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DIFFERENTIAL SCANNING CALORIMETRY OF UNIVALENT DIHYDROGEN PHOSPHATES AND ARSENATES

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ABSTRACT

The high temperature phase relations (> 20°C) of LiH_2PO_4, NaH_2PO_4, KH_2PO_4, RbH_2PO_4, CsH_2PO_4, $NH_4H_2PO_4$, KH_2AsO_4, RbH_2AsO_4, CsH_2AsO_4 and $NH_4H_2AsO_4$ have been studied. All materials decompose at higher temperatures. Solid–solid transitions are studied when present and transition temperatures, transition enthalpies, decomposition temperatures, decomposition enthalpies and decomposition products are discussed.

INTRODUCTION

The univalent dihydrogen phosphates and arsenates with general formula XH_2YO_4, where $X = $ Li, Na, K, Rb, Cs, NH_4 and $Y = $ P or As, have attracted much attention because many of the compounds are hydrogen-bonded ferroelectrics[1]. Most studies have been directed at the low-temperature ferroelectric transitions. The present study was undertaken to establish the high-temperature phase behaviour of these compounds.

KH_2PO_4 (KDP) is the best-known ferroelectric compound in the group and also the most studied. Its phase behaviour serves as a model for the group and therefore the main features are summarized here. The ferroelectric phase is stable at low temperatures; it is orthorhombic space group C_{2v}^{19}-$Fdd2$. As the temperature is raised this phase transforms to a paraelectric tetragonal phase with space group D_{2d}^{12}-$I\bar{4}2d$. At still higher temperatures (> 150°C) decomposition occurs when KH_2PO_4 loses water with the resultant formation of KPO_3[2]. This decomposition complicates the interpretation of the high-temperature phase behaviour. High pressures inhibit this decomposition and therefore high-pressure differential thermal analysis studies have been vital in determining the high-temperature phase relations[3–5]. KDP shows a quasi-irreversible transition at ~180°C to a monoclinic phase with uncertain space group[1, 3, 6]. A further phase transition is encountered at ~233°C before melting takes place at 260°C.

The phase relations for RbH_2PO_4 (RDP), CsH_2PO_4 (CDP), $NH_4H_2PO_4$ (ADP) and KH_2AsO_4 (KDA) have been studied at high pressures and temperatures and the overall crystal chemical similarities have been discussed[3-5]. The single study conducted at atmospheric pressure where most information was presented for the group of compounds is that of Gallagher[2]. Using thermogravimetric (TG) and differential thermogravimetric (DTG) experimental techniques Gallagher[2] was able to determine the temperatures at which decomposition occurred and to propose what some of the decomposition products in the series of compounds were.

The present study was undertaken to study the high-temperature phase behaviour of the following compounds: LiH_2PO_4 (LDP), NaH_2PO_4 (SDP), KH_2PO_4 (KDP), RbH_2PO_4 (RDP), CsH_2PO_4 (CDP), $NH_4H_2PO_4$ (ADP), KH_2AsO_4 (KDA), RbH_2AsO_4 (RDA), CsH_2AsO_4 (CDA) and $NH_4H_2AsO_4$ (ADA). The study was aimed at determining transition temperatures, decomposition temperatures, enthalpies of solid–solid transitions and decomposition, and finally decomposition products.

EXPERIMENTAL

The DSC measurements were made in a commercial differential scanning calorimeter (Du Pont 990 Thermal Analysis System). The samples and reference (alumina) were contained in aluminium cups and heating rates of 2 and 5°C min^{-1} were used. The calorimeter sensitivity was varied in the range 0.1 to 2 mcal sec^{-1} in^{-1}. Transition temperatures were measured in the conventional manner, i.e. the intersection between the extension of the linear portion of the leading edge of the curve and the baseline. When determining enthalpies of transition an alumina reference was replaced by an empty aluminium cup and time was measured on the abcissa. The peak area used in enthalpy determination was the area enclosed by the curve and a line drawn between the points where the curve begins to deviate from and returns to the baseline. Instrument scales were calibrated in each case using pure indium, tin and lead standards in the appropriate temperature ranges. Sample weight was typically 15 mg and weight losses were monitored intermittently with an accuracy of 0.02 mg.

Certain DSC traces showed gross instability during decomposition processes. If the samples were diluted by adding alumina the traces were smoothed and peak areas become easier to measure. In some cases where alumina was used the results were also repeated using aluminium powder, to verify reproducibility of results.

Samples and decomposition products were characterized using high resolution Guinier X-ray powder diffraction techniques with monochromatic Cu $K\alpha_1$ (λ = 1.5405) radiation.

ADP, KDA (British Drug Houses Ltd.) LDP (Rocky Mountain Research Inc.), KDP, SDP monohydrate (Merck) and SDP dihydrate (Hopkin and Williams Ltd.) were all available with states purities of better than 99.0%. The remaining compounds were prepared as discussed previously[5].

TABLE 1

THERMAL DATA ON UNIVALENT DIHYDROGEN PHOSPHATES AND ARSENATES

Compound	*Solid–solid transition (T>O°C)*		*Decomposition process*			
	T(°C)	*ΔH(kJ mole⁻¹)*	*Start (°C)*	*Finish (°C)*	*Transition Temp. (°C)*	*ΔH(kJ mole⁻¹)*
LiH_2PO_4			150	220	199	42.03
NaH_2PO_4			175	215	205	45.94
KH_2PO_4	~180[a] ~233		204	266	222	61.12
RbH_2PO_4	90[a] 281	4.67[a]	207	270	221	63.44
CsH_2PO_4	149[a] 230	1.07[a] 7.62	195	268	235.5	61.32
$(NH_4)H_2PO_4$			140	240	190	69.45
KH_2AsO_4			200	280	211	69.41
RbH_2AsO_4			192	264	197	81.70
CsH_2AsO_4	166	11.5	260	293	278	43.54
			175	215	180	91.00
			225	250	229	9.59
$(NH_4)H_2AsO_4$			255	320	284	25.43
			410	435	428	17.26

[a] Data are taken from refs. 3, 5 and 14.

RESULTS AND DISCUSSION

All compounds studied showed decomposition prior to melting. Each compound will be discussed separately and the results are summarized in Table 1.

LiH_2PO_4 (LDP)

LDP is orthorhombic with space group C_{2v}^9-$P2_1cn$ at room temperature[7]. At higher temperatures it was reported to decompose into $Li_2H_2P_2O_7$ and then into $LiPO_3$ at 160–260°C and 260–400°C, respectively[8, 9]. The decomposition process was reported to be a complex one, with a number of non-stoichiometric polyphosphates appearing[9].

The LDP used was checked prior to use by X-ray powder diffraction. The compound was heated to ~140°C without any thermal events occurring. Figure 1 shows a typical DSC curve obtained for LDP diluted with alumina. As can be seen the DSC curve deviates from the baseline at ~150°C with the bulk of the thermal event being completed by ~220°C. The decomposition reaction started with the formation of a clear viscous liquid which seemed to be polymeric in nature. This is similar to results obtained previously on alkali dihydrogen phosphates[2]. Intermittent weight loss measurements showed that a measurable weight loss started occurring at ~150°C and this was terminated above ~260°C.

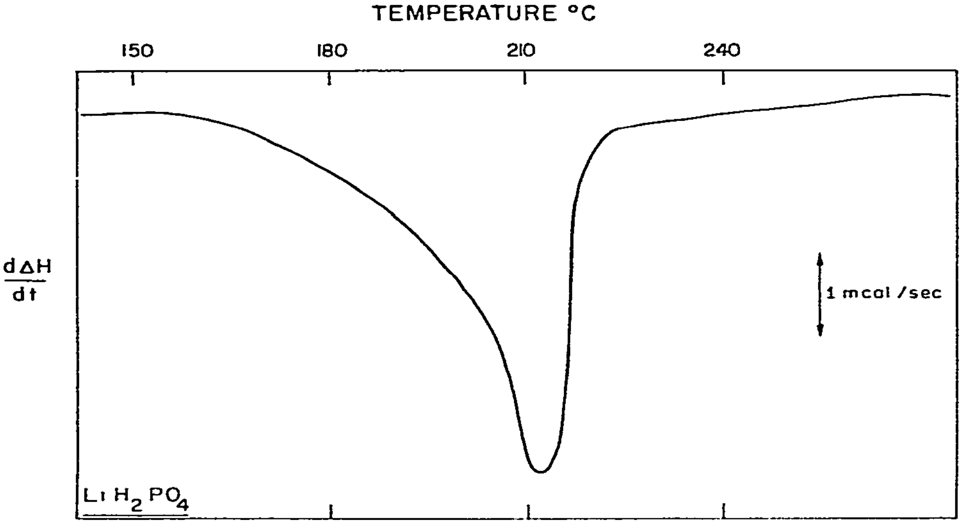

Fig. 1. Typical DSC trace for LiH_2PO_4 diluted with alumina.

X-ray diffraction patterns of partially decomposed products indicated a lack of crystallinity in the additional products. The additional diffraction lines were diffuse and difficult to identify, but LDP remained clearly identifiable.

The total decomposition enthalpy measured was 42.03 kJ mole^{-1}. It is, however, clear from a comparison of the present data with those obtained previously[8, 9] that the thermal event refers to a decomposition process which takes place in steps rather than a single event. The final products rpoduced by total decomposition were glassy solids which were extremely deliquescent and were not identified by X-ray diffraction.

NaH_2PO_4 (SDP)

SDP was obtained in the dihydrate and monohydrate forms. $NaH_2PO_4 \cdot 2H_2O$ is orthorhombic[10], space group D_2^4-$P2_12_12_1$, $NaH_2PO_4 \cdot H_2O$ is orthorhombic[11], space group C_{2v}^9-$Pna2_1$ and NaH_2PO_4 is monoclinic[12], space group C_{2h}^5-$P2_1/c$. Recently, it has been proposed that $NaH_2PO_4 \cdot 2H_2O$ and $NaH_2PO_4 \cdot H_2O$ are structurally very similar. In both compounds it is reported that P tetrahedra form a framework by two systems of bent chains. The structural similarities allowed a mechanism to be proposed[11] for the following solid-state reaction

$$NaH_2PO_4 \cdot 2H_2O \rightleftarrows NaH_2PO_4 \cdot H_2O + H_2O$$

The thermal decomposition of NaH_2PO_4 has been discussed in detail[9]. More recent reviews[13] identify the following decomposition reaction

$$2NaH_2PO_4 \xrightarrow{200\,^\circ C} Na_2H_2P_2O_7 + H_2O$$

The present X-ray diffraction data revealed small quantities of $NaH_2PO_4 \cdot H_2O$ in the $NaH_2PO_4 \cdot 2H_2O$ sample, thus confirming remarks made about the relative stabilities of these compounds by Catti and Ferraris[11]. The DSC traces indicate

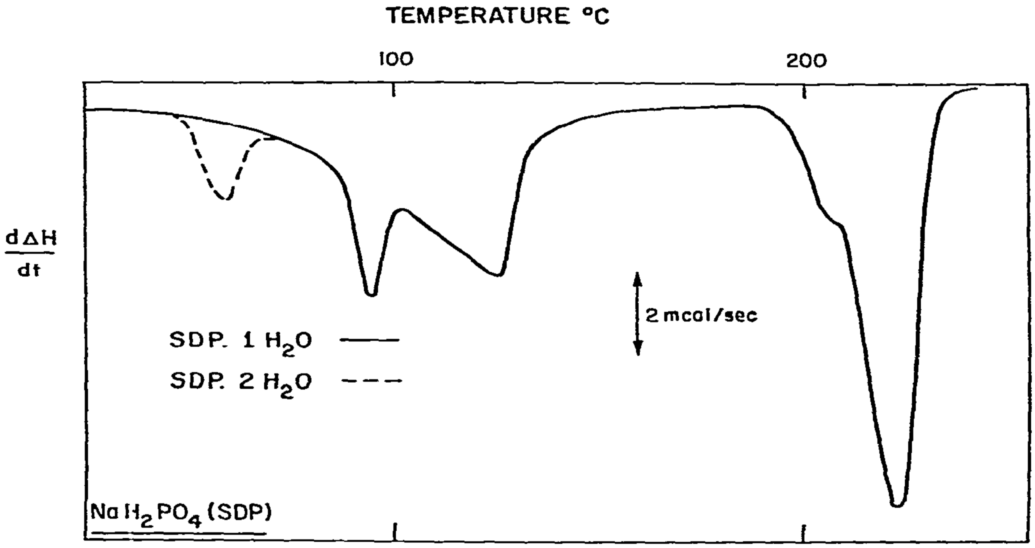

Fig. 2. Typical DSC trace for $NaH_2PO_4 \cdot H_2O$.

thermal events at 47 and 67 °C for the dihydrate and at 67 °C in the monohydrate. The DSC trace for pure $NaH_2PO_4 \cdot H_2O$ is shown in Fig. 2. The event at 47 °C represents the conversion of the dihydrate into the monohydrate, with pure NaH_2PO_4 being prepared with the subsequent loss of water starting at 67 °C. The reaction

$$NaH_2PO_4 \cdot H_2O \rightarrow NaH_2PO_4 + H_2O$$

is spread over a wide temperature range (67–130 °C), however, Fig. 2 shows that at ~100 °C a secondary thermal event occurs. X-ray diffraction patterns show that at ~100 °C, i.e. after the initial event at 67 °C, the material is pure NaH_2PO_4. The enthalpy for this event is 10.43 kJ $mole^{-1}$. The secondary event does not produce any structural changes and could be due to adsorbed water being driven off the surface of the particles, or capsule surface. This was found when the starting material was the mono- or dihydrate. No attempt was made to estimate ΔH for the event at 47 °C as the sample was known to contain $NaH_2PO_4 \cdot 2H_2O$ and $NaH_2PO_4 \cdot H_2O$ as discussed previously.

NaH_2PO_4 decomposed at ~205 °C forming a viscous liquid similar to that found for LDP and ADP. The observed enthalpy was 45.94 kJ $mole^{-1}$. This thermal event corresponds well with the reported decomposition of NaH_2PO_4 with the formation of $Na_2H_2P_2O_7$.

KH_2PO_4 (KDP), RbH_2PO_4 (RDP) and CsH_2PO_4 (CDP)

All salts have been discussed in detail previously[2, 3, 5, 14] except for the enthalpy value related to decomposition. The solid–solid transitions were confirmed and all salts decomposed in the region 200–220 °C. Weight loss measurements suggest that the decomposition reaction is

$$MH_2PO_4 \rightarrow MPO_3 + H_2O$$

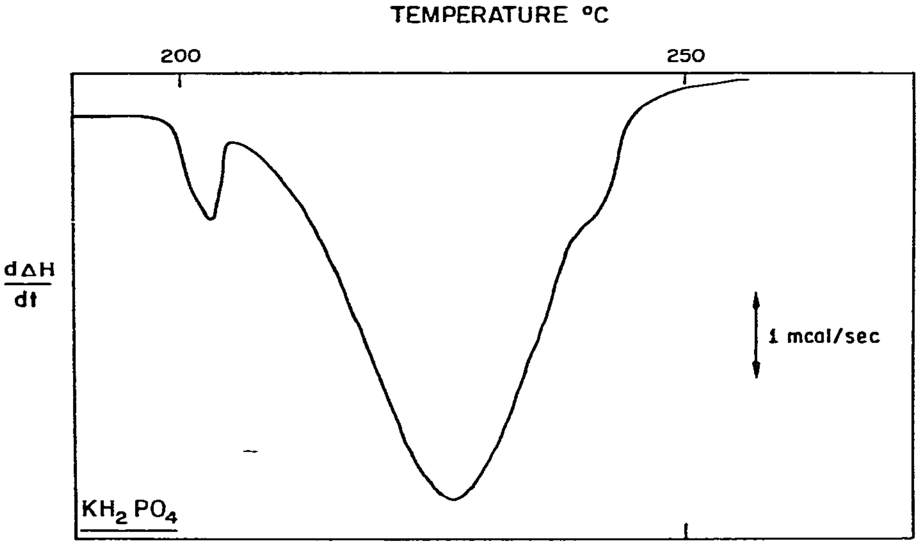

Fig. 3. Typical DSC trace for KH_2PO_4 diluted with alumina.

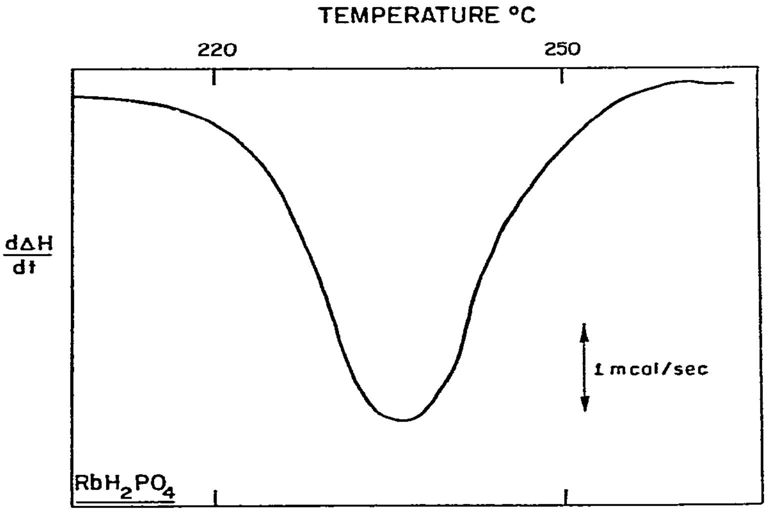

Fig. 4. Typical DSC trace for RbH_2PO_4 diluted with alumina.

KDP and CDP have solid–solid transitions[14] and immediately afterwards or during the transition process decomposition takes place. The events cannot be completely separated for the purpose of enthalpy measurements. (In the case of RDP the events are well separated). Figures 3–5 illustrate this point and also show the typical decomposition events. For this reason the enthalpy values quoted refer to the total enthalpies with the previously reported enthalpies subtracted from the total. The measured decomposition enthalpies for KDP, RDP and CDP were 61.12, 63.44, and 61.321 kJ mole^{-1}, respectively. The temperatures at which decomposition started were 204, 207 and 195°C, respectively. In the case of CDP it will be noted that slight decomposition appears to start prior to the transition at 230°C. The feature was also discussed in detail by Metcalfe and Clark[14]. The decomposition temperatures for KDP and RDP are in good agreement with Gallagher[2].

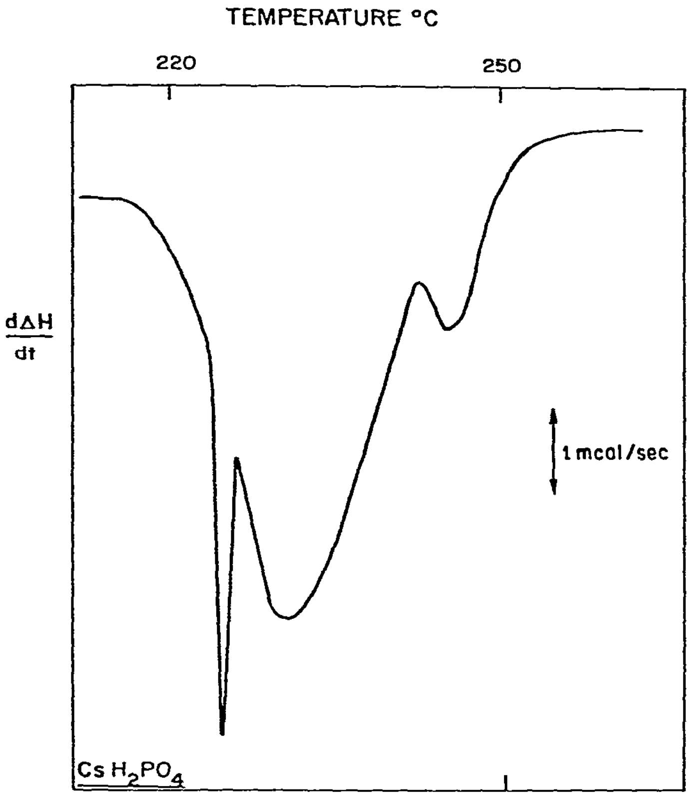

Fig. 5. Typical DSC trace for CsH_2PO_4 diluted with alumina.

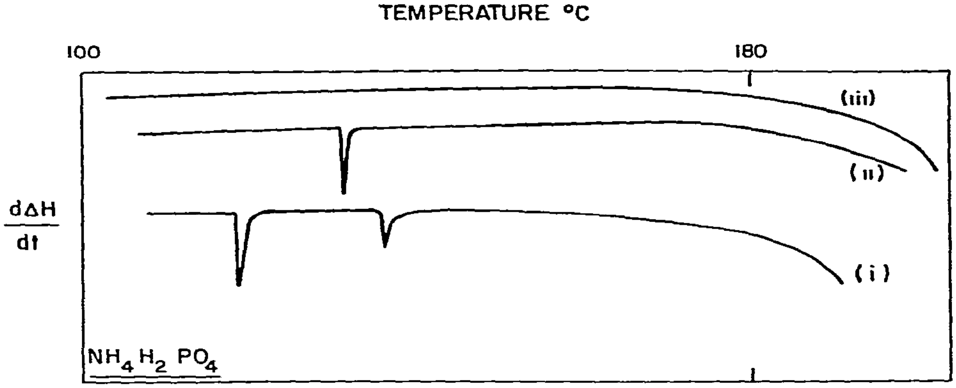

Fig. 6. Typical DSC trace for $NH_4H_2PO_4$ below decomposition temperature.

$NH_4H_2PO_4$ (ADP)

ADP has been discussed in detail[4]. With the recent discovery of quasi-irreversible transitions prior to decomposition for RDP and CDP[14], it was decided to check for such a transition in ADP. The material, used as supplied, initially yielded irreproducible results. Approximately 90 DSC traces were completed which yielded small sharp thermal events as shown in Fig. 6(i) and (ii). The thermal events were spread between 90 and 170°C, with most events occurring around 110°C. Detailed investigation of single crystals of ADP showed unusual surface details. These were removed by

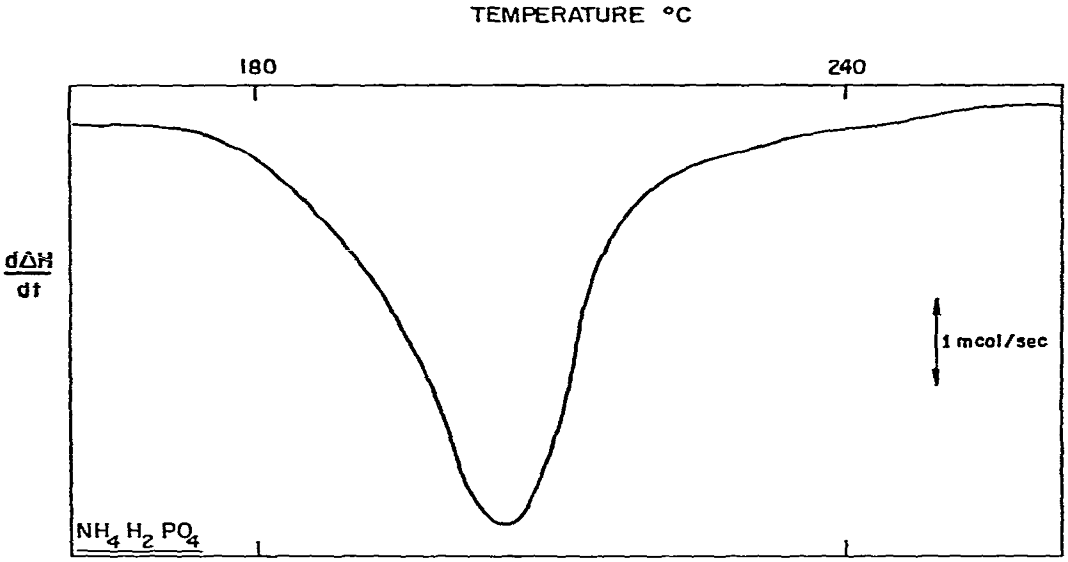

Fig. 7. Typical DSC trace for $NH_4H_2PO_4$ decomposition diluted with alumina.

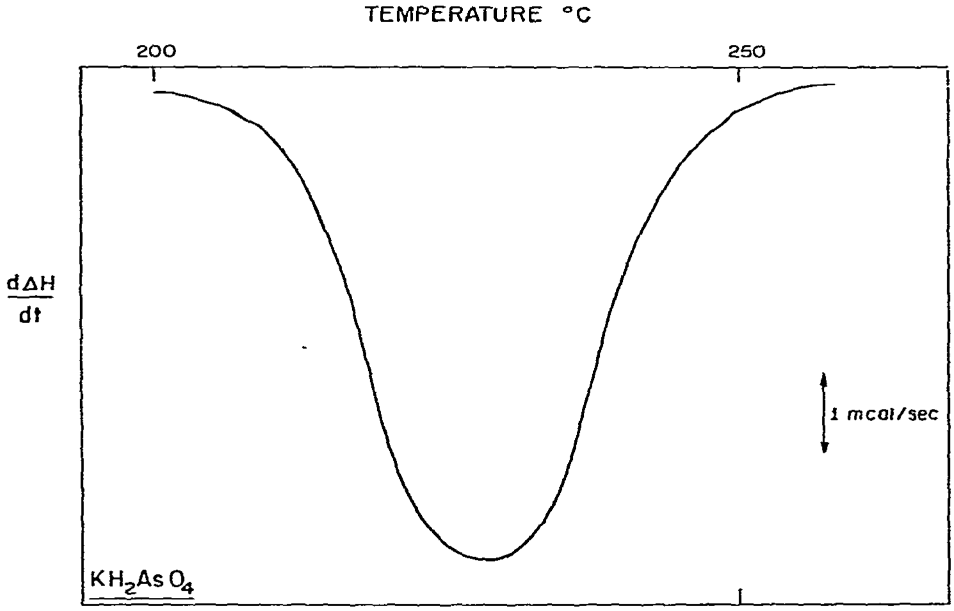

Fig. 8. Typical DSC trace for KH_2AsO_4.

washing the crystals in acetone. Upon reinvestigation using DSC all stray thermal events were removed and the DSC trace was absolutely smooth, as shown in Fig. 6(iii). As shown in Fig. 7, decomposition occurred at ~190°C with an enthalpy of 69.45 kJ mole^{-1}. Decomposition was, however, not affected by the surface imperfections. If the clean crystals were exposed to the atmosphere for ~2 h the effect was found to reappear. The decomposition temperature is in good agreement with Gallagher[2].

Partially decomposed products were examined by X-ray diffraction. In addition to ADP being present, there was evidence of an additional poorly crystallized phase, which could not be identified.

KH_2AsO_4 (KDA)

KDA has been described previously in some detail[4]. It is reported[2] to decompose at atmospheric pressure at ~225°C with no solid–solid transitions prior to decomposition.

Figure 8 shows a typical DSC trace obtained for KDA. No solid–solid transitions were found prior to decomposition which takes place at 211 °C and is spread over some 80°C wsith an enthalpy of 69.41 kJ mole^{-1}. Weight loss measurements indicate that the decomposition reaction was as follows

$$KH_2AsO_4 \rightarrow KAsO_3 + H_2O$$

Post-mortem X-ray analysis strongly suggested that the bulk of the material was $KAsO_3$. The ASTM reference diffraction data for $KAsO_3$ were of poor quality and a more positive identification would have been possible if the reference data had been better.

RbH_2AsO_4 (RDA)

RDA is tetragonal[15], space group V_d^{12}-$I\bar{4}2d$ at room temperature. It is reported to decompose[2, 15, 16] at ~200°C without any solid–solid transitions taking place prior to decomposition.

Figure 9 shows a typical DSC trace for RDA with decomposition starting at ~192°C, spread over ~70°C with an enthalpy change of 81.70 kJ mole^{-1}. Post mortem X-ray analysis clearly showed the presence of a new phase with many similarities to the phase formed for KDA. No reference data exist in the ASTM files for $RbAsO_3$, so a positive identification is impossible.

CsH_2AsO_4 (CDA)

CDA is tetragonal, space group V_d^{12}-$I\bar{4}2d$ at room temperature. It is reported to

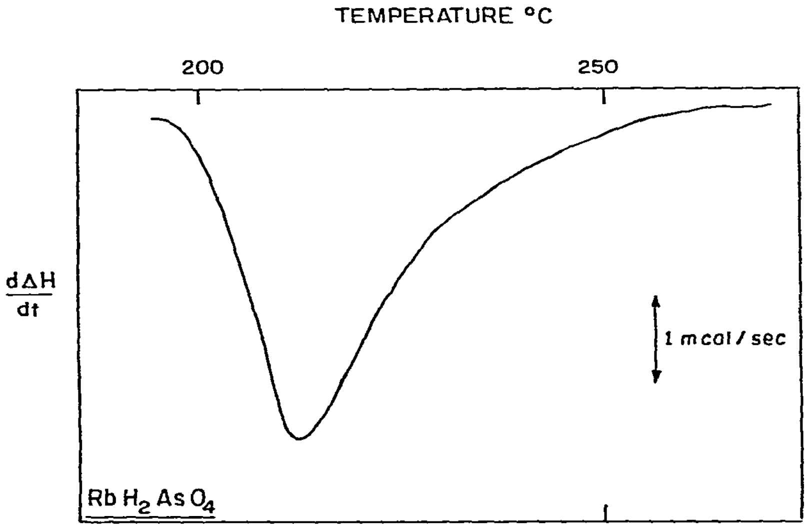

Fig. 9. Typical DSC trace for RbH_2AsO_4.

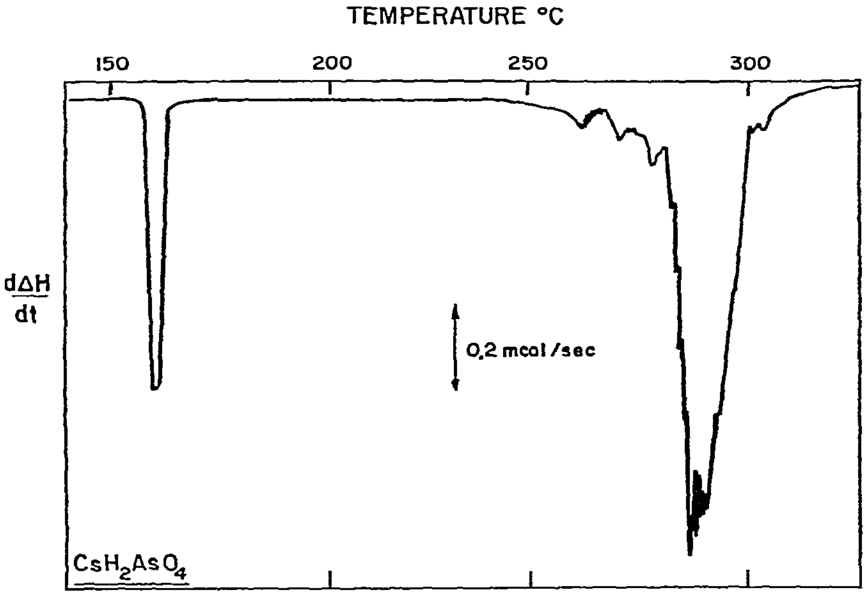

Fig. 10. Typical DSC trace for CsH_2AsO_4.

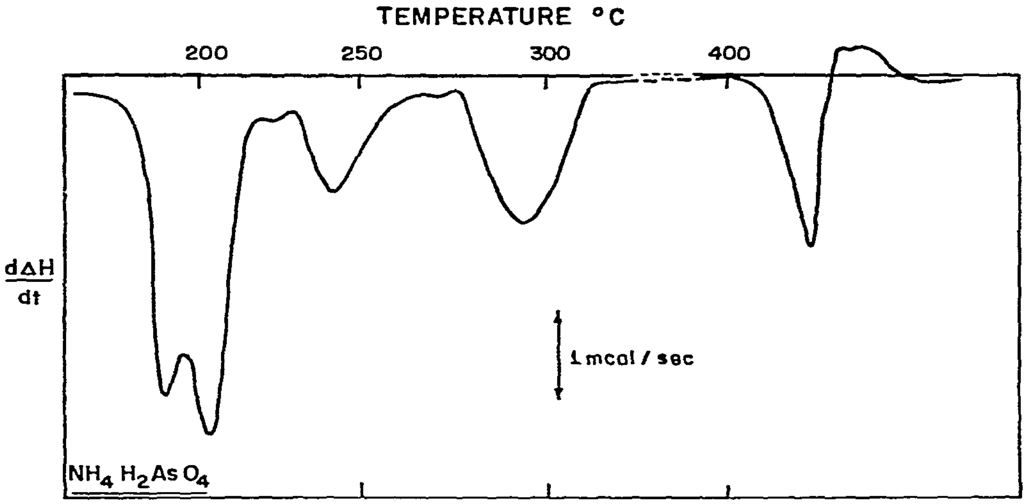

Fig. 11. Typical DSC trace for $NH_4H_2AsO_4$.

undergo a solid–solid transition[15] at 150 °C with decomposition[2, 15] taking place at ~220 °C. However, other reports[16, 18] (and references therein) indicate three transitions at 156, 178 and 190 °C, and even suggest decomposition at 109 °C.

Figure 10 shows a typical DSC trace for CDA. A single solid–solid transition is found at 166 °C with an enthalpy of 11.5 kJ $mole^{-1}$. The transition was found to be fully reversible with the cooling signal occurring at 136 °C. Repeated cycling showed that the base of the DSC signal increased slightly from ~10 to ~16 °C, but that the enthalpy values remained constant.

Decomposition occurred at ~278 °C but started at ~250 °C with an enthalpy of 43.54 ± 3.2 kJ $mole^{-1}$. Weight loss data indicated the following reaction

$CsH_2AsO_4 \rightarrow CsAsO_3 + H_2O$

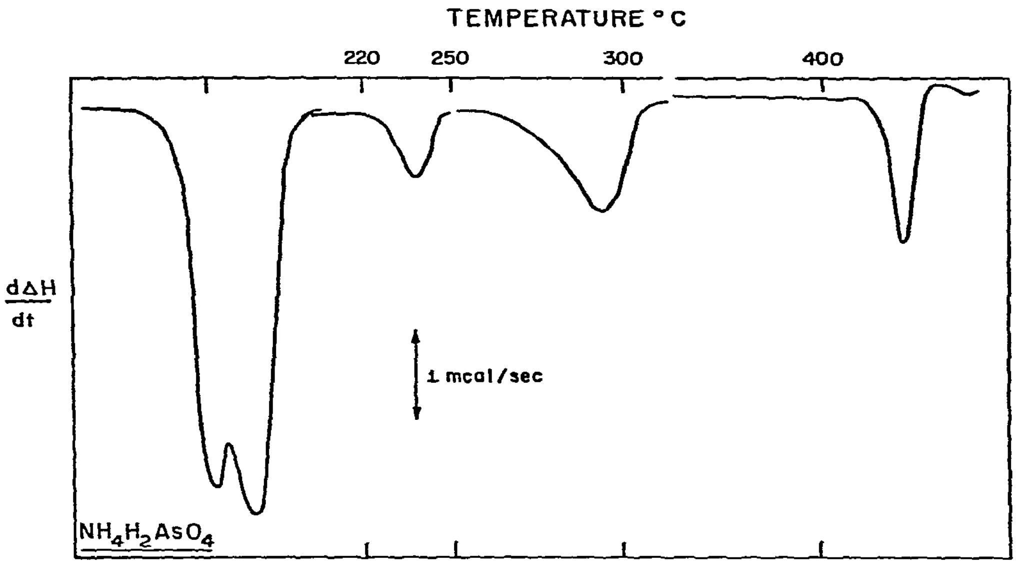

Fig. 12. Interrupted DSC trace for $NH_4H_2AsO_4$ where each thermal event is resolved separately.

Once again post-mortem X-ray diffraction analysis is hampered by a lack of diffraction data for $CsAsO_3$. The diffraction pattern showed clear evidence of the formation of the new products and they were clearly poorly crystallized.

$NH_4H_2AsO_4$ (ADA)

ADA is tetragonal[17], space group V_d^{12}-$I\bar{4}2d$ at room temperature. It is reported from EGA experiments to decompose[2] at ~200°C with subsequent loss of NH_3 and H_2O, with the formation of As_2O_3.

Figures 11 and 12 show the typical results obtained for the decomposition of ADA. The decomposition behaviour is clearly complex and occurs between 180 and 450°C.

The complex DSC trace could be resolved into four discrete thermal events (Fig. 12) by interrupting heating and allowing some form of thermal equilibrium to be established. The first event (actually a double event) is associated with the loss of water and has an enthalpy of 91.00 kJ mole^{-1}. The following two thermal events at ~230 and ~280°C showed further weight losses and the products at various stages had diffraction patterns which showed strong similarities, with the main product being As_2O_5. The enthalpies are 9.59 and 25.43 kJ mole^{-1}. Weight loss data[2] suggest the loss of ammonia and water at 230°C. The final thermal event at 428°C has a slight exothermic component at the end of the thermal event. The enthalpy was 17.26 kJ mole^{-1}.

The identification of As_2O_5 as the main solid product of decomposition is not in agreement with previous assumptions of the formation of As_2O_3 as the main decomposition product. The relative stabilities of As_2O_5 and As_2O_3 are not well understood[19, 20]. The bulk of evidence does, however, suggest that the As_2O_5 could be an intermediate product which transforms into As_2O_3 at higher temperatures.

CONCLUSIONS

(1) The high-temperature phase relations including decomposition behaviour have been studied for LDP, SDP, KDP, RDP, CDP, ADP, KDA, RDA, CDA and ADA. The results are summarized in Table 1.

(2) The nature of the solid–solid transitions, prior to decomposition, for CDA has been resolved. One reversible transition occurs on heating at 166°C and on cooling at 136°C, with an enthalpy of 11.5 kJ mole^{-1}.

(3) Weight loss measurements and the X-ray diffraction data obtained indicate that the most probably decomposition reaction is

$XH_2YO_4 \rightarrow XYO_3 + H_2O$

Exceptions are found for NaH_2PO_4 and $NH_4H_2AsO_4$ where the probable solid products are $Na_2H_2P_2O_7$ and As_2O_5.

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