Fig. 2 — Plots of log C/C_0 against x/l [× naphthalene-catechol system; ⊙ naphthalene-p-chloronitrobenzene system]

For the case of non-mixing, Eq. (3) is followed:

$$C = C_0\left[1 + \left(\frac{C_e}{C_0} - 1\right)\exp\left(\frac{-xv}{D}\frac{P_s}{P_1}\right)\right] \qquad ...(3)$$

where D is the diffusion coefficient and v is the velocity of zone movement.

From Eq. (2) it follows that for complete mixing there should not be any change in the concentration with change in the value of x. This is not true in the present case. Hence, complete mixing does not take place in the zone melting of the samples studied in the present case. In order to test Eq. (3), log $(1 - C/C_0)$ was plotted against x. Straight lines were not obtained. Hence it follows that the equation for non-mixing is also not applicable. Since the rate of zone movement is large and Eqs. (2) and (3) do not fit the data, it appears that partial mixing occurs in the present eutectic systems.

Since the value of effective distribution coefficient is less than unity in both the systems, the impurities are preferentially rejected by the solid and pile up in the liquid close to the interface. Further, greater the deviation from unity in the value of k, the greater is the separation efficiency. The separation efficiency in the naphthalene-p-chloronitrobenzene system is greater than in the naphthalene-catechol system.

References

1. Pfann, W. G., Trans. metall. Soc., AIME, **194** (1952), 794.
2. Yue, A. S., Trans. metall. Soc., AIME, **248** (1970), 19.
3. Yue, A. S., Trans. metall. Soc., AIME, **212** (1958), 88.
4. Wilcox, W. R. & Herington, Zone melting of organic compounds (John Wiley, New York), 1963.
5. Timmermans, J., Physicochemical constants of pure organic compounds (Elsevier, Houston, Texas), 1950.
6. Rastogi, R. P. & Ram Verma, K. T., J. chem. Soc. (1956),
7. Nippon Nojima, H., Kagaku Zasshi, **91** (1970), 810.
8. Rastogi, R. P., Singh, N. B. & Singh, Narsingh Bhadur, J. Cryst. Growth, **37** (1977), 329
9. Wilcox, W. R., Segundo, El., Friedenberg, R & Back, Nathan, Chem. Rev., **64** (1964), 187.

High Temperature X–Ray Diffraction Study of Barium Pyrophosphate

Safia Mehdi, M. Raza Hussain & B. Rama Rao

Regional Research Laboratory, Hyderabad 500009

High temperature X-ray diffraction study of barium hydrogen phosphate has been undertaken in order to find out whether any phase changes take place in it. It has been observed that this compound gets completely converted into barium pyrophosphate at 550°. On heating the latter to further higher temperatures there is no change in phase but the d-values decrease after 850°. This behaviour is similar to that of UP_2O_7. X-ray powder pattern of barium pyrophosphate has been indexed. The system is orthorhombic with the following crystal data: $a = 9\cdot200$ Å, $b = 14\cdot120$ Å, $c = 5\cdot420$ Å, $z = 4$, $D_m = 4\cdot45$ g cm^{-3} and space group symmetry is P_{mmm} or P_{mm2} or P_{222}.

THE effect of heat on barium hydrogen phosphate has been investigated by X-ray methods and the results are described in this paper.

X-ray diffraction patterns were taken on a Philips PW 1010 X-ray diffractometer employing nickel filtered CuK radiation. The samples were heated by means of a high temperature attachment to the diffractometer. Pure barium hydrogen phosphate was heated up to 1000° starting from room temperature, and X-ray patterns were taken at intervals of 100°. The accuracy of temperature measurement and uniformity of temperature have been checked by known lattice spacing-temperature relation of silver. Calibration at room temperature was done from the positions of high angle peaks by extrapolation methods.

It is observed that the conversion of barium hydrogen phosphate into barium pyrophosphate begins at 270° and is complete at about 550°. The X-ray pattern of this pyrophosphate is similar to the pattern of δ-pyrophosphate reported in literature[1] (except for the presence of a few extra weak reflections, which could be located by us because the patterns were taken on a diffractometer and not on a camera). But the temperature of formation of δ-barium pyrophosphate observed here is much less than that reported. The low temperature or α-phase has not been observed at all. The pattern obtained at 550° is completely that of δ-pyrophosphate. It is stable at room temperature and is unaffected by further heating even up to 1400°. Also, there is no indication of the formation of another phase. However an interesting phenomenon has been observed. The values of the interplanar spacings increase when the temperature reaches about 850° and then start decreasing on heating to higher temperatures. This can be seen from the plots in Fig. 1, where the variation in d-spacings with temperature is shown for four strong reflections. This unusual behaviour of barium pyrophosphate is similar to that of uranium pyrophosphate[2] which expands up to about 400° and then contracts till 1200°. Since the structure of
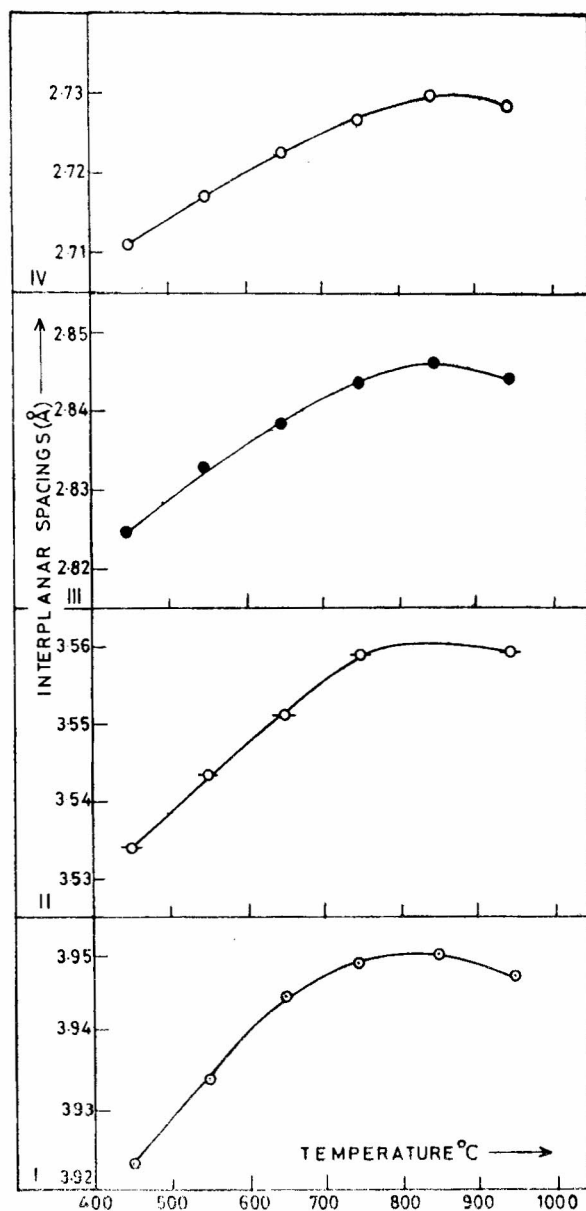
Fig. 1 — Variation of d-spacings with temperature for four strong reflections in X-ray pattern of barium pyrophosphate

barium pyrophosphate is not yet known, it is not possible to give a conclusive explanation for this phenomenon. However, if its structure consists of PO_4 tetrahedra linked together to form P_2O_7 groups, then the decrease in the cell dimensions could perhaps be explained on the basis of the tilting theory[3], because tilting is probable in structures where polyhedra are linked by their corners only.

The peculiar behaviour of barium pyrophosphate as well as its diffraction pattern suggest that this substance is not isomorphous with calcium and strontium pyrophosphates. This is in agreement with the observations of Ranby et al.[1] who have mentioned that the δ-form has no isomorphs at all. Therefore, the general statement that barium pyrophosphate is isomorphous with strontium and calcium pyrophosphates[4] is not wholly correct.

TABLE 1 — INDEXED X-RAY POWDER PATTERN OF BARIUM PYROPHOSPHATE

d in Å	I	hkl	d in Å	I	hkl
5·331	6	001	2·153	31	042
4·334	3	210	2·108	27	161
3·915	100	121	2·037	4	302
3·529	25	040	1·956	11	052
3·354	6	211	1·909	4	152
3·254	6	131	1·865	8	332, 360
3·223	3	230	1·832	4	500
3·070	11	300	1·805	4	003
3·011	3	310	1·769	4	080, 361
2·967	4	041	1·722	5	123
2·828	55	050	1·668	4	213
2·708	39	002	1·586	7	233, 143
2·351	5	202, 060	1·538	6	600
2·318	27	340	1·482	9	551
2·265	11	410	1·411	12	413
2·219	18	222	1·402	7	516, 480
			1·354	8	004

The powder pattern of barium pyrophosphate has been indexed and is given in Table 1. The system is orthorhombic with P_{mmm}, P_{mm2} or P_{222} as the probable space group. The crystal data is as follows:
$a = 9 \cdot 200$ Å, $b = 14 \cdot 120$ Å, $c = 5 \cdot 420$ Å, $z = 4$ and $\rho_m = 4 \cdot 45$ g cm^{-3}.

References

1. RANBY, P. W., MASH, D. H. & HENDERSON, S. T., Brit. J. appl. Phys., Supplement 4 (1955), 18.
2. KIRCHNER, H. P., MERZ, K. M. & BROWN, W. R., J. Am. ceram. Soc., 40 (1963), 137.
3. MEGAW, H. D., Mat. Res. Bull., 6 (1971), 1007.
4. PLUMIER, R., Bull. Classe. Sci. Acad. roy Belg. (1957), 43.

Thermochemical Studies of Diaquodiacetatodioxouranium(VI)

LAMBODAR THAKUR*, MD FAIZ AHMAD & RAJENDRA PRASAD†
Department of Chemistry, Bhagalpur University
Bhagalpur 812007

The heats of solution of anhydrous diacetatodioxouranium(VI) and diaquodiacetatodioxouranium(VI) in water and 2N acetic acid at 300°K, are $-11 \cdot 3 \pm 0 \cdot 6$, $-22 \cdot 4 \pm 0 \cdot 5$; $22 \cdot 6 \pm 0 \cdot 4$, and $10 \cdot 7 \pm 0 \cdot 2$ KJ mol^{-1} respectively. The standard heat of formation of anhydrous UO_2Ac_2 is $-1991 \cdot 9$ KJ mol^{-1}. The gas phase enthalpy of reaction between UO_2Ac_2 and one mole of water is $-60 \cdot 6$ KJ mol^{-1}, commensurate with the dative uranium-oxygen bond strength.

ANHYDROUS diacetatodioxouranium(VI) in the crystalline state, dissolves in water or in aqueous acetic acid giving a clear yellow solution which on

*To whom all correspondence should be addressed.
†Present address: A. N. S. College, Barh (Magadh University).