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Note

Effect of impurities on orthorhombic (II) – hexagonal (I) transformation of potassium sulphate

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Potassium sulphate has been said to invert from an orthorhombic modification to a hexagonal modification around 590 °C according to Bredig[1], who has determined the structure of the high-temperature phase. Even though there are several papers [2, 3, 4, 10] in the literature describing the crystallography, reversibility, quantitative thermodynamic and kinetic aspect of this transformation, there is limited information regarding the effect of impurities on the enthalpy, kinetics and energetics of the transformation. We have now investigated this aspect and such a study is of particular importance owing to the fact that impurities markedly affect the phase transformation of solids[5]. Moreover, this study may throw some light on the mechanism of this transformation.

In the present investigation, the kinetics and energetics of orthorhombic(II)–hexagonal(I) transformation of potassium sulphate in the presence of known amounts of different impurity cations have been studied. The values of enthalpy of transformation (ΔH) and energy of activation (E_a) for different impurity-doped samples of potassium sulphate have been evaluated from DTA data.

EXPERIMENTAL

All the samples of pure and doped potassium sulphate were prepared according to the method adopted by Rao et al.[6] Known amounts of impurity cations (Na^+, Li^+, NH_4^+, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) were taken in the form of sulphates along with the pure potassium sulphate. The impurity cations were chosen on the basis of their ionic size. All the chemicals used were of analytical grade.

The DTA curves were obtained by employing a "Fisher Differential thermalyzer" Model 260, fitted with an automatic voltage stabilizer, recorder and amplifier. The curves were recorded with a constant heating rate of 10 °C min^{-1}, under controlled conditions (packing, particle size, etc.). Calcined α-alumina was used as reference material. The activation energy was calculated following the method of Borchardt and Daniels[7]. ΔH values were computed by comparing the area of transformation

TABLE 1

VALUES OF $Tf_{(i)}$, $Tf_{(P)}$, $Tr_{(P)}$, ΔHf, ΔHr AND E_af FOR ORTHORHOMBIC (II)–HEXAGONAL (I) TRANSFORMATION OF VARIOUS DOPED SAMPLES OF POTASSIUM SULPHATE

Sample No.	*Impurity*[a] *(%)*	$Tf_{(i)}$ *(°C)*	$Tf_{(P)}$ *(°C)*	$Tr_{(P)}$ *(°C)*	*Hf*[b] *kcal mole*$^{-1}$	*Hr*[b] *kcal mole*$^{-1}$	E_af *kcal mole*$^{-1}$	*Ionic radii (nm)*
1	None	552	581	570	2.14	2.40	229	K^+ = 0.133
2	Na (0.5)	534	580	570	2.00	2.40	144	
3	Na (1.0)	537	578	565	1.90	2.10	160	
4	Na (2.0)	542	578	564	1.80	1.90	179	Na^+ = 0.095
5	Na (5.0)	544	576	561	1.70	1.70	190	
6	Na (10.0)	547	576	561	1.10	0.80	233	
7	Li (1.0)	533	576	561	1.80	2.30	122	
8	Li (5.0)	553	575	562	1.80	2.20	192	Li^+ = 0.060
9	Li (10.0)	556	573	561	1.70	2.10	210	
10	Li (20.0)	561	573	561	1.50	1.60	220	
11	NH_4 (0.5)	553	578	568	2.10	2.30	275	
12	NH_4 (1.0)	555	577	568	1.90	2.30	345	
13	NH_4 (2.0)	557	575	568	1.90	2.20	370	NH_4^+ = 0.148
14	NH_4 (5.0)	561	572	567	1.80	2.10	400	
15	NH_4 (10.0)	564	568	564	1.60	2.00	428	
16	Cu (0.5)	555	569	557	2.10	2.50	313	
17	Cu (1.0)	557	568	556	1.80	2.20	355	
18	Cu (2.0)	560	568	555	1.70	2.10	370	Cu^{2+} = 0.072
19	Cu (5.0)	559	567	555	1.30	1.50	358	
20	Cu (10.0)	556	565	553	1.10	1.30	349	
21	Ni (0.5)	550	570	553	2.30	2.60	195	
22	Ni (1.0)	550	568	550	1.90	2.40	200	
23	Ni (2.0)	555	568	550	1.80	2.20	223	Ni^{2+} = 0.069
24	Ni (5.0)	557	567	543	1.70	1.40	242	
25	Ni (10.0)	559	566	538	1.50	1.20	260	
26	Zn (1.0)	553	564	547	1.20	1.60	134	
27	Zn (2.0)	555	565	546	1.00	1.40	205	Zn^{2+} = 0.074
28	Zn (5.0)	558	566	545	0.80	1.00	283	
29	Cd (0.5)	542	576	567	1.60	1.90	220	
30	Cd (1.0)	522	550	541	1.90	2.10	174	
31	Cd (2.0)	511	537	520	2.10	2.40	121	Cd^{2+} = 0.097
32	Cd (5.0)	502	527	497	2.40	2.60	103	
33	Cd (10.0)	499	526	497	2.60	2.80	96	

[a] Impurity concentrations are in atomic percent.
[b] ΔH of transformation of pure potassium sulphate was used as an internal standard. The value indicated is from Kelly, as quoted in ref. 8.

peak for the doped samples with the transformation (orthorhombic(II)–hexagonal(I)) peak of pure potassium sulphate[8].

RESULTS AND DISCUSSION

The ΔH values estimated from the peak areas may have an uncertainty of $\pm$ 5%. However, better values of enthalpy cannot be obtained from DTA for smeared or higher order phase transformations which occur over a wide temperature range. This difficulty in the measurement of ΔH by DTA has been pointed out in the transformation of potassium sulphate[7].

Strictly speaking one cannot define ΔH values in the case of doped samples with higher percentage of impurity, because the values have been evaluated per mole of potassium sulphate. But the ΔH values have been calculated for the purpose of comparison with that of pure potassium sulphate. The energy of activation (E_a) could be obtained by the method of Borchardt and Daniels[7] with in an uncertainty of $\pm$ 10%. Although there is considerable controversy regarding the quantitative evaluation of E_a from DTA curves, it may be reasonable to compare values in a related series of systems[9, 10]. Further, good linear plots of log k against $1/T$ seem to serve as satisfactory criteria for obtaining meaningful values of E_a. Such linear plots were found in the present study.

The temperature at the starting point of the peak for the forward transformation, $Tf_{(i)}$, forward transformation temperature $Tf_{(P)}$, backward transformation temperature $Tr_{(P)}$, ΔH values for the forward (ΔHf) and reverse transformations (ΔHr) and E_a values of the forward transformation (E_af) for the pure and doped samples are listed in Table 1.

It is evident from Table 1 that the incorporation of impurities affects $Tf_{(i)}$, $Tf_{(P)}$, $Tr_{(P)}$, ΔHf, ΔHr and E_af values. The E_a value of 229 kcal mole^{-1} for the transformation of pure potassium sulphate agrees well with the earlier reported data[10]. E_a values for the various doped samples range from 96 to 428 kcal mole^{-1} in comparison to 229 kcal mole^{-1} for the pure potassium sulphate[11]. The variation in the values of ΔHf and ΔHr is also fairly large, ranging from 0.80 to 2.60 kcal mole^{-1} and 0.80 to 2.80 kcal mole^{-1}, respectively, in comparison to 2.14 and 2.40 kcal mole^{-1} for the pure potassium sulphate.

As shown in Table 1, the hysteresis in the transformation temperatures of pure potassium sulphate is ~11 °C. Hysteresis is a necessary consequence of the coexistence of two phases[11] and the magnitude of hysteresis is determined by the relative volumes of the high and low temperature phases. The increased hysteresis, i.e., 15°, 13°, 12°, 24°, 21°, 30° occurring by the addition of 5 atomic percent Na^+, Li^+, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} ions, respectively and the decreased hysteresis (~5°) occurring by the addition of 5 atomic percent NH_4^+ are likely to be due to the variation in ΔV caused by the presence of smaller and bigger cations, respectively. Unfortunately no crystallographic data are available on the low and high temperature forms of potassium sulphate with these impurities.

The increase of sodium, lithium, and ammonium ion impurity from 0.5 to 10 atomic percent decrease ΔH values and increase E_a values. The transformation temperatures, i.e., $Tf_{(P)}$ and $Tr_{(P)}$ follow the trend of ΔH values in all cases. With the increase in Cu^{2+} ion impurity from 0.5 to 2 atomic percent, the ΔH value decreases, the E_a value increases, and with further increase of Cu ion content both ΔH and E_a values decrease. The $Tf_{(P)}$, $Tr_{(P)}$ and $Tf_{(i)}$ follow the trend of ΔH and E_a values, respectively.

In the case of Ni^{2+} and Zn^{2+} ion-doped samples, as the impurity percentage is increased, ΔH values decrease and E_a values increase. The transformation temperatures $Tf_{(P)}$, $Tr_{(P)}$ and $Tf_{(i)}$ follow the trend of ΔH and E_a values in both cases. Contrary to this, on increasing Cd^{2+} ion impurity content from 0.5 to 10 atomic percent, ΔH values increase and E_a values decrease.

A perusal of the data given in Table 1 for the doped samples shows that as the E_a values increase, the starting point of the forward transformation peak also shifts to a higher temperature and with the decrease in ΔH values the transformation temperatures, i.e., $Tf_{(P)}$ and $Tr_{(P)}$ decrease, except in the case of cadmium-doped samples, wherein the $Tf_{(P)}$ and $Tr_{(P)}$ decrease with the increase in enthalpy values.

The present findings reveal that for alkali cation impurity-doped samples (Na^+, Li^+, NH_4^+) having the same valency state and electronic configuration but different ionic radii, the trend in the variation of E_a and ΔH values is more or less similar, although there is a contrast in their behaviour when the absolute values of E_a and ΔH are considered. As regards the Cu^{2+} and Ni^{2+} ion-doped samples (for 2–10% impurity) the different trend in the variation of E_a values may probably be due to their different electronic configuration.

The different trend in the variation of E_a and ΔH values in the case of Cd and Zn ion-doped samples is not explainable with the existing data.

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