Thermochimica Acta, 76 (1984) 301–309
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DISSOLUTION OF $Ca_3(AsO_4)_2 \cdot 2\ H_2O$ IN THE SYSTEM $CaO–As_2O_5–H_2O$ AT 35, 40, 45 AND 50°C AND THE RELATED THERMODYNAMIC DATA

P.P. MAHAPATRA *, L.M. MAHAPATRA and C.N. NANDA **

Post-Graduate Department of Chemistry, Khallikote College, Berhampur, GM 760 001 (India)

(Received 21 November 1983)

ABSTRACT

Calcium arsenate dihydrate is precipitated at pH 7.0 and its dissolution in aqueous solutions at temperatures of 35, 40, 45 and 50°C and a pH of between 3.0 and 8.0 is investigated. The thermodynamic parameters ΔG^0, ΔS^0 and ΔH^0 for the process are evaluated. Temperature dependence of solubility is obtained by the equations

$$-\log K_{\mathrm{TCA}} = \frac{9078.138}{T} - 34.0468 + 0.0821421\ T$$

INTRODUCTION

Nelson and Haring [1] and Pearce [2] indicated the existence of calcium arsenate $Ca_3(AsO_4)_2 \cdot 2\ H_2O$ (TCA), although in the system calcium oxide–arsenic oxide–water its behaviour was not clearly defined. Chukhlantsev [3] reported its solubility product (6.76×10^{-19}) at 20°C. While Robinson [4] reported its solubility at 25°C, Smith [5] observed that TCA did not attain saturation in aqueous solutions. Therefore, this communication reports the dissolution of TCA under equilibrium conditions between 35 and 50°C and pH 3.0–8.0, as part of an investigation on the thermodynamics of interactions of different phases of the system $CaO–As_2O_5–H_2O$ with aqueous solvents. The thermodynamic functions ΔG^0, ΔH^0 and ΔS^0 at equilibrium are calculated and reported.

EXPERIMENTAL

The sample of $Ca_3(AsO_4)_2 \cdot 2\ H_2O$ was prepared by the addition of 300 ml calcium nitrate solution (0.166 M) to 300 ml $Na_2AsO_4 \cdot 7\ H_2O$ solution

---

* Author for correspondence at the present address: Department of Chemistry, Science College, Chatrapur GM 761 020, India.

** Present address: Department of Chemistry, Ravenshaw College, Cuttack, India.

(0.10 M) over 30 min. Both solutions were scrupulously maintained at pH 7.0 by 0.005 M NaOH. The product was filtered, washed with doubly-distilled water, heated at 110°C for 3 h, and confirmed by chemical analysis and IR spectra. The formation of the TCA phase was pre-established by a series of pH-metric titration experiments and the identification of the product at different pH values by chemical analysis and IR spectra.

The solubility behaviour of TCA was investigated between 35 and 50°C and pH 3.0–8.0 under a constant ionic environment of 0.05 M $NaNO_3$, by the method of equilibration used earlier [6]. Different concentrations of As_2O_5 (BDH) in water for pH 3.0–6.5 and sodium hydroxide (4.125×10^{-5} and 8.25×10^{-5} M) for pH 7.5 and 8.0 were used. The saturated solutions obtained after the desired period of equilibration were analysed for Ca and As complexometrically [7].

CALCULATION

From a knowledge of the pH of total dissolved Ca and As in solution at equilibrium, concentrations of the free ionic species AsO_4^{3-}, $HAsO_4^{2-}$ and $H_2AsO_4^-$ were calculated from eqns. (1)–(3) as follows

$$(AsO_4^{3-}) = As_{Total} \Big/ \left[\frac{(H^+)^3}{K_1 K_2 K_3} + \frac{(H^+)^2}{K_2 K_3} + \frac{(H^+)}{K_3 f_{HAsO_4^{2-}}} + \frac{1}{f_{AsO_4^{3-}}} \right] \qquad (1)$$

$$(HAsO_4^{2-}) = As_{Total} \Big/ \left[\frac{(H^+)^2}{K_1 K_2} + \frac{(H^+)}{K_2 f_{H_2AsO_4}} + \frac{1}{f_{HAsO_4^{2-}}} \right] \qquad (2)$$

$$(H_2AsO_4^-) = As_{Total} \Big/ \left[\frac{(H^+)}{K_1} + \frac{1}{f_{H_2AsO_4}} \right] \qquad (3)$$

where K_1, K_2 and K_3 are dissociation constants of orthoarsenic acid [8,9] and $f_{AsO_4^{3-}}$, $f_{HAsO_4^{2-}}$ and $f_{H_2AsO_4^-}$ are the activity coefficients for AsO_4^{3-}, $HAsO_4^{2-}$ and $H_2AsO_4^-$ ions, respectively, parentheses indicate activities. Assuming the activity coefficient in the above equations unity, the concentration of Ca^{2+}, H^+ and OH^-, the approximate ionic strength (μ) was obtained using the equation

$$\mu = \tfrac{1}{2} \Sigma C_i Z_i^2$$

The activity coefficient of the three arsenate ions are obtained from the extended Davies' equation [10]

$$\log f_i = -\frac{A\sqrt{\mu}\, Z_i^2}{1 + \sqrt{\mu}} - 0.3\mu$$

The activity coefficients obtained from the above equations are used in eqns.

(1)–(3) and a new value for μ is determined. Iteration was continued until convergence in μ was attained and the activity coefficients are determined. The true activity coefficients of the three arsenate species were obtained. The solubility product of TCA (K_{TCA}) was calculated as follows

$$K_{TCA} = [Ca^{2+}]^3 f^3_{Ca^{2+}} [AsO_4^{3-}]^2 f^2_{AsO_4^{3-}}$$

In the present communication the purpose of calculation is to obtain the solubility product (K_{TCA}) as a function of temperature and the dependence of solubility on the pH of the dissolving medium. The calculations satisfied at least two conditions:
(1) saturation with respect to TCA: $(Ca^{2+})^3(AsO_4^{3-})^2 - K_{TCA} = 0$;
(2) congruent dissolution of TCA: $Ca/(As-As_0) - R = 0$
where R is the expected value for a ratio of 3/2. The values of K_{TCA} at different temperatures were computed by least squares estimation of the coefficient A_i in the expression

$$\log K_{TCA} = \frac{A_1}{T} + A_2 + A_3T$$

where T is the absolute temperature.

The thermodynamic quantities (ΔG^0, ΔH^0 and ΔS^0) of dissolution of TCA described by the reaction $Ca_3(AsO_4)_2 = 3\ Ca^{2+} + 2\ AsO_4^{3-}$ were calculated using the standard thermodynamic equations [11].

RESULTS AND DISCUSSION

The chemical analysis of the sample which gave (wt.%): CaO, 39.27; As_2O_5, 55.29 (calcd. (wt.%): CaO, 38.74; As_2O_5, 52.99) and with a Ca/As ratio of 1.46, corresponded to $Ca_3(AsO_4)_2 \cdot 2\ H_2O$. Formation of the hydrated TCA was indicated from its IR spectra (Fig. 1) and the thermal

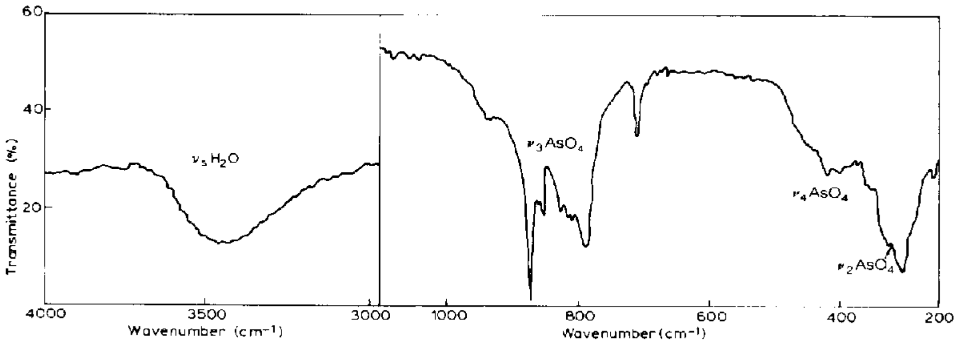

Fig. 1. IR spectra of $Ca_3(AsO_4)_2 \cdot 2\ H_2O$.

TABLE 1

Dissolution of $Ca_3(AsO_4)_2 \cdot 2\ H_2O$ in aqueous solutions and its solubility product (K_{TCA}) at 35°C ($pK_w = 13.68$)

Soln. No.	Initial As_2O_5 conc. in water ($M \times 10^{-3}\ As_0$)	pH of medium		Concentration in solution (g atom $\times 10^{-3}\ l^{-1}$)		$\frac{Ca}{As - As_0}$	K_{TCA}
		Initial	Final	Ca	As		
1	3.592	3.0	7.2	14.4	16.785	1.50	1.7716
2	0.898	3.5	7.4	11.0	9.130	1.499	1.7672
3	0.1796	4.0	7.6	8.7	6.159	1.500	1.8265
4	0.1526	4.5	7.8	7.0	4.985	1.495	1.9257
5	0.05388	5.0	8.0	5.7	3.90776	1.500	2.0339
6	0.0449	5.5	8.10	5.0	3.4298	1.497	2.2027
7	0.00898	6.0	8.20	4.6	3.08396	1.500	2.0430
8	0.00898	6.5	8.3	4.2	2.80898	1.500	1.61586
9	—	7.5	8.3	4.05	2.70	1.50	1.8399
10	—	8.0	8.3	4.05	2.70	1.50	1.8399

Average $K_{TCA} = 1.8868$. Standard deviation = 0.178171.

dehydration corresponded to a loss of about 9% water for the dihydrate of TCA.

The results of the analysis of saturated solutions obtained after equilibration at different temperatures are given in Tables 1–4. The experimental conditions assured the attainment of equilibrium of the solutions of variable

TABLE 2

Dissolution of $Ca_3(AsO_4)_2 \cdot 2\ H_2O$ in aqueous solutions and its solubility product (K_{TCA}) at 40°C ($pK_w = 13.535$)

Soln. No.	Initial As_2O_5 conc. in water ($M \times 10^{-3}\ As_0$)	pH of medium		Concentration in solution (g atom $\times 10^{-3}\ l^{-1}$)		$\frac{Ca}{As - As_0}$	K_{TCA}
		Initial	Final	Ca	As		
1	3.592	3.0	7.15	16.2	17.985	1.50	2.3981
2	0.898	3.5	7.35	12.4	10.620	1.50	2.4423
3	0.1796	4.0	7.50	10.10	7.369	1.44	2.4689
4	0.1526	4.5	7.7	8.20	5.772	1.499	2.3702
5	0.05388	5.0	8.0	6.30	4.307	1.50	2.3986
6	0.0449	5.5	8.0	5.80	3.956	1.499	2.2829
7	0.00898	6.0	8.1	5.20	3.487	1.498	2.2655
8	0.00449	6.5	8.2	4.70	3.223	1.499	2.2908
9	—	7.5	8.25	4.30	2.870	1.498	1.9742
10	—	8.0	8.3	4.0	2.670	1.498	1.8507

Average $K_{TCA} = 2.2742$. Standard deviation 0.2044939.

TABLE 3

Dissolution of $Ca_3(AsO_4)_2 \cdot 2\ H_2O$ in aqueous solutions and its solubility product (K_{TCA}) at 45°C ($pK_w = 13.40$)

Soln. No.	Initial As_2O_5 conc. in water ($M \times 10^{-3}\ As_0$)	pH of medium		Concentration in solution (g atom × 10^{-3} l^{-1})		$\frac{Ca}{As - As_0}$	K_{TCA}
		Initial	Final	Ca	As		
1	3.592	3.0	7.15	18.2	19.318	1.50	2.7211
2	0.898	3.5	7.30	14.0	11.136	1.498	2.8583
3	0.1796	4.0	7.45	11.5	8.0265	1.499	2.81462
4	0.1526	4.5	7.60	9.5	6.6393	1.499	3.009
5	0.05388	5.0	7.70	7.7	5.24176	1.499	3.009
6	0.0449	5.5	7.95	6.3	4.2898	1.50	2.6246
7	0.00898	6.0	8.0	6.0	4.0279	1.496	2.7045
8	0.00449	6.5	8.1	5.35	3.57598	1.499	2.6170
9	—	7.5	8.2	4.80	3.205	1.497	2.6043
10	—	8.0	8.2	4.80	3.205	1.497	2.6043

Average $K_{TCA} = 2.7288$. Standard deviation 0.2341246.

initial arsenic oxide concentration in water with solid TCA. Congruent dissolution is indicated from the $Ca/(As - As_0)$ ratio which remained almost 3/2 at all temperatures. The potential diagram (Fig. 2) where the saturated condition is defined by a straight line, the slope corresponding to the reciprocal of Ca/As of the solid governing the solubility equilibria. The

TABLE 4

Dissolution of $Ca_3(AsO_4)_2 \cdot 2\ H_2O$ in aqueous solutions and its solubility product (K_{TCA}) at 50°C ($pK_w = 13.262$)

Soln. No.	Initial As_2O_5 conc. in water ($M \times 10^{-3}\ As_0$)	pH of medium		Concentration in solution (g atom × 10^{-3} l^{-1})		$\frac{Ca}{As - As_0}$	K_{TCA}
		Initial	Final	Ca	As		
1	3.592	3.0	6.95	23.0	22.519	1.499	3.1108
2	0.898	3.5	7.20	16.0	12.463	1.499	3.1092
3	0.1796	4.0	7.30	14.0	9.69325	1.499	3.1334
4	0.1526	4.5	7.50	11.0	7.63932	1.499	3.2887
5	0.05388	5.0	7.60	9.3	6.30776	1.50	2.9093
6	0.00449	5.5	7.90	6.7	4.5558	1.50	2.9831
7	0.00898	6.0	7.95	6.2	4.15196	1.499	3.3819
8	0.00449	6.5	8.00	6.0	4.01898	1.496	2.9990
9	—	7.5	8.15	5.2	3.466	1.50	3.2422
10	—	8.0	8.15	5.2	3.466	1.50	3.2422

Average $K_{TCA} = 3.1399$. Standard deviation 0.1450537.

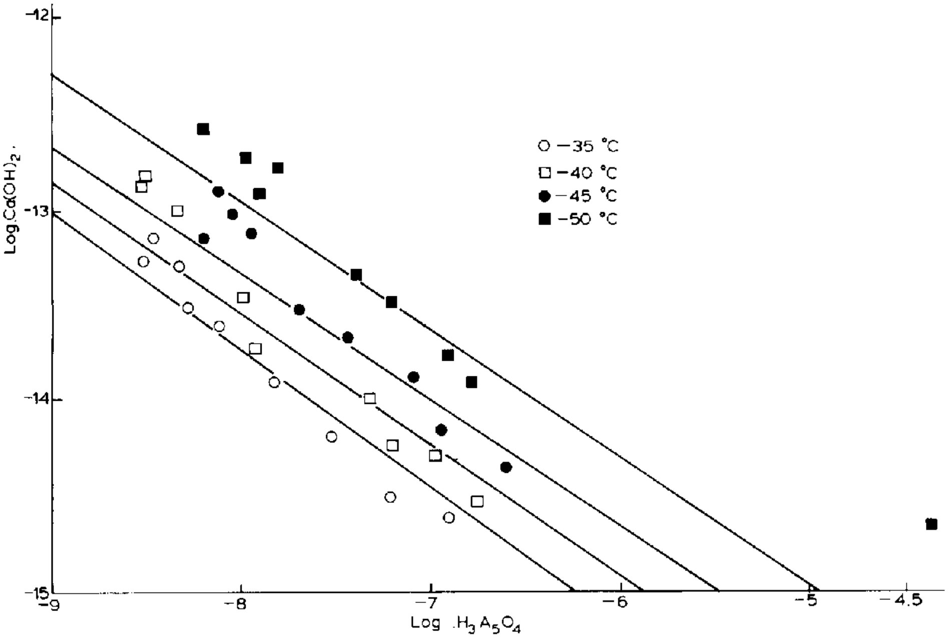

Fig. 2. Chemical potential diagram of log[Ca(OH)$_2$] vs. log[H$_3$AsO$_4$] for the dissolution of Ca$_3$(AsO$_4$)$_2$·2 H$_2$O.

values ranged from 1.42 to 1.49 between 35 and 50°C, respectively which correspond to a Ca/As ratio of about 1.5 (with minor deviation) in all cases.

The solubility of TCA decreased with increasing pH of the dissolving medium (Fig. 3). Similar smooth curves are also obtained when the values of As are plotted against pH at different temperatures. The effect of pH is understood from the consideration of the chemical potential diagram (Fig. 2) of the dissolution process. In the isotherm the region of higher calcium ion concentration is characterized by a decrease in chemical potential of calcium hydroxide because of low pH values. This decrease is compensated by the increase in chemical potential of arsenic acid so that the left-hand side of the following equation remains constant

$$\Delta F^0_{\mathrm{TCA}} + 6\mu \mathrm{H_2O} = 3\mu \mathrm{Ca(OH)_2} + 2\mu \mathrm{H_3AsO_4}$$

where ΔF^0 is the standard heat of dissolution of the process. Thus, when the medium is basic the solution is supersaturated and leads to a decrease in solubility while in an acidic medium it becomes under-saturated and the composition will not move further down the isotherm. Figure 4 shows the solubility isotherm for TCA in terms of log (total calcium concentration) as a function of pH. It is evident from the relative position of the curves that the solubility of the salt increases with increasing temperature; in this respect its behaviour differs from that of dicalcium arsenate [12]. Dependence of

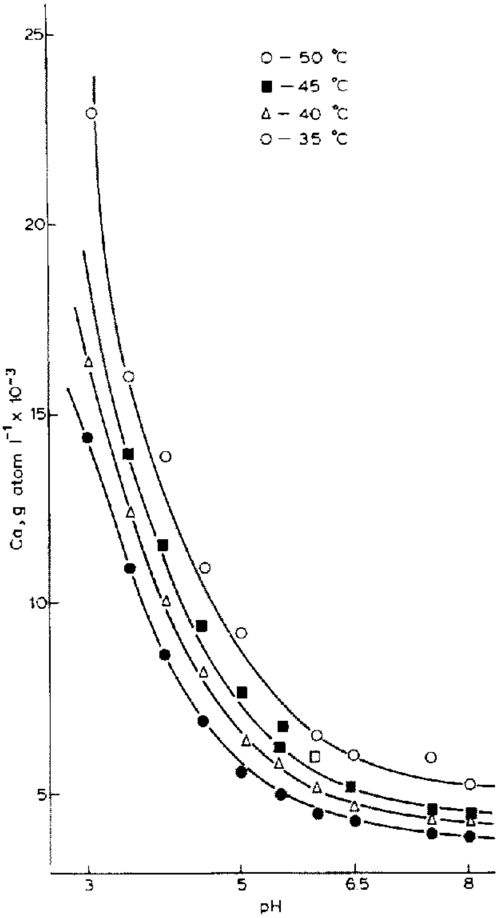

Fig. 3. Dependence of the solubility of $Ca_3(AsO_4)_2 \cdot 2\ H_2O$ on pH of the dissolving medium at different temperatures.

K_{TCA} on pH of the medium is illustrated in Fig. 5. The linear nature of the curves shows a possibility of the non-appearance of ion-pairs under the conditions of equilibration, otherwise a concave, downwards, curve should have resulted [13].

The temperature dependence of the dissolution of TCA and the standard thermodynamic quantities (ΔG^0, ΔS^0 and ΔH^0) are calculated for this reaction by

$$-\log K_{TCA} = \frac{9078.138}{T} - 34.0468 + 0.0821421\ T$$

and are presented in Table 5. An increase in solubility, and hence solubility product, with temperature is observed. The trends in the calculated thermodynamic parameters lend support to its temperature facile dissolution.

It is interesting to note that although tricalcium arsenate (TCA) and

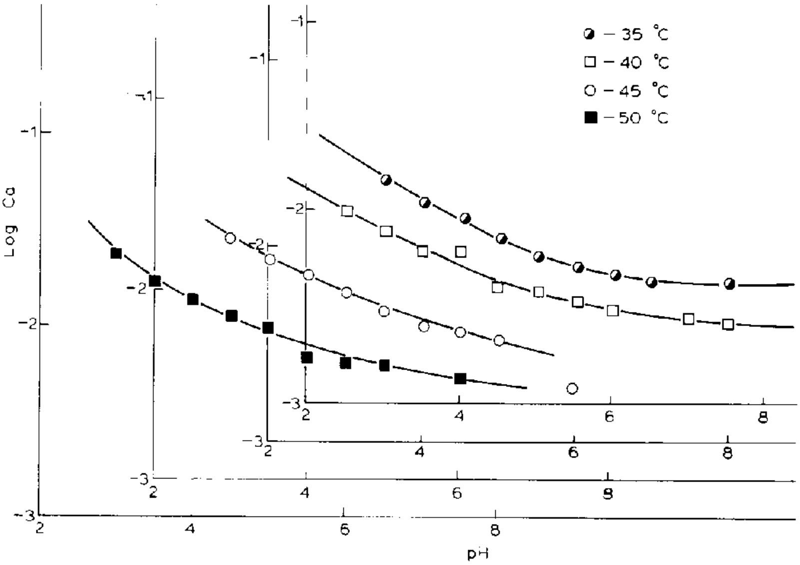

Fig. 4. Solubility isotherm of $Ca_3(AsO_4)_2 \cdot 2\ H_2O$ in terms of log (Ca Total) as a function of pH between 35 and 50°C.

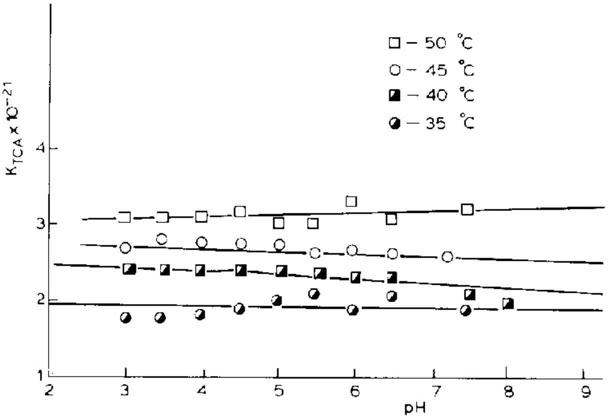

Fig. 5. Dependence of the solubility product (K_{TCA}) of $Ca_3(AsO_4)_2 \cdot 2\ H_2O$ with pH of the medium between 35 and 50°C.

TABLE 5

The temperature dependence of dissolution of TCA, and the standard thermodynamic quantities

Soln. No.	Temp. (°C)	Theor. K_{TCA}	Exptl. K_{TCA}	ΔG^0 (kJ mol^{-1} K^{-1})	ΔS^0 (J mol^{-1} K^{-1})	ΔH^0 (kJ mol^{-1} K^{-1})
1	35	1.8730	1.8868	122.2151	−316.88	24.615
2	40	2.1512	2.2742	123.838	−332.60	19.732
3	45	2.3878	2.7288	125.541	−348.33	14.771
4	50	2.5657	3.1399	127.322	−364.05	9.731

tricalcium phosphate (TCP) belong to the same isomorphous family their temperature dependence of solubility is opposite in nature; TCP exhibits a retrograde solubility with temperature [14]. The higher dissolution of TCA (K_{TCA} at 35°C is 1.88×10^{-21}) than TCP (K_{TCP} at 35°C is 1.15×10^{-29}) could be due to the introduction of more ionic character in the crystal lattice due to the presence of a large arsenate ion.

ACKNOWLEDGEMENTS

We thank Dr. S.C. Padhi, Professor of Chemistry, for the provision of laboratory facilities and the University Grants Commission, New Delhi for the award of a Teacher Fellowship to L.M.M.

REFERENCES

1 O.A. Nelson and M.M. Haring, J. Am. Chem. Soc., 59 (1937) 2216.
2 G.W. Pearce, J. Am. Chem. Soc., 59 (1938) 1258.
3 V.G. Chukhlantsev, Zh. Neorg. Khim., 1 (1956) 1975.
4 R.A. Robinson, J. Agric. Res., 13 (1918) 281.
5 L.M. Smith, J. Am. Chem. Soc., 42 (1920) 259.
6 P.P. Mahapatra and N.S. Chickerur, J. Inorg. Nucl. Chem., 40 (1978) 131.
7 P.P. Mahapatra, L.M. Mahapatra and C.N. Nanda, Indian J. Chem., submitted.
8 L.G.C. Sillen, A.E. Martell, E. Hogfeldt and R.H. Smith, Chem. Soc. Spec. Publ., 25 (1971).
9 A.L. Agafonova and I.L. Agafonov, Zh. Fiz. Khim., 27 (1963) 1137.
10 M.F.C. Ladd, Structure and Bonding in Solid State Chemistry, Wiley, New York, 1979, p. 131.
11 P.P. Mahapatra, H. Misra and N.S. Chickerur, Thermochim. Acta, 59 (1982) 383.
12 P.P. Mahapatra, L.M. Mahapatra and C.N. Nanda, unpublished results.
13 E.C. Morend, T.M. Gregory and W.E. Brown, J. Res. Natl. Bur. Stand., Sect. A, 70(6) (1966) 545.
14 T.M. Gregory, E.C. Moreno, J.M. Patel and W.E. Brown, J. Res. Natl. Bur. Stand., Sect. A, 78(6) (1974) 667.