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DTA STUDY OF THE REACTIONS OF V_2O_5 WITH METAL (II) OXIDES

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Vanadate formation during reactions of V_2O_5 with CoO, NiO, ZnO, MgO and MnO has been studied. The initial products of solid–solid reaction with ZnO, MgO and MnO are $Zn_2V_2O_7$, $Mg_3V_4O_{13}$ and MnV_2O_6 respectively. CoO and NiO predominantly form the vanadate which corresponds to the stoichiometry of the initial oxide mixture. Subsequent formation of ortho-, pyro- and metavanadates as intermediates indicate that the principal mechanistic process is the transport of V_2O_5 to the reaction interface.

Phase-equilibrium studies of the binary systems $MO-V_2O_5$ (M = Ni, Co, Mn, Zn, Mg) have been reported [1–8]. However, there may be evidence that phases formed during cooling of melts are not those formed by solid–solid reaction below liquidus temperatures. For example, Brisi [4] reports the formation of $Mn_2V_2O_7$ by solid–solid reaction between oxides but Dorm and Marinder [9] could prepare this phase only in a melt reaction. Similarly Speranskaya [7] could not prepare MgV_2O_6 by solid reaction, although Pollard [6] reports this phase in his phase diagram obtained from cooling-curve data.

Not only is there doubt about the products of some of these reactions but there is evidence that they may be mechanistically complex. Thus Pollard [8] suggests that the phase $7ZnO \cdot 2V_2O_5$ may be an intermediate in the reaction of ZnO with V_2O_5 and has also noted the successive formation of ortho-, pyro- and metavanadate in reactions of MgO with V_2O_5 [6].

This paper, the first of a series dealing with the reactions of V_2O_5, presents results of DTA studies of the ortho-, pyro- and meta-vanadates of Ni, Co, Mn, Zn and Mg and discusses the use of DTA in elucidating both the nature of the intermediates formed in the solid–solid reactions of the component oxides and the probable mechanism of these reactions.

Experimental

V_2O_5, MgO and ZnO were laboratory-grade oxides preheated at 870 K (V_2O_5) and 1270 K for 24 hours. MnO was prepared by pyrolysis in N_2 of AR $Mn(COO)_2 \cdot 2H_2O$ at 1270 K. CoO and NiO were prepared by pyrolysis in N_2 of the AR hydrated sulphates at 1270 K. All oxides were ground by hand and mesh, sieved to 63 – 75μm. Experimental analytical % metal in the oxides, with theory % in parenthesis, were V_2O_5, 56.00 (56.02); NiO, 78.44 (78.59); CoO, 78.48 (78.65); ZnO, 80.31 (80.34); MnO, 77.50 (77.45); MgO, 60.28 (60.32).

Reaction mixtures were prepared by weighing the oxides in the appropriate molar ratios into sealed polythene containers and were blended by prolonged shaking. This procedure was used in preference to grinding, so that identical particle sizes were maintained in all mixtures subjected to DTA. Samples of the vanadates were prepared by heating the mixtures at temperatures up to 1070 K for 1 week [1 – 8]. Since some of the oxides are susceptible to air oxidation, a N_2 atmosphere was used. Heating was accomplished with a nichrome wound tube furnace regulated to ±2 degrees by a proportional controller. Samples were contained in platinum boats placed in a 30-mm diameter silica sheath through which dry de-oxygenated N_2 was passed at a flow rate of 1 cm^3 s^{-1} and a pressure of 122 010 Nm^{-2} absolute. During heating mixtures were periodically removed and thoroughly ground to ensure complete reaction.

Each vanadate was characterised by X-ray powder diffractometry using a Philips PW 1010/30 X-ray set (Mo K_α radiation). With the exception of $Mn_3V_2O_8$, powder-diffraction patterns agreed closely with previously published powder data [1, 2, 4, 6]. For $Ni_3V_2O_8$ [10], CoV_2O_6 [11], $Co_2V_2O_7$ [11], $Co_3V_2O_8$ [10], $Mn_2V_2O_7$ [9], $Mg_2V_2O_7$ [12], $Mg_3V_2O_8$ [13], ZnV_2O_6 [14], $Zn_2V_2O_7$ [15] and $Zn_3V_2O_8$ [16] whose structures have been determined, the *d* spacings were also in close agreement with the values computed from the cell dimensions. $Mn_3V_2O_8$ could not be prepared from MnO/V_2O_5 mixtures. Below 950 K the only product of reaction was MnV_2O_6. Above 950 K some oxidation-reduction occurred and reaction products were mixtures of Mn_2O_3, $Mn_2V_2O_7$ and MnV_3O_7 [4].

DTA curves were obtained using a Standata 5 – 50 fitted with Platinum / 13% Rhodium-platinum thermocouples. The reference material was Al_2O_3 previously ignited at 1270 K. Samples and reference (0.2 g) were contained in 8-mm × 6.2-mm Pt crucibles set in a demountable ceramic block. The heating rate was 10 degrees min^{-1}. For CoO and MnO reactions N_2 was passed over the specimens to avoid air oxidation. The flow rate was 3 cm^3 s^{-1} at a pressure of 122 010 Nm^{-2} absolute. The apparatus was calibrated with AR K_2SO_4, the extrapolated onset temperature of the $\alpha - \beta$ transition being found at 856 ± 2 K in exact agreement with McAdie [17]. Unless otherwise stated, peak temperatures are quoted as extrapolated onset temperatures [18] and peak heights and widths are quoted in arbitrary units, these being cm at an instrument attenuation of 50 μV and a chart speed of 0.5 cm min^{-1}.

Results and discussion

Thermal properties of the vanadates

Extrapolated onset temperatures, peak heights, peak widths and assignments of the DTA curves of the ortho-, pyro- and meta-vanadates are given in Table 1. Temperatures are in good agreement with literature values [1 – 8], the greatest disparity being for the peritectic melting of CoV_2O_6 here reported at 1013 K but given by Brisi [1] at 978 K. Assignments of peaks, except those of CoV_2O_6, $Zn_3V_2O_8$ and MnV_2O_6 which are discussed below, are in total agreement with known thermal behaviour [1 – 8].

On the basis of extra lines found in the X-ray powder patterns of some CoO/V_2O_5 compositions heated above 950 K, Brisi [1] has suggested that CoV_2O_6 may undergo a phase transformation at about this temperature. The small endothermic effect shown by CoV_2O_6 at 935 K is therefore assigned to this transformation.

The thermal behaviour of $Zn_3V_2O_8$ has been the subject of some controversy. Brown and Hummel [2] consider that an $\alpha - \beta$ phase transition occurs at 1068 K, a $\beta - \gamma$ phase transition occurs at 1088 K and $\gamma - Zn_3V_2O_8$ melts congruently at 1163 K. Makarov et al. [3] found no $\alpha - \beta$ transition and consider that at 1088 K

Table 1

DTA data for some metal(II) vanadates

Compound	Extrapolated onset temperature, K	Peak* height, cm	Peak width, cm	Assignment
CoV_2O_6	935	5.5	2.2	Phase transition
	1013	30.0	3.0	CoV_2O_6 peritectic melting
	1105	13.5	3.8	$Co_2V_2O_7$ peritectic melting
$Co_2V_2O_7$	1105	20.5	5.5	$Co_2V_2O_7$ peritectic melting
$Co_3V_2O_8$	no thermal effects to 1300 K			
NiV_2O_6	1020	15.1	3.4	NiV_2O_6 peritectic melting
	1135	9.4	2.0	$Ni_2V_2O_7$ peritectic melting
$Ni_2V_2O_7$	1140	10.6	3.0	$Ni_2V_2O_7$ peritectic melting
$Ni_3V_2O_8$	no thermal effects to 1300 K			
ZnV_2O_6	918	29.5	5.0	ZnV_2O_6 peritectic melting
	1140	16.5	2.8	β-$Zn_2V_2O_7$ melting
$Zn_2V_2O_7$	888	9.4	1.8	α-β $Zn_2V_2O_7$ phase transition
	1145	20.0	5.0	β-$Zn_2V_2O_7$ melting
$Zn_3V_2O_8$	1065	1.1	0.2	α-β $Zn_3V_2O_8$ phase transition
	1088	10.0	2.3	β-$Zn_3V_2O_8$ decomposition
	1148	19.6	5.0	β-$Zn_2V_2O_7$ melting
	1185	10.5	1.2	$Zn_4V_2O_9$ peritectic melting
MgV_2O_6	1038	27.0	5.5	MgV_2O_6 peritectic melting
	1190	3.0	0.8	α-β $Mg_2V_2O_7$ phase transition
$Mg_2V_2O_7$	1190	8.8	1.2	α-β $Mg_2V_2O_7$ phase transition
$Mg_3V_2O_8$	no thermal effects to 1300 K			
MnV_2O_6	825	3.2	1.7	Phase transition
	1098	27.8	5.8	MnV_2O_6 peritectic melting
	1296	12.6	4.2	$Mn_2V_2O_7$ melting
$Mn_2V_2O_7$	1293	19.6	4.9	$Mn_2V_2O_7$ melting

* All peaks are endothermic

$Zn_3V_2O_8$ undergoes solid–state decomposition into $\beta-Zn_2V_2O_7$, melting at 1163 K, and $Zn_4V_2O_9$, melting at 1183 K. The DTA curve of $Zn_3V_2O_8$ (Table 1) is in excellent agreement with that of Makarov et al. [3], but in addition shows a very small endotherm at 1065 K, which may be too small to be resolved by less sensitive apparatus. X-ray diffraction of $Zn_3V_2O_8$ heated above 1088 K and of $4ZnO + V_2O_5$ mixtures heated at 1100 K confirm the formation of $Zn_4V_2O_9$, the observed *d* spacings being in excellent agreement with those of Makarov et al. [3]. This investigation therefore confirms that the thermal behaviour of $Zn_3V_2O_8$ is as suggested by Makarov et al. [3], but that it also undergoes the slow $\alpha-\beta$ transition noted by Brown and Hummel [2].

The DTA curve of MnV_2O_6 shows two effects (Table 1). The large 1098 K endotherm can be ascribed to peritectic melting in accordance with reported temperatures of 1078 K [5] and 1073 K [4]. The small endotherm at 825 K, which is a reversible effect, has not been previously reported and is presumably due to a phase transition similar to that found for CoV_2O_6.

Reaction of CoO with V_2O_5

DTA curves of the reactions $CoO + V_2O_5$, $2CoO + V_2O_5$ and $3CoO + V_2O_5$ are given in Figure 1 (a–c). In the 900–1000 K region each curve is characterized by a small broad exothermic rise, a sharp endotherm and a sharp exotherm. The exothermic rises are due to the commencement of reaction and since the onset temperatures (780–790 K) are below that of the lowest temperature eutectic, 908 K [1], these are solid–solid reactions. This eutectic which has a composition 25 mol% CoO, shows as the sharp endotherm in each curve at 920 K. With the appearance of a melt phase the rate of reaction rapidly increases and this is reflected in the DTA curves by the appearance of sharp exotherms with peak maxima at 948 K, 935 K and 931 K, respectively, for $CoO + V_2O_5$, $2CoO + V_2O_5$ and $3CoO + V_2O_5$. The reaction exotherm is sharpest and of greatest height for the $3CoO + V_2O_5$ reaction and is broadest and of least height for the $CoO + V_2O_5$ reaction. However, the peak areas are approximately equal, indicating that the heats of these reactions are of similar magnitude. The shapes of the reaction exotherms therefore suggest that the rates of reaction increase in the order $CoO + V_2O_5 < 2CoO + V_2O_5 < 3CoO + V_2O_5$. This conclusion is substantiated firstly by the relative heights of the initial exothermic rises, which increase with increasing mol% CoO and therefore indicate a greater conversion to product in the $3CoO + V_2O_5$ reaction than in the $CoO + V_2O_5$ reaction, and secondly by the relative heights of the 920 K eutectic endotherms, which decrease markedly with increasing mol% CoO. Although the decrease in the proportion of V_2O_5 in the original mixtures is a major factor responsible for the decrease in height of the eutectic endotherm, the decrease in peak height is disproportionately greater than the decrease in the proportion of V_2O_5 in the original mixtures and therefore clearly indicates that the rate of solid–solid reaction is fastest for $3CoO + V_2O_5$ and slowest for $CoO + V_2O_5$.

At temperatures above that of the reaction exotherm, the CoO + V_2O_5 curve shows two large endotherms at 1013 K and 1103 K. These correspond to peritectic melting of CoV_2O_6 and $Co_2V_2O_7$, respectively (Table 1). The 2CoO + V_2O_5 curve shows a very small endotherm at 1017 K and a large endotherm at 1103 K. Thus a small amount of CoV_2O_6 is formed during the reaction 2CoO + V_2O_5 in addition to the major product $Co_2V_2O_7$. Since $Co_3V_2O_8$ shows no thermal effects to 1300 K, it is not possible to note whether some $Co_3V_2O_8$ is also formed. The

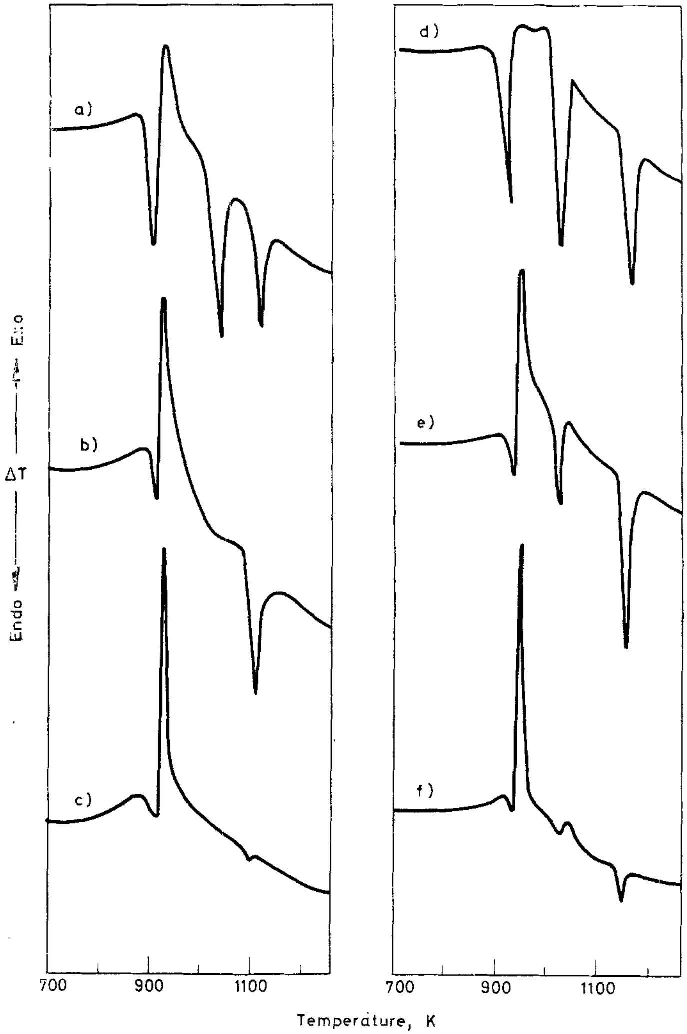

Fig. 1. DTA curves of (a) CoO + V_2O_5; (b) 2CoO + V_2O_5; (c) 3CoO + V_2O_5; (d) NiO + V_2O_5; (e) 2NiO + V_2O_5; (f) 3NiO + V_2O_5

curve of the 3CoO + V_2O_5 reaction shows no peritectic melting of CoV_2O_6, but does show a small endotherm at 1100 K indicating that some $Co_2V_2O_7$ is formed in this reaction.

In no case is there evidence of the formation of the low temperature polymorph of $Co_3V_2O_8$ reported by Joubert and Durif [19] to transform at 834 K.

Reaction of NiO with V_2O_5

DTA curves of the reactions NiO + V_2O_5, 2NiO + V_2O_5 and 3NiO + V_2O_5 are given in Figure 1 (d – f). These curves are similar to those of the corresponding CoO/V_2O_5 reactions but differ in detail. The initial exothermic rises are much less pronounced indicating that the solid – solid reactions may be slower than the CoO/V_2O_5 reactions. The endotherms at 928 K which show the same variation of peak height as the CoO/V_2O_5 reactions are due to melting of the 20-mol% NiO/V_2O_5 binary eutectic reported by Brisi [1] at 913 K. The reaction exotherms all occur at 954 K but in the NiO + V_2O_5 reaction this is a double peak with the second component at 990 K. The latter component is probably the true NiV_2O_6 formation peak, the first component being that of $Ni_2V_2O_7$ and $Ni_3V_2O_8$ formation. This assignment is in agreement with the observed peak temperatures of the CoO/V_2O_5 reactions in which the temperatures of peak maxima for $Co_2V_2O_7$ and $Co_3V_2O_8$ formation were very similar (935 K and 931 K, respectively) and that for CoV_2O_6 formation was rather higher (948 K).

All three NiO/V_2O_5 reactions show an endotherm at 1015 K largest in the NiO + V_2O_5 reaction and smallest in 3NiO + V_2O_5. This peak corresponds to peritectic melting of NiV_2O_6 (Table 1) and shows that NiV_2O_6 is formed not only in the reaction NiO + V_2O_5, but also in significant amounts in the reactions 2NiO + V_2O_5 and 3NiO + V_2O_5. The small exothermic effects which follow the appearance of this melt phase indicate that reaction is not complete in the NiO/V_2O_5 reactions at 1015 K, in agreement with the previous observation that the NiO/V_2O_5 reactions are less rapid than their CoO/V_2O_5 counterparts.'

All three curves also show an endothermic peak at 1130 K corresponding to peritectic melting of $Ni_2V_2O_7$ (Table 1). Relative peak heights suggest that $Ni_2V_2O_7$ is formed in all three reactions, as is NiV_2O_6. From the data given in Table 1 for NiV_2O_6, the peritectic melting of $Ni_2V_2O_7$ produces an endotherm of approximately two-thirds the area of that of NiV_2O_6. In the NiO + V_2O_5 reaction these endotherms are of approximately equal area suggesting that $Ni_2V_2O_7$, in addition to NiV_2O_6, is a major product of this reaction and verifying the double reaction exotherm of NiO + V_2O_5. The inflection points at about 990 K clearly visible in the 2NiO + V_2O_5 curve and just detectable in the 3NiO + V_2O_5 curve, are probably also due to formation of NiV_2O_6 in both reactions.

Reaction of ZnO with V_2O_5

DTA curves of the reactions ZnO + V_2O_5, 2ZnO + V_2O_5 and 3ZnO + V_2O_5 are given in Figure 2 (a – c). Each curve shows an exothermic rise commencing at

725–730 K due to the onset of solid–solid reactions, followed by a pair of endotherms. The first small endotherm at 888 K co-incides exactly with the temperature of the $Zn_2V_2O_7$ $\alpha-\beta$ reversible transformation (Table 1), showing that $Zn_2V_2O_7$ is a major product of solid–solid reaction in all three reactions. The second endotherm peaks at 903 K in ZnO + V_2O_5 and at 895 K in both 2ZnO + V_2O_5 and 3ZnO + V_2O_5 can be assigned to the melting of the 26-mol% ZnO/V_2O_5 eutectic reported variously at 898 K [3], 900 K [2] and 907 K [8].

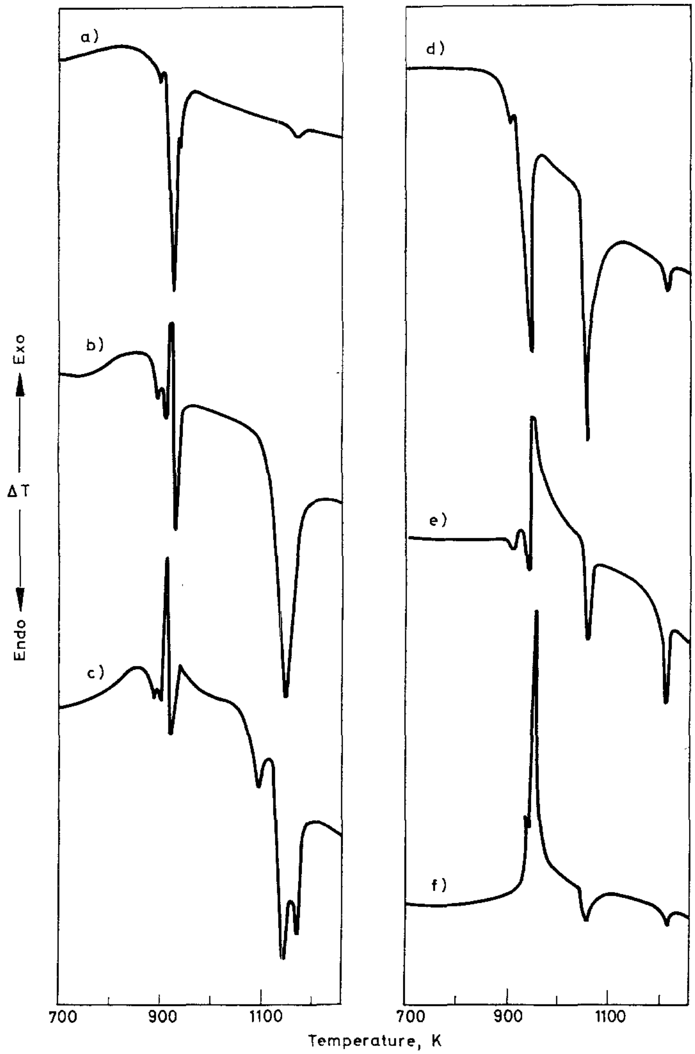

Fig. 2. DTA curves of (a) ZnO + V_2O_5; (b) 2ZnO + V_2O_5; (c) 3ZnO + V_2O_5; (d) MgO + V_2O_5; (e) 2MgO + V_2O_5; (f) 3MgO + V_2O_5

In $2ZnO + V_2O_5$ and $3ZnO + V_2O_5$ this eutectic endotherm is immediately followed by a sharp exotherm peaking at 904 K and of greatest height in $3ZnO + V_2O_5$. This suggests, as in the CoO/V_2O_5 reactions, that either the heat of reaction or the rate of reaction increases in the order $ZnO + V_2O_5 < 2ZnO + V_2O_5 < 3ZnO + V_2O_5$. The heights of the initial exothermic rises and of the eutectic endotherms suggest that the latter alternative is the more probable. This conclusion is also substantiated by the endotherms at 920 K of greatest height in $2ZnO + V_2O_5$. The temperature of these endotherms corresponds to that of the peritectic melting of ZnV_2O_6 (Table 1) and its small height in $ZnO + V_2O_5$ is further confirmation that $ZnO + V_2O_5$ is the kinetically slowest reaction. The formation of ZnV_2O_6 in large amounts in the $2ZnO + V_2O_5$ reaction and in smaller but nevertheless significant amounts in the $3ZnO + V_2O_5$ parallels similar observations in the NiO/V_2O_5 reactions.

The reaction $3ZnO + V_2O_5$ shows an endotherm at 1088 K. This corresponds to the decomposition of $\beta-Zn_3V_2O_8$ (Table 1) but is absent in both the $ZnO + V_2O_5$ and $2ZnO + V_2O_5$ curves, indicating that $Zn_3V_2O_8$ is not a significant product of these reactions up to 1088 K.

The endotherms shown by all three curves at 1145 K are due to melting of $\beta-Zn_2V_2O_7$ (Table 1) and their relative heights are in agreement with the previous observations. The $3ZnO + V_2O_5$ curve shows a further endotherm at 1183 K which corresponds to melting of the phase $Zn_4V_2O_9$ [3] and further confirms that $Zn_3V_2O_8$ is a major product only in the $3ZnO + V_2O_5$ reaction.

Reaction of MgO with V_2O_5

DTA curves of the reactions $MgO + V_2O_5$, $2MgO + V_2O_5$ and $3MgO + V_2O_5$ are given in Figure 2 (d–f). Initial exothermic rises are not apparent except in the $3MgO + V_2O_5$ reaction.

The $MgO + V_2O_5$ and $2MgO + V_2O_5$ curves each show a very small endotherm at 903 K not present in the $3MgO + V_2O_5$ curve. This peak cannot be assigned to any thermal effect of MgV_2O_6, $Mg_2V_2O_7$ or $Mg_3V_2O_8$ (see Table 1) and is probably due to decomposition of the phase $Mg_3V_4O_{13}$ known to form in solid–solid reaction of MgO with V_2O_5 [7]. That it is decomposition of this phase which occurs at 903 K is shown in Figure 3. (a) of this figure shows the DTA curve of the product formed in the reaction $MgO + V_2O_5$ at 900 K for 1 week. The small endotherm at 848 K is the $\alpha-\beta$ phase transformation of $Mg_3V_4O_{13}$ given by Speranskaya [7] at 849 K. The double endotherm has peaks at 903 and 923 K. The latter co-incides with the melting temperature of the 15-mol% MgO/V_2O_5 eutectic previously reported at 923 K [7] and 931 K [6]. The product of this reaction at 900 K therefore contains an excess of V_2O_5. The 903 K component of the double endotherm co-incides with the endotherms found in the $MgO + V_2O_5$ and $2MgO + V_2O_5$ curves. Figure 3(b) shows the DTA curve of the product formed in the reaction $MgO + V_2O_5$ at 925 K for 1 week and is identical to that of that of MgV_2O_6 (Table 1), indicating that $Mg_3V_4O_{13}$ is not formed above 900 K.

All three MgO/V_2O_5 reactions show an endotherm at 920 K, very large in $MgO + V_2O_5$ and very small in $3MgO + V_2O_5$. As noted above, this peak corresponds to eutectic melting and is immediately followed in $2MgO + V_2O_5$ and $3MgO + V_2O_5$ by a sharp exotherm peaking at 930 K. As in the reactions of V_2O_5 with NiO, CoO and ZnO relative peak heights and widths indicate the rates of reaction to increase in the order $MgO + V_2O_5 < 2MgO + V_2O_5 < 3MgO + V_2O_5$.

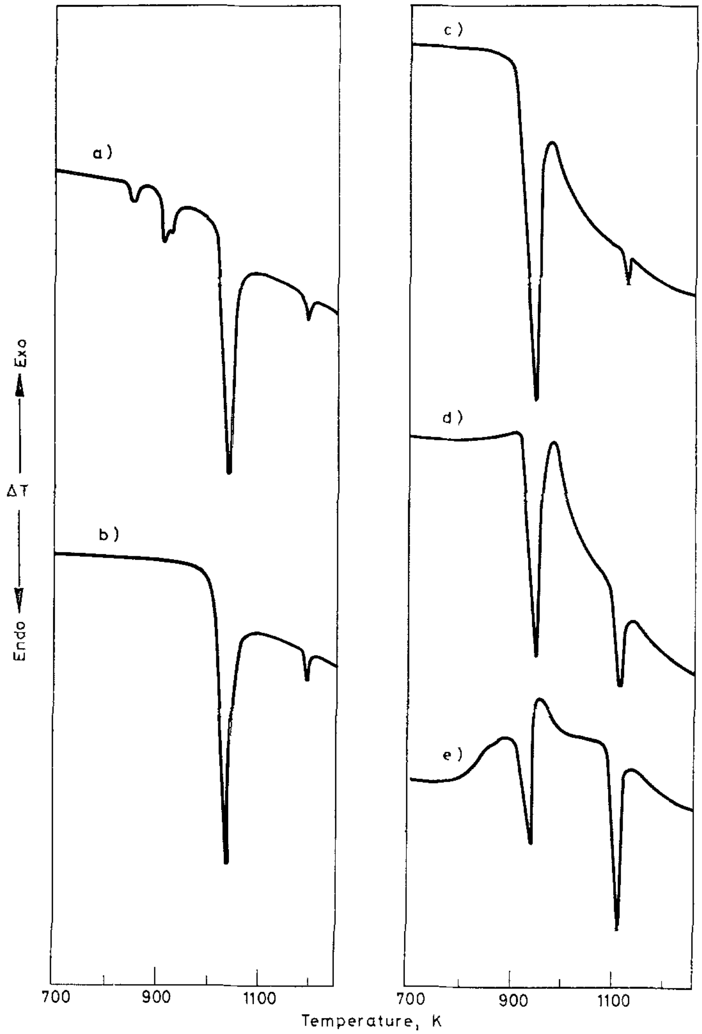

Fig. 3. DTA curves of (a) $MgO + V_2O_5$ product at 900K; (b) $MgO + V_2O_5$ product at 925K; (c) $MnO + V_2O_5$; (d) $2MnO + V_2O_5$; (e) $3MnO + V_2O_5$

Each curve shows an endotherm at 1035 K which corresponds to peritectic melting of MgV_2O_6 (Table 1). As expected this is of greatest height in $MgO + V_2O_5$ and smallest in $3MgO + V_2O_5$ but nevertheless shows, in common with the CoO and ZnO reactions, that the metavanadate is a product of all three reactions. The pyrovanadate $Mg_2V_2O_7$ is also a significant product of all three reactions as evidenced by the endotherm at 1190 K shown in each curve. This corresponds to the $\alpha-\beta$ phase transition of $Mg_2V_2O_7$ [6, 7].

Reaction of MnO with V_2O_5

DTA curves of the reactions $MnO + V_2O_5$, $2MnO + V_2O_5$ and $2MnO + V_2O_5$ are given in Figure 3 (c–e). The three curves each show two endotherms, one at 918 K and one at 1098 K. The former whose height varies in the order $MnO + V_2O_5 > 2MnO + V_2O_5 > 3MnO + V_2O_5$ is due to MnV_2O_6/V_2O_5 eutectic melting [5] and its decrease in height is a reflection of the decreasing V_2O_5 content. The 1098 K endotherm corresponds to MnV_2O_6 peritectic melting (Table 1) and its increase in height with increasing MnO content indicates that, in spite of the apparently unfavourable stoichiometry, a greater conversion to MnV_2O_6 occurs in the $3MnO + V_2O_5$ reaction than in the $MnO + V_2O_5$ reaction. This is substantiated by the appearance in the $3MnO + V_2O_5$ curve of an exothermic rise commencing at about 800 K and an exotherm at 950 K following the eutectic endotherm, and is also in accord with the other MO/V_2O_5 reactions in which vanadate formation also proceeds more rapidly in mixtures of high MO content.

That MnV_2O_6 is the only product of reaction of MnO with V_2O_5 at temperatures below the melting point of MnV_2O_6 is in agreement with the attempted preparation of $Mn_3V_2O_8$ in which it was found by X-ray powder diffraction that MnV_2O_6 was always formed below 950 K in the reaction $3MnO + V_2O_5$. Dorm and Marinder [9] also found that a temperature of at least 1070 K was required for the preparation of $Mn_2V_2O_7$ by the reaction $2MnO + V_2O_5$.

Conclusion

The unique ability of DTA to detect and identify chemically similar phases in complex admixtures has been of particular value in determining the products of the MO/V_2O_5 reactions. Despite the chemical and structural similarities of the systems studied, they show remarkable variation not only in the identity of the initial product of solid–solid reaction but also in the identities and relative amounts of subsequent intermediates. Thus the initial products of solid–solid reaction of V_2O_5 with ZnO, MgO and MnO, irrespective of initial stoichiometry, are $Zn_2V_2O_7$, $Mg_3V_4O_{13}$ and MnV_2O_6, respectively, whereas NiO and CoO form that vanadate which corresponds to the stoichiometry of the initial oxide mixture. Whether this complex situation arises from mechanistic or thermodynamic considerations, is not clear and requires further investigation.

The presence of metavanadate as an intermediate of all the $2MO + V_2O_5$ reactions and of some $3MO + V_2O_5$ reactions suggests that the mechanism of these reactions may involve transport of MO to the reaction interface. However, the absence of low-temperature thermal effects for the orthovanadates and the presence of significant amounts of pyrovanadate in the $MO + V_2O_5$ reactions conversely suggests the chemically more acceptable transport of V_2O_5 to the reaction interface. Also, the observation that reaction progresses most rapidly in MO/V_2O_5 mixtures of highest MO content favours the transport of V_2O_5 as mechanistically the more important process since it is in these mixtures that the area of available reaction interface for this process is greatest.

Note added in proof:

Recent work of this laboratory [20] and others [21, 22] indicates that in the $MgO-V_2O_5$ system the phase $Mg_3V_4O_{13}$ may not form in solid—solid reactions but that it is a further polymorphic form of $Mg_2V_2O_7$ stable below 900 K.

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Résumé — On a étudié la formation de vanadates par réaction de V_2O_5 avec CoO, NiO ZnO, MgO et MnO. Les produits initiaux de la réaction dans l'état solide avec ZnO, MgO et MnO sont respectivement $Zn_2V_2O_7$, $Mg_3V_4O_{13}$ et MnV_2O_6. CoO et NiO donnent surtout le vanadate correspondant au mélange stoechiométrique initial des oxydes. La formation ultérieure des ortho-, méta- et paravanadates comme produits intermédiaires indique que le mécanisme principal est constitué par la migration de V_2O_5 vers l'interface réactionnel.

ZUSAMMENFASSUNG — Die Vanadatbildung im Verlauf der Reaktion von V_2O_5 mit CoO, NiO, ZnO, MgO und MnO wurde untersucht. Die Anfangsprodukte der Festphasenreaktion mit ZnO, MgO und MnO sind $Zn_2V_2O_7$, $Mg_3V_4O_{13}$, bzw. MnV_2O_6. CoO und NiO bilden vorwiegend das Vanadat, welches der Stöchiometrie des anfänglichen Oxidgemisches entspricht. Die darauffolgende Bildung von Ortho-, Pyro- und Metavanadat als Zwischenprodukte weist darauf hin, daß der mechanistische Hauptvorgang in dem Transport von V_2O_5 zu der Reaktionsgrenzfläche besteht.

Резюме — Было изучено образование ванадатов при реакции V_2O_5 с CoO, NiO, ZnO, MgO и MnO. Первоначальными продуктами реакции типа твердое тело — твердое тело V_2O_5 с ZnO, MgO и MoO являются соответственно $Zn_2V_2O_7$, $Mg_3V_4O_{13}$ и MnV_2O_6. CoO и NiO образуют преимущественно ванадаты, состав которых соответствует стехиометрии первоначальных смесей окислов. Последующее образование орто-, про- и метаванадатов, как промежуточных продуктов, указывает на то, что основным процессом механизма реакции является перенос V_2O_5 на реакционную поверхность раздела.