328	21						
		1.210	7						
		1.203	7						
		1.174	6						
		1.152	6						
		1.107	6						
		1.104	6						

combined oxide. These data are more accurate than that of previous work[7,8], where only the few main lines of each compound with approximate relative intensities of the identified lines were investigated. Our results are shown in Table 1.

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[a] The three main lines of sodium vanadate compounds.

REFERENCES

1 B. Burwell, *J. Metals*, 13 (1961) 562.
2 M. H. Tikkanen, *Extraction of Vanadium-Containing Magnetic Iron Concentrate*, Dechema Monograph, 26 (1957) 260.
3 N. P. S. Sidak, *Stal'*, 22 (1962) 7.
4 F. N. Shenouda, G. A. Kolta and N. S. Petro, *Erzmetall*, (1970) 427.
5 G. W. Cunningan and A. Brasunas, *Corrosion*, 12 (1956) 35.
6 A. A. Fotiev and B. V. Slobodin, *J. Inorg. Chem. USSR*, 10 (1965) 80.
7 B. V. Slobodin and A. A. Fotiev, *J. Appl. Chem.*, 38 (1965) 801.
8 I. Lukacs, C. Strusievici and C. Liteana, *Akad. Rep. Populare Romine, Filiala Cluj, Studii Cercetari Chim.*, 13 (1962) 171.
9 F. Holzberg, A. Reisman, M. Berry and M. Berkenblit, *J. Amer. Chem. Soc.*, 78 (1956) 1536.
10 G. A. Kolta, I. F. Hewaidy and N. S. Felix, *Thermochim. Acta*, 4 (1972) 151.
11 G. A. Kolta, I. F. Hewaidy and N. S. Felix, *Erzmetall*, in press.
12 I. Lukacs, C. Strusievici and C. Liteana, *Z. Anorg. Allg. Chem.*, 326 (1964) 331.
13 A. A. Fotiev and B. V. Slobodin, *J. Appl. Chem. USSR*, 38 (1965) 499.
14 I. N. Balyaev and T. G. Golovanova, *J. Inorg. Chem. USSR*, 7 (1962) 2760.
15 ASTM cards, *Index of the X-ray Powder Data*, File 196.