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THERMODYNAMIC STUDY OF THE SOLID–LIQUID EQUILIBRIA IN THE MPO_3–LaP_3O_9 SYSTEMS (M = Li, Na, K, Rb, Cs, Ag, Tl)

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ABSTRACT

The enthalpies of fusion of the MPO_3 (M = Li, Na, K, Rb, Cs, Ag, Tl) polyphosphates were determined by calorimetry.

The MPO_3–LaP_3O_9 binary systems were investigated for the first time by DTA. The study shows in all cases the existence of one or both of the two intermediate compounds: $MLa(PO_3)_4$ and $M_2La(PO_3)_5$.

The solid–liquid equilibria of the MPO_3–LaP_3O_9 systems were submitted to a thermodynamic exploitation. With the exception of lithium, silver and thallium polyphosphates, whose crystallization fields are very limited, the liquidus curves of the other polyphosphates were put in equation. The melting point of LaP_3O_9, which undergoes a chemical decomposition before melting, was calculated and the obtained value was in agreement with the results of the thermogravimetric analysis.

Starting with simplified hypotheses, the liquidus curves were recalculated and the thermodynamic functions characterizing the stable or metastable melting of the corresponding solid phases were obtained.

Comparison of the measured and calculated values of the melting enthalpy of MPO_3 polyphosphates shows, for the concentrations rich in alkali polyphosphates, the existence of associations in the liquid state.

1. INTRODUCTION

During the last decade, the various studies on condensed phosphates of rare earths and alkali metals [1–5] have shown, in some cases, interesting physical properties, such as laser emission, ionic conduction or ferromagnetism.

Thus, we have undertaken a systematic research oriented towards the elaboration and study of new compounds of the following type: $M^I_xM^{III}_y(PO_3)_{x+3y}$(with M^I = Li, Na, K, Rb, Cs, Ag, Tl, NH_4 and M^{III} = La[6–11], Sm[12], Ce[13–18]).

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Analysis, processing and thermodynamic exploitation of solid–liquid equilibria curves of MPO_3–LaP_3O_9 systems (M = Li, Na, K, Rb, Cs, Ag, Tl) are presented in this paper. In order to refine and to interprete the experimental data, we have applied to these systems a semi-empirical equation [19–21] already used with success for many water–salt binary systems.

A complementary study using calorimetry was undertaken to control thermodynamic values of monovalent metal polyphosphates determined by liquidus curves computation.

2. EXPERIMENTAL

The melting enthalpies of monovalent metal polyphosphates were determined with a Setaram DSC 111 differential calorimeter, coupled to a Hewlett–Packard calculator allowing, through an appropriate program, to integrate by the scanning method different thermal ‘effects’. The calorimeter correction factor was introduced in the program. Samples of 0.2 g, in a stainless steel measuring cell, were used and the heating rate of the furnace was 10 K min^{-1}.

The phase equilibrium diagrams of MPO_3–LaP_3O_9 binary systems were established by using differential thermal analysis (DTA), according to Mazieres method [22], with a M5 Micro DTA Setaram apparatus. The heating rate of the furnace was 10 K min^{-1}. Samples of different concentration ratios of MPO_3 and $LaP_3O_9 \cdot 3H_2O$, reduced to a fine powder, were prepared in silica crucibles. The temperature and the annealing time of the samples varied with their composition.

For the differential thermal analysis, the crucibles containing the previous samples and the reference α-Al_2O_3 were made of platinium. Pt/Pt–Rh thermocouples were used at temperatures higher than 1273 K. Below this temperature a Pt/Platinel thermocouple was sufficient.

TABLE 1

Melting enthalpies of MPO_3 polyphosphates (M = Li, Na, K, Rb, Cs, Ag, Tl)

MPO_3	ΔH_{fus} (kJ mol^{-1})
$LiPO_3$	25.5
$NaPO_3$	22.2
KPO_3	10.9
$RbPO_3$	11.1
$CsPO_3$	10.1
$AgPO_3$	11.7
$TlPO_3$	17.2 [a]

[a] The value given is the melting enthalpy of the α-phase.

TABLE 2

Phase transformations in the $LiPO_3$–LaP_3O_9 system

x [a]	T_E(K) [b]	T_P(K) [c]	T_F(K) [d]
0.00	–	–	939
0.05	919	–	–
0.07	923	–	1073
0.10	916	–	1128
0.15	915	–	1178
0.20	918	–	1213
0.25	914	–	1224
0.30	921	1233	1233
0.35	923	1243	1283
0.40	921	1233	1318
0.50	917	1238	1378
0.55	–	1241	1393
0.60	–	1237	1418
0.70	–	1239	1448
0.80	–	1238	1473
0.90	–	1242	1503
1.00	–	–	1523

[a] x, Mole fraction of LaP_3O_9.
[b] T_E, Eutectic temperature.
[c] T_P, Peritectic temperature.
[d] T_F, Melting temperature.

TABLE 3

Phase transformations in the $NaPO_3$–LaP_3O_9 system

x [a]	T_E(K) [b]	T_P(K) [c]	T_F(K) [d]
0.000	–	–	905
0.025	902	–	–
0.050	900	–	900
0.100	899	–	1028
0.125	898	–	1055
0.150	897	–	1073
0.200	898	–	1109
0.250	896	–	1134
0.300	893	1145	1213
0.350	891	1146	1257
0.400	893	1147	1293
0.450	889	1145	1327
0.500	–	1146	1349
0.550	–	1139	1379
0.600	–	1144	1405
0.700	–	1139	1443
0.750	–	1139	1463
0.800	–	1133	1477
0.900	–	1133	1503
1.000	–	–	1523

[a] x, Mole fraction of LaP_3O_9.
[b] T_E, Eutectic temperature.
[c] T_P, Peritectic temperature.
[d] T_F, Melting temperature.

TABLE 4

Phase transformations in the KPO_3–LaP_3O_9 system

x [a]	T_E(K) [b]	T_{P_1}(K) [c]	T_{P_2}(K) [c]	T_F(K) [d]
0.00	–	–	–	1083
0.05	978	–	–	1053
0.10	978	–	–	988
0.15	980	–	–	1018
0.20	976	–	–	1052
0.27	978	1050	–	1113
0.33	–	1043	–	1158
0.40	–	1043	1153	1243
0.50	–	–	1153	1319
0.60	–	–	1153	1388
0.80	–	–	1153	1458
1.00	–	–	–	1523

[a] x, Mole fraction of LaP_3O_9.
[b] T_E, Eutectic temperature.
[c] T_{P_1}, T_{P_2}, Peritectic temperature.
[d] T_F, Melting temperature.

TABLE 5

Phase transformations in the $RbPO_3$–LaP_3O_9 system

x [a]	T_E(K) [b]	T_{P_1}(K) [c]	T_{P_2}(K) [c]	T_F(K) [d]
0.050	972	–	–	1036
0.075	970	–	–	1015
0.100	972	–	–	–
0.150	970	–	–	1020
0.175	970	–	–	1029
0.200	969	–	–	1038
0.250	965	–	–	1057
0.300	–	1055	–	1168
0.333	–	1033	–	1178
0.350	–	1046	–	1183
0.400	–	1045	1188	–
0.450	–	–	1193	1303
0.500	–	–	1188	1327
0.600	–	–	1183	1388
0.700	–	–	1183	1438
0.800	–	–	1178	–
0.900	–	–	1173	–
1.000	–	–	–	1523
0.000	–	–	–	1068

[a] x, Mole fraction of LaP_3O_9.
[b] T_E, Eutectic temperature.
[c] T_{P_1}, T_{P_2}, Peritectic temperature.
[d] T_F, Melting temperature.

TABLE 6

Phase transformations in the $CsPO_3$–LaP_3O_9 system

x [a]	T_E(K) [b]	T_{P_1}(K) [c]	T_{P_2}(K) [c]	T_F(K) [d]
0.050	918	–	–	976
0.075	920	–	–	947
0.100	918	–	–	–
0.150	918	–	–	988
0.175	923	–	–	1027
0.200	909	–	–	1045
0.250	909	–	–	1071
0.300	–	–	–	1107
0.333	–	1095	–	1188
0.400	–	1080	1197	–
0.450	–	–	1199	1302
0.500	–	–	1193	1338
0.600	–	–	1185	1403
0.700	–	–	1180	1433
0.800	–	–	1175	–
0.900	–	–	1173	–
1.000	–	–	–	1523
0.000	–	–	–	1004

[a] x, Mole fraction of LaP_3O_9.
[b] T_E, Eutectic temperature.
[c] T_{P_1}, T_{P_2}, Peritectic temperature.
[d] T_F, Melting temperature.

TABLE 7

Phase transformations in the $AgPO_3$–LaP_3O_9 system

x [a]	T_E(K) [b]	T_P(K) [c]	T_F(K) [d]
0.00	–	–	761
0.05	765	–	994
0.10	763	–	1051
0.20	764	1075	–
0.30	770	1076	1241
0.40	759	1073	1313
0.50	–	1080	1373
0.60	–	1067	1423
0.70	–	1067	1453
0.80	–	1063	–
0.90	–	1063	–
1.00	–	–	1523

[a] x, Mole fraction of LaP_3O_9.
[b] T_E, Eutectic temperature.
[c] T_P, Peritectic temperature.
[d] T_F, Melting temperature.

3. RESULTS

The calorimetric study of melting enthalpies was limited owing to two factors: on one hand, the apparatus available did not allow measurements at temperatures higher than 1100 K and, on the other, the binary intermediate compounds presented a peritectic decomposition upon heating.

The melting enthalpy of MPO_3 (M = Li, Na, K, Rb, Cs, Ag, Tl) monovalent elements are presented in Table 1. Those of lithium and sodium polyphosphates were higher than the values of potassium, rubidium, caesium and silver polyphosphates, which were all similar. On the other hand. The $TlPO_3$ compound presented a phase transition [23] at a temperature very close to the melting point: therefore, the value given for this compound is the melting enthalpy of the α-phase.

The DTA results for the MPO_3–LaP_3O_9 are presented in Tables 2–7. The phase equilibrium diagrams obtained are described in Figs. 1–7.

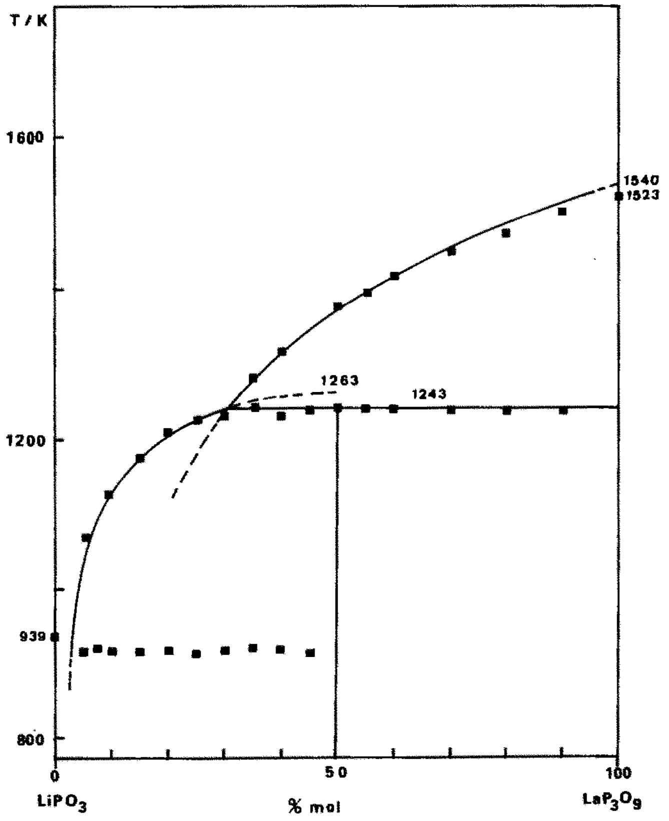

Fig. 1. Equilibrium diagram of the $LiPO_3$–LaP_3O_9 system: (–) liquidus curve recalculated; (■) experimental points.

TABLE 8

Phase transformations in the $TlPO_3$–LaP_3O_9 system

x [a]	T_E(K) [b]	T_{P_1}(K) [c]	T_{P_2}(K) [c]	T_F(K) [d]
0.00	–	–	–	711
0.05	709	–	–	824
0.07	707	–	–	886
0.10	707	–	–	898
0.15	708	923	–	1006
0.20	710	929	–	1066
0.25	705	924	–	1088
0.30	–	923	–	1100
0.33	–	922	–	1101
0.40	–	920	1093	1293
0.50	–	–	1090	1348
0.60	–	–	1072	1413
0.80	–	–	1078	1473
1.00	–	–	–	1523

[a] x, Mole fraction of LaP_3O_9.
[b] T_E, Eutectic temperature.
[c] T_{P_1}, T_{P_2}, Peritectic temperature.
[d] T_F, Melting temperature.

The study showed the existence of two intermediate compounds: $MLa(PO_3)_4$, $M_2La(PO_3)_5$ with M = K, Rb, Cs, Tl and only one compound $MLa(PO_3)_4$ with M = Li, Na, Ag.

4. DISCUSSION

A semi-empirical equation of a stoichiometric phase liquidus curve previously obtained in the water–salt systems [19–21] was re-examined and applied to molten salt systems. The analytical expression perfectly describes the liquidus of all solid phases of the MPO_3–LaP_3O_9 systems and has the general formula:

$$\sum_i \nu_{i0} \ln(x_i/x_{i0}) = A/T + B \ln T + C \qquad (1)$$

ν_{i0} is the stoichiometric coefficient of the species i in the solid, x_{i0} and x_i are, respectively, the mole fractions of species i in the solid and the liquid phases, and A, B and C are constants and can be calculated by a least squares method. These constants may be expressed by the relations:

$$\begin{aligned} A &= (\Delta C_P T_0 - \Delta H_0)/R - \alpha \\ B &= \Delta C_P/R - \beta \\ C &= \Delta H_0/(RT_0) - \Delta C_P(1 + \ln T_0)/R - \gamma \end{aligned} \qquad (2)$$

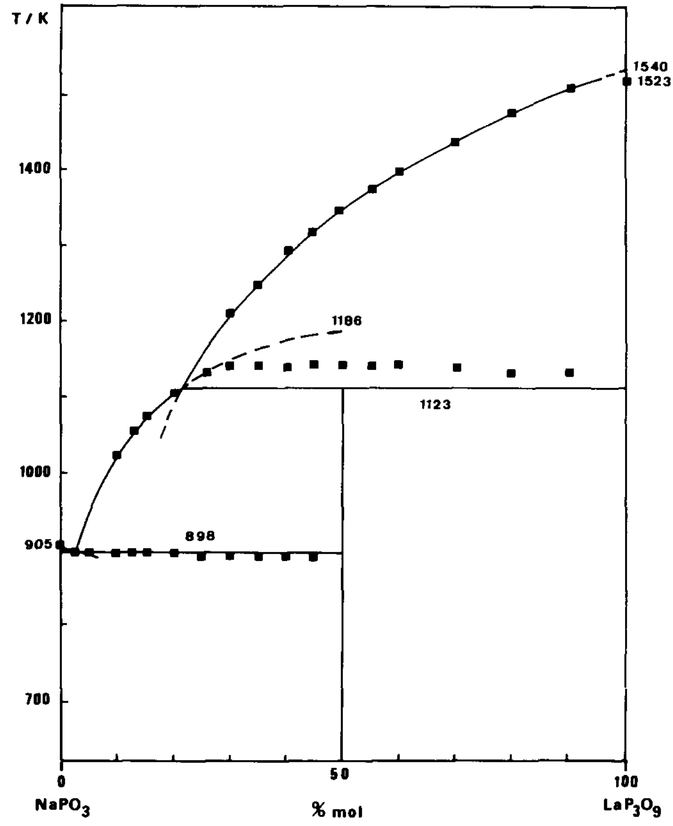

Fig. 2. Equilibrium diagram of the NaPO$_3$-LaP$_3$O$_9$ system: (–) liquidus curve recalculated; (■) experimental points.

R is the perfect gas constant and T_0 is the stable or metastable melting point of the pure substance. ΔH_0 and ΔC_P are, respectively, the variations of heat enthalpy and heat capacity at the fusion of the pure substance. α, β and γ coefficients may be expressed by an equation of the algebraic type:

$$\sum_i \nu_{i0} \ln(\gamma_i/\gamma_{i0}) = \alpha/T + \beta \ln T + \gamma \tag{3}$$

in which γ_i and γ_{i0} are the activity coefficients of species i in the liquid and in the solid phase.

A, B and C parameters calculation is carried out using the N experimental points (xj, Tj) and minimizing the following expression:

$$Q = \sum_{j=1}^{N} \left(\sum_i \nu_{i0} \ln(x_i/x_{i0}) - (A/T + B \ln T + C) \right)^2 \tag{4}$$

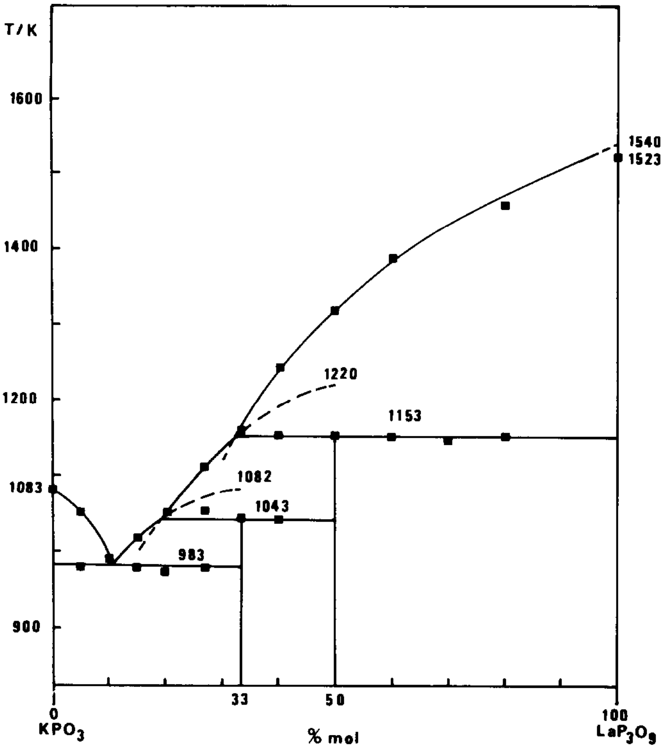

Fig. 3. Equilibrium diagram of the KPO_3–LaP_3O_9 system: (–) liquidus curve recalculated; (■) experimental points.

Analysis of the liquidus curves

In general, lanthanide (Ln) metaphosphates have a high decomposition temperature, which varies from one author to another [24,25], and the following reaction represents this decomposition:

$$LnP_3O_9 \rightarrow LnPO_4 + \tfrac{1}{2}P_4O_{10} \tag{5}$$

For the lanthane metaphosphate, the existence of this decomposition was confirmed by thermogravimetric analysis. In fact, a 50 mg sample heated at 10 K min^{-1} in a GDTD 24 Setaram thermoanalyser undergoes a loss of mass of about 3% characterized by an endothermic peak at 1523 K. The metastable melting point of LaP_3O_9 can be determined by many different measures under pressure, then by extrapolation at atmospheric pressure. However, it is easier to extrapolate a liquidus curve obtained by elimination of the experimental values affected by the decomposition. In the case of lanthane metaphosphate, eqn. (1) becomes

$$\ln x = A/T + B \ln T + C \tag{6}$$

where x is the mole fraction of LaP_3O_9 in the liquid phase.

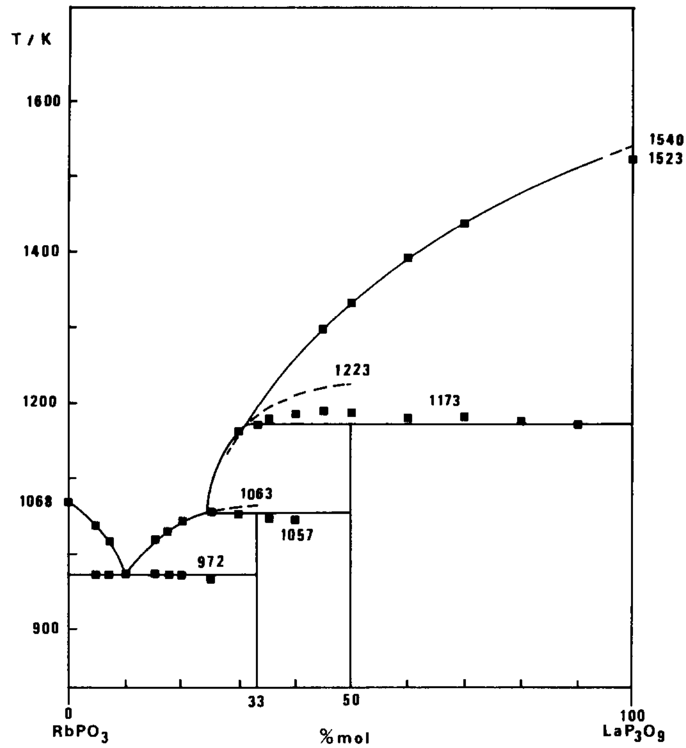

Fig. 4. Equilibrium diagram of the $RbPO_3$–LaP_3O_9 system: (–) liquidus curve recalculated; (■) experimental points.

The coefficients A, B and C were calculated in the MPO_3–LaP_3O_9 ($M = Na$, Ag) systems, in which the LaP_3O_9 experimental liquidus curve is the best to be defined. By eliminating the experimental values higher than 1473 K, a common metastable melting point is obtained at 1540 K, a result which is confirmed by thermogravimetric analysis: $LaPO_4$ formed in the reaction (5) lowers the melting point of the lanthane metaphosphate. The determination of the LaP_3O_9 heat enthalpy, which is presented next, leads to a cryoscopic lowering of 21 K and consequently the melting point of LaP_3O_9 is approximately 1544 K. The parameters of the liquidus equation of LaP_3O_9 were calculated in each system. They are given in Table 9.

In general, the liquidus curves of the MPO_3 metaphosphates were defined by a small number of experimental values. Because the melting point T_0 of pure solids is more precisely known than the solubility determined values, the liquidus curves must pass through the points. If we suppose that the species of the liquid phase are only MPO_3 and LaP_3O_9, eqn. (1) becomes:

$$\ln(1 - x) = A(1/T - 1/T_0) + B \ln(T/T_0) \qquad (7)$$

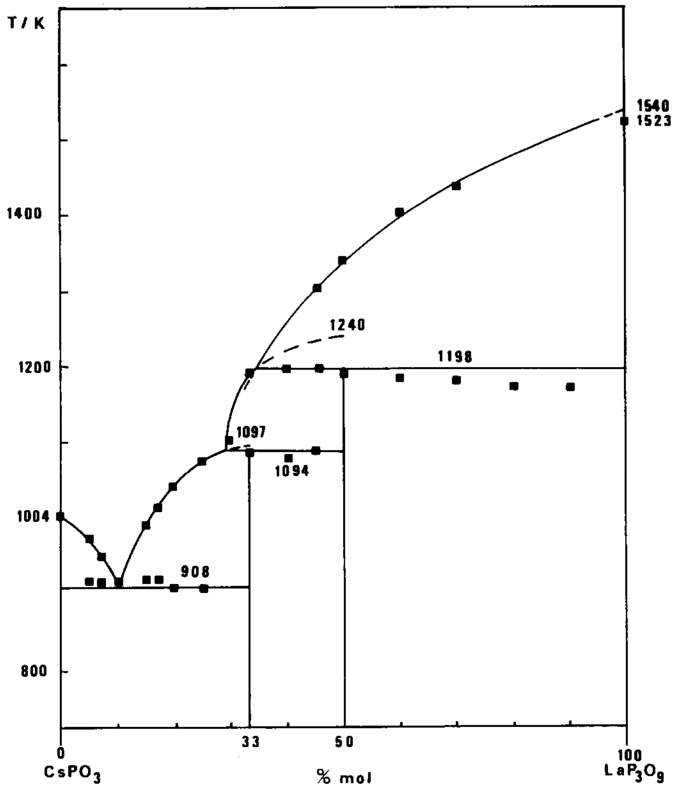

Fig. 5. Equilibrium diagram of the $CsPO_3$–LaP_3O_9 system: (–) liquidus curve recalculated; (■) experimental points.

The parameters A and B of the different MPO_3 liquidus equations are presented in Table 10.

The stoichiometry of the intermediate binary compounds found in the different systems corresponds to the formula: $M_pLa(PO_3)_{3+p}$ with $p = 1$ or

TABLE 9

MPO_3–LaP_3O_9 system: liquidus of LaP_3O_9

MPO_3	A(K)	B	C	ΔH_0 (kJ mol^{-1})	ΔS_0 (J K^{-1} mol^{-1})	ΔC_P (J K^{-1} mol^{-1})	T_0 (K)
$LiPO_3$	14106.7	15.732	−124.63	84.2	54.6	130.8	1540
$NaPO_3$	7662.9	10.672	−83.31	72.9	47.3	88.7	1540
KPO_3	11830.7	12.800	−101.63	65.5	42.6	106.4	1540
$RbPO_3$	10564.8	12.168	−96.17	68.0	44.1	101.1	1540
$CsPO_3$	16172.0	16.207	−129.45	73.1	47.4	134.7	1540
$AgPO_3$	13369.9	15.242	−120.55	84.0	54.5	126.7	1540
$TlPO_3$	24158.4	22.233	−178.87	83.8	54.4	184.8	1540

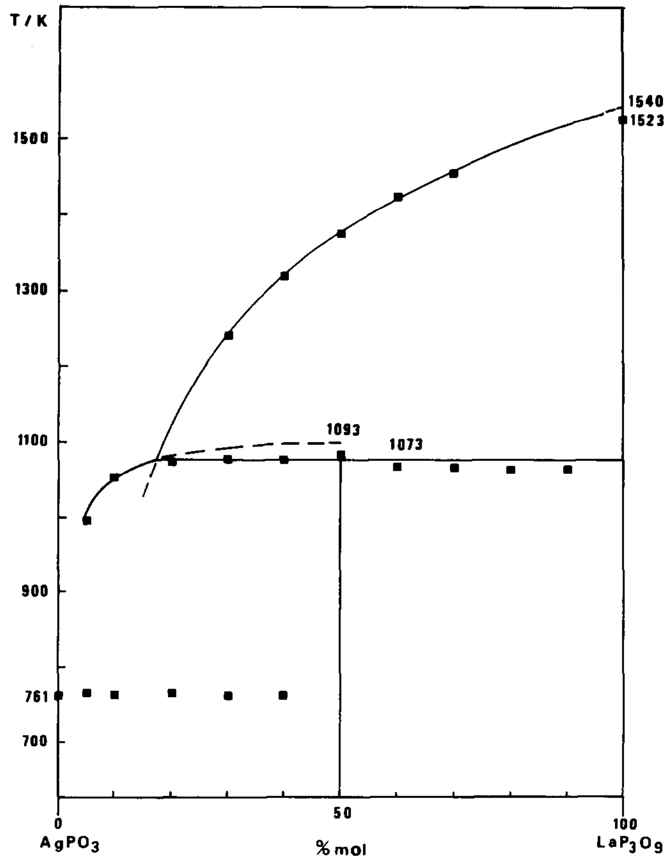

Fig. 6. Equilibrium diagram of the $AgPO_3$–LaP_3O_9 system: (–) liquidus curve recalculated; (■) experimental points.

2 and eqn. (1) can be expressed as:

$$\ln\left(x(1-x)^p(1+p)^{(1+p)}/P^p\right) = A/T + B\ln T + C \tag{8}$$

All these solid phases undergo a peritectic decomposition. Their metastable

TABLE 10

MPO_3–LaP_3O_9 system: liquidus of MPO_3

MPO_3	A(K)	B	ΔH_0 (kJ mol^{-1})	ΔS_0 (J K^{-1} mol^{-1})	ΔC_P (J K^{-1} mol^{-1})	T_0 (K)
$NaPO_3$	648436.4	724.271	81.9	90.5	6046.5	905
KPO_3	22160.4	22.57	19.1	17.6	187.7	1083
$RbPO_3$	18871.2	19.646	17.6	16.4	163.3	1068
$CsPO_3$	15320.4	17.122	15.6	15.5	142.4	1004

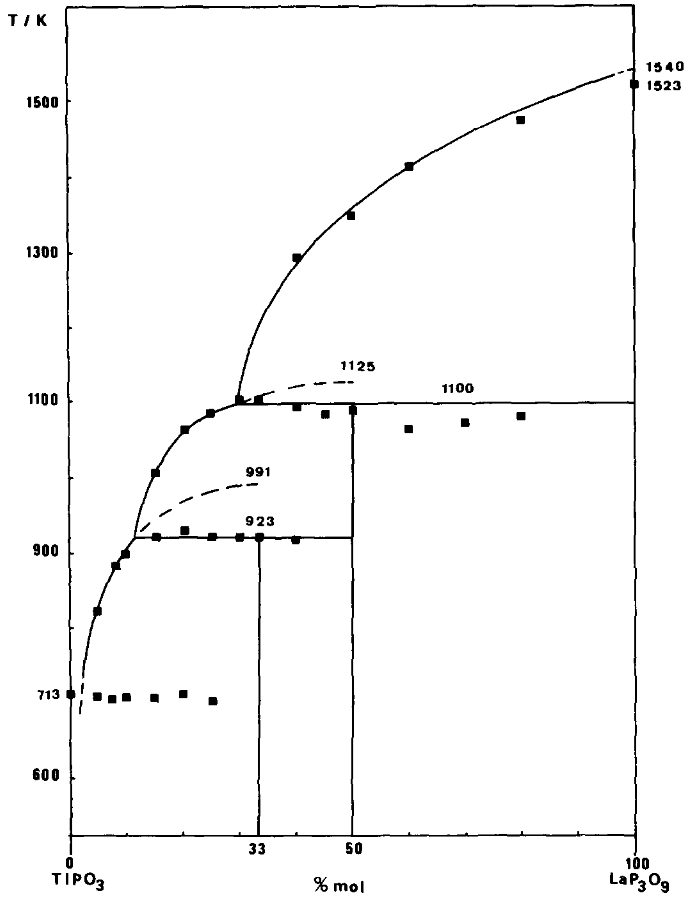

Fig. 7. Equilibrium diagram of the TlPO$_3$–LaP$_3$O$_9$ system: (–) liquidus curve recalculated; (■) experimental points.

TABLE 11

MPO$_3$–LaP$_3$O$_9$ system: liquidus of M$_p$La(PO$_3$)$_{3+p}$ ($p = 1, 2$)

M$_p$La(PO$_3$)$_{3+p}$	A(K)	B	C	ΔH_0 (kJ mol^{-1})	ΔS_0 (J K^{-1} mol^{-1})	ΔC_P (J K^{-1} mol^{-1})	T_0 (K)
LiLa(PO$_3$)$_4$	24187.3	29.243	−227.98	105.9	83.9	243.1	1263
NaLa(PO$_3$)$_4$	−16566.7	−7.848	69.52	60.3	50.9	−65.2	1186
KLa(PO$_3$)$_4$	−16855.8	−11.877	98.22	19.7	16.1	−98.7	1220
RbLa(PO$_3$)$_4$	34050.4	31.935	−254.87	41.8	34.1	265.5	1223
CsLa(PO$_3$)$_4$	44948.8	39.928	−320.65	37.8	30.5	331.9	1240
AgLa(PO$_3$)$_4$	300203.0	305.666	−2413.33	283.8	259.5	2541.3	1093
TlLa(PO$_3$)$_4$	42004.0	45.721	−358.56	78.6	69.8	380.1	1125
K$_2$La(PO$_3$)$_5$	−42047.8	−34.950	283.04	35.1	32.4	−290.6	1082
Rb$_2$La(PO$_3$)$_5$	11960.2	18.432	−139.70	63.5	59.7	153.2	1063
Cs$_2$La(PO$_3$)$_5$	716.9	3.741	−26.84	28.1	25.7	31.1	1097
Tl$_2$La(PO$_3$)$_5$	5197.9	12.307	−90.15	58.2	58.7	102.3	991

melting points were calculated and are presented in Table 11 with the parameters of eqn. (8).

Thermodynamic exploitation of liquidus curves

The heat enthalpy of lanthane metaphosphate cannot be measured by calorimetry due to decomposition of this compound at high temperature. However, when the liquidus equation is known, the thermodynamic functions characteristic of the metastable fusion can be calculated for the ideal solution ($\alpha = \beta = \gamma = 0$) from eqn. (2).

The values thus obtained in the different systems are relatively coherent among themselves (Table 9).

At the temperature of 1540 K, the average values are the following: $\Delta H_0 = 76$ kJ mol^{-1}, $\Delta C_p = 125$ J K^{-1} mol^{-1}.

All the intermediate phases have a peritectic decomposition on heating and their fusion was not studied further by calorimetry. The fusion thermodynamic functions were calculated at the metastable melting point. The results are displayed in Table 11. These values are given only as an indication, since they are calculated on the assumption that the solution is ideal and the liquid phase is only formed by MPO_3 and LaP_3O_9. Important discrepancies can be observed with different hypotheses, as shown in the following analysis.

The liquidus study of the MPO_3 polyphosphates was limited to the sodium, potassium, rubidium and caesium salts, whose experimental liquidus curves were sufficiently well defined to allow a thermodynamic exploitation. Based on the assumption that the solution is ideal, the values of the calculated heat enthalpy are, in all cases, superior to calorimetric determinations (Tables 1 and 11). These discrepancies can be explained by association phenomena in the liquid. In the solid, the two phosphates MPO_3 and LaP_3O_9 form stoichiometric compounds whose relative composition and saturation field are given in the equilibrium diagram.

We postulated that, in the range of concentrations and temperatures studied, the chemical species in the liquid phase are the same as those in the

TABLE 12

Comparison between intermolecular association degrees in solid and liquid phases

$M_pLa(PO_3)_{3+p}$	n[a]	z[b]
$NaLa(PO_3)_4$	3.8	4
$K_2La(PO_3)_5$	1.9	2
$Rb_2La(PO_3)_5$	1.8	2
$Cs_2La(PO_3)_5$	1.7	2

[a] n, Number of molecules in liquidus phase.

[b] z, Number of molecules by unit cell in solid phase.

TABLE 13

Liquidus of MPO_3: association in the liquid phase

MPO_3	A(K)	B	T_0(K)	ΔH_0 (kJ mol^{-1})		ΔS_0 (J K^{-1} mol^{-1})	ΔC_P (J K^{-1} mol^{-1})
				Calc.	Calorim.		
$NaPO_3$	160718.9	180.319	905	20.0	22.2	22.9	1499
KPO_3	9160.6	9.609	1083	10.4	10.9	9.6	80
$RbPO_3$	8216.2	8.800	1068	9.8	11.1	9.2	73
$CsPO_3$	5422.4	6.411	1004	8.4	10.1	8.4	53

solid phase. In this case, the liquid phase contains not only MPO_3 polyphosphates but also $(NaLa(PO_3)_4)_n$ or $(M_2La(PO_3)_5)_n$ for M = K, Rb, Cs.

Then, eqn. (1) becomes:

$$\ln\{(1-(p+1)x/[1-(p+1-1/n)x]\} = A(1/T - 1/T_0) + B\ln(T/T_0) \quad (9)$$

with $p = 1$ for M = Na and $p = 2$ for M = K, Rb, Cs. If we suppose that these associations are the cause of the deviation to the ideality previously observed, the number n can be calculated in each case. The results are given in Table 12 and are compared with the number z of molecules by unit cell in solid phase [7–9]. The values of n and z are relatively coherent among themselves. The thermodynamic functions are calculated again neglecting the activity coefficients and taking for n the corresponding z value. The results are shown in Table 13; given the precision and the number of experimental determinations, they can be considered to be in concordance.

5. CONCLUSION

A semi-empirical equation of the liquidus curve, already established in the water–salt binary systems was applied with success to salt–salt systems.

This equation is useful for an intermediate or limit phase in the complete range of temperatures and compositions. The analytical expression obtained perfectly describes the experimental liquidus curves of all the solid phases in the MPO_3–LaP_3O_9 systems. Moreover, the metastable melting point of intermediate phases was determined. The melting point of LaP_3O_9, which cannot be obtained by experimentation, was calculated by extrapolation of the liquidus curves in the MPO_3–LaP_3O_9 (M = Na, Ag) systems. The final common value is in line with the liquidus curves of the other systems and with the results of thermogravimetric analysis.

The thermodynamic function characteristic of the fusion was calculated with a simplified hypothesis for all the solid phases whose experimental liquidus curves have been determined.

Comparison of the measured and calculated values of heat enthalpies shows, in the range of concentrations rich in alkali polyphosphates, the existence of associations in the liquid state.

The assumption that the associations are the same in the liquid and in the solid state agrees with the experimental data.

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